JI, LIWEN. Lithium Alloy-Carbon Composite Nanofibers for Energy Storage by Electrospinning and Carbonization. (Under the directions of Professor Xiangwu Zhang and Professor Peter S. Fedkiw).

The development of high-performance rechargeable lithium-ion batteries (LIBs) for efficient energy storage has become one of the key components in today’s information-rich mobile society. LIBs can offer energy densities 2-3 times and power densities 5-6 times higher than conventional Ni-Cd and Ni-MH batteries. As a result, they weigh less, take less space, and deliver more energy. As one of the most promising energy technologies, LIBs are dominantly powering most of today’s portable electronics. However, their automobile applications in advanced hybrid electric vehicles and plug-in electric vehicles are hampered by high cost, poor durability, and relatively low energy and power densities. Faced with these problems, we have developed novel porous, Li-active, and Li-inactive nanoparticle-loaded carbon nanofibers (CNFs), which can be directly used to store energy in LIBs with enhanced high energy and power densities via a judicious combination of electrospinning technology and carbonization process. Furthermore, these CNF-based anodes eliminate the presence of non-active materials and facilitate the easy access of Li ions to the inner sites of anodes, which dramatically reduces Li ion diffusion distance, thereby improving the electron transfer rate. As a result, LIBs using porous CNFs and composite CNFs as anodes offer advantages, such as improved energy and power densities, fast-charging capability, long cycle life, easy fabrication, low cost, and environmental benignity. Hopefully, the technological impact of designing CNFs with controlled structures and compositions will open up new opportunities.
to develop future generations of electrode materials for high-performance LIBs, which are the dominant power sources for consumer devices and electric vehicles, and also have a critical role to play in solving the worldwide critical energy issue.
DEDICATION

I dedicate my dissertation to my respected parents, my elder brother, my little sister, and all of my teachers and friends. A special feeling of gratitude to my loving parents, who make perhaps everything through my life and also all things I got, for their feeding, teaching, