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Ti-based nanostructured materials for lithium-ion batteries

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Institute of Superconducting and Electronic Materials
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Ti-based Nanostructured Materials for Lithium-ion Batteries

This thesis is presented as part of the requirements for the Award of the Degree of

Doctor of Philosophy

from the

University of Wollongong

by

Jae-Geun Kim

Institute of Superconducting and Electronic Materials
Faculty of Engineering
February 2014
ABSTRACT

Worldwide efforts to reduce the consumption of fossil fuels and to preserve the environment have been promoted the development of renewable energy systems which require energy storages to preserve electric energy. Lithium rechargeable battery is one of promising storage devices because of high energy and power density and reliable safety. Ti-based oxides are attractive candidates for use as an anode for lithium ion batteries due to low cost, excellent functionality, non-toxicity, thermal stability, and environmental friendliness. The morphology, phase formation and electronic structure of Ti-based oxide materials on the nanoscale definitely determine their electrochemical properties in energy storage systems. In this thesis, one-dimensional nanostructured Ti-based oxides, including nitrogen-doped TiO$_2$, Ag-Li$_4$Ti$_5$O$_{12}$ Zr-doped Li$_4$Ti$_5$O$_{12}$ and a core-shell Si@TiO$_2$ fibrous structure, were fabricated and their morphology, phase formation, electronic structure and electrochemical properties were investigated for application in anodes of lithium ion batteries.

1D Ag (1.75 at%)-Li$_4$Ti$_5$O$_{12}$ composite nanofibers showed enhanced specific capacity, rate capability, and cycling stability compared to bare Li$_4$Ti$_5$O$_{12}$ nanofibers, due to the Ag nanoparticles (<5 nm), which were mainly distributed at interfaces between Li$_4$Ti$_5$O$_{12}$ primary particles. This structural morphology resulted in 20% higher rate capability than bare Li$_4$Ti$_5$O$_{12}$ nanofibers by facilitating the charge transfer kinetics. For Zr$^{4+}$ doping into Li$_4$Ti$_5$O$_{12}$, as the doping content increased, there was no distinct change in the morphology and electronic structure, whereas the average lattice was increased from ~8.360 Å for the bare Li$_4$Ti$_5$O$_{12}$ to 8.361-8.362 Å for the Zr-doped Li$_4$Ti$_5$O$_{12}$ and the amount of ZrO$_2$ impurity was increased.
Incorporating a small fraction of Zr\(^{4+}\) ions in the Ti\(^{4+}\) sites of the Li\(_4\)Ti\(_5\)O\(_{12}\) led to enhanced lithium ion battery performance, which was due to the structural distortion through an increase in the average lattice constant, and thereby, enlarged Li\(^+\) diffusion paths, rather than changes to the electronic structure. However, insulating ZrO\(_2\) nanoparticles that were present between the Li\(_4\)Ti\(_5\)O\(_{12}\) grains due to the low Zr\(^{4+}\) solubility had a negative effect on the Li\(^+\) extraction capacity.

In the case of nitrogen-doped TiO\(_2\) nanofibers, it was speculated that substitutional nitrogen would be spread widely in the bulk, while interstitial nitrogen atoms were mostly located near the surface. The nitrogen-doped TiO\(_2\) nanofibers showed the improved cyclic retention and rate capability compared to TiO\(_2\) nanopowders and TiO\(_2\) nanofibers. This result was due to higher conductivity and faster Li\(^+\) diffusion of the 1D nanostructure. For core-shell structured Si-nanoparticles@TiO\(_{2-x}\)/C composite microfibers, the core-shell composite exhibits high reversible capacity, excellent rate capability and improved cycle performance were found. In addition, the exothermic behaviour was remarkable suppressed, which can prevent possible thermal runaway and safety problems of the cells. The improved electrochemical and thermal properties are attributed to the mechanically, electrically, and thermally robust architecture of the TiO\(_{2-x}\)/C nanocomposite encapsulating the Si-nanoparticles. These findings could provide promising material architectures for robust, high performance Li\(_4\)Ti\(_5\)O\(_{12}\)- and TiO\(_2\)-based anodes of lithium rechargeable batteries.
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<table>
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<tr>
<td>0D</td>
<td>Zero-dimensional</td>
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<tr>
<td>1D</td>
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<tr>
<td>2D</td>
<td>Two-dimensional</td>
</tr>
<tr>
<td>3D</td>
<td>Three-dimensional</td>
</tr>
<tr>
<td>BET</td>
<td>Brunauer-Emmett-Teller</td>
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<tr>
<td>BFTEM</td>
<td>Bright field transmission electron microscopy</td>
</tr>
<tr>
<td>BJH</td>
<td>Barrett–Joyner–Halenda</td>
</tr>
<tr>
<td>CB</td>
<td>Conduction band</td>
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<tr>
<td>FTIR</td>
<td>Fourier transform infrared spectroscopy</td>
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<tr>
<td>PDOSs</td>
<td>Projected density of states</td>
</tr>
<tr>
<td>PEC</td>
<td>Photoelectrochemical</td>
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<tr>
<td>PMMA</td>
<td>Poly(methyl methacrylate)</td>
</tr>
<tr>
<td>PP</td>
<td>Polypropylene</td>
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<tr>
<td>PVDF</td>
<td>Polyvinylidene fluoride</td>
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<tr>
<td>PVP</td>
<td>Polyvinylpyrrrolidone</td>
</tr>
<tr>
<td>PWSCF</td>
<td>Plane-wave self-consistent field code</td>
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<td>SADPs</td>
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<tr>
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<td>SiNPs@C</td>
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<td>SiNPs@T/C</td>
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</tr>
<tr>
<td>STEM</td>
<td>Scanning transmission electron microscopy</td>
</tr>
<tr>
<td>TEM</td>
<td>Transmission electron microscopy</td>
</tr>
<tr>
<td>TGA</td>
<td>Thermogravimetric analysis</td>
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<tr>
<td>TTIP</td>
<td>Titanium (IV) isopropoxide</td>
</tr>
<tr>
<td>VASP</td>
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<tr>
<td>VB</td>
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<tr>
<td>XPS</td>
<td>X-ray photoelectron spectroscopy</td>
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<td>XRD</td>
<td>X-ray diffraction</td>
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</table>
1 INTRODUCTION

As population increases, the consumption of fossil fuels has increased, which causes environmental pollutions such as global warming and air pollution because of greenhouse gas emissions. To solve the environmental issues, the alternative clean energy sources such as solar, wave and wind have been required. One method to reduce the emission of carbon dioxide into the atmosphere is to replace with renewable energy sources, and development of energy storage system, including fuel cells, supercapacitors and batteries, is very important to preserve the electric energy provided from renewable energy system.

Lithium ion battery is one of the green energy storage technologies because of its several advantages such as high energy and power density, long cycle life and low (or no) self-discharge in comparison with other energy storage system. It is widely used in portable devices (laptop, mobile phone, digital cameras, etc.) as power source. Even though lithium ion battery has a number of advantages, it still needs to enhance its performance. For example, electric vehicles using lithium ion battery can travel only short distance compared to common vehicles used by gasoline. The development of the lithium rechargeable batteries has been reported through theoretical and experimental analyses. The lithium rechargeable batteries possess a higher capacity, better rate performance and greater safety as use of nanosized electrode materials because of their desired properties such as shortened Li$^+$ diffusion pathways, improved electron transport and higher surface area compared to bulk materials.

These advantages of nanomaterials are able to promote specific charge capacity and stability at high current rate during electrochemical reaction.
In this doctoral work, Ti-based one-dimensional nanostructured materials were fabricated by using an electrospinning technique to improve the electrochemical performance for application in lithium ion battery anode. The phase formation, microstructure, electronic structure, and electrochemical properties of the Ti-based nanostructured materials were examined through experimental and theoretical methods.

An overview of the chapter in this work:

Chapter 2 presents a comprehensive background on nanostructured materials, experimental parameters and mechanisms of electrospinning, and literature review of Ti-based materials for lithium rechargeable batteries.

Chapter 3 introduces the synthesis and electrochemical performance of 1D TiO$_2$N$_x$ nanofibers. 1D TiO$_2$ nanostructure materials offered better cycle stability than TiO$_2$ nanoparticles due to their morphological advantages, and nitrogen doping in the form of TiO$_2$N$_x$ also caused further improvement because of the high conductivity and fast Li$^+$ diffusion. The site for nitrogen doping was clarified through experimental investigation along with first-principle calculation.

Chapter 4 presents 1D nanostructured Ag-Li$_4$Ti$_5$O$_{12}$ composite fibers as a promising anode material. Ag-Li$_4$Ti$_5$O$_{12}$ nanofibers were rationally designed and synthesized to meet the requirements of one-dimensional (1D) morphology and superior electrical conductivity. 1D Ag-Li$_4$Ti$_5$O$_{12}$ nanofibers improved specific capacity, rate capability, and cycle stability compared to bare Li$_4$Ti$_5$O$_{12}$ nanofibers, due to the Ag nanoparticles, which were uniformly distributed throughout the Li$_4$Ti$_5$O$_{12}$ material.
Chapter 5 shows the Zr$^{4+}$ doping effect on Li$_4$Ti$_5$O$_{12}$ lattice, electronic structure, and resultant electrochemical properties of Li-ion batteries. A small fraction of Zr$^{4+}$ ions in the Li$_4$Ti$_5$O$_{12}$ structure gave rise to enhanced electrochemical performance due to the structural imperfection. However, insulating ZrO$_2$ nanoparticles that were present between the Li$_4$Ti$_5$O$_{12}$ grains due to the low Zr$^{4+}$ solubility had a negative effect on the Li$^+$ extraction capacity.

Chapter 6 introduces Si-nanoparticles@TiO$_{2-x}$/C core/shell mesoporous microfiber composite by using a coaxial spinneret. The role of TiO$_{2-x}$/C shell to suppress the disintegration of the Si-nanoparticles during cycling as a buffer layer and the oxygen-deficient TiO$_2$ and carbon as well as the in situ formed Li$_x$TiO$_2$ phase during lithiation can provide electrical pathway of high conductivity. Furthermore, enhanced thermal stability of the Si composite can also be obtained because of intrinsically-stable thermal property of TiO$_2$. Si-nanoparticles@TiO$_{2-x}$/C mesoporous microfiber exhibited not only high reversible capacity, excellent rate capability and cycle stability but also thermal property. It is expected as a promising material architecture for a safe and reliable Si-based lithium ion battery.

Chapter 7 contains the conclusions and summary of this thesis. Suggestions for further investigation and direction are also suggested.
2 LITERATURE REVIEW

2.1 Overview of nanostructured materials

Nanostructured materials have received great interests because of their unique physical, electronic, magnetic and chemical properties superior to their bulk counterparts. [1-8] It is well known that nanostructured materials strongly depend on the dimensionality, morphologies, shapes and size, which are the major factors to their applications. Based on their dimension, nanostructured materials can be divided into zero-dimensional (0D), one-dimensional (1D), two-dimensional (2D) and three-dimensional (3D) nanostructure (Figure 1). A large number of synthetic techniques have been suggested with the development of state-of-the-art

![Figure 2.1](image)

**Figure 2.1** Schematic diagrams of (a) 0D, (b) 1D, (c) 2D and (d) 3D structure. [9]
nanotechnology for 0D, 1D, 2D and 3D nanostructured materials, which have great potential in a wide range of applications. The major feature that distinguishes various types of nanostructures is their dimensionality.

Firstly, 0D nanostructured materials such as core-shell quantum dots, uniform particles arrays and hollow spheres have been studied in light emitting diodes, single-electron transistors, lasers, solar cells and various energy storage systems through a variety of chemical and physical synthetic methods. [10-17]

Secondly, 1D nanostructures such as nanowires, nanotubes, nanorods, nanobelts, nanoribbon, nanofibers and hierarchical nanostructures have attracted great attention due to their morphological advantages and unique properties. It is generally accepted that 1D nanostructured materials provide an idea system to investigate novel phenomena, size reduction and dimensionality at the nanoscale. Their functional units and interconnects also play an important role in electronic and optical devices, sensors, catalysis, energy, biomedical and environmental applications. [4, 18-42]

Thirdly, 2D nanostructured materials have certain geometries with unique shape-dependant characteristics and the atomic scale thickness as building blocks for functional components. They are especially interesting not only for understanding of growth mechanism, but also for novel applications in sensors, nanocontainers, nanoreactors and photocatalysts owing to their salient properties. [43-49]

Lastly, 3D nanostructures with high dimensionality and complex morphology have received much research interests because of their advanced geometric structure, large surface area, and exploitation of novel properties. Such nanomaterials with high
porosity in 3D are very important in many areas such as magnetic materials, catalysts and electrode materials for rechargeable batteries. [50-62]
2.2 Synthetic methods for 1D nanostructured materials

1D nanostructures have attracted great attention due to their different electronic physical and chemical properties compared to bulk materials. A variety of synthetic methods have been developed for 1D nanostructured materials with controlled structure, size and morphology. One of the common methods is an evaporation technique such as ion assisted and thermal evaporation. In thermal evaporation method, the gas atoms or molecules of source materials evaporated at high temperatures are deposited on a substrate to form desired nanostructures. [63-65]

Sol-gel process is a wet chemical route that can be used to fabricate clusters in a liquid or suspension of colloidal particles (sol). A chemical solution (sol) acts as precursor for a solid network (gel) with a solvent and the wet gel can be converted into various nanostructured materials when the solvent is removed. [66-68] It is also possible to control the size and morphology of materials by changing experimental process with proper surfactants. However, the sol-gel processing is rather complicated because of different activities between network-modifying components and network-forming reaction parameters.

Hydrothermal method is to synthesize crystallized materials from aqueous solutions at high temperature and pressure. [69-71] The crystal growth in hydrothermal synthesis is conducted in a steel vessel (autoclave) to fabricate 1D nanostructured materials with controlled temperature and pressure. This is suitable for growing high-quality crystals with retaining a proper control. The hydrothermal method, however, has disadvantages such as requirement of expensive hydrothermal vessel and impossibility of observing crystal growth behaviour.
Chemical vapor deposition (CVD) for 1D nanostructured materials is a chemical process to form high quality crystals or various composite materials through decomposition of volatile precursors and their chemical reaction with substrate surface. [72-73] CVD, however, has several disadvantages such as complicated reaction mechanisms and use of expensive equipments.

Electrospinning is a facile method for synthesising 1D architectures with diverse compositions, morphologies and dimensions including hollow structures, core-shell structure and uniaxially aligned arrays. [35-42, 74-75] Moreover, it also enables homogeneous coating or doping and mass production for commercialisation with use of multiple nozzles. Therefore, electrospinning yields various functional 1D nanostructures of polymers, ceramics or composites.
2.3 Electrospinning

2.3.1 Overview

A schematic diagram of setup for electrospinning is shown in Figure 2.2. It has three major components such as a high voltage power supply, a metal nozzle and a collector. In a typical process, a precursor is injected from a syringe with use of a syringe pump to a small metal nozzle at a constant and controllable rate. The drop of polymer solution at the tip of metal nozzle becomes electrified when a high voltage is applied in the range of 1 to 30 kV. As a result, the liquid drop is distorted into a conical object (Taylor cone) due to two major electrostatic forces such as the electrostatic repulsion between the surface charges and the Coulombic force exerted by applied electric filed. A liquid jet is ejected from the metal nozzle because the electrostatic force can overcome the surface tension of the droplet when the applied electric field reaches a threshold value. The liquid jet then goes through whipping

![Figure 2.2 A schematic illustration for electrospinning.](image)
and stretching processes. A solid fiber mat is formed on the collector due to the electrostatic repulsion of the surface charges and evaporation of the solvent. The diameter of electrospun fibers can be controlled in the range of a few micrometers to tens of nanometers. A variety of types of organic polymers have already been reported as fibers with the use of relatively simple and straightforward electrospinning technique. [36, 76-118]

The electrospinning mechanism is rather complicated, even though the setup of electrospinning is very simple. An electrified jet during electrospinning is mainly caused by the bending instability, resulting in formation of solid polymeric fibers after solvent evaporation. [119-122] The photographs of an electrified jet are shown in Figure 2.3. [122] As mentioned above, when an electrified jet is ejected from the metal nozzle to the collector, the jet begins at the end of Taylor cone. The spinning jet is a nearly straight line from Taylor cone, then it become unstable (cone-shaped). The cone-shaped spinning jet in unstable region (bending instability) is consisted of

![Figure 2.3](image)

**Figure 2.3** The photographs illustrating the bending instability region of the spinning jet. The capture time was (a) 1/250 s and (b) 18 ns.
multiple jets, however, only single jet is observed at the bending instability region of the spinning jet when using a high-speed photography, as can be seen in Figure 2.3(b). Several groups have performed theoretical and experimental studies on electrospinning phenomenon. Reneker and co-workers offered a good explanation for formation of bending instability using a mathematical model. [119, 121] The calculated results agreed well with their experimental observations. Also, Rutledge and co-workers reported that the electrospinning process is related to whipping of electrified jet. [122-125] The electrostatic interactions between the surface charges on the spinning jet and the external electric field cause mainly the whipping instability. In the instability region, stretching and acceleration of the spinning jet lead to formation of thin fibers.

These theoretical and experimental studies provide a better understanding of electrospinning mechanism, which can be used to control structure and diameter of electrospun fibers.

2.3.2. Experimental parameters on the fiber formation

The morphology and diameter of fibers are determined by a number of parameters which are generally divided into three kinds of factors as followings: (i) electrospinning solution (intrinsic properties), (ii) operational condition of electrospinning, (iii) ambient condition during electrospinning.

Solution parameters

Electrospinning solution is a very important to form fibers and determine the diameter. The solution parameters include sorts, molecular weight, and concentration of polymer, surface tension, solvent dielectric effect, viscosity and solution
conductivity. The viscosity and electrical conductivity of the spinning solution influence the stretching and acceleration of the spinning jet, which directly affects the morphology of resultant fibers. The surface tension plays an important role to control the bead formation along the fiber length.

The diameter of fiber is determined using above processing and solution parameter as followings: [234]

\[
h_f = \left( \frac{\gamma E Q^2}{I^2 \pi (2 \ln \varphi - 3)} \right)^{1/3}
\]

(2.1)

where \( h_f \) is the diameter of fiber, \( \gamma \) is the surface tension, \( E \) is the applied voltage (5-30 kV), \( Q \) is the feeding rate (0.2-15 ml h\(^{-1}\)), \( I \) is the electric current, the tip-to-collector screen distance: 5-20 cm, and \( \varphi \) is the dimensionless parameter of instability.

**Processing parameters**

Although the setup of electrospinning is very simple, there are a number of external parameters that can affect the morphology and diameter. The diameter of fiber is decreased with low feeding rate or high applied voltages, whereas it is possible to form fibers containing beads at low applied voltages or high feeding rate. The distance between tip and collector has also an effect on the morphology and diameter and it needs to be optimized for beads-free fibers. The fiber diameter is decreased with increasing distance to collector.

**Environmental parameters**
The interaction between the electrospinning solution and environmental parameters (e.g. humidity, temperature, pressure and type of atmosphere) can have an effect on morphology and diameter of fibers. Pores are formed on the surface because of different humidity level, from the inner region of electrospun fibers, which makes more difficult reproduction of electrospun fibers from the literature. Moreover, the evaporation rate of the solvent in electrospinning solution is determined by ambient humidity and temperature.

Apart from the above-mentioned parameters, the formation of electrospun fibers can be strongly influenced by various tools of electrospinning such as collectors, nozzles and collector substrates. The role of various parameters on the morphology and diameter is described in Table 1.
<table>
<thead>
<tr>
<th>Parameters</th>
<th>Effects on diameter and morphology of fibers</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Processing parameters</strong></td>
<td></td>
</tr>
<tr>
<td>Applied voltage [126]</td>
<td>Increase in applied voltage:</td>
</tr>
<tr>
<td></td>
<td>decreased fibers diameter and increased beading.</td>
</tr>
<tr>
<td>Feeding rate [94]</td>
<td>Decrease in feeding rate: decreased fibers diameter.</td>
</tr>
<tr>
<td></td>
<td>Increase in feeding rate: increased beading</td>
</tr>
<tr>
<td>Distance between tip and collector [127]</td>
<td>Increase in distance between tip and collector: decreased fiber diameter</td>
</tr>
<tr>
<td><strong>Solution parameters</strong></td>
<td></td>
</tr>
<tr>
<td>Viscosity [128]</td>
<td>Low viscosity: no continuous fiber</td>
</tr>
<tr>
<td></td>
<td>High viscosity: problem in ejection of jets</td>
</tr>
<tr>
<td>Solution conductivity [94]</td>
<td>Increase in solution conductivity: defect-free fiber and smaller diameter fiber</td>
</tr>
<tr>
<td>Polymer concentration [129]</td>
<td>Increase in polymer concentration: bigger fiber diameter and decreased beading</td>
</tr>
<tr>
<td>Polymer molecular weight [130]</td>
<td>Increase in polymer molecular weight: decreased beading</td>
</tr>
<tr>
<td>Solvent dielectric effect [131]</td>
<td>Increase in dielectric constant: decreased bead formation</td>
</tr>
<tr>
<td>Surface tension [132]</td>
<td>Important parameter to control bead formation</td>
</tr>
<tr>
<td>Solution temperature [128]</td>
<td>Higher solution temperature:</td>
</tr>
<tr>
<td></td>
<td>more uniform diameter.</td>
</tr>
<tr>
<td><strong>Environmental parameters</strong></td>
<td></td>
</tr>
<tr>
<td>Humidity [94]</td>
<td>High humidity: formation of pores on the surface</td>
</tr>
<tr>
<td>Temperature [94]</td>
<td>High temperature: smaller diameter fiber</td>
</tr>
<tr>
<td>Pressure [133]</td>
<td>Below atmospheric pressure:</td>
</tr>
<tr>
<td></td>
<td>Electrospinning is not possible</td>
</tr>
</tbody>
</table>
2.3.3. Modification

It is possible to fabricate desired structure through various electrospinning set-ups (a modification of spinneret or collector). Highly ordered and aligned structures are required for many applications such as photonic and electronic devices. To obtain aligned fibers, rotating drum collectors (Figure 2.4(a)) have been used at high speed by several groups. The aligned fibers are collected in the large area. Matthews and co-workers demonstrated the influence of the rotating speed of a drum collector on the degree of aligned electrospun fibers. When the rotating speed was less than 500

Figure 2.4 Schematic diagrams of (a) a rotating drum collector, (b) a knife-edge rotating disc collector, (c) a pair of spilt electrodes, (d) array of counter electrodes, (e) a coaxial spinneret and (f) multiple spinnerets. [85]
rpm, the fibers showed random orientation, however, the alignment of electrospun fibers was significant improved at 4500 rpm. [135] Even though aligned fibers were obtained by rotating drum collector, the degree of orientation was still far from perfect. Therefore, it is difficult to fabricate fibers with high alignment by using a drum collector and the resultant fibers could be easily broken when the rotating speed is too high.

To overcome these limitations, a knife-edge rotating disc collector has been developed to obtain highly aligned electrospun fibers (Figure 2.4(b)). [85] It has advantages of rotating motion and the convergence of electrospinning jet toward the disc collector because of electric field line. Highly aligned fibers are collected on the knife-edge rotating disc collector, however, when a mat is thicker on the knife-edge rotating disc collector, it is unable to retain the alignment of fibers at the same rotating speed. Li and co-workers demonstrated a pair of spilt electrodes to collect aligned fibers as a collector (Figure 2.4(c)). [98] The electrospun fibers were uniaxially aligned in the gap of a pair of electrodes whereas they had random orientation on a pair of electrodes during electrospinning process. The aligned fibers can be easily transferred to another substrate, however, there is a limitation of length. It is possible to form a pattern of the electrospun fibers by using a similar concept. The arrangement and pattern of fibers is determined as the location of electrodes (Figure 2.4(d)).

Coaxial spinneret design in Figure 2.4(e) is utilized for hollow fibers and core-shell structure. [98] By removing the core material through an extraction process or a thermal treatment after electrospinning, hollow fibers can be fabricated. The core-shell nanofibers can be obtained with desired functions and properties by two
different polymer solutions using a coaxial spinneret. However, coaxial electrospinning is rather complicated because of interface interaction, individual behaviour and mixing problem of two materials. Bi-component spinneret is a similar concept of a coaxial spinneret design. Bi-component fibers can be produced by two spinnerets side by side for unique functions.

Electrospinning is a limitation of fiber production due to small nozzle and low feeding rate of spinning solution. To solve this problem, a straightforward method has been employed by using multiple spinnerets (Figure 2.4(f)) which are devised for mass production of fibers. [136] Multiple spinnerets also have additional advantage of a composited electrospun mat.
2.4 Lithium ion batteries

Lithium ion batteries are one of the promising storage devices for portable electronics, large electric power storage units, electric vehicles (EVs) and power tools, which were commercialized by Sony in the early 1990s. Recently, lithium ion batteries have been used as a main power source for these devices because of their numerous advantages compared to other rechargeable batteries, such as lead acid, nickel cadmium, sodium-metal chloride and nickel-metal hydride. Lithium ion batteries have high energy density in comparison to other electrochemical storage systems because lithium has very light weight, the lowest redox potential and small ionic radius. They also have very low self-discharge rates and long cycle life.

2.4.1. Basics of operation

A lithium ion battery is an electrochemical cell which converts from chemical energy to electrical energy. It consists of three main components of a positive electrode (cathode), a negative electrode (anode) and an electrolyte. Li ions are intercalated into a negative electrode from a positive electrode via an electrolyte by external electrical energy during the charge process. The external electrical energy is then stored as chemical energy. During the discharge process, Li ions intercalated in the negative electrode are transferred through the electrolyte into the positive electrode while electrons go through a closed external circuit. A schematic diagram of conventional lithium ion cell (Graphite/LiCoO$_2$) is shown in Figure 2.5. The following equations show the reaction mechanisms of conventional lithium ion cell:

$$LiCoO_2 \leftrightarrow Li_{1-x}CoO_2 + xLi^+ + xe^- \quad (2.2)$$
\[ C + xLi^+ + xe^- \leftrightarrow Li_xC \] (2.3)

### 2.4.2. Nanomaterials for lithium ion batteries

Nanomaterials have attracted considerable attention for lithium ion storage devices because of significantly altered materials properties. The first-generation lithium ion battery consists of electrodes of millimeter-sized powder, and millimeter-sized pores of a separator trap the electrolyte. Even though the first-generation lithium ion battery has a high energy density, the battery is a low power device (slow

**Figure 2.5** A schematic diagram of conventional lithium rechargeable battery (Graphite/LiCoO$_2$). [138]
charge/discharge). The use of nanomaterials enhances the performance of lithium ion batteries, such as high intercalation/deintercalation rates and short lithium diffusion lengths due to their reduced dimensions however, there are also some disadvantages of nanomaterials. [139]

**Advantages**

First of all, a new reaction mechanism, so-called conversion can occur in a reaction between lithium and nanostructured electrodes, resulting in higher capacity and power density. Such new mechanisms of transition metal oxide, sulfides, nitrides and fluorides at the nanoscale have been reported as anode materials. [140-143] The reaction mechanism is different from classical Li insertion/extraction or Li alloying process. The classical and conversion mechanism is described by the following equations: [144]

\[
M_1 + xLi^+ + xe^- \leftrightarrow Li_xM_1
\]  
\[
M_2X + yLi^+ + ye^- \leftrightarrow M_2 + Li_yX
\]

where \(M_1\) is Si, Sn, Pb, Bi, Ag or a multicomponent alloy, \(M_2\) is transition metals (Fe, Ni, Cu, Co, etc.) and \(X\) is anions (N,P, F,S, O, etc.). The major difference from classical mechanism is the involvement of formation and decomposition of \(Li_xX\) or a Li alloy. [144]

Second, nanostructured materials can provide shortened Li\(^+\) diffusion pathways for enhanced electrochemical performances because of the reduced particle size. [145] Especially, Li\(^+\) transport plays an important role during high rate charge/discharge process. The Li\(^+\) diffusion in host electrode materials is related with Li\(^+\) diffusion
length and diffusion coefficient. The characteristic time for diffusion is given by following equation: [145]

\[ \tau = \frac{L^2}{D} \]  

(2.6)

where \( L \) is \( \text{Li}^+ \) diffusion length which is associated with the particle size for intercalation. \( D \) is \( \text{Li}^+ \) diffusion coefficient, which depends on property of electrode materials. The time (\( \tau \)) for intercalation decreases with square of the \( \text{Li}^+ \) diffusion length. Therefore, reducing particle size is an effective way for enhancing the rate capability in lithium rechargeable batteries because of shortened \( \text{Li}^+ \) diffusion pathways.

Lastly, nanomaterials offer a higher contact area between the electrode and electrolyte compared to electrodes of micron-sized particle owing to the large surface area, resulting in high capacity, stable cycle and high rate performance. [144] The overall capacity of surface Li storage depends on the surface area and the accessible site for \( \text{Li}^+ \) in the host materials. The amount of surface-stored \( \text{Li}^+ \) rises with a reduction of particle size because the surface site and near surface site have higher activity than the bulk site. A large electrode/electrolyte contact area is thus beneficial for enhanced electrochemical properties.

**Disadvantages**

Nanostructured materials generally exhibit low density in comparison to micro-sized materials. Consequently, the packing density of nanostructured electrodes is lower than that of micro-sized electrodes. The low volumetric energy density limits applications of nanomaterials, especially for electric vehicle. To solve this issue, Zhou and co-workers suggested that two kinds of nanomaterials with different
morphology (nanowires and nanoparticles) were mixed to increase the density of electrode. [146-147] This method is an effective way to enhance not only the packing density but also the electronic transfer. In addition, mixing nanomaterials and micromaterials also should be an effective method to raise the packing density of the electrode because the nano-sized materials can occupy the interspace among the micro-sized materials.

The high surface area of nanostructured materials may, however, lead to the risk of more significant side reactions between electrode and electrolyte, which results in poor cycle performance and high irreversibility. Surface coating can be a solution to alleviate the undesired surface reaction. For example, carbon coating on the electrode surface can prevent the direct contact between the nanomaterials and electrolyte, since Li ions can pass through the coating layer while the solvent molecules of electrolyte cannot pass through the carbon coating layer. [148] It is also difficult to uniformly control the morphology and dimensions.

2.4.3. Core-shell structure for lithium rechargeable battery electrodes

Core-shell structures (Figure 2.6) [149] provide a prospective strategy to solve the existing obstacles, such as their poor electronic transport and large volume changes, in lithium rechargeable battery electrodes during charge/discharge processes. In general, the core is an active material for the lithium rechargeable battery, while the shell acts as a protection layer to enhance the performance of the core component or to bring physical or chemical properties. [150] The enhanced performance of core-shell structure is contributed to the advantages as followings:
1) The exterior shell can shield the core material as a protective layer between the core and electrolyte.

2) The outer shell can suppress the disintegration of core materials due to the repeated volume changes during cycling.

3) The shell can serve as an enhanced electrical pathway by its high conductivity.

4) The shell can strengthen physical or chemical properties of the core-shell structured electrodes.

5) The exterior shell can allow ions or molecules to selectively percolate into the

![Figure 2.6](image)

**Figure 2.6** Schematic illustrations of various core-shell structures with (a) a single core, (b) multiple cores, (c) multiple shells, and (d) a raspberry-like core. [149]
Core-shell structures for cathode and anode materials in lithium ion batteries have been fabricated by various methods, such as chemical vapor deposition (CVD), thermal vapor deposition (TVD), hydrothermal, solvothermal, sol-gel, and atomic layer deposition (ALD). These methods, however, need two step processes and it is difficult to control desired morphologies. Alternatively, electrospinning is a simple technique to fabricate fibrous core-shell structures using a coaxial spinneret. Compared with single-component structure, core-shell structures often exhibit superior mechanical, thermal and electrical properties.

### 2.4.4. Porous materials for lithium rechargeable battery electrodes

Porous materials have been widely used in various applications, such as catalysts, gas storages, sensors, energy storages, etc. [151] They can be classified according to their pore size (micropores: < 2 nm, mesopores: 2-50 nm, and macropores: >50 nm) and morphologies (ordered and disordered). One can also distinguish between “textural porosity” and “integral porosity. The pores are created by voids from the packing of particles on a current collector (textural porosity), and the pores are an integral part of a continuous solid framework (integral porosity). Therefore, the pore size is usually correlated to the particle size in texturally porous materials, whereas integrally porous materials are independent of their particle size.

The porous materials offer important benefits in cathodes and anodes for electrochemical energy storage systems in the followings [152]:

1) Porous materials allow an easy access of the electrolyte due to existence of the pores.
2) Porous materials offer shortened Li\(^+\) diffusion pathways because the walls surrounding the pores in active materials are very thin.

3) The surface area is relatively large, so that charge transfer in the interface between electrode and electrolyte is enhanced.

4) The porous structure of active materials makes it possible to be fully used their surface area due to their high surface-area-to-volume-ratio, so that specific capacities can be improved at high charge/discharge rates.

The reserved void spaces of active materials can help to alleviate huge volume changes of active materials during repeated charge/discharge processes.

2.4.5. Ti-based oxide materials for lithium rechargeable batteries

Titanium-oxide-based materials are considered as potential anode materials for energy storage systems due to their advantages such as cost-effectiveness, excellent functionality, long term stability, non-toxicity, thermal stability, and environmental friendliness. [139, 153] Among Ti-based nanostructured materials, titanium dioxides (TiO\(_2\)) and lithium titanium oxide (Li\(_4\)Ti\(_5\)O\(_{12}\)) are promising materials as an anode for lithium ion batteries. These materials have several advantages: (i) intrinsic safety without lithium plating on the electrode because of higher electrochemical lithium reaction voltages than graphite, (ii) low or negligible volume change during charging/discharging process. Therefore, outstanding structure stability of these materials provides long cycle life in Lithium ion batteries.

2.4.5.1. TiO\(_2\)

TiO\(_2\) are well-known to have various polymorphs including rutile, anatase, brookite,
TiO$_2$-B (bronze), TiO$_2$-R (ramsdellite), TiO$_2$-H (hollandite), TiO$_2$-II (columbite) and TiO$_2$-III (baddeleyite), and the theoretical calculated capacity is 335 mAh g$^{-1}$. [154-165] TiO$_2$ polymorphs follow the electrochemical reaction of TiO$_2$ during intercalation/deintercalation:

$$\text{TiO}_2 + x\text{Li}^+ + xe^- \leftrightarrow \text{Li}_x\text{TiO}_2$$  \hspace{1cm} (2.7)

where x is varied from 0 to 1 according to TiO$_2$ polymorphs, morphologies and their sizes. This redox reaction implies the creation of electrons compensating Ti$^{III}$ cations in the Ti$^{IV}$ sublattice as well as the insertion of positively charged Li$^+$. This is supported by theoretical calculations and observed in X-ray photoelectron spectroscopy (XPS) experiments. [166,167]

Rutile TiO$_2$ is the most thermodynamically stable form of TiO$_2$. Figure 2.7 shows the structure of rutile TiO$_2$. [164] The bulk rutile TiO$_2$ can accommodate a negligible amount of Li ions (<0.1 Li per TiO$_2$ unit) at room temperature, [168-170] however, the lithium reactivity is increased at 120°C, resulting in full lithium loading ($x=1$). [170,171] Rutile TiO$_2$ is thus thermodynamically favorable during Li$^+$ insertion. Li$^+$ diffusion of rutile TiO$_2$ is highly anisotropic because Li$^+$ diffusion coefficient along the $c$-direction (diffusion coefficient is about $10^{-6}$ cm$^2$s$^{-1}$) is faster than that of the $ab$-plane (diffusion coefficient is about $10^{-15}$ cm$^2$s$^{-1}$). [172-174] Moreover, the repulsive interactions between Li ions in the $c$-direction and the trapped Li ions pairs in $ab$-planes obstruct further Li$^+$ insertion. [172,173] However, Liu and co-workers reported that mesoporous rutile TiO$_2$ accommodated excellent Li insertion activity up to 0.7 mol of Li at the first discharge and showed excellent cycle performance over 100 cycles at 1C rate. [179] Therefore, it is very difficult for bulk rutile TiO$_2$ to insert Li$^+$ and only a negligible amount of Li ions can be accommodated into rutile
Table 2.2 Morphology and electrochemical performance of rutile TiO$_2$.

<table>
<thead>
<tr>
<th>Morphology</th>
<th>Particle size (nm)</th>
<th>Current rate (mA g$^{-1}$)</th>
<th>Reversible capacity (mAh g$^{-1}$)</th>
<th>Capacity retention (cycle number)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Commercial nanoparticles [175]</td>
<td>15</td>
<td>50</td>
<td>264</td>
<td>90% (n = 2–20)</td>
</tr>
<tr>
<td>Commercial nanoparticles [176]</td>
<td>50</td>
<td>30</td>
<td>37</td>
<td>94% (n = 1–15)</td>
</tr>
<tr>
<td>Nanorod [176]</td>
<td>200</td>
<td>30</td>
<td>160</td>
<td>94% (n = 1–50)</td>
</tr>
<tr>
<td>Nanoparticles [177]</td>
<td>40–50</td>
<td>33</td>
<td>225</td>
<td>89% (n = 2–30)</td>
</tr>
<tr>
<td>(N,F) co-doped TiO$_2$ [178]</td>
<td>10–20</td>
<td>30</td>
<td>210</td>
<td>80% (n = 2–60)</td>
</tr>
</tbody>
</table>

Figure 2.7 Structure of rutile TiO$_2$. [164]
TiO$_2$ while nanostructured rutile TiO$_2$ could be significantly improved. The electrochemical properties of nanostructured rutile TiO$_2$ are described in Table 2.2.

Anatase TiO$_2$ can accommodate more Li ions in comparison to rutile TiO$_2$. The crystal structure of anatase TiO$_2$ is shown in Figure 2.8. [164] Li$^+$ can be delivered up to 0.5 mol in the bulk anatase TiO$_2$ with a flat voltage profile, which indicates a classic bi-phase electrochemical reaction during Li insertion/extraction. [180-182] During the insertion, anatase TiO$_2$ converts into a mixture of tetragonal Li$_{0.05}$TiO$_2$ and Li rich orthorhombic Li$_{0.5}$TiO$_2$. The overall orthorhombic distortion from anatase TiO$_2$ to lithium titanate is small and symmetrical, which leads to less than 4% volume change. [191] Therefore, it has been reported that bulk anatase TiO$_2$ can be accommodated up to 0.5 mol Li ion with a small volume change as the maximum electrochemical insertion. Similar to rutile TiO$_2$, anatase nanoparticles alter electrochemical reaction and Li$^+$ reactivity, and nanostructured anatase TiO$_2$ leads to improved capacity over 0.5 Li because of different Li reaction mechanisms and surface-confined charge storage. [192, 193] The cycle performance of nanostructured

![Figure 2.8 Structure of anatase TiO$_2$. [164]](image-url)
Table 2.3 Morphology and cycle performance of nanostructured anatase TiO$_2$.

<table>
<thead>
<tr>
<th>Morphology</th>
<th>Particle size (nm)</th>
<th>Current rate$^a$</th>
<th>Reversible capacity (mAh g$^{-1}$)</th>
<th>Capacity retention (cycle number)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mesoporous [183]</td>
<td>9 (XRD)</td>
<td>8 C (1C = 168 mA g$^{-1}$)</td>
<td>157</td>
<td>84% (n = 1–50)</td>
</tr>
<tr>
<td>Hollow nanospheres [184]</td>
<td>28</td>
<td>0.5 C</td>
<td>198</td>
<td>94% (n = 50)</td>
</tr>
<tr>
<td>Nanosheets [185]</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Nanoparticles [186]</td>
<td>20</td>
<td>0.5C (1C = 160 mA g$^{-1}$)</td>
<td>180</td>
<td>89% (n = 2–150)</td>
</tr>
<tr>
<td>Hollow peanuts [187]</td>
<td>100–200</td>
<td>0.1 C</td>
<td>156 (2nd discharge)</td>
<td>77% (n = 2–30)</td>
</tr>
<tr>
<td>Hollow Microspheres with nanotubes [188]</td>
<td>30 diam, 5 thickness (TEM)</td>
<td>1C</td>
<td>220</td>
<td>68% (n = 2–500)</td>
</tr>
<tr>
<td>Rice grain shape [190]</td>
<td>20 (XRD)</td>
<td>0.45 C</td>
<td>162</td>
<td>81% (n = 10–800)</td>
</tr>
<tr>
<td>Rice grain/4 wt % CNT composite [189]</td>
<td>21</td>
<td>0.45 C</td>
<td>139</td>
<td>93% (n = 10–800)</td>
</tr>
<tr>
<td>Nanofibers [189]</td>
<td>18</td>
<td>0.45C</td>
<td>144</td>
<td>92% (n = 10–800)</td>
</tr>
<tr>
<td>Nanoparticles [190]</td>
<td>9</td>
<td>1 C</td>
<td>160</td>
<td>83% (n = 50)</td>
</tr>
</tbody>
</table>

$^a$ current rate 1C = 335 mA g$^{-1}$
anatase TiO₂ is given in Table 2.3.

Bronze or TiO₂-B, which is a monoclinic (space group $C2/m$) structure consisting of edge- and corner-sharing TiO₆ octahedra (Figure 2.9), [164] is a promising host for Li⁺ insertion among all TiO₂ polymorphs because of a one-dimensional infinite channel, which indicates more open crystal structure with density of 2.73 g cm⁻³ compared to anatase (3.89 g cm⁻³) and rutile TiO₂ (4.25 g cm⁻³). [194] The open framework structure can accommodate the volume change without distortion of TiO₂-B structure and permit facile Li transport within TiO₂-B. The insertion amount of Li⁺ in TiO₂-B is up to about 0.85 mol at room temperature. [195] Therefore, TiO₂-B is a superior insertion host for Li⁺ in comparison to other TiO₂ polymorphs. Electrochemical performance of TiO₂-B is summarized in Table 2.4.

Even though nanostructuring TiO₂ polymorphs leads to enhanced Li insertion properties due to shortened Li⁺ diffusion pathways, the charge transport of TiO₂ is considerably slow due to its low electrical conductivity, which limits the overall Li electrochemical activity of TiO₂. For example, nanostructured TiO₂ polymorphs such

![Figure 2.9 Structure of TiO₂-B. [164]](image-url)
Table 2.4 Morphology and electrochemical properties of TiO$_2$-B.

<table>
<thead>
<tr>
<th>Morphology</th>
<th>Particle size (nm)</th>
<th>Current rate (mA g$^{-1}$)</th>
<th>Reversible capacity (mAh g$^{-1}$)</th>
<th>Capacity retention (cycle number)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nanowires [196]</td>
<td>20–40</td>
<td>50</td>
<td>205</td>
<td>90% (n = 2–100)</td>
</tr>
<tr>
<td>Nanotubes [165]</td>
<td>diameter: 10</td>
<td>thickness: 2.5</td>
<td>20</td>
<td>237</td>
</tr>
<tr>
<td>Nanoparticles [161]</td>
<td>10</td>
<td>35</td>
<td>210</td>
<td>76% (n = 2–40)</td>
</tr>
<tr>
<td></td>
<td>16</td>
<td>35</td>
<td>148</td>
<td>40% (n = 2–50)</td>
</tr>
<tr>
<td></td>
<td>33</td>
<td>35</td>
<td>45</td>
<td>78% (n = 2–50)</td>
</tr>
<tr>
<td>Nanosheets [197]</td>
<td>thickness: 5–10</td>
<td>10 C</td>
<td>216</td>
<td>94% (n = 2–200)</td>
</tr>
<tr>
<td>Nanoparticles [198]</td>
<td>20–25</td>
<td>0.2C</td>
<td>200</td>
<td>86% (n = 2–10)</td>
</tr>
</tbody>
</table>
as nanoparticles, nanowires and nanotubes still have a substantial irreversible capacity at the first cycles due to the poor electronic conductivity. Nanostructured composite structures with the electrically conductive additives have been developed a promising approach due to both shortened Li transport distances and fast electron transport. Guo and co-workers reported superior electrochemical performance of nanostructured mesoporous TiO$_2$ (anatase) through efficient hierarchical mixed provided good electrical conductivity and highly conducting paths for electrons in a three-dimensional network. [199] This nanostructured network gave very fast Li$^+$ diffusion, enhanced electrical conductivity, and possibly faster phase transformation reactions. The TiO$_2$ with RuO$_2$ showed a specific capacity of about 214, 190, 147, and 125 mAh g$^{-1}$ at 0.2, 1, 5, and 10 C rate, respectively. At a high rate of 30 C, the specific charge capacity is still 91 mAh g$^{-1}$, which is about two times larger than that of anatase TiO$_2$ (48 mAh g$^{-1}$) with 5 nm in size and nine times larger than that of mesoporous anatase TiO$_2$ spheres (10 mAh g$^{-1}$) without a conductive additive. Liu and co-workers [200] reported self-assembled rutile TiO$_2$/graphene hybrid nanostructures. This nanostructured material demonstrated enhanced Li-ion insertion/extraction kinetics at high charge/discharge process and an excellent cycle performance. Indeed, the electrochemical performance of rutile TiO$_2$/graphene composite is even better than that of the hierarchical TiO$_2$/RuO$_2$ composite. The specific capacity of the rutile TiO$_2$/graphene hybrid composite was 87 mAh g$^{-1}$, which is more than two times the high capacity (35 mAh g$^{-1}$) of the bare rutile TiO$_2$ at a rate of 30C due to the high electron conductivity of graphene.

Recently, Han and co-workers have investigated nitridated hollow TiO$_2$ as the anode for lithium ion batteries. [201] The nitridated hollow TiO$_2$ was fabricated by an electrospinning with a core-sheath nozzle through an ammonia treatment. The
nitridated nanotubes exhibited a higher capacity than TiO$_2$ nanofibers due to the larger surface area, the shortened diffusion length of the lithium ions and high conductivity. Park and co-workers further investigated SnO$_2$@TiO$_2$ nanotubes through a coaxial electrospinning as anode materials for lithium ion batteries. The specific capacity of hollow SnO$_2$@TiO$_2$ nanofibers was around 500 mAh g$^{-1}$ after 100 cycles, and the hollow nanofibers could provide large reaction surface area and reserved void space, undergoing the repeated volume change during the lithiation and delithiation processes.

2.4.5.2. Li$_4$Ti$_5$O$_{12}$

Spinel Li$_4$Ti$_5$O$_{12}$ (LTO), as an alternative anode to carbon, is a promising candidate for high power Li rechargeable batteries as well as hybrid supercapacitors. It can accommodate 3 mol of Li during intercalation, with a theoretical capacity of 175 mAh g$^{-1}$, resulting in a structural transition from spinel-Li$_4$Ti$_5$O$_{12}$ to rock-salt phase Li$_7$Ti$_5$O$_{12}$. [202] The structure of spinel-Li$_4$Ti$_5$O$_{12}$ and rock-salt Li$_7$Ti$_5$O$_{12}$ are illustrated in Figure 2.10, and the following equation shows the electrochemical reaction of Li$_4$Ti$_5$O$_{12}$ during intercalation/deintercalation:

$$Li_4Ti_5O_{12} + 3Li^+ + 3e^- \leftrightarrow Li_7Ti_5O_{12} \quad (2.8)$$

During Li$^+$ intercalation/deintercalation, Li$_4$Ti$_5$O$_{12}$ undergoes a negligible volume change of only 0.2% as zero strain material, resulting in long-term cycling stability. [203-205] Furthermore, it has little electrolyte decomposition and safe operation due to its high equilibrium potential, showing relatively high operating voltage (~1.55 V vs. Li/Li$^+$). Despite its several merits, it still shows poor rate capability due to a very low electrical conductivity at room temperature ($10^{-13}$ Scm$^{-1}$) because of empty Ti 3d
state with band energy of around 2 eV, which is inherently insulating properties. [206,207] In order to overcome this issue, various methods have been suggested to improve electrical conductivity via surface coating with conductive materials, reducing particle size or doping metal elements to achieve metallic substitution. Zhu and co-workers reported Li₄Ti₅O₁₂/graphene composites, which had a specific surface area of 170 m² g⁻¹, by electrospinning, and the nanosized Li₄Ti₅O₁₂ were coated by a uniform graphene sheet. [208] The Li₄Ti₅O₁₂/graphene composites exhibited high C-rate capability and excellent cycling stability. The specific capacity of Li₄Ti₅O₁₂/graphene composites was 164 and 137 mAh g⁻¹ at 0.2 C and at 8 C, respectively. At 22 C rate, the Li₄Ti₅O₁₂/graphene gave a specific capacity of 110 mAh g⁻¹, which is more than twice the capacity of the Li₄Ti₅O₁₂ nanofibers (47 mAh g⁻¹). The composite retained 91% of the initial capacity after 1300 cycles. Jung and co-workers investigated bare and Carbon-coated Li₄Ti₅O₁₂. [209,210] The electronic

**Figure 2.10** Structure of (a) spinel Li₄Ti₅O₁₂. Blue tetrahedra represent lithium, and green octahedra represent disordered lithium and titanium. (b) rock salt Li₇Ti₅O₁₂. Blue octahedra represent lithium, and green octahedra represent disordered lithium and titanium. [202]
conductivity of C-coated Li$_4$Ti$_5$O$_{12}$ increased from $1.58 \times 10^{-9}$ to $5.24 \times 10^{-3}$ S cm$^{-1}$. C-coated Li$_4$Ti$_5$O$_{12}$ showed excellent cycle performance because of its high conductivity. The specific capacity of C-coated Li$_4$Ti$_5$O$_{12}$ was 165 mAh g$^{-1}$ up to 100 cycles at 1 C rate while the bare Li$_4$Ti$_5$O$_{12}$ showed much smaller capacity, which was 55 mAh g$^{-1}$ at 1 C. Therefore, carbon materials provided excellent electrochemical performance particularly, good rate capability and cycle performance because of highly conductive characteristics.

Ion doping is an effective and direct way to improve the intrinsic material properties of Li$_4$Ti$_5$O$_{12}$ materials. Such doping of ion into the Li$_4$Ti$_5$O$_{12}$ lattice offers enhanced electronic conductivity through the substitution of metal ions on the Ti$^{4+}$ or Li$^+$ sites and hence, an increase in the amount of mixed Ti$^{3+}$/Ti$^{4+}$ states as charge compensation, consequently increasing the concentration of electrons. [211-220] Various cations and anions, such as Mg$^{2+}$, La$^{3+}$, Ni$^{3+}$, Mn$^{3+}$, Al$^{3+}$, Co$^{3+}$, Fe$^{3+}$, Ga$^{3+}$, La$^{3+}$, Cr$^{3+}$, V$^{4+}$, Mo$^{4+}$, Zr$^{4+}$, V$^{5+}$, F$^-$ and Br$^-$ have been used to be doped into Li$^+$, Ti$^{4+}$ and O$^{2-}$ sites. The ion valence and distribution, structural properties and conductive characteristics were also investigated. [211-244] The doping ions could enter the Li$_4$Ti$_5$O$_{12}$ lattice to strongly affect its structure and change of the electrochemical performances such as specific capacity, cycle stability and rate capability. The electrochemical performances of Li$_4$Ti$_5$O$_{12}$ are summarized in Table 2.5.
Table 2.5 Morphology and Electrochemical performance of spinel Li₄Ti₅O₁₂.

<table>
<thead>
<tr>
<th>Morphology</th>
<th>Particle size (nm)</th>
<th>Current rate (mA g⁻¹)</th>
<th>Reversible capacity (mAh g⁻¹)</th>
<th>Capacity retention (cycle number)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Submicrosized LTO [245] submicro-sized</td>
<td>0.2C</td>
<td>140</td>
<td></td>
<td>98% (n = 35–100)</td>
</tr>
<tr>
<td>Mg-substituted LTO [246] diameter: 10</td>
<td>0.5 C</td>
<td>169</td>
<td></td>
<td>87% (n = 2–8)</td>
</tr>
<tr>
<td>Nanowires [247]</td>
<td>0.3C</td>
<td>142</td>
<td></td>
<td>86% (n = 1–15)</td>
</tr>
<tr>
<td>3D network nanoarchitecture [248]</td>
<td>&lt;100</td>
<td>0.5C</td>
<td>140</td>
<td>73% (n = 1–30)</td>
</tr>
<tr>
<td>Nano flowers [249] diameter: 300–500</td>
<td>0.2C</td>
<td>167</td>
<td></td>
<td>77% (n = 1–100)</td>
</tr>
<tr>
<td>Porous 3D network [250] 20–50</td>
<td>1C</td>
<td>158</td>
<td></td>
<td>98% (n = 2–100)</td>
</tr>
<tr>
<td>Nanofibers [251]</td>
<td>200</td>
<td>1C</td>
<td>148</td>
<td>97% (n = 50–380)</td>
</tr>
<tr>
<td>LTO/CNT composites [252] ∼50</td>
<td>1C</td>
<td>170</td>
<td></td>
<td>99% (n = 2–100)</td>
</tr>
<tr>
<td>Porous microsphere [253] Spheres: 4μm, particles: 33 nm</td>
<td>2C</td>
<td>147.4</td>
<td>95% (n = 2–200)</td>
<td></td>
</tr>
<tr>
<td>Nanostructured spherical LTO [254] Spheres: 1-2 μm</td>
<td>1C</td>
<td>155</td>
<td>95% (n = 2–200)</td>
<td></td>
</tr>
</tbody>
</table>
2.4. 6. Si-based materials for lithium rechargeable batteries

Silicon is considered as one of the most promising anode materials for Li rechargeable batteries because it has the highest volumetric and gravimetric capacity and is also abundant, cost-effective and environmentally friendly. Each Si atom can accommodate 4.4 mol of Li during alloying process. [255] Silicon reacts with lithium to form several intermetallic compounds such as Li_{12}Si_{7}, Li_{7}Si_{3}, Li_{13}Si_{4}, and Li_{22}Si_{5} during electrochemical reactions. [256] The theoretical capacity of Li_{22}Si_{5} is 4200 mAhg\(^{-1}\), which is more than 10 times in comparison with graphite. During the lithiation process, Si converts into the amorphous at room temperature and the electrochemical reaction of Si is described by the following equation:

\[
Si + xLi^{+} + xe^{-} \leftrightarrow Li_{x}Si
\]  

Si has the low reaction potential of about 0.4V against Li/Li\(^+\), which enables high voltage battery. Although Si has the high specific capacity, however, it exhibits over 300% volume expansion, [255] which leads to rapid mechanical degradation of the Si materials during repeated electrochemical reaction, resulting in poor cycle performance. Furthermore, the volume expansion and contraction during cycling will cause irreversible capacity because of formation of new surfaces arising from pulverization. To overcome this issue, Si nanowires have been investigated to overcome the issue by Chan and co-workers, showing a reversible capacity of over 3000 mAhg\(^{-1}\) for 10 cycles with little capacity fading. [257] In addition, porous silicon structures, reduction of Si particles size, and core-shell structure are also effective methods. [258-261] For example, Hwang and co-workers fabricated a core–sheath Si@carbon nanofibers consisted of a porous assembly of Si-nanoparticles as the core, and the carbon wall as the shell structure for lithium ion batteries. [262] The
Si@carbon extraction capacity was 1491 mAh$^{-1}$ at 0.1 C in the first cycle. At 0.2 C rate, Si@carbon nanofibers exhibited a high discharge capacity around 1250 mAh g$^{-1}$ with a nearly 100% retention over 100 cycles and excellent cycling performance after 300 cycles at a high rate of 3 C. The electrochemical performance was determined mainly by the stability of the solid electrolyte interphase (SEI) and the contact between Si nanoparticles and carbon matrix. Because the Si volume expansion at high current rates was not that considerable, the SEI layers were more stable and thus more reversible charge–discharge reaction occurred.
2.5 References


3 STRUCTURALLY AND ELECTRONICALLY DESIGNED TiO$_2$N$_x$ NANOFIBERS FOR LITHIUM RECHARGEABLE BATTERIES

3.1 Introduction

Titanium dioxide, TiO$_2$, is a window semiconductor material for photocatalysts, photovoltaic cells, gas sensors, and other electrochemical devices, [1,2] owing to its wide band gap (3.2 eV), cost-effectiveness, and non-toxic nature. In particular, rationalizing the morphology of TiO$_2$ undoubtedly plays a key role in enhancing its electronic or electrochemical performance. From the viewpoint of an electrode material for the lithium rechargeable battery, TiO$_2$ can yield a considerable advantage in terms of its rate performance governed by electronic conductivity, as well as in electrochemical versatility due to its various polymorphs. [3-14] Based on previous report, [2,14] the TiO$_2$-B polymorph is an ideal host for Li$^+$ intercalation because it has a relatively open tunnel structure compared to anatase, rutile, and brookite. Anatase also has the same sort of mesoporous structure, and in addition, its long voltage plateau obtained during Li$^+$ insertion/extraction is definitely ideal for use in lithium rechargeable batteries. However, repeated charge and discharge tend to quickly drive down the capacity of anatase due to its poor Li$^+$ conductivity and electronic conductivity. As various synthetic methods have been suggested with the development of nanotechnology, it might be expected that the lithium storage performance of polymorph TiO$_2$ nanostructures could be superior to the current state-of-the-art performance if a favourable architecture for electron or Li$^+$ transport is found. To achieve these aims, the one-dimensional (1D) nanostructure has been regarded as one of the most promising types. In particular, the 1D architecture has received great attention due to not only its unique structural characteristics, but also
because of its tuneable intrinsic properties, [15-18] i.e., \( \text{Li}^+ \) intercalation and conductivity. For this purpose, application of the electrospinning process can be suggested as an easy and economical way to improve the lithium storage performance of TiO\(_2\) due to the merits of 1D structure that are associated with it, such as facilitated ion transport and enhanced electronic conductivity.

In this chapter, therefore, nitrogen-doped TiO\(_2\) nanofibers were fabricated by electrospinning, in which diethylenetriamine was used as nitrogen source for preparation of the precursor solution. The effect of nitrogen doping on the phase formation, microstructure, electronic structure, and electrochemical properties of TiO\(_2\) nanofibers was examined for application of lithium rechargeable batteries. The site for nitrogen doping will be clarified by correlating the experimental probe with first-principle calculation for nitrogen-doped TiO\(_2\) nanofibers.
3.2 Experimental

3.2.1 Preparation of bare TiO$_2$ and TiO$_2$N$_x$ nanofibers and structural characterization

For the two kinds of TiO$_2$ nanofibers, 1.5 g of titanium isopropoxide was mixed with ethanol and 0.5 ml of acetic acid. After 1 hour, this solution was added into 5 ml of ethanol, containing of 4.5 wt% polyvinylpyrrolidone (PVP), followed by magnetic stirring for 1 hour. For nitrogen-doped TiO$_2$ nanofibers, 0.1 ml of diethylenetriamine as nitrogen source was added to the Ti precursor solution. The yellow transparent spinning solution was immediately loaded into a plastic syringe equipped with a 23 gauge needle. The needle was connected to a high voltage supply, and the feeding rate for the precursor was set at 0.5 mlh$^{-1}$. A distance of 9 cm and voltage of 15 kV were maintained between the tip of the needle and the drum collector. After the electrospinning, the as-spun nanofibers were left in air for 24 hours to obtain anatase TiO$_2$ nanofibers. The nanofibers were heat-treated in air at 450$^\circ$C for 1 hour to remove PVP. The morphology and structure of the nanofibers were characterized by field emission-scanning electron microscopy (FE-SEM), and transmission electron microscopy (TEM). Nitrogen doping into TiO$_2$ was further studied by using X-ray photoelectron spectroscopy (XPS) and Fourier transform infrared spectroscopy (FTIR).

3.2.2 Electrochemical performance

Coin-type half cells (CR2016) were assembled to evaluate the anodic performances of the two kinds of 1D TiO$_2$ nanofibers and the TiO$_2$ nanoparticles. In this experiment, 1D TiO$_2$ nanofibers or TiO$_2$ nanoparticles were used as the active
electrode. Each electrode was fabricated by mixing each active material, acetylene black, and polyvinylidene fluoride (PVDF) at a weight ratio of 75:17:8 using N-methylpyrrolidone (NMP) as a solvent. After coating the slurry on Al foil, they were dried at 120 °C for 5 h under vacuum. The assembly was carried out in an Ar-filled glove box with less than 0.1 ppm each of oxygen and moisture. Li metal foil was used as the counter and reference electrode, and 1M LiPF₆ dissolved in a 1:1 (by volume) mixture of ethylene carbonate (EC) and diethyl carbonate (DEC) was employed as the electrolyte. A polypropylene (PP) film was used as separator.

Charge (Li⁺ insertion)-discharge (Li⁺ extraction) tests were performed up to the 40 cycles in the range of 1 to 3 V (vs. Li/Li⁺). Electrochemical impedance spectroscopy (EIS) analysis of the coin half-cells were performed using a Iviumstate potentiostat/galvanostat (Ivium Technologies, Netherlands). The EIS frequency ranged from 100 kHz to 0.1Hz and the EIS ac perturbation amplitude was 5mV for room temperature measurements. Data acquisition and analysis were done respectively using the electrochemical impedance software, ZPlot and Zview (Version 3.0, Scribner Associates, Inc., USA).

3.2.3 First principles calculations

Spin-polarized density functional theory (DFT) calculations were performed using the periodic plane wave approach, as implemented in the Vienna Ab-initio Simulation Package (VASP) code [19,20] in the generalized gradient approximation (GGA) using the Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional. [21] Frozen-core projector augmented wave pseudopotentials were used.[22,23] A special 3 × 3 × 1 k-point sampling was applied for the surface Brillouin zone integration. The plane wave basis set was restricted by the cut-off energy of 400 eV.
The anatase (101) surface was modelled with a periodically repeated slab of four TiO$_2$ layers (twelve atomic layers) separated by a vacuum of 20 Å width. A super cell contained 96 atoms, with surface cell parameters $u = 10.972$ Å, $v = 7.569$ Å, $\alpha = 110.18^\circ$. These optimized lattice parameters are taken from another calculation on bulk anatase phase. Total energies are converged to $10^{-6}$ eV. All structures were fully optimized, with the largest residual force smaller than 0.01 eV Å$^{-1}$. The atoms in the bottom layer were fixed to their bulk positions during geometry optimizations, in order to simulate the presence of the bulk underneath.
3.3 Results and discussion

The configuration and crystalline microstructure of the bare and nitrogen-doped TiO$_2$ fibers produced in this work can be directly seen in the scanning electron microscope (SEM) and high magnification transmission electron microscope (TEM) images in Figure 3.1. In the Figure 3.1(a) and (b), the diameters of the two kinds of fibers were estimated to be 100-200 nm. Interestingly, there was no noticeable change through nitrogen doping. The morphology of the two types of TiO$_2$ fibers was further observed by bright field TEM, as shown in Figure 3.1(c) and (d). The fiber surface obtained was smooth and uniform. The two kinds of TiO$_2$ fibers mainly consisted of nanosized particles 10 nm in size. Moreover, the two types of fibers had typical mesoporous morphology, which is an ideal host for Li$^+$ intercalation, as shown by annular dark field scanning TEM (STEM) images (Figure 3.1(e) and 1(f)). These fibers commonly also showed a random orientation and the lack of any impurity phases, as in the high resolution TEM (HR-TEM) images in Figure 3.1 (g) and (h), and their fast Fourier transforms (FFT). It is worth noting that phases of bare and nitrogen-doped TiO$_2$ fibers also show no noticeable differences in X-ray diffraction (XRD) analysis (Figure 3.2). They both show only typical anatase phase without any impurity.

If nitrogen atoms are present in either interstitial or substitutional sites, a natural question is then where the nitrogen is. Very recently, TiO$_2$ hollow nanofibers were synthesized via the eletrospinning using a dual nozzle. These hollow nanofibers heathed with TiO$_x$N$_y$ and TiN layers on the surfaces were designed as a highly conducting layer for considering the dominant rate capability determining factors, i.e., lithium ion diffusivity, especially, solid state diffusion of lithium ion, and electronic
Figure 3.1 SEM images of (a) TiO$_2$ and (b) nitrogen-doped TiO$_2$ nanofibers after calcination. Bright field TEM images of (c) TiO$_2$ and (d) nitrogen-doped TiO$_2$ nanofibers and their SAED patterns (inset), which correspond anatase phase. Annular dark field STEM images of (e) TiO$_2$ and (f) nitrogen-doped TiO$_2$ nanofibers. HR-TEM images of (g) TiO$_2$ and (h) nitrogen-doped TiO$_2$ nanofibers and the corresponding FFT patterns.
conductivity but nitrogen site was not still clarified. [24] To clarify the nitrogen site, the surface of nitrogen-doped TiO\textsubscript{2} was further investigated by energy-dispersive X-ray spectroscopy (EDS), Fourier transform infrared spectroscopy (FTIR), and X-ray photoelectron spectroscopy (XPS), as shown in Figure 3.3. First, EDS was evaluated for the presence of nitrogen doping. According to the element mapping, the nitrogen was seen in nitrogen-doped TiO\textsubscript{2} nanofibers, as in Figure 3.3(d). FTIR spectroscopy was then conducted. In the FTIR spectrum of nitrogen-doped TiO\textsubscript{2}, there were three peaks at 470, 1630, and 3450 cm\textsuperscript{-1} (Figure 3.3(e)). These peaks are also observed in commercial Degussa P25, which is composed of anatase and rutile crystallities, from earlier reports. [25] Interestingly enough, new peaks were found at 1460 and 2920 cm\textsuperscript{-1}, respectively (Figure 3.3(e)). The first peak (2920 cm\textsuperscript{-1}) can be related to the C-H vibration in remnant organic compounds in TiO\textsubscript{2} nanofibers. [25] The small peak at 1460 cm\textsuperscript{-1}, which was produced by -NO\textsubscript{x} (−Ti−O−N−Ti−), indicated that nitrogen

**Figure 3.2** XRD patterns of TiO\textsubscript{2} and nitrogen-doped TiO\textsubscript{2} nanofibers after calcination at 450 °C.
Figure 3.3 (a) TEM image of (a) nitrogen-doped TiO$_2$ nanofibers, (b) its titanium, (c) Oxygen and (d) nitrogen mapping. FTIR spectrum of nitrogen-doped TiO$_2$ nanofibers (e). XPS spectra of nitrogen-doped TiO$_2$ nanofibers: (f) N$_{1s}$ peak, (g) O$_{1s}$ peak.
atoms in the nitrogen-doped TiO₂ sample existed in the form of –NOₓ. [26] Even after EDS and FTIR, however, controversy still remains. In order to further clarify the nitrogen positions, XPS analysis was also undertaken. Based on literature surveys, [27-32] the broad peak at 398.2 - 400.7 eV can be interpreted as the result of nitrogen atoms occupying interstitial sites in the TiO₂ lattice (TiO₂Nx), while the peak at 396 - 397 eV could be derived from substitution of nitrogen on the oxygen site in TiO₂ (TiO₂-xNx) or adsorbed NHₓ species, i.e., molecular nitrogen on the surface. [28] N 1s was found to be around 400.0 eV, four peaks were also found from O 1s, as can be seen in Figure 3.3(f) and (g). Two peaks of 532.0 eV and 533 eV were reported to be related to NOₓ. [25] In addition, the peaks at 529.9 eV and 531.3 eV can be attributed to Ti-O bond and Ti-O-N bonds, respectively. Even if the spectra of O 1s observed at 531.8 eV was reported to be Ti oxynitride (TiOₓNx), [33] neither TEM nor XRD (Figure 3.2) revealed any other evidence beyond anatase. The Ti oxynitride is well-known to be rock-salt crystal structure of osbornite. The nitrogen site is considered as either an interstitial or a substitution in anatase TiO₂.

To again confirm this issue, a series of first principles calculations on the nitrogen-doped TiO₂ surface was carried out. Substitutional nitrogen doping was simulated by replacing one oxygen atom per supercell with a nitrogen atom, and interstitial nitrogen doping was simulated by adding one nitrogen atom to a neighboring site to an oxygen atom in the surface slab model: this corresponds to TiO₂-xNx (TiO₂Nx) with x = 0.021. The main concern is to establish whether the nitrogen defect in the surface is favored with respect to that in a sublayer. To this end, various possible nonequivalent surface and subsurface substitutional nitrogen sites (Ns) and interstitial nitrogen sites (Ni) have been considered. For all Ns configurations, no significant structural variation is observed upon substitution: the Ti-N bonds are only
slightly (less than 0.1 Å) elongated with respect to the corresponding Ti-O bonds. For the most stable interstitial doping, nitrogen atoms bond with three neighbors, one with surface oxygen \(d_{\text{N-O}} = 1.27 \text{ Å}\) and the others with Ti atoms \(d_{\text{Ti-N}} = 1.96 \text{ Å}, 2.16 \text{ Å}\), respectively. The surface oxygen, when bonded with an N atom, was kicked out of the surface, ~1 Å above the initial position. Figure 3.4(a) shows the relative defect energies \(E_d\) for various nitrogen atom positions. The defect energy of bulk TiO\(_2\) in anatase phase and the height of the outermost oxygen atom in pristine (101) were set as the origin of the y-axis and abscissa, respectively. The nitrogen atom substitution occurs preferentially in the subsurface layer (-0.18 eV at 3.47 Å below the TiO\(_2\) surface). On the other hand, the most stable interstitial nitrogen atom resides in a surface site (Figure 3.4(c) and (e); -1.63 eV at 0.26 Å above the TiO\(_2\) surface). That is, substitutional nitrogen would be spread widely in the bulk, while interstitial nitrogen atoms were mostly located near the surface.

Figure 3.4 Energetic graph of a nitrogen atom site (a), geometry of the TiO\(_2\) structure (b), and interstitial sites on the surface of nitrogen-doped TiO\(_2\) structure (c). The atomic geometries ((d) and (e)) are viewed in (001) direction for the corresponding samples. Herein dashed lines show the surface unit cell.
Table 3.1 Relative energies (eV) for substitutional (Es) and interstitial (Ei) Nitrogen in different positions of anatase TiO$_2$ (001) surface slab model.

<table>
<thead>
<tr>
<th>N substitution</th>
<th>N interstitial</th>
</tr>
</thead>
<tbody>
<tr>
<td>depth (Å)</td>
<td>Es wrt. bulk (eV)</td>
</tr>
<tr>
<td>0.093</td>
<td>0.054</td>
</tr>
<tr>
<td>-0.553</td>
<td>0.110</td>
</tr>
<tr>
<td>-1.578</td>
<td>-0.031</td>
</tr>
<tr>
<td>-2.432</td>
<td>-0.049</td>
</tr>
<tr>
<td>-3.468</td>
<td>-0.175</td>
</tr>
<tr>
<td>-4.431</td>
<td>0.038</td>
</tr>
<tr>
<td>-5.123</td>
<td>0.016</td>
</tr>
<tr>
<td>-6.029</td>
<td>-0.104</td>
</tr>
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</table>

The work function variation in each configuration is also investigated (Table 3.1). The work function is defined as the energy of the vacuum level (determined by applying a dipole correction to the super cell [34]) with respect to the Fermi energy, $E_F$, in each configuration. For the substitutional doping, the work function deviates a little (~0.3 eV) from that of the pristine surface (7.34 eV), although the work function of interstitial doping is much reduced (~1.3 eV) from that of the pristine surface. The high work function, i.e., the lower lying valence band maximum is the main obstacle to the use of TiO$_2$ as a photocatalyst or as an electrode of a photoelectrochemical (PEC) cell. Work function engineering by nitrogen interstitial doping may be valuable for various applications of TiO$_2$ material, such as in photocatalysis, PEC cells, and solar cells.

It is well known that a small fraction of nitrogen doping as impurity in semiconductor material, especially TiO$_2$, can improve electrical conductivity. Here,
the internal conductivity is considered as investigated by electrochemical impedance spectroscopy of TiO$_2$ nanoparticles, TiO$_2$ nanofibers and nitrogen-doped TiO$_2$ nanofibers, as shown in Figure 3.5. In the electrochemical impedance spectra (EIS) of TiO$_2$, the high frequency semicircle can be attributed to the contact resistance or the solid electrolyte interphase (SEI) film, the medium frequency semicircle indicates the charge transfer resistance at the interface between the electrolyte and the electrode material, and the inclined lines correspond to the Li$^+$ diffusion process inside the electrode material. When the experimental data was fitted using a typical equivalent circuit (shown in the inset of Figure 3.5), the different sizes of the semicircle among these materials were primarily associated not with contact resistance or SEI film, but with charge transfer resistance. So, the more restrained semicircle of bare TiO$_2$ nanofibers (1301 Ω) compared to that of TiO$_2$ nanoparticles.

![Figure 3.5 Nyquist plots of TiO$_2$ nanoparticles, TiO$_2$ nanofibers, and nitrogen-doped TiO$_2$ nanofibers. The inset figure corresponds to the equivalent circuit used to interpret the impedance spectra.](image-url)
(2370 Ω) clearly proves that the electrode materials with 1D structure feature enhanced kinetic properties because of their innately conductive electronic structure. [35,36] Finally, that the smallest resistance (1170 Ω) was observed in nitrogen-doped TiO2 nanofibers confirms that the doped nitrogen results in enhancing electrical conductivity due to an electron acceptor. [29] Interestingly, the linear Warburg region (at low frequencies), which correspond to the Li+ diffusion process inside the electrode materials, for the nitrogen-doped TiO2 nanofibers exhibit slightly steeper slope. That is to say, this result demonstrates that nitrogen doping plays an important role for fast charge transfer and Li+ diffusion which would affect electrochemical performance.

The electrochemical performance of the two different TiO2 nanofibers for use as anode in the lithium rechargeable battery is shown in Figure 3.6. Anatase TiO2 nanoparticles were also tested as a reference. More details on the sample preparation can be found in the Experimental section. The galvanostatic profiles of the three TiO2 configurations show a clear voltage plateau during Li+ insertion/extraction, indicating that all TiO2 samples have a typical anatase phase. The preferential use of anatase phase compared to rutile phase for the lithium rechargeable battery is due not only to the voltage plateau characteristics of anatase, but also to its better electrochemical performance, such as higher capacity and better cyclic retention. The nitrogen-doped TiO2 nanofibers shown in Figure 3.6(b) have a specific charge (Li+ insertion) capacity of around 224 mAhg⁻¹, and further cycling leads to around 185 mAhg⁻¹ retention after 40 cycles. This indicates that the superior cycling performance can be attributed to the morphological advantage for Li+ storage as well as faster Li+ diffusion. As pointed out by Park et al. [37] 1D nanostructures such as in urchin-like structures or nanorod structures on the surface of spherical particles
can supply the most optimized environment for facilitating the charge/discharge process of Li\(^+\) because of their dual merits, including a suitable surface area, excluding large irreversible capacity, and the high aspect ratio necessary for fast electron transport. After 1\(^{\text{st}}\) cycle, the coulombic efficiency of nitrogen-doped TiO\(_2\) nanofiber and TiO\(_2\) nanofiber is better compared to that of TiO\(_2\) nanoparticle proving the enhanced reversibility associated with 1D structure (Figure 3.6(c)). Furthermore, the comparison between nitrogen-doped TiO\(_2\) nanofiber and bare TiO\(_2\) nanofiber clearly proves the effect of nitrogen doping on the rate performance of TiO\(_2\) in Figure 3.6(d). The nitrogen-doped TiO\(_2\) nanofibers show enhanced rate capability compared to bare TiO\(_2\) nanofiber from 0.1 C to 2 C. This result indicates that nitrogen doping is contributed to fast Li\(^+\) transfer and electron transfer with higher conductivity.

Figure 3.6 Nyquist plots of TiO\(_2\) nanoparticles, TiO\(_2\) nanofibers, and nitrogen-doped TiO\(_2\) nanofibers. The inset figure corresponds to the equivalent circuit used to interpret the impedance spectra.
Therefore, mesoporous 1D structure results in higher specific surface area, strongly facilitating Li$^+$ diffusion, which produces enhanced cyclic retention.
3.4 Summary

1D mesoporous TiO$_2$N$_x$ was prepared by electrospinning, and their phase formation, microstructure, nitrogen site and electrochemical performance were studied for application of lithium rechargeable batteries. The nitrogen interstitially located near surface in the form of TiO$_2$N$_x$, improving conductivity and changing work function, based on the first principles calculations. The nitrogen-doped TiO$_2$ nanofibers (185 mAh g$^{-1}$) show much higher cyclic retention than the nanopowders (60 mAh g$^{-1}$) after 40 cycles due to the intrinsic properties of the nitrogen-doped TiO$_2$ such as higher conductivity and faster Li$^+$ diffusion.
3.5 References


4 CONTROLLED AG-DRIVEN SUPERIOR RATE-CAPABILITY OF 
\(\text{Li}_4\text{Ti}_5\text{O}_{12}\) ANODE FOR LITHIUM RECHARGEABLE BATTERY

4.1 Introduction

Ti-based oxide anode materials have attracted much attention due to their potential advantages, which include excellent thermal stability, low cost, and environmental friendliness [1-2]. In particular, spinel \(\text{Li}_4\text{Ti}_5\text{O}_{12}\) has been intensively studied as a promising anode to meet the requirements for electric vehicles (EVs) and large-scale energy storage systems (ESSs) [3-6]. It is well known that \(\text{Li}_4\text{Ti}_5\text{O}_{12}\) shows some promise, largely due to its two key advantages: (i) long cycle life arising from its zero-strain structure and (ii) little electrolyte decomposition due to its higher equilibrium potential, showing a voltage plateau at 1.55 V vs. Li/Li\(^+\) [7-10]. \(\text{Li}_4\text{Ti}_5\text{O}_{12}\) material has a low electrical conductivity of about \(10^{-13}\) S cm\(^{-1}\) [11], however, resulting in poor rate capability and an initial capacity loss. To improve this, several methods have been considered to preferentially enhance the electrical conductivity. The most efficient methods are applying a surface coating or doping to achieve metallic substitution [12-23]. Surface coating with a conductive material, i.e., carbon, is not an ideal solution, because it is hard to make a homogeneous thin layer. Severe aggregation of metallic additive is also known to be difficult to avoid.

One-dimensional (1D) nanostructures have remarkable electrical, thermal, and mechanical properties. [24-33] It is accepted that 1D nanostructures have clear morphological advantages due to the shortened Li\(^+\) diffusion pathways and improved electron transport in lithium rechargeable batteries. Even if small-sized \(\text{Li}_4\text{Ti}_5\text{O}_{12}\) particles synthesized through the solid-state reaction, hydrothermal, and sol-gel methods are known to be the most direct approach [34-36], using these methods with
metallic dopants/additives usually leads to severe inhomogeneity or difficulty in mass production [37]. Liu et al. reported that Ag nanoparticles (< 10 nm) located within Li$_4$Ti$_5$O$_{12}$ particles improved rate performance and led to long life cycle due to enhanced electrical conductivity [38]. However, no quantitative analysis has ever been carried out. From this point of view, it might be expected that the electrochemical performance of 1D Li$_4$Ti$_5$O$_{12}$ nanostructures in energy storage could be improved if metal nanoparticles were distributed all throughout the Li$_4$Ti$_5$O$_{12}$ material. Furthermore, Ag additive could improve the electrochemical performance of Li$_4$Ti$_5$O$_{12}$ nanofibers by enhancing intra- or inter-grain connectivity.

In this chapter, 1D Ag-Li$_4$Ti$_5$O$_{12}$ nanofibers was fabricated by a simple one-step synthesis using electrospinning method. The as-prepared Ag-Li$_4$Ti$_5$O$_{12}$ nanofibers showed excellent rate capability and cycling stability with enhanced electrical conductivity and maximized kinetic properties because of the shortened diffusion length for Li$^+$ transport and the fast electron transport.
4.2 Experimental

4.2.1 Bare \( \text{Li}_4\text{Ti}_5\text{O}_{12} \) and Ag-\( \text{Li}_4\text{Ti}_5\text{O}_{12} \) nanofibers and their structural characterization

For the \( \text{Li}_4\text{Ti}_5\text{O}_{12} \) nanofibers, 1.48 mL titanium (IV) isopropoxide and 0.413 g lithium acetate were mixed with 10 mL ethanol and 7 mL acetic acid. After dissolving for 1 h, 0.8 g polyvinylpyrrolidone (PVP) was added into this solution, followed by magnetic stirring for 1 h. For Ag-doped \( \text{Li}_4\text{Ti}_5\text{O}_{12} \) nanofibers, 0.045 g silver nitrate was dissolved in 16 mL ethanol and 1.48 mL titanium (IV) isopropoxide, and 0.413 g lithium acetate and 1 mL acetic acid were added into the dissolved Ag solution. The yellow transparent spinning solution was immediately loaded into a plastic syringe equipped with a 23 gauge needle. The needle was connected to a high voltage supply, and the feeding rate for the precursor was set at 0.7 mL h\(^{-1} \). A distance of 13 cm and voltage of 20 kV were maintained between the tip of the needle and a drum collector. A schematic illustration of the electrospinning set-up for obtaining \( \text{Li}_4\text{Ti}_5\text{O}_{12} \) and Ag-\( \text{Li}_4\text{Ti}_5\text{O}_{12} \) nanofibers is shown in Figure 1(a). After the electrospinning, the electrospun nanofibers were detached from the drum collector. Finally, the nanofibers were heat-treated at 750 °C for 3 h in air. The morphology and microstructure of the nanofibers were characterized by X-ray diffraction (XRD), field emission-scanning electron microscopy (FE-SEM), and transmission electron microscopy (TEM).

4.2.2 Electrochemical performance

The electrodes were prepared by coating aluminum foil substrates with slurries containing the active material, carbon black (Super-P), and polyvinylidene fluoride
(PVDF) at a weight ratio of 80:10:10 using N-methylpyrrolidone (NMP) as the solvent. After coating the slurry on Al foil, the electrodes were dried at 120 °C for 12 h under vacuum. The mass of the active material was approximately 2 mg cm⁻². 2032 coin cells were assembled in a dry room. A porous polyethylene film was used as the separator, 1 M LiPF₆ dissolved in a 1:2 (by volume) mixture of ethylene carbonate (EC) and dimethyl carbonate (DMC) was employed as the electrolyte solution, and lithium foil was used as the counter electrode. Discharge (Li⁺ intercalation)-charge (Li⁺ de-intercalation) tests were performed up to 200 cycles in a voltage window of 1 to 3 V (vs. Li/Li⁺). The first and second cycles were conducted galvanostatically at a current density of 0.1 C (where 1 C was set as 170 mA g⁻¹), and measurements of the rate capability at various current densities and cycling tests at 1 C were performed. Electrochemical impedance spectroscopy (EIS) was performed after the first discharge under a three-electrode electrochemical system, in which the reference and counter electrodes were Li metal. The EIS frequency ranged from 10⁶ to 10⁻² Hz, and the voltage perturbation amplitude was 5 mV. Data acquisition and analysis were carried out using the electrochemical impedance software packages ZPlot and Zview (Version 3.0, Scribner Associates, Inc., USA), respectively.
4.3 Results and discussion

The configuration and crystalline microstructure of the two kinds of nanofibers were directly confirmed by XRD, SEM, and TEM analyses. As shown in Figure 4.1(a) and (b), only small differences were observed between the bare Li$_4$Ti$_5$O$_{12}$ (LTO) and the Ag-Li$_4$Ti$_5$O$_{12}$ nanofibers. The randomly aligned nanofibers have average diameters

![SEM images of (a) Li$_4$Ti$_5$O$_{12}$ and (b) Ag-Li$_4$Ti$_5$O$_{12}$ nanofibers after calcination. (c) Energy spectrum from the elemental mapping.](image)

<table>
<thead>
<tr>
<th>Element</th>
<th>Wt%</th>
<th>At%</th>
</tr>
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<tbody>
<tr>
<td>OK</td>
<td>33.54</td>
<td>61.49</td>
</tr>
<tr>
<td>AgL</td>
<td>6.43</td>
<td>1.75</td>
</tr>
<tr>
<td>TiK</td>
<td>60.04</td>
<td>36.76</td>
</tr>
</tbody>
</table>

**Figure 4.1** SEM images of (a) Li$_4$Ti$_5$O$_{12}$ and (b) Ag-Li$_4$Ti$_5$O$_{12}$ nanofibers after calcination. (c) Energy spectrum from the elemental mapping.
of 50-200 nm and lengths extending to several tens of micrometers. Interestingly, it is hard to distinguish the Ag particles from the SEM image of Ag-Li$_4$Ti$_5$O$_{12}$ nanofibers in Figure 1(b), however, 1.75 at% of Ag is confirmed by energy-dispersive X-ray spectroscopy (EDS) in Figure 4.1(c). From the XRD patterns in Figure 4.2(a), however, all reflections were identical to the standard peaks of Li$_4$Ti$_5$O$_{12}$ and metallic Ag. This indicates that the Li$_4$Ti$_5$O$_{12}$ and Ag-Li$_4$Ti$_5$O$_{12}$ nanofibers were successfully synthesized during the heat treatment without
introducing any impurity such as rutile TiO₂. The microstructure of the Ag-Li₄Ti₅O₁₂ nanofibers was further observed by high-angle annular dark-field (HAADF) scanning TEM (STEM), as shown in Figure 4.2(b) and (c). The Ag-Li₄Ti₅O₁₂ nanofibers exhibited smooth and uniform surfaces, and the Ag particles were distinguished in the STEM images by showing bright contrast. These results indicate that the Ag-Li₄Ti₅O₁₂ nanofibers have the form of a secondary 1D Ag-Li₄Ti₅O₁₂ composite consisting of Ag and Li₄Ti₅O₁₂ primary particles, as shown in Figure 4.2(c).

The schematic diagram of the structure of an Ag-Li₄Ti₅O₁₂ nanofiber in Figure 4.3(a) illustrates the TEM results. The Ag particles (∼100 nm) have been successfully incorporated and are interconnected between the Li₄Ti₅O₁₂ nanoparticles, as can be seen in Figure 4.3(b). These interconnected Ag particles could improve the electrical contact between the Li₄Ti₅O₁₂ particles and the current collector. Furthermore, the Ag nanoparticles were observed to be less than 5 nm in size, mostly spherical in shape, and embedded in the Li₄Ti₅O₁₂ host matrix (Figure 4.3(c)). In fine detail, the high resolution TEM (HR-TEM) images confirmed that the interconnected Ag particles were single-crystal from their selected area diffraction patterns (SADPs), and the exposed surfaces of the Ag particles were determined to be {002} and {0-22} facets, as in Figure 4.3(d). The Li₄Ti₅O₁₂ particles also show a strong crystalline structure. The lattice spacing parallel to the side wall is ∼2.95 Å, in accordance with the (-220) planes of Li₄Ti₅O₁₂ in Figure 4.3(e). As a result, the two important configurations that could enhance the electrical conductivity are (i) interconnected large-sized Ag particles and (ii) embedded Ag nanoparticles. Even though it is generally argued that embedded Ag nanoparticles mainly play a supporting role in term of electrical conductivity, it would be difficult to conclude that they are the predominant factor. For that purpose, the interface between the Li₄Ti₅O₁₂ particles...
Figure 4.3 Schematic illustration of Ag-Li$_4$Ti$_5$O$_{12}$ nanofibers (a). Low magnification TEM images of Ag-Li$_4$Ti$_5$O$_{12}$ nanofibers (b, c). High resolution TEM (HR-TEM) images of (d) Ag and (e) Li$_4$Ti$_5$O$_{12}$ nanoparticles and the corresponding SADPs.
was further investigated using a Cs-corrected scanning TEM (STEM), as shown in Figure 4.4. Here, the nanosized Ag particles were observed to be concentrated along the grain boundaries. Their size was less than 5 nm, which can improve charge transfer between the Li$_4$Ti$_5$O$_{12}$ nanoparticles, predominantly due to enhanced electrical conductivity. The insets show the grain boundaries (dashed lines) and Ag nanoparticles (dots). If conducting agents, such as RuO$_2$ or Fe$_2$P, were distributed at the boundaries of active material, it would affect rate capability due to the enhanced electrical conductivity, according to the literatures [23, 39]. Therefore, Li$_4$Ti$_5$O$_{12}$ primary particles have intimate electrical contact with aids of Ag particles at the grain boundaries that might be effective for fast electron transfer. The Ag particles could be observed all over the Li$_4$Ti$_5$O$_{12}$ nanofibers, which would be expected to enhance electrochemical performance. To explore the possibilities of Ag-Li$_4$Ti$_5$O$_{12}$ nanofibers for use as the anode in Li rechargeable batteries, galvanostatic discharge–charge cycling was carried out to investigate the lithium storage properties of the

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**Figure 4.4** HAADF STEM images of grain boundaries in Ag-Li$_4$Ti$_5$O$_{12}$ nanofibers. The insets show the grain boundaries (dashed lines) and Ag particles (dots).
Li$_4$Ti$_5$O$_{12}$ and Ag-Li$_4$Ti$_5$O$_{12}$ nanofibers. Figure 4.5(a) shows the first discharge/charge voltage profiles of the Li$_4$Ti$_5$O$_{12}$ and Ag-Li$_4$Ti$_5$O$_{12}$ nanofibers at current density of 0.1 C. The discharge and charge capacities of the Ag-Li$_4$Ti$_5$O$_{12}$ nanofibers were 195.7 and 164.2 mAh g$^{-1}$ at the first cycle, respectively. They thus exhibited a larger initial discharge capacity than the bare Li$_4$Ti$_5$O$_{12}$ nanofibers (178.1 mAh g$^{-1}$). The initial irreversible capacities of both types of nanofibers were estimated to be 21.1 (Li$_4$Ti$_5$O$_{12}$) and 31.5 mAh g$^{-1}$ (Ag-Li$_4$Ti$_5$O$_{12}$). Although the Ag-Li$_4$Ti$_5$O$_{12}$ exhibited a slightly larger initial irreversible capacity, which probably originated from different electrolyte decomposition behavior [18, 40], this electrode still showed increased reversible capacity compared to the bare Li$_4$Ti$_5$O$_{12}$. The rate-capability and cycling performances of the Li$_4$Ti$_5$O$_{12}$ and Ag-Li$_4$Ti$_5$O$_{12}$ nanofibers were also evaluated at various current rates from 0.1 to 30 C, as shown in Figure 4.5(b). The Ag-Li$_4$Ti$_5$O$_{12}$ nanofibers show enhanced rate performance compared to the bare Li$_4$Ti$_5$O$_{12}$ nanofibers at all current rates. At current densities below 10 C, the capacities of the Ag-Li$_4$Ti$_5$O$_{12}$ nanofibers vary from 150 to 165 mAh g$^{-1}$. Furthermore, the Ag-Li$_4$Ti$_5$O$_{12}$ nanofibers still have a specific capacity of 140 mAh g$^{-1}$, which is larger than that of the bare Li$_4$Ti$_5$O$_{12}$ nanofibers at the high current density of 10 C. Most notably, the Ag-Li$_4$Ti$_5$O$_{12}$ nanofibers exhibit remarkable rate performance at 10 C, which is much better than the performances of the carbon-coated, surface-nitried, phosphidated, and nanostructured Li$_4$Ti$_5$O$_{12}$ reported in the literature [14, 28, 41-42]. At the highest rate of 30 C, corresponding to a time of 2 min to fully discharge/charge the materials, the specific capacity of the Ag-Li$_4$Ti$_5$O$_{12}$ nanofibers is 107.5 mAh g$^{-1}$, which is significantly higher than that of the bare Li$_4$Ti$_5$O$_{12}$ nanofibers (82.2 mAh g$^{-1}$). After the galvanostatic rate capability test, an additional cycling performance test was carried out at a current density of 1 C. The
Ag-Li\textsubscript{4}Ti\textsubscript{5}O\textsubscript{12} nanofibers regained their Li\textsuperscript{+} de-intercalation capacity of around 163.5 mAh g\textsuperscript{-1}, while further cycling led to around 160 mAh g\textsuperscript{-1} retention after 200 cycles.

Figure 4.5 shows differential capacity plots of the Li\textsubscript{4}Ti\textsubscript{5}O\textsubscript{12} and Ag-Li\textsubscript{4}Ti\textsubscript{5}O\textsubscript{12} nanofibers at various current densities. Even if there is only a small difference in overpotential between the bare Li\textsubscript{4}Ti\textsubscript{5}O\textsubscript{12} nanofibers and the Ag-Li\textsubscript{4}Ti\textsubscript{5}O\textsubscript{12} nanofibers at 0.1 C, the Ag-Li\textsubscript{4}Ti\textsubscript{5}O\textsubscript{12} nanofibers exhibit remarkably lower overpotential than the bare Li\textsubscript{4}Ti\textsubscript{5}O\textsubscript{12} nanofibers with increasing current density.

**Figure 4.5** (a) Discharge–charge curves in the first cycle, (b) rate performance and coulombic efficiency (inset), and (c) differential capacity (dQ/dV) vs. voltage curves of Li\textsubscript{4}Ti\textsubscript{5}O\textsubscript{12} and Ag-Li\textsubscript{4}Ti\textsubscript{5}O\textsubscript{12} nanofibers, (d) the overpotential of the samples at different current densities.
which results from a decrease in the polarization resistance because of the improved electrical conductivity of the Ag-Li$_4$Ti$_5$O$_{12}$ nanofibers. These results indicate that the superior rate capability and cycling performance can be attributed to the increased electrical conductivity of the Li$_4$Ti$_5$O$_{12}$ nanofibers due to the incorporation of Ag nanoparticles, which greatly enhances the charge transport during the charge/discharge process and thus leads to significant improvement in the electrochemical performance.

Electrochemical impedance spectroscopy (EIS) measurements were also conducted to examine the internal conductivity of the Li$_4$Ti$_5$O$_{12}$ and Ag-Li$_4$Ti$_5$O$_{12}$ nanofibers. Nyquist plots of the AC-impedance spectra obtained for the lithiated Li$_4$Ti$_5$O$_{12}$ and Ag-Li$_4$Ti$_5$O$_{12}$ nanofibers are presented in Figure 4.6. The parameters were

![Nyquist plots](figure)

**Figure 4.6** Nyquist plots of the Li$_4$Ti$_5$O$_{12}$ and Ag-Li$_4$Ti$_5$O$_{12}$ nanofibers. The inset figure corresponds to the equivalent circuit used to interpret the impedance spectra.
determined by the complex nonlinear least squares (CNLS) fitting method with an equivalent circuit (inset) and are summarized in Table 1. $R_{\text{el}}$ is the resistance of the electrolyte solution, the high frequency semicircle can be attributed to the surface layer resistance associated with the solid electrolyte interphase ($R_{\text{SEI}}$), and the medium frequency semicircle indicates the charge transfer resistance ($R_{\text{ct}}$) at the interface between the electrolyte and the electrode material. The more modest medium frequency semicircle of the Ag-Li$_4$Ti$_5$O$_{12}$ nanofibers (788 $\Omega$) compared to that of the Li$_4$Ti$_5$O$_{12}$ nanofibers (1143 $\Omega$) clearly proves that the electrode material with incorporated Ag particles features enhanced charge transfer due to improved electrical conductivity. The inclined lines in the Warburg region correspond to the Li$^+$ diffusion process inside the electrode material (W). The Ag-Li$_4$Ti$_5$O$_{12}$ nanofibers exhibit a larger slope than the bare Li$_4$Ti$_5$O$_{12}$ nanofibers, which implies high Li$^+$ mobility in the solid phase [43]. This result clearly demonstrates that incorporated Ag particles can boost electron transfer and Li$^+$ transfer, which significantly influence electrochemical performance.

Table 4.1 Best-fit values of EIS data with the equivalent circuit in Fig. 4.6.

<table>
<thead>
<tr>
<th></th>
<th>Li$_4$Ti$<em>5$O$</em>{12}$ ($\Omega$)</th>
<th>Ag-Li$_4$Ti$<em>5$O$</em>{12}$ ($\Omega$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$R_{\text{SEI}}$</td>
<td>263</td>
<td>203</td>
</tr>
<tr>
<td>$R_{\text{ct}}$</td>
<td>1143</td>
<td>788</td>
</tr>
</tbody>
</table>
4.4 Summary

As an anode material, Li$_4$Ti$_5$O$_{12}$ is a promising candidate for lithium rechargeable batteries to solve the safety issues, although the low kinetics associated with its poor electrical conductivity limits the electrochemical performance from the viewpoint of practical application. Incorporation of Ag nanoparticles is an effective way to improve the kinetics of Li$_4$Ti$_5$O$_{12}$ toward fast Li$^+$ intercalation/de-intercalation. The Ag-Li$_4$Ti$_5$O$_{12}$ nanofibers exhibit high specific capacity, and remarkably high rate capability and cycling performance due to higher conductivity and faster Li$^+$ diffusion. The controlled incorporation of Ag nanoparticles into 1D Li$_4$Ti$_5$O$_{12}$ nanostructures would be a promising (or advanced) approach to improve electrochemical performance in Li$^+$ storage devices.
4.5 References


5 ATOMIC INSIGHTS INTO ZR$^{4+}$ DOPING IN LI$_4$TI$_5$O$_{12}$ ANODE FOR THE LITHIUM RECHARGEABLE BATTERY: OPEN LI$^+$ DIFFUSION PATHS THROUGH STRUCTURAL IMPERFECTION

5.1 Introduction

Lithium ion batteries (LIBs) have attracted great interest as efficient portable storage devices for renewable energy, owing to their great advantages, such as high energy density, absence of a memory effect, and long cycling life in comparison to other rechargeable batteries. [1-4] Carbon-based anode materials in currently available LIBs, however, exhibit a relatively low energy density and have serious safety issues due to lithium dendritic growth when operating under high current densities. There have thus been numerous studies on developing alternative anodes with higher energy density, enhanced safety, and longer cycling performance. Among the various metal oxide candidates, spinel Li$_4$Ti$_5$O$_{12}$ (LTO) has been considered as a promising anode material for LIBs, since it has inherent structural stability due to its ‘zero-strain’ characteristic and relatively high operating voltage (~1.55 V vs. Li/Li$^+$), which can ensure excellent cyclability and safe operation during Li$^+$ intercalation/de-intercalation processes. [5-9] In spite of those advantages, Li$_4$Ti$_5$O$_{12}$ anodes still show poor rate capability due to its low electrical conductivity ($< 10^{-13}$ S cm$^{-1}$). [10]

In order to resolve this issue, various methods have been investigated, including surface coating with conductive TiN or carbon layers, doping with metal ions (such as Mg$^{2+}$, Al$^{3+}$, Ga$^{3+}$, Co$^{3+}$, Cr$^{3+}$, Ta$^{5+}$, or Zr$^{4+}$) or non-metal ions (such as F$^-$ or Br$^-$), and reducing Li$_4$Ti$_5$O$_{12}$ particle size. [11-22] Among those approaches, metal ion doping could be an effective and direct way for improving the intrinsic material
properties. Such doping of metal ions into the Li$_4$Ti$_5$O$_{12}$ lattice offers enhanced electronic conductivity through the substitution of metal ions on the Ti$^{4+}$ or Li$^+$ sites and hence, an increase in the amount of mixed Ti$^{3+}$/Ti$^{4+}$ states as charge compensation, consequently improving the rate capability of LIBs. In addition, the metal doping has been reported to reduce the size of the Li$_4$Ti$_5$O$_{12}$ particles in the case of doping with Zr$^{4+}$ and Cr$^{3+}$, which could partly enhance the rate capability due to the size effect. [14,17,21]

One-dimensional (1D) nanomaterials have been examined extensively as promising anode structures in lithium rechargeable batteries, since they provide shortened Li$^+$ diffusion pathways and facile accessibility of the electrolyte, and hence, improve the electrochemical properties such as reversible capacity and rate capability. [23] From this point of view, it is expected that utilization of 1D Li$_4$Ti$_5$O$_{12}$ nanostructures in conjunction with an appropriate metal ion doping could improve the electrochemical performance of LIBs.

In this chapter, 1D Li$_4$Ti$_5$O$_{12}$ nanofibers with Zr$^{4+}$ doping were fabricated by an electrospinning method, which is a simple and mass-producible way to synthesize 1D nanostructures with controlled size and composition. [24-37] In contrast to most previous studies, in which benefits were claimed for the doping effect on the basis of enhanced electronic conductivity, [11,14,21] the structural change due to Zr$^{4+}$ doping at different doping levels was addressed through a theoretical study using first principles calculations, as well as an experimental investigation, and the two were correlated to understand the structural configuration of 1D Zr-doped Li$_4$Ti$_5$O$_{12}$ nanostructures and the resultant electrochemical performance.
5.2 Experimental

5.2.1 Preparation of 1D Li$_4$Ti$_5$O$_{12}$ and Zr-doped Li$_4$Ti$_5$O$_{12}$ nanofibers and structural characterization

_Synthesis of 1D Li$_4$Ti$_5$O$_{12}$ and Zr-doped Li$_4$Ti$_5$O$_{12}$ nanofibers:_ 1D Li$_4$Ti$_5$O$_{12}$ and Zr-doped Li$_4$Ti$_5$O$_{12}$ nanofibers were fabricated by an electrospinning process. First, in order to prepare the precursor solutions with $x = 0$, 0.05, 0.1, and 0.15 in Li$_4$Ti$_{5-x}$Zr$_x$O$_{12}$, Li-acetate dihydrate (Li(CH$_3$COO)$_2$H$_2$O, Aldrich), Ti-isopropoxide (Ti(OCH(CH$_3$)$_2$)$_4$, Aldrich), and Zr-butoxide (Zr(OC(CH$_3$)$_3$)$_4$, Aldrich) were dissolved in a mixed solvent of 10 mL ethanol and 7 mL acetic acid under magnetic stirring for 1 h. 0.8 g polyvinylpyrrolidone (PVP, (C$_6$H$_9$NO)$_n$, M$_w$ 1,300,000, Aldrich) was then added into the solutions. After magnetic stirring for 1 h, the light yellow transparent spinning solution was immediately loaded into a plastic syringe equipped with a 23 gauge needle, which was connected to a high voltage supply. The solution was then subjected to electrospinning under the following conditions: the DC voltage, feeding rate of the precursor solution, and distance between the tip of the needle and the Al-foil-wrapped drum collector were 22 kV, 0.7 mL/h, and 13 cm, respectively. The electrospun nanofibers were detached from the drum collector and finally heat-treated at 750 °C for 3 h in air.

_Characterizations:_ The morphology and microstructure of the nanofibers were observed by field-emission scanning electron microscopy (FESEM, JEOL JSM-7000F) and transmission electron microscopy (FETEM, JEM-2100F, Japan Electronic Optics Ltd.). The phase and crystal structure were characterized by using X-ray diffraction (XRD, GBC MMA), electron diffraction, and fast-Fourier transform (FFT) patterns. The chemical binding state and electronic structure were
examined by X-ray photoelectron spectroscopy (XPS, Thermo Scientific Sigma Probe) with Al Kα X-rays.

5.2.2 Electrochemical performance

The electrodes were prepared by coating Al foil substrates with slurries containing the active material, carbon black (Super-P), and polyvinylidene fluoride (PVDF) at a weight ratio of 80:10:10 using N-methylpyrrolidone (NMP) as the solvent. After coating the slurry on the Al foil, the electrodes were dried at 120 °C for 12 h under vacuum. The mass load of the active material was approximately 1.0 mg/cm². 2032 coin cells were assembled in a dry room. A porous polyethylene film and Li foil were used as the separator and counter electrode, respectively. 1 M LiPF₆ dissolved in a mixture of ethylene carbonate (EC) and dimethyl carbonate (DMC) with a volume ration of 1:2 was employed as the electrolyte solution. Discharge (Li⁺ de-intercalation) – charge (Li⁺ intercalation) testing was performed for up to 100 cycles in a voltage window of 1 to 3 V (vs. Li/Li⁺). The first and second cycles were conducted galvanostatically at a current density of 0.1 C (where 1 C was set as 170 mA/g), and measurements of the rate capability at various current densities and cycling tests at 1 C were performed. The cyclic voltammetry (CV) was carried out with a VSP-300 potentiostat (BioLogic). A potential sweep with a scan rate of ±50 mV s⁻¹ was applied to the Li₄Ti₅O₁₂ working electrode in a three-electrode electrochemical cell, where Li metal was used as counter and reference electrodes. The specific surface area of the electrodes was measured by the BET method (Tristar II 3020).
5.2.3 First principles calculations

The first principles calculations were performed using plane-wave self-consistent field code (PWSCF) implemented in the Quantum-Espresso package, [38] which is a density functional theory code, working in a plane wave basis set. Electron-ion interactions were described using the ultrasoft pseudopotential method. [39] For exchange and correlation, the functional form of Perdew-Burke-Ernzerhof was adopted. [40] Supercells were constructed for the calculations on undoped and Zr-doped Li₄Ti₅O₁₂ systems to conform with the chemical stoichiometry, and their size was 1×1×3 conventional unit cells. For the supercells used throughout most of the calculations, the k-point sampling was restricted to the Γ point and a plane-wave cut-off energy of 40 Ry was used for the energy calculations. A denser Monkhorst-Pack k-point mesh was used for the sampling of the Brillouin zone in order to analyze the electronic structure. [41] Geometric optimization procedures were performed by fully relaxing the positions of all of the atoms in a supercell until the residual forces were less than 10⁻³Ry/Bohr (2.6 × 10⁻² eV/Å).
5.3 Results and discussion

The 1D Li$_4$Ti$_5$O$_{12}$ and Zr-doped Li$_4$Ti$_5$O$_{12}$ nanofibers were fabricated by the electrospinning system. All the nanofibers exhibited long and slightly winding morphology, with an average diameter of 100-300 nm and lengths of a few millimetres (Figure 5.1(a-d)). It has been reported that the Li$_4$Ti$_5$O$_{12}$ particle size gradually decreases with an increasing amount of metal ion dopant. [17,21] This size reduction can affect the LIB performance due to the reduced diffusion pathways of Li$^+$ ions within the Li$_4$Ti$_5$O$_{12}$ particles and the enhanced contact area between the Li$_4$Ti$_5$O$_{12}$ and electrolyte. It should be noted that there were no distinct differences in

![Figure 5.1 SEM images of (a) Li$_4$Ti$_5$O$_{12}$, (b) LTO-Zr0.05, (c) LTO-Zr0.1, and (d) LTO-Zr0.15 nanofibers after the calcination.](image)

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the morphology and average diameter between the undoped and doped Li$_4$Ti$_5$O$_{12}$ fibers, which allows any size effect on the electrochemical properties to be excluded. The XRD patterns showed that all the samples had a polycrystalline Li$_4$Ti$_5$O$_{12}$ phase with spinel structure after the heat treatment (Figure 5.2(a)). With increasing Zr$^{4+}$ dopant content, the primary Li$_4$Ti$_5$O$_{12}$ (111) peak was shifted towards low 2$\theta$, as

![Figure 5.2](image)

**Figure 5.2** (a) XRD patterns of the Li$_4$Ti$_5$O$_{12}$ and Zr-doped Li$_4$Ti$_5$O$_{12}$ nanofibers, and enlarged views of the (b) LTO (111) and (c) ZrO$_2$ main peaks. LTO-Zr0.15 nanofibers after the calcination.
shown Figure 5.2(b): the average lattice constant estimated based on the Rietveld refinement was ~8.360 Å for the Li$_4$Ti$_5$O$_{12}$, and it increased to 8.361-8.362 Å for the Zr-doped Li$_4$Ti$_5$O$_{12}$. This expansion of the Li$_4$Ti$_5$O$_{12}$ lattice by the Zr$^{4+}$ doping was attributed to the larger ionic radius of Zr$^{4+}$ (0.080 nm) than that of Ti$^{4+}$ (0.068 nm). Moreover, ZrO$_2$ impurity peaks (marked by an asterisk) were found for nominal Zr contents over $x = 0.05$ (LTO-Zr0.1 and LTO-Zr0.15), as can be seen in Figure 5.2(a) and (c), indicating that only a small amount of Zr$^{4+}$ should be substituted for Ti$^{4+}$ in the Li$_4$Ti$_5$O$_{12}$ lattice. The XRD results reveal that the solubility limit of Zr in the Li$_4$Ti$_{5-x}$Zr$_x$O$_{12}$ composition.
In order to clarify the doping effect of Zr⁴⁺ on the phase formation and microstructure, transmission electron microscope (TEM) observations were conducted, and the Zr-doped Li₄Ti₅O₁₂ samples with \( x = 0.05 \) and \( x = 0.1 \) (LTO-Zr0.05 and LTO-Zr0.1) were compared, as shown in Figure 5.3. From the high-angle annular dark-field (HAADF) scanning TEM (STEM) images (Figure 2(a) and (d)), the spherical ZrO₂ nanoparticles were distinguished from the Li₄Ti₅O₁₂ nanofibers by their bright contrast: the LTO-Zr0.05 had a few ZrO₂ particles, even though the ZrO₂ phase was not detected in the XRD pattern, whereas the LTO-Zr0.1 contained a large number of ZrO₂ particles. The high-resolution TEM (HRTEM) images (Figure 5.3(b) and (e)) revealed that both the Zr-doped Li₄Ti₅O₁₂ nanofibers had rough surfaces due to the

![Figure 5.3](image)

**Figure 5.3** (a, d) HAADF STEM and (b, c, e, f) HRTEM images of the Zr-doped Li₄Ti₅O₁₂ nanofibers: (a-c) LTO-Zr0.05 and (d-f) LTO-Zr0.1. The arrows in (a) and (d) indicate the ZrO₂ precipitates on the LTO, and the insets of (c) and (f) show the corresponding fast Fourier transform and SAED patterns, respectively.
polygonal-shaped (faceted) grains that were of comparable size (~100 nm) to the fiber diameter and the cubic spinel structure (see the inset of Figure 5.3(c)). It is noteworthy that the ZrO$_2$ particles (~30 nm), as was confirmed by the corresponding selected area electron diffraction (SAED) pattern (inset of Figure 5.3(f)), were present between the Li$_4$Ti$_5$O$_{12}$ grains in the case of the LTO-Zr0.1 sample (Figure 5.3(e)). These results indicate that only a certain amount of Zr$^{4+}$ was incorporated into the Li$_4$Ti$_5$O$_{12}$ lattice, while the residue was precipitated in the form of ZrO$_2$ nanoparticles throughout the Li$_4$Ti$_5$O$_{12}$ grain boundary, which confirms that the solubility limit of Zr in the Li$_4$Ti$_{5-x}$Zr$_x$O$_{12}$ is below $x = 0.05$ in Li$_4$Ti$_{5-x}$Zr$_x$O$_{12}$. ZrO$_2$ is known to be a promising coating material for cathodes in lithium batteries, even though it has a low electrical conductivity. [42-44] It typically acts as a protector by preventing direct contact between the cathode material and electrolyte at high operation potentials, while allowing the Li$^+$ to pass through during charge/discharge processes. [42-44] There is still controversy, however, on the role of ZrO$_2$, since the operation potential of Li$_4$Ti$_5$O$_{12}$ is about 1.55 V (vs. Li/Li$^+$), which is lower than that of a cathode material such as LiMn$_2$O$_4$ (4.0 V vs. Li/Li$^+$). [42] Furthermore, the effect of Zr$^{4+}$ substitution for Ti$^{4+}$ in Li$_4$Ti$_5$O$_{12}$ has not been clearly
Figure 5.4 XPS (a) Ti 2p and (b) Zr 3d spectra of the undoped and Zr-doped Li$_4$Ti$_5$O$_{12}$ nanofibers. The dashed lines indicate the maximum binding energies of the spectra.
revealed. To address those issues, analysis of the electronic structure of the undoped and Zr-doped Li$_4$Ti$_5$O$_{12}$ was conducted by X-ray photoelectron spectroscopy (XPS) and first-principles calculations.

First, the surface chemistry of the Li$_4$Ti$_5$O$_{12}$ and Zr-doped Li$_4$Ti$_5$O$_{12}$ nanofibers was investigated to determine changes in the chemical state of the Li$_4$Ti$_5$O$_{12}$ surface induced by Zr$^{4+}$ incorporation, and the resulting XPS spectra are shown in Figure 5.4. All the Zr 3d and Ti 2p spectra were referenced by a charge correction method based on an adventitious C 1s excitation (284.5 eV). In the Ti 2p spectra (Figure 5.4(a)), two characteristic peaks were observed at 457.7 eV and 463.5 eV, which are matched with typical values of Ti 2p$_{3/2}$ and Ti 2p$_{1/2}$, respectively, corresponding to Ti$^{4+}$ in Li$_4$Ti$_5$O$_{12}$. [45] Interestingly, there was no notable change, such as the formation of the Ti$^{3+}$ state, with changing Zr content in the Ti 2p spectra. Figure 5.4(b) shows the Zr 3d spectra from the undoped and doped samples. The Zr 3d signals (d$_{5/2}$ and d$_{3/2}$) clearly appeared at 181.4 eV and 183.8 eV for all the Zr-doped Li$_4$Ti$_5$O$_{12}$ samples, indicating that the Zr$^{4+}$ has an ionic bonding characteristic. [46] It should be noted that no prominent change in the binding energy with increasing Zr$^{4+}$ doping was detected. The negligible changes in the Ti 2p and Zr 3d spectra are likely to be a result of the small amount of Zr$^{4+}$ incorporation in the Li$_4$Ti$_5$O$_{12}$ and/or a minute change in the surface state from the Zr$^{4+}$ doping.

Next, density functional theory (DFT) band calculations were carried out to probe the changes in the energy band structure and lattice structure from Zr$^{4+}$ doping. Figure 5.5(a) illustrates the (111) plane of the Li$_4$Ti$_5$O$_{12}$ unit cell used for constructing a stoichiometric 1×1×3 supercell. The structural parameters such as bond angle ($\gamma$), longitudinal distance ($a_1$), and vertical distance ($b_1$) are indicated to express a
lithium diffusion path for the tetrahedral 8a sites. Figure 5.5(b-d) plots the calculated projected density of states (PDOSs) of the pure Li₄Ti₅O₁₂ and the two Zr-doped cases with x = 0.05 and x = 0.1. The Li₄Ti₅O₁₂ exhibited typical insulating behavior, with an energy band gap of around 2.5 eV: the valence and conduction bands mainly consisted of O-\(p\) and Ti-\(d\) bands, respectively (Figure 5.5(b)). For the undoped Li₄Ti₅O₁₂, the bands corresponding in predominance to the interaction of O\(p_z\)-Ti\(d_{z^2}\) and O\(p_y\)-Ti\(d_{x^2-y^2}\) orbitals were in the energy range from -6.0 eV to the Fermi level.

**Figure 5.5** (a) Structural model of the Li₄Ti₅O₁₂ unit cell in the [110] direction: purple, grey, and red spheres indicate Li, Ti, and O atoms, respectively. The bond angle (\(\gamma\)), longitudinal distance (a₁), and vertical distance (b₁) are indicated to show the occupation sites for lithium (tetrahedral 8a sites) corresponding to a lithium diffusion path; Partial density of states projected onto the spherical harmonics of Ti/Zr and O atoms for Li₄Ti₅₋ₓZrxO₁₂ with (b) x = 0, (c) x = 0.05, and (d) x = 0.1. The valence band maximum was set to zero energy level.
When Zr$^{4+}$ was substituted into Ti$^{4+}$ sites, the interaction between the Zr-O atoms showed similar behavior to the Ti-O, but more $O_p y$-$Zr d_{x^2-y^2}$ bonding character (Figure 5.5(c) and (d)). It should be noted that the Zr-related states did not appear between the O-$p$ and Ti-$d$ bands in the Li$_4$Ti$_5$O$_{12}$. Consequently, the Zr$^{4+}$ doping is considered to give rise to no obvious change within the band gap.

By increasing the Zr$^{4+}$ doping content, the calculated average lattice parameter ($a$) increased gradually, which was in line with the XRD results (Figure 5.2(b)). Quite interestingly, the Zr$^{4+}$ doping resulted in increases in $a l$ and $b l$, while decreasing $\gamma$, as summarized in Table 5.1. The changes in the lattice structure, however, seemed to be saturated at the composition of $x = 0.05$. These structural changes could provide a hint for understanding the difference in electrochemical performance caused by Zr$^{4+}$ doping.

**Table 5.1** Calculated lattice parameter change ($\Delta a$), Zr substitution energy ($E_{\text{sub}}$), bond angle ($\gamma$), longitudinal ($a l$) and vertical ($b l$) distances for the lithium diffusion sites in the LTO and Zr-substituted ($x = 0.05$ and 0.1) supercells, as depicted in Figure 5.5(a).

<table>
<thead>
<tr>
<th>Composition</th>
<th>Lattice parameter change, $\Delta a$ (Å)</th>
<th>Substitution energy, $E_{\text{sub}}$ (eV/substituted atom)</th>
<th>$\gamma$ (degree)</th>
<th>$a l$ (Å)</th>
<th>$b l$ (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li$_4$Ti$<em>5$O$</em>{12}$</td>
<td>0</td>
<td>91.166</td>
<td>3.359</td>
<td>4.427</td>
<td></td>
</tr>
<tr>
<td>Li$<em>4$Ti$</em>{4.95}$Zr$<em>{0.05}$O$</em>{12}$</td>
<td>+0.028</td>
<td>-0.739</td>
<td>89.821</td>
<td>3.479</td>
<td>4.451</td>
</tr>
<tr>
<td>Li$<em>4$Ti$</em>{4.9}$Zr$<em>{0.1}$O$</em>{12}$</td>
<td>+0.049</td>
<td>-0.756</td>
<td>89.819</td>
<td>3.486</td>
<td>4.466</td>
</tr>
</tbody>
</table>
doping. The lattice expansion of Li$_4$Ti$_5$O$_{12}$ through the substitution of Zr$^{4+}$ with a relatively large ionic radius for Ti$^{4+}$ might have benefits for facile and fast intercalation/de-intercalation of lithium ions in terms of lithium diffusion behaviour, even though the Zr$^{4+}$ incorporation did not cause new states to appear within the band gap or mixed Ti$^{3+}$/Ti$^{4+}$ states, by which the electronic conductivity is enhanced due to the increase in the amount of charge carriers. [47] This result may be also in accordance with the absence of mixed Ti$^{3+}$/Ti$^{4+}$ states in the XPS spectra (Figure 5.4(a)).

The electrochemical performance of the undoped and Zr-doped Li$_4$Ti$_5$O$_{12}$ nanofiber anodes was evaluated using a galvanostatic discharge (de-intercalation) ––charge (intercalation) measurement. Figure 5.6(a) presents the first discharge/charge voltage profiles of the Li$_4$Ti$_5$O$_{12}$ and Zr-doped Li$_4$Ti$_5$O$_{12}$ samples at a current density of 0.1 C. All the samples exhibited a plateau at ~1.55 V, which is characteristic of Li$_4$Ti$_5$O$_{12}$ due to the two-phase reaction. [8] The initial discharge capacity of the undoped Li$_4$Ti$_5$O$_{12}$ nanofiber was 145.8 mAh g$^{-1}$, with an initial coulombic efficiency of 89.2 %. On the other hand, the LTO-Zr0.05 sample displayed a higher initial discharge capacity of 151.1 mAh g$^{-1}$, with an initial coulombic efficiency of 90.3 %. Increasing the Zr$^{4+}$ doping content further (LTO-Zr0.1 and LTO-Zr0.15), however, led to decreased capacity.

In addition, the Zr$^{4+}$ doping improved the rate capability and cycling performance, as can be seen in Figure 5.6(b). The LTO-Zr0.05 sample showed remarkably enhanced rate capability compared to the Li$_4$Ti$_5$O$_{12}$ sample, and the better performance at high current densities in particular was obvious. The discharge capacity of the LTO-Zr0.05 was 120.9 mAh g$^{-1}$ at 30 C, which was higher than that of the Li$_4$Ti$_5$O$_{12}$
Figure 5.6 (a) Discharge–charge curves in the first cycle and (b) rate capability and cycling performance of the Li$_4$Ti$_5$O$_{12}$ and Zr-Li$_4$Ti$_5$O$_{12}$ anodes. The first and second cycles were conducted at a current density of 0.1 C (with 1 C set as 170 mA g$^{-1}$), and the rate capability at various current densities (0.1 C to 30 C) and cycling performance at 1 C were evaluated.
(101.5 mAh g⁻¹). Although tZr⁴⁺ ions at higher doping levels (LTO-Zr0.1 and LTO-Zr0.15) degraded the discharge capacity at low current densities (0.1 C to 5 C), the doping was still clearly found to enhance the rate capability from comparison of the capacities at the high C rates of 20 C and 30 C.

To further investigate the Zr⁴⁺ doping effect on the reversibility of Li⁺ diffusion kinetics, cyclic voltammetry (CV) was conducted on the Li₄Ti₅O₁₂ and LTO-Zr0.05 electrodes at different scan rates, as shown in the inset of Figure 5.7(a). For both the samples, the separation between the redox peaks increased with increasing scan rate. From the CV profiles under the different scan rates, the plots of the normalized peak current (iₚ) with respect to the square root of the scan rate (ν¹/²) are presented in Figure 5.7(a). The linear relationship between iₚ and ν¹/² indicates that the Li⁺ intercalation/de-intercalation of both the samples corresponded to the diffusion-limited process and followed the Randles-Sevcik equation:

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

where \(i_p\) is the normalized peak current (A g⁻¹), \(n\) is the electron concentration (1 for Li⁺), \(A\) is the surface area of the electrode (cm² g⁻¹), which was measured by the Brunauer-Emmett-Teller (BET) method, \(D\) is the diffusion coefficient of Li⁺ (cm² s⁻¹), \(C\) is the bulk concentration of Li⁺ in the electrode (mol cm⁻³), and \(v\) is the scan rate (V s⁻¹). The surface areas of the Li₄Ti₅O₁₂ and Zr-doped Li₄Ti₅O₁₂ electrodes were estimated by N₂ adsorption/desorption isotherms and used to obtain Li⁺ diffusion coefficients during the intercalation and de-intercalation. From the N₂ sorption isotherms (Figure 5.7(b), the surface area was measured to be 96454 cm² g⁻¹
Figure 5.7 (a) Relationship between the peak current \( (i_p) \) and the square root of the scan rate \( (\nu^{1/2}) \) for Li\(^+\) intercalation/de-intercalation. The inset shows the cyclic voltammetry profiles at various scan rates. (b) N\(_2\) sorption isotherms and comparison of the measured specific surface areas (inset) for the Li\(_4\)Ti\(_5\)O\(_{12}\) and LTO-Zr0.05 samples.
and 64085 cm² g⁻¹ for the Li₄Ti₅O₁₂ and LTO-Zr0.05, respectively (see the inset of Figure 5.7(b)). Using the slope of the fitted lines, the Li⁺ diffusion coefficients during the intercalation and de-intercalation were calculated based on Equation (1): the diffusion coefficient during the intercalation was 5.91 × 10⁻¹⁴ and 2.00 × 10⁻¹³ cm² s⁻¹ for the Li₄Ti₅O₁₂ and LTO-Zr0.05, respectively, and the value during the de-intercalation was 1.08 × 10⁻¹³ and 2.87 × 10⁻¹³ cm² s⁻¹. In the case of both the intercalation and de-intercalation, the diffusion coefficients of the Zr-doped sample were larger than those of the undoped one, suggesting that the Zr⁴⁺ doping is effective for enhancing the electrochemical reaction kinetics of Li⁺ intercalation/de-intercalation. This improvement of the Li⁺ diffusivity appeared as a result of the lattice expansion, rather than electronic structure change by the Zr⁴⁺ substitution, as assessed based on the above theoretical and experimental investigations.

It should be noted that the Li₄Ti₅O₁₂ sample doped with the smallest amount of Zr⁴⁺ (LTO-Zr0.05) clearly exhibited improved electrochemical performance, but on the other hand, the electrochemical properties deteriorated abruptly for the LTO-Zr0.1 sample. In order to elucidate the origin of the different electrochemical performance of the LTO-Zr0.1 from that of LTO-Zr0.05, the microstructure of the LTO-Zr0.1 sample was further studied by using detailed TEM observations. Figure 5.8(a) displays bright field (BF) TEM (left) and HRTEM (right) images of the region (the interface between the Li₄Ti₅O₁₂ grains) highlighted by the dotted square on the LTO-Zr0.1 nanofiber. It was clearly observed that a few ZrO₂ nanoparticles with a size of less than 4 nm were present along the grain boundaries (see also the HAADF STEM image of Figure 5.8 (b)), which could be caused by the excessive doping over the solubility limit. This presence of the insulating ZrO₂ particles possibly hindered
Li$^+$ diffusion within the Li$_4$Ti$_5$O$_{12}$ nanofibers, and it could be responsible for the initial
Figure 5.8 (a) BF TEM (left), corresponding HRTEM (right) of the area marked by the dotted square, and (b) HAADF STEM images of an LTO-Zr0.1 nanofiber. The arrows indicate the ZrO$_2$ nanoparticles that are present on the LTO grain boundary.
discharge capacity fading of the LTO-Zr0.1 and LTO-Zr0.15 samples in the electrochemical performance testing.
5.4 Summary

The structural configuration induced by Zr$^{4+}$ doping in the 1D Li$_4$Ti$_5$O$_{12}$ nanofibers was explored through the correlation between the theoretical and experimental analyses. The Zr$^{4+}$ doping in the Li$_4$Ti$_5$O$_{12}$ lattice barely changed the fiber dimensions and electronic structure, but it increased the average lattice constant and Li$^+$ diffusion coefficient. For the Li$_4$Ti$_5$O$_{12}$ nanofiber doped with $x = 0.05$ (LTO-Zr0.05), it was found that the specific capacity, rate capability, and cycling properties were improved compared with the undoped one. These enhancements were attributed to the increased Li$^+$ diffusivity due to the lattice distortion (expansion) as a result of the Zr$^{4+}$ doping rather than an electronic structure change affecting the electronic conductivity. On further increasing the doping level, however, a number of ZrO$_2$ nanoparticles were formed at the Li$_4$Ti$_5$O$_{12}$ gain boundary, and they played a negative role in the electrochemical performance.
5.5 References


6 CORE-SHELL STRUCTURED SI-NANOPARTICLES@TIO2,X/C
MESOPOROUS MICROFIBER COMPOSITE AS A SAFE AND
HIGH-PERFORMANCE LI-ION BATTERY ANODE

6.1 Introduction

Considerable attention has been paid to the use of Si-based anode materials for LIBs because they theoretically possess much higher capacity than graphite (3590 mAh g\(^{-1}\) for Li\(_{3.75}\)Si and 372 mAh g\(^{-1}\) for LiC\(_6\)). Although the Si anodes deliver high specific capacity, they suffer from volume expansion, which leads to mechanical degradation of the Si materials during repeated cycling, and thereby poor cycle performance. [1,2] Research and development of Si-based anodes has been accelerated with the advance of nanotechnology since Fuji announced amorphous tin composite oxide (ATCO) as an anode material in 1997. [3] Nanostructured Si-based anode materials have been known to facilitate stain/stress relaxation and also shorten the Li diffusion length, so that an improved capacity, rate-capability, and cycle performance can be achieved. [4] Several types of Si-nanomaterials, such as active/inactive nanocomposites, [5] nano-sized particles with various morphologies, [6,7] and meso/macro-porous materials, [8,9] have been explored. Some of them are deployed in commercial LIB, as found in Hitachi Maxell’s cell where a SiO material was adopted as part of the anode composition. [10] The content of SiO in the anode was, however, limited under 10 wt.% because of the intrinsic volume expansion and the low initial coulombic efficiency as well as the unguaranteed safety issue with increasing energy density of the cell. Thus, Si-based anode materials should be further researched and developed for a competitively upgraded Si-based LIB having higher energy density, compared with the currently-used graphite-based LIB.
High capacity and long cycle-life have to be given priority in development of Si-based anode materials. However, concerns on the safety issue with the increased high energy density of a Si-employed LIB must be addressed before its practical application. Generally, the lithiated anode material is thermodynamically unstable and reacts exothermally with an electrolyte at an elevated temperature. [11] Unlike graphite anode material, however, only a few studies on the thermal properties of lithiated Si-based anode have been reported. [12-14] Previously, Jeong and co-workers reported the thermal properties of Si and SiO materials. [15] The large heat generation including a severe exotherm in the 300-400 °C range was observed for the Si-based materials, approximately threefold larger than the heat generation of graphite. The undesirable exothermic behavior was still observed for carbon-coated Si where the carbon has been regarded as a typical material of choice for improving the electrochemical performance of LIB electrode materials. Consequently, the larger heat generation in Si-based anodes is considered a potential risk factor inducing violent explosion of the battery under hazardous conditions. To suppress the undesirable exotherm, the carbon-coat was replaced by TiO$_2$ layer, and finally, could thus stabilize the thermal behavior of the SiO. However, the electrochemical performance was not much improved, probably due to the low electrical conductivity, so further development is necessary to achieve well-balanced cell performance for practical applications.

In this chapter, Si-nanoparticles@TiO$_{2-x}$/C mesoporous microfiber composite was fabricated by electrospinning with core-shell nozzle for 1D architecture for a high-performance and safety-reliable Si-based anode material, which has the features of a mechanically, electrically, and thermally robust microstructure. For a core-shell structured Si-nanoparticles@TiO$_{2-x}$/C mesoporous microfiber composite, the
Figure 6.1 Schematic illustration of a core-shell structured Si-nanoparticles@TiO_{2-x}/C mesoporous microfiber composite as an anode material for Li-ion batteries, which has the features of a mechanically, electrically, and thermally robust architecture. The molecules expressed with ball and stick model indicate EMC, EC, and LiPF_6 in the electrolyte solution (counterclockwise from top) and the ΔH means an exothermic enthalpy in the reaction between Li_xSi and electrolyte.

Expected function is three-fold as following (Figure 1): (i) Encapsulation of Si-nanoparticles inside a one-dimensional hollow and rigid TiO_{2-x}/C composite scaffold, with reserved void space therein, can suppress the disintegration of the Si-nanoparticles undergoing repeated volume change during cycling, and thereby improve the cycle performance (mechanically robust structure). (ii) Oxygen-deficient titania (TiO_{2-x}) and carbon as the shell components can provide an enhanced
electrical pathway of high conductivity for the electrochemical reaction between Li and Si, thereby improving the cell performance. Oxygen-deficient TiO₂ has been intensively studied for various application fields owing to its narrower band-gap enabling relatively high electrical conductivity. [16-23] For a battery material, a black TiO₂, showing oxygen-deficiency, has showed promising anode performance compared with a typical white TiO₂, by resolving the problem of the initial low electrical conductivity. [20] An oxygen-deficient TiO₂ as well as the in situ formed LiₓTiO₂ phase [24,25] during lithiation can support a favorable electrical environment with carbon in the shell structure (electrically robust structure). (iii) Introducing the TiO₂ as a main shell component, enhanced thermal stability of the Si composite can also be obtained. [15] The reason is that the TiO₂-shell is anticipated to act as a physical/chemical interfacial barrier retarding exothermic reaction between the highly lithiated Si phase and the electrolyte solution, combined with the intrinsically-stable thermal property of the TiO₂ itself (thermally robust structure). [26,27]
6.2 Experimental

6.2.1 Preparation of Si-nanoparticles@TiO$_2$/C and Si-nanoparticles@C

*Preparation of Si-nanoparticles@TiO$_2$/C:* For the core polymer solution, 0.5 g of Si nanoparticles (Nanostructured & Amorphous materials, 50-70 nm) was dispersed in 10 ml of $N,N$-dimethylformamide (DMF, Sigma-Aldrich) and 1.045 g of poly(methyl methacrylate) (PMMA, Mw=350,000, Sigma-Aldrich) was dissolved in dispersed Si solution by stirring at 90 °C for at least 8 hours. On the other hand, the shell solution was prepared by dissolving 1.567 g PMMA in 10 ml of DMF and 5 ml of acetic acid (Sigma-Aldrich). After dissolving over 8 hours, 2 ml of titanium (IV) isopropoxide (TTIP, Sigma-Aldrich) was added in PMMA solution, followed by magnetic stirring for 1 hour. The brown core polymer solution was immediately loaded into a plastic syringe equipped with the inner channel of a dual nozzle (NNC-DN-1723, NanoNC, Korea), which has a 23-gauge inner needle (OD: 0.63 mm, ID: 0.33 mm) and a 17-gauge outer needle (OD: 1.47 mm, ID: 1.07 mm). The light yellow transparent shell polymer solution was loaded into another plastic syringe which was connected to outer channel at the dual nozzle. The dual nozzle was connected to a high voltage supply, and the feeding rate of the core and shell solutions was set at 1.5 and 3.0 ml h$^{-1}$, respectively. A distance of 21.5 cm and voltage of 15 kV were maintained between the tip of the dual nozzle and a drum collector. After the electrospinning, the electrospun nanofibers were peeled off from the drum collector. Finally, the electrospun nanofibers were heat-treated at 800 °C for 3 h in nitrogen atmosphere.

*Preparation of Si-nanoparticles@C:* 1.0 g of Si nanoparticles and 1.093 g of PMMA (Mw=960,000, Sigma-Aldrich) were dispersed in 4.75 g of DMF and 4.75 g of acetone (Sigma-Aldrich) by stirring at 90 °C for at least 8 hours as the core polymer solution.
For the shell polymer solution, 1.425 g of polyacrylonitrile (PAN, Mw=150,000, Sigma-Aldrich) was dissolved in 10 ml of DMF at 90 °C for at least 8 hours. The core and shell polymer solution were loaded into the plastic syringes which were connected to the inner and outer dual nozzle, respectively. The distance between the needle and the drum collector was 11 cm, and the high voltage of 17 kV was applied to the dual-nozzle. The feeding rates of the core and shell solutions were 2.0 and 3.0 ml h⁻¹, respectively. After the electrospinning, the electrospun microfibers were detached from the drum collector and stabilized at 280 °C for 1 hour in air. The carbonization was performed at 900 °C for 5 h in nitrogen atmosphere.

**Characterizations:** The morphology, microstructure, and compositional analysis of the synthesized materials were examined using a field emission scanning electron microscope (FESEM, JEOL JSM-7000F), a high-resolution transmission electron microscopy (HRTEM, ARM-200F, JEOL) having a probe C₈ aberration corrector (CEOS GmbH) and an energy-dispersive spectroscopy (EDS) system that was attached to the TEM system. The crystalline structure analysis of the synthesized materials was performed using an Empyrean diffractometer (PANalytical) equipped with monochromated Cu Kα₁ radiation (λ = 1.54056 Å). For ex situ XRD analyses of the discharged or charged electrode, a gas-tight sample holder filled with Ar and covered with a polyimide (Kapton) tape was used. After cell reacted up to certain level, the electrode was carefully disassembled from the cell and then rinsed with dimethyl carbonate (DMC) in an Ar-filled glove box to remove residual electrolyte. The electrodes was then dried under vacuum for 3 h and transferred to the ex situ XRD holder. The morphology change and cross-sectional image of electrodes after cycling was analyzed by FESEM. Similar to the ex situ XRD analysis, the cells were carefully disassembled and the electrodes were subsequently rinsed with DMC. They
were then dried under vacuum for 3 h and transferred to the chamber of SEM equipment. The chemical binding state and electronic structure were examined by X-ray photoelectron spectroscopy (XPS, Thermo Scientific Sigma Probe) with Al Kα X-rays. Diffuse reflectance UV-vis spectra of powders were measured on JASCO spectrophotometer (V-670, Japan) and all the samples were measured under ambient conditions. The surface area and pore volume of the synthesized materials were measured by Brunauer–Emmett–Teller (BET) and Barrett–Joyner–Halenda (BJH) methods, respectively, using a surface area and porosimetry analyzer (TristarII 3020, Micromeritics). The electrical conductivity of powder-type samples was measured by a direct volt-ampere method (MCP-PD51, Mitsubishi Chemical Analytech) in which a sample was pressurized and contact with a four-point probe. Differential scanning calorimetry (DSC) was performed using a Model Star system (Mettler Toledo), and the lithiated electrode samples were prepared by discharging the 2032 coin half cells to 0.005 V at a slow rate of 60 mA g⁻¹. These cells were disassembled in a dry room (the dew point of less than -60 °C), and the electrodes were rinsed with DMC and dried under vacuum. Then, 1.5 mg of the electrode and 0.5 mg of fresh electrolyte solution were sealed in a high-pressure DSC pan. The heating rate and temperature range of the DSC tests were 5 °C min⁻¹ and 25–400 °C, respectively.

### 6.2.2 Electrochemical performance

The electrodes were prepared by coating copper foil substrates (thickness: 10 mm) with slurries containing the active material powders (80 wt%), carbon black (Super-P, 10 wt%), and poly(acrylic acid) (PAA, 10 wt%) dissolved in water. After coating, they were dried at 80 °C for 30 min in a convection oven to evaporate the water and then heat-treated at 120 °C for 6 h under vacuum. The electrodes were cut into discs
(12 mm in diameter), in which the mass of the active material was approximately 1–3 mg. 2032 coin cells were assembled in a dry room that provided humidity at a dew point of less than -60 °C, using a polypropylene separator (Asahi Kasei Chemicals); 1 M LiPF₆ in a mixture of ethylene carbonate (EC) and ethyl methyl carbonate (EMC) (EC/EMC = 1/2 ratio) containing 20% fluoroethylene carbonate (FEC) as an electrolyte solution; and lithium foil (14 mm in diameter) as a counter-electrode. The assembled cells were aged overnight at room temperature and then electrochemically tested using a TOSCAT-3100U (Toyo system Co.) battery measurement system under the following protocols. The first cycle was operated at a constant current (CC) mode of 50 mA g⁻¹ within a voltage window of 0.005–2.5 V vs. Li/Li⁺. The test protocol for cycle and rate performance was a constant current followed by a constant voltage (CCCV) mode for discharging (lithiation). In this mode, 0.2C (1C was set as 1100 mAg⁻¹) was used for the CC step and 0.005 V finished at 0.1C for the CV step. For charging (delithiation), the CC mode with various current densities was used and cut off by 1.4 V.
6.3 Results and discussion

A core-shell structured Si-nanoparticles@TiO$_{2-x}$/C mesoporous microfiber composite (hereafter denoted as SiNPs@T/C) was prepared by an electrospinning method using a dual nozzle. Si-nanoparticles dispersed in a poly(methyl methacrylate) (PMMA) solution were injected into the core channel of the nozzle, whereas titanium (IV) isopropoxide dissolved in a PMMA solution was injected into the shell channel of the nozzle. After the single electrospinning step, the product was heated to 800 °C to obtain TiO$_{2-x}$/C nanocomposite in the electrospun. Details of materials and experimental methods are described in the Experimental Details. The morphology and crystalline microstructure of the electrospun were directly confirmed by scanning electron microscopy (SEM), transmission electron microscopy (TEM), scanning TEM (STEM), and X-ray diffraction (XRD). As shown in Figure 6.2(a), the electrospun revealed the randomly aligned microfibers having average diameters of ~2 µm and length extending to several tens of micrometers. The core-shell structure was observed by SEM (the inset in Figure 6.2(a)) and was further clearly confirmed by the high-angle annular dark-field (HAADF) STEM images and the corresponding energy dispersive spectroscopy (EDS) elemental mapping for Si, Ti, O and C (Figure 6.2(b) and (c)). The core region was full of Si-nanoparticles (50–100 nm diameter for each Si-nanoparticle) with reserved void space that may be produced by unzipping of PMMA [28,29] used in the solution for the core channel in the dual-nozzle electrospinning. The outer-shell section composed of Ti, O and C showed a thickness of 200–300 nm and also porous characteristics. The pore structure of the electrospun was further investigated by nitrogen sorption measurement (Figure 6.2(d)). The N$_2$ adsorption/desorption isotherm indicates the characteristics of mesoporous materials. The Brunauer–Emmett–Teller (BET)
The surface area was 163 m$^2$ g$^{-1}$ and the average pore volume of Barrett–Joyner–Halenda (BJH) was 0.33 cm$^3$ g$^{-1}$, which strongly confirmed the mesoporous structure of the electrospun. The identified porosity may be helpful in accessing the electrolyte solution and to accommodate the volume expansion of the Si-nanoparticles when the

Figure 6.2 (a) SEM images of the electrospun SiNPs@T/C. (b) A HAADF STEM image of SiNPs@T/C and (c) the EDS elemental mapping for silicon, titanium, oxygen, and carbon. (d) N$_2$ adsorption/desorption isotherm and the pore size distribution (inset) of SiNPs@T/C: the BET surface area is 163 m$^2$ g$^{-1}$ and the average pore volume is 0.33 cm$^3$ g$^{-1}$. HRTEM images and the corresponding FFTs (inset) for (e) the core region and (f) the shell region of SiNPs@T/C: the observed crystallites in the HRTEM image correspond to rutile TiO$_2$ and the amorphous regions correspond to carbon.
microfiber is used as an anode material for LIBs. [8,9] The phase information corresponding to the core and shell region was identified by the high-resolution TEM (HRTEM) image and the corresponding fast Fourier transform (FFT). The HRTEM images and FFTs indicated the crystalline Si (Figure 6.2(e)) for the core section, the nanocomposite of rutile TiO₂ and amorphous carbon for the shell (Figure 6.2(f)),

![Graphical representation of XRD pattern and Raman spectra](image)

**Figure 6.3** (a) XRD pattern and (b) Raman spectra of the SiNPs@T/C.
which conclusively proved that crystalline Si-nanoparticles were encapsulated by TiO$_2$/C nanocomposite in the electrospun fibrous composite. Additional phase identification by using XRD and Raman spectroscopy (Figure 6.3(a) and (b)) supported the presence of polycrystalline rutile TiO$_2$, Si, and amorphous carbon. The presence of carbon in the shell of the SiNPs@T/C deserves mention. The content of carbon in the TiO$_2$/C shell was about 14 wt.%, measured by thermogravimetric analysis (Figure 6.4). The carbon is considered to originate from the PMMA used in the solution for the shell channel in the dual-nozzle electrospinning. Generally, PMMA leaves no residue after pyrolysis even in inert atmosphere. [28,30] In certain

**Figure 6.4** The TGA curve of the TiO$_{2-x}$/C nanocomposite as the shell structure.
cases, however, PMMA can be carbonized. [31,32] According to the literature, TiO$_2$-gel in the PMMA partly terminates the chain degradation of PMMA by intercepting some of the free radicals during depolymerization, which leads to the formation of carbon in SiNPs@T/C material.

The basic material characterization of the Si-nanoparticles@C (hereafter denoted as SiNPs@C) were displayed in Figure 6.5. As shown in Figure 6.5(a), the electrospun revealed the randomly aligned microfibers having average diameters of 1~2 mm and length extending to several tens of micrometers. The core-shell structure was

![Figure 6.5](image)

**Figure 6.5** SEM images of the electrospun SiNPs@C mat at (a) low and (b) high magnification. (c) XRD pattern of the SiNPs@C and (d) Thermogravimetric analysis (TGA) result of the SiNPs@C indicating the Si-content (54 wt%) in the composite.
observed by SEM in Figure 6.5(b). From the XRD patterns, all reflections were identical to the standard peaks of Si in Figure 6.5(c). The content of carbon in the SiNPs@C was about 54 wt.%, measured by thermogravimetric analysis in Figure 6.4(d).

As shown in Figure 6.6, the SiNPs@T/C has dark-green color. Many reports have discussed coloration of TiO$_2$ in relation with the electronic structure. [16-23,33,34] The coloration in the sample also implied the presence of nonstoichiometric TiO$_2$, and the electronic structure of the TiO$_2$ in the SiNPs@T/C and the effect on electrical conductivity were investigated. Figure 6.6 presents the Tauc plot [35] derived from the diffusive reflectance UV-vis spectroscopy analysis for the SiNPs@T/C. It revealed that the optical band gap of SiNPs@T/C was 2.44 eV whereas the band gap

Figure 6.6 Tauc plots representing band gap energy of SiNPs@T/C, SiNPs, and white TiO$_2$. 
of white TiO$_2$ as a reference was 3.18 eV. The band gap energy of SiNPs is higher than 1.1 eV known as a typical value for silicon, because of the native silicon oxide and/or nano-size effect of SiNPs. [36] In the latter, the SiNPs@T/C exhibited a broad absorption extending to the near-infrared (NIR) region of the spectrum (Figure 6.7), which gave it a dark-green coloration. To clarify the physical origin of the visible-NIR light absorption of the SiNPs@T/C, its electronic properties were investigated by using X-ray photoelectron spectroscopy (XPS) measurement. Although both SiNPs@T/C and white TiO$_2$ showed typical Ti 2p core-level XPS spectra with Ti$^{4+}$ characteristics (Ti 2p$_{3/2}$ peak at 459.0 eV of binding energy), SiNPs@T/C also exhibited a shoulder near 457.7 eV, which is characteristic of Ti$^{3+}$ (Figure 6.8(a)).[21]
The ratio of Ti$^{3+}$ to Ti$^{4+}$ was calculated to be 9.7/90.3, assumed to be TiO$_{1.952}$. According to the literature, [33,37] defects can be generated in TiO$_2$ structure in inert atmosphere due to partial oxygen loss leading to reduction and vacancy generation and the reduction to Ti$^{3+}$ strongly influences the density of the state distribution.

Figure 6.8 (a) Ti 2$p_{3/2}$ XPS spectra for SiNPs@T/C and white TiO$_2$. The measured spectra were deconvoluted by Ti$^{4+}$ and Ti$^{3+}$. (b) Valence band XPS spectra of SiNPs@T/C and white TiO$_2$. Of the two main bands in the valence band, the low binding energy state (5~6 eV) is assigned to O 2$p$–Ti 4$s,p$ bonding, and the electronic band at high binding energy (7~8 eV) is predominantly due to O 2$p$–Ti 3$d$ bonding. [17] Thin blue lines show the linear extrapolation of the curves used for deriving the band edge position of the samples.

The ratio of Ti$^{3+}$ to Ti$^{4+}$ was calculated to be 9.7/90.3, assumed to be TiO$_{1.952}$. According to the literature, [33,37] defects can be generated in TiO$_2$ structure in inert atmosphere due to partial oxygen loss leading to reduction and vacancy generation and the reduction to Ti$^{3+}$ strongly influences the density of the state distribution. Figure 6.8(b) exhibits valence band (VB) XPS of SiNPs@T/C and white TiO$_2$. A white TiO$_2$ displayed the VB maximum edge at 2.17 eV and, since the optical band gap is 3.18 eV from the above UV–vis measurement, the conduction band (CB) minimum will occur at -1.01 eV. On the other hand, VB XPS of SiNPs@T/C showed notable differences: the main absorption onset was located at 1.73 eV, whereas the
maximum energy associated with the band tail blue-shifted further toward the vacuum level at about -0.09 eV. Chen et al. [16] reported a substantial shift (2.18 eV) of the VB maximum edge for hydrogenated black TiO\(_2\) nanoparticles, and Naldoni et al. [18] also presented very similar VB spectra for both white and black TiO\(_2\). The TiO\(_{2-x}\) of the shell component in the SiNPs@T/C also has a distinctive density of states (DOS) structure. If for the TiO\(_{2-x}\) the same CB energy shape is assumed as for white TiO\(_2\) reference, a remarkable narrowing in the band gap (0.62 eV) can be observed (Figure 6.9). Therefore, electronic transition from tailed VB to CB in the narrowing band gap, which is induced by the presence of Ti\(^{3+}\), is responsible for the

**Figure 6.9** The schematic DOS for white TiO\(_2\) and the TiO\(_{2-x}\) in SiNPs@T/C. Both representations were built using experimental data from UV-vis spectroscopy and XPS analyses.
Figure 6.10 Electrical conductivities of SiNPs@T/C, SiNPs@C, and carbon black powders.

TiO$_{2-x}$ shell in the SiNPs@T/C. As expected from the reduction in the band gap energy of TiO$_2$ and the presence of carbon in the shell of the SiNPs@T/C, the electrical conductivity of the SiNPs@T/C was found to be relatively high, i.e., $3 \times 10^{-1}$ S cm$^{-1}$ (Figure 6.10). Although the value is lower than those of carbon black and SiNPs@C (a core-shell structured Si-nanoparticles@carbon fibrous composite was prepared for comparison in Figure 6.5, which was already reported as a promising anode material. [29]), it is much higher than those of white TiO$_2$ and Si-nanoparticles: the electrical conductivities of white TiO$_2$ and Si-nanoparticles could not be measured in this study because of their too low conductivities. With the references, [38,39] the known electrical conductivities of rutile TiO$_2$ (white) and Si-nanoparticle are $7 \times 10^{-7}$ and $10^{-8} - 10^{-7}$ S cm$^{-1}$ respectively. Consequently, the
The electrochemical performance of the SiNPs@T/C anodes was evaluated using a galvanostatic discharge—charge measurement. Figure 6.11(a) shows the first and second voltage profiles of the SiNPs@T/C anode material. The discharge (lithiation) and charge (delithiation) capacities were 1710 and 1260 mAh g⁻¹, respectively. The significantly increased electrical conductivity of SiNPs@T/C appears to enhance the electrochemical performance of an LIB anode material.
initial coulombic efficiency (ICE) corresponded to 74% which exceeded that of the pure Si-nanoparticles anode (68%). It implies that the well-integrated core-shell structure of the SiNPs@T/C suppresses the possible structural collapse produced by the volume change of Si, enhancing reversibility of the Li-Si electrochemical reaction. The preservation of the core-shell structure and the expansion ratio of the electrode after the first lithiation were verified by SEM images (Figure 6.11 (b)-(d)). The overall fibrous morphology was clearly maintained and the expansion ratio was ~57% which is comparable to the already-reported advanced Si anode materials, such as, a Si nanotube (~54%) [40] and an urchin-like Si/SiOₓ nanocomposite (~50%). [41]

It is important to further check whether high capacity of an anode material is really increasing the energy density of the full-cell battery where the anode is employed. The reason is that not only the reversible capacity of an anode but the ICE, the electrode density (especially, lithiated, i.e., expanded state in a case of Li-alloy anode), and operational voltage of the full-cell are also critical factors determining the energy density of a full-cell battery. To compare the volumetric energy density of the SiNPs@T/C-employed full-cell with a graphite-employed one, a single full-cell configuration was established by applying LiCoO₂ (LCO) as a cathode. Estimation of volumetric energy density and voltage profile was carried under the following conditions:

1) 1-dimensional single-stacked full cell (see the Figure 6.12) was considered as a model structure for estimation of volumetric energy density.

2) Charging voltage of full cells; 4.2 V.
3) Discharge cut-off voltage for the full cell employing SiNPs@T/C is 2.0 V, corresponding to ca. 2.0 V vs Li/Li\(^+\) of cut-off potential for the anode in the half-cell. Discharge cut-off voltage for the full cell employing graphite is 3.0 V.

4) Loading of cathode

- Loading of cathode composite film (LiCoO\(_2\)+carbon black+binder) was fixed at 23.8 mg cm\(^{-2}\), corresponding to 3.6 mAh cm\(^{-2}\) of charging capacity.

5) Electrode density of anodes

- 1.3 g cm\(^{-3}\) of electrode density was employed for SiNPs@T/C anode, which is corresponding to the experimental value for the firstly lithiated SiNPs@T/C electrode.

**Figure 6.12** Design with 1.1 N/P ratio and 3.6 mAh/cm\(^2\) for charging capacity (4.2V).
6) Loading and thickness of anodes
   - By negative/positive (N/P) ratio (=1.1) and the electrode densities, loading and thickness of the anodes were determined.

7) Voltage profile and energy density
   - Voltage profiles and volumetric energy densities of the full cells were obtained from the experimental voltage profiles of anode and cathode in their half-cells, using the OriginPro 8 SR4 program.

![Figure 6.13](image)

**Figure 6.13** Simulated voltage profiles versus volumetric capacity of the SiNPs@T/C−LiCoO$_2$ and the graphite−LiCoO$_2$ of unit full-cell stack. The loading of the LiCoO$_2$ cathode and charging voltage were fixed at 3.6 mAh cm$^{-2}$ and 4.2 V, respectively. The detailed design parameters and simulated results are listed in the Table 6.1.
Table 6.1. Estimation of volumetric energy density of a single full-cell of SiNPs@T/C–LiCoO₂ and the comparison with a graphite–LiCoO₂ full-cell.

<table>
<thead>
<tr>
<th>Design parameters</th>
<th>SiNPs@T/C anode</th>
<th>Graphite anode</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Cathode (LiCoO₂)</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Charge capacity / mAh g⁻¹ *</td>
<td>158</td>
<td>←</td>
</tr>
<tr>
<td>Discharge capacity / mAh g⁻¹</td>
<td>153</td>
<td>←</td>
</tr>
<tr>
<td>Initial Coulombic efficiency / %</td>
<td>96.8</td>
<td>←</td>
</tr>
<tr>
<td>Ratio of active material / %</td>
<td>96</td>
<td>←</td>
</tr>
<tr>
<td>Ratio of binder / %</td>
<td>2</td>
<td>←</td>
</tr>
<tr>
<td>Ratio of carbon black / %</td>
<td>2</td>
<td>←</td>
</tr>
<tr>
<td>Electrode density / g cm⁻³</td>
<td>3.7</td>
<td>←</td>
</tr>
<tr>
<td>Charge capacity per unit area / mAh cm⁻²</td>
<td>3.6</td>
<td>←</td>
</tr>
<tr>
<td>Loading level / mg cm⁻²</td>
<td>23.8</td>
<td>←</td>
</tr>
<tr>
<td>Electrode thickness / μm</td>
<td>64</td>
<td>←</td>
</tr>
<tr>
<td><strong>Anode</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Charge capacity / mAh g⁻¹</td>
<td>1710</td>
<td>378</td>
</tr>
<tr>
<td>Discharge capacity / mAh g⁻¹ **</td>
<td>1180</td>
<td>350</td>
</tr>
<tr>
<td>Initial Coulombic efficiency / %</td>
<td>69</td>
<td>93</td>
</tr>
<tr>
<td>Ratio of active material / %</td>
<td>80</td>
<td>90</td>
</tr>
<tr>
<td>Ratio of binder / %</td>
<td>10</td>
<td>10</td>
</tr>
<tr>
<td>Ratio of carbon black / %</td>
<td>10</td>
<td>0</td>
</tr>
<tr>
<td>Electrode density / g cm⁻³</td>
<td>1.3⁺</td>
<td>1.4</td>
</tr>
<tr>
<td><strong>Others</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>N/P ratio</td>
<td>1.1</td>
<td>←</td>
</tr>
</tbody>
</table>
Table 6.1. (continue)

<table>
<thead>
<tr>
<th>Simulated results</th>
<th>SiNPs@T/C anode</th>
<th>Graphite anode</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Anode</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Loading level / mg cm(^{-2})</td>
<td>2.90</td>
<td>11.65</td>
</tr>
<tr>
<td>Electrode thickness / (\mu m)</td>
<td>34</td>
<td>83</td>
</tr>
<tr>
<td><strong>Single-stacked full cells</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Discharge capacity per unit area / mAh cm(^{-2})</td>
<td>2.486</td>
<td>3.336</td>
</tr>
<tr>
<td>Volume of stack / cm(^3)</td>
<td>0.00983</td>
<td>0.01474</td>
</tr>
<tr>
<td>Stack-volumetric capacity / Ah L(^{-1})</td>
<td><strong>253</strong></td>
<td><strong>226</strong></td>
</tr>
<tr>
<td>Operating mid-voltage / V</td>
<td>3.58</td>
<td>3.7</td>
</tr>
<tr>
<td>Stack-volumetric energy density / Wh L(^{-1})</td>
<td><strong>906</strong></td>
<td><strong>837</strong></td>
</tr>
</tbody>
</table>

* 4.2 V of charging cutoff voltage for the full cells
** 2.0 V of discharging cutoff voltage for the SiNPs@T/C–LiCoO\(_2\) full cell (The value corresponds to 2.0 V vs. Li/Li\(^+\) in the half-cell of the SiNPs@T/C anode), and 3.0 V of discharge cutoff voltage for the graphite– LiCoO\(_2\) full cell
† The value corresponds to the first lithiated (expanded) state.
Figure 6.14 (a) DCPs of SiNPs@T/C half-cell during the first and second cycles.

(b) Evolution of the XRD patterns of SiNPs@T/C during the first cycle; (i) the fresh electrode, (ii) discharged by 1.0 V (vs. Li/Li$^+$), (iii) discharged by 0.005 V, (iii) charged by 1.4 V, and (iv) charged by 2.5 V.
As presented in Figure 6.13 and Table 6.1, the SiNPs@T/C-LCO system revealed ~8% higher energy density than that of the graphite-LCO. For a more competitive energy density to replace a graphite-system, however, the ICE and the volume expansion as well as capacity need to be further perfected.

As indicated in the differential capacity plot (DCP) of the SiNPs@T/C (Figure 6.14(a)), the main discharge/charge reaction is based on alloying/de-alloying between Li and Si. Besides the Li-Si electrochemistry, the rutile TiO$_{2-x}$ as a shell structure in the SiNPs@T/C also takes part in the initial electrochemical reaction. As well-noted in the literature, [42] a nanostructured rutile TiO$_2$ is one of the candidates for an anode material in LIBs. Li-ion can insert into TiO$_2$ during the initial discharge process at about 1.7~1.8 V, leading to the formation of Li$_{0.5}$TiO$_2$. It has been well known that the in situ formed Li$_x$TiO$_2$ also has an enhanced electrical conductivity due to the existence of Ti$^{3+}$, [24,25] as well as TiO$_{2-x}$, and thus can also be advantageous for electrical pathways similar to the traditional carbon-coat on electrode materials for LIBs. Several DCP peaks (inset in Figure 6.14(a)) could be observed in the potential range of 0.82.4 V in the initial discharge process of the SiNPs@T/C. A peak at 1.8 V corresponds to Li-ion insertion into the TiO$_{2-x}$ and other DCP peaks are related with electrolyte decomposition on the surface of SiNPs@T/C. The phase evolution of the rutile TiO$_{2-x}$ during insertion/extraction of Li-ion can be identified by ex situ XRD analysis as shown in Figure 6.14(b). When a SiNPs@T/C was lithiated by 1.0 V (vs. Li/Li$^+$), the corresponding XRD pattern showed no change versus the fresh electrode. It indicates that the lithiated SiNPs@T/C, more specifically, the lithiated TiO$_{2-x}$ of the shell component in the composite initially retains a rutile-type structure upon lithiation. Further lithiation down to 0.005 V leads to the appearance of LiTiO$_2$ phase of cubic rock-salt structure.
(2θ= 43.8 and 63.5°, JCPDS #16-0223) in addition to the Li_{3.75}Si alloy phase formed by lithiation of Si-nanoparticles of the core component. On the reverse charging process, the LiTiO₂ phase still remains even in the fully delithiated state, indicating the irreversible trapping of Li in TiO₂-x. The above observed phase evolution of rutile TiO₂-x and Si in the first cycle matches well to the previous results in the literature. [25,43-45] Although the irreversible LiTiO₂ phase causes the low coulombic efficiency in the first cycle, it has a positive effect, as previously mentioned, on the following cycle or rate performance of the SiNPs@T/C by providing an electrical scaffold structure having an enhanced electrical conductivity.

Figure 6.15(a) exhibits the cycling performance of the SiNPs@T/C. For comparison, the simply-mixed Si-TiO₂-C electrode in the same weight ratio with the SiNPs@T/C electrode is also tested. When cycled at 0.2 C, the SiNPs@T/C displayed good capacity retention, i.e., 90% of the initial capacity after 50 cycles, showing obviously a superior performance to the simply-mixed Si-TiO₂-C. When cycled at a higher current density of 1C, the SiNPs@T/C still delivered excellent cycling performance where the capacity and its retention were almost the same as to the performance at 0.2 C. The SiNPs@T/C also exhibited outstanding rate capability (Figure 6.15(b)), where a high capacity of 939 mAh g⁻¹ is observed even at a significantly high current density of 12 C (12 A g⁻¹), i.e., 89% of the initial capacity at 0.2 C. These outstanding electrochemical performances indicate that the fibrous core-shell structure of the SiNPs@T/C resolves some serious issues in Si-based anode materials, such as, collapse of electrical network in the electrode due to the mechanical degradation by volume change of the Si. The mechanically robust TiO₂-x/C shell can suppress the disintegration of the Si nanoparticles in the SiNPs@T/C composite. Also, the initial TiO₂-x and the in situ formed Li₅TiO₂ phase in the shell structure
Figure 6.15 (a) Capacity retention of SiNPs@T/C during cycling and the corresponding voltage profiles (inset). (b) Delithiation rate capability of SiNPs@T/C and the corresponding voltage profiles (inset). For the cycle and rate capability tests, lithiation current density was fixed as 0.2C/0.1C(5 mV) CCCV mode. (c) A SEM image of SiNPs@T/C after 50 cycles (lithiated state). The cross-sectional SEM images of SiNPs@T/C electrode (d) before cycling and (e) after 50 cycles (lithiated state). The observed expansion ratio was ~53%.
promote the electron/Li-ion path in the SiNPs@T/C, and thereby improve the
electrochemical performance of the SiNPs@T/C. Figure 6.15(c-e) show the SEM
images of the SiNPs@T/C particle and the cross section of the SiNPs@T/C electrode
after 50 cycles. The fibrous core-shell structure free of a significant collapse can be
clearly observed even after 50 cycles. Also, the volume expansion after the 50th
discharge is still ~53% which is almost the same as the value after the 1st discharge
step (see again Figure 6.10), indicating stable volume change during cycling.

In addition to the electrochemical performance, the thermal property of the lithiated
SiNPs@T/C was also investigated, focusing on the effect of the TiO2-x shell structure.
Figure 6.16 shows differential scanning calorimetry (DSC) scans of the different
lithiated anode materials including the SiNPs@T/C. All the measurements were
performed at 100% SOC (state of charge) in the presence of the entrapped electrolyte.
Compared with the graphite which showed a relatively low exotherm in the overall
temperature range (5.7 kJ g\(^{-1}\)), the bare Si-nanoparticles (SiNPs) exhibited larger
exothermic enthalpy (11.4 kJ g\(^{-1}\)), especially with an abrupt exothermic peak in the
350–400 °C range. Although a more systematic clarification of the DSC behavior of
the bare SiNPs, beyond the scope of this paper, is required, the larger exothermic
enthalpy including the abrupt exotherm above the 350 °C is regarded as an intense
reaction between the highly-lithiated Li\(_x\)Si and the electrolyte solution as previously
reported. \[15\] The large exothermic behavior of Si material can be problematic in
respect to safety concerns in the development of a Si-based LIB, because the thermal
behavior can lead to a cell explosion under extreme conditions, such as, penetration
or high-temperature exposure. For a more specific investigation of the thermal
property of the SiNPs@T/C, the thermal property of the SiNPs@C material was also
examined because the carbon-coating or carbon-composite for a Si anode has been
regarded as the most effective material engineering for enhancing the electrochemical performance. The SiNPs@C exhibited less exothermic enthalpy in the overall temperature range (6.0 kJ g\(^{-1}\)) than the bare SiNPs. However, the heat generation in the 150−300 °C range was still the same as for bare SiNPs, which indicates that the carbon-shell structure cannot perfectly suppress the intensive exothermic reaction between Li\(_x\)Si and the electrolyte.

Unlike the bare SiNPs and SiNPs@C, the SiNPs@T/C exhibited a significantly reduced exotherm in the overall temperature range (4.2 kJ g\(^{-1}\)), which is comparable to graphite. This remarkable thermal stabilization is considered to originate from the TiO\(_{2-x}\) shell structure. The shell which is mainly composed of TiO\(_{2-x}\) possibly retards

**Figure 6.16** (a) DSC curves and (b) the corresponding accumulated heat curves of SiNPs@T/C, SiNPs@C, SiNPs, and graphite anode materials. All samples were fully lithiated (discharged to 5 mV) for the first cycle.
the intensive thermal reaction between the highly lithiated Si and the electrolyte solution. In addition, the well-noted thermal stability of lithiated TiO$_2$ and its solid-electrolyte-interphase are considered to be other possible reasons for the suppressed exothermic reaction in the SiNPs@T/C. The quantitative relationship between the DSC results and the actual safety characteristics of LIB is not linearly dependent. The present results, however, suggest that the thermal stability of the fully lithiated Li$_x$Si phase is definitely improved when the Si-nanoparticles are encapsulated by TiO$_{2-x}$.
6.4 Summary

Achievement of the high energy density and the long cycle-life of a Si-based LIB should be accompanied with guaranteed safety. A core-shell structured Si-nanoparticles@TiO$_{2-x}$/C mesoporous microfiber composite as an anode for LIBs was prepared by a simple method using electrospinning. The microstructure was identified by various analytical methods as a core-shell fibrous composite consisting of a porous assembly of Si-nanoparticles as the core, and the mesoporous wall of rutile TiO$_{2-x}$/C nanocomposite as the shell structure. The SiNPs@T/C exhibited high reversible capacity, excellent rate capability, and good cycle performance. Furthermore, it showed remarkable suppression of exothermic behavior in comparison with bare SiNPs and a SiNPs@C fibrous composite. The stabilized thermal property can prevent possible thermal runaway and safety problems of a Si-based LIB. The improved electrochemical and thermal properties are ascribed to the mechanically, electrically, and thermally robust shell-structure of the TiO$_{2-x}$/C nanocomposite encapsulating the Si-nanoparticles. In many efforts for the commercialization of Si-based LIBs, the core-shell structured Si-nanoparticles@TiO$_{2-x}$/C mesoporous microfiber composite can thus offer a promising material architecture for a safe and reliable Si-based LIB of high energy density.
6.5 References


7 CONCLUSION

This thesis has investigated the electrochemical properties of Ti-based nanostructured materials fabricated by an electrospinning technique as alternative anodes materials for lithium rechargeable batteries. 1D Ti-based oxide materials has clearly demonstrated that their electrochemical performance is related to their morphological advantages. The effect of doping (such as silver, zirconium and nitrogen) into Ti-based oxide materials was investigated through correlation between experimental results and theoretical study. The remarkably improved electrochemical properties of 1D nanostructured Ti-based oxide materials originated from the effect of 1D nanostructure affording shortened Li$^+$ diffusion pathways and fast electron charge transport.

In the first part, on the basis of structural characterizations, it was found that anatase TiO$_2$N$_x$ nanofibers (100-200 nm) were formed after calcination below 500 °C. To clarify the nitrogen site, the surface of nitrogen-doped TiO$_2$ was investigated by first principles calculations as well as EDS, FTIR, and XPS. The nitrogen was interstitially located near surface of anatase TiO$_2$, enhancing the conductivity and changing the work function. The nitrogen-doped TiO$_2$ nanofibers (185 mAhg$^{-1}$) showed much higher cycle stability than the commercial nanopowders (60 mAhg$^{-1}$) after 40 cycles, and enhanced rate capability from 0.1 C to 2 C because of strongly facilitated Li$^+$ diffusion and electron transport.

In the second, the electrochemical performance of 1D Li$_4$Ti$_5$O$_{12}$ with novel metal doping was investigated. To improve electrical conductivity, Li$_4$Ti$_5$O$_{12}$ nanofibers were rationally designed by Ag doping. It was found that Ag nanoparticles (1.75
at.%) were mainly distributed all throughout the Li$_4$Ti$_5$O$_{12}$ matrix. The Ag-Li$_4$Ti$_5$O$_{12}$ nanofibers showed high rate capability and cycle stability compared to the bare Li$_4$Ti$_5$O$_{12}$ nanofibers from 0.1 to 30 C, however, the initial irreversible capacity of Ag-Li$_4$Ti$_5$O$_{12}$ (31.5 mAh g$^{-1}$) exhibited a slightly larger than that of the bare Li$_4$Ti$_5$O$_{12}$, (31.5 mAh g$^{-1}$), which probably originated from different electrolyte decomposition behaviors. At the highest rate of 30 C, the specific capacity of the Ag-Li$_4$Ti$_5$O$_{12}$ nanofibers was still 107.5 mAh g$^{-1}$, which was significantly larger than that of the bare Li$_4$Ti$_5$O$_{12}$ nanofibers (82.2 mAh g$^{-1}$). This result clearly demonstrates that incorporation of Ag nanoparticles can be attributed to fast electron transfer and Li$^+$ transfer due to enhanced electrical conductivity.

Thirdly, the structural configuration induced by Zr$^{4+}$ doping (0.05-0.15 mol) in Li$_4$Ti$_5$O$_{12}$ nanofibers was systematically explored through the correlation between the theoretical and experimental analyses. By increasing the Zr$^{4+}$ doping level, the calculated average lattice parameter was increased gradually, however, there were no noticeable changes in the morphology and size between the bare Li$_4$Ti$_5$O$_{12}$ and the Zr-doped Li$_4$Ti$_5$O$_{12}$ nanofibers. The expansion of lithium diffusion path was clearly found to be at 0.05 mol of Zr$^{4+}$ substitution in 1D Li$_4$Ti$_5$O$_{12}$ through first principle calculation. The discharge capacity of the Li$_4$Ti$_{4.95}$Zr$_{0.05}$O$_{12}$ was 120.9 mAh g$^{-1}$ at 30 C, which was higher than that of the Li$_4$Ti$_5$O$_{12}$ (101.5 mAh g$^{-1}$). In addition, the diffusion coefficient during the intercalation was $5.91 \times 10^{-14}$ and $2.00 \times 10^{-13}$ cm$^2$ s$^{-1}$ for the Li$_4$Ti$_5$O$_{12}$ and Li$_4$Ti$_{4.95}$Zr$_{0.05}$O$_{12}$, respectively, and the value was $1.08 \times 10^{-13}$ and $2.87 \times 10^{-13}$ cm$^2$ s$^{-1}$ during the de-intercalation. Therefore, the Zr$^{4+}$ doping could be an effective way to enhance the electrochemical reaction kinetics during Li$^+$ intercalation/de-intercalation.
Lastly, a core-shell Si-nanoparticles@TiO$_{2-x}$/C mesoporous microfiber composite was fabricated by electrospinning with a coaxial spinneret. The core-shell composite was rationally designed as the mechanically, electrically, and thermally robust structure of the TiO$_{2-x}$/C shell encapsulating the Si-nanoparticles core, which was confirmed by various analytical methods. The Si-nanoparticles@TiO$_{2-x}$/C mesoporous microfibers exhibited an outstanding rate capability, i.e., a high capacity of 939 mAh g$^{-1}$ at a significantly high current density of 12 C (12 A g$^{-1}$). Furthermore, thermal stability of the lithiated Si-nanoparticles@TiO$_{2-x}$/C was better than Si nanoparticles, graphite and Si-nanoparticles@C because of the TiO$_{2-x}$ shell structure. Therefore, the core-shell structured Si-nanoparticles@TiO$_{2-x}$/C mesoporous microfiber architecture can offer higher energy density and safety as a promising anode material for Si-based lithium ion batteries.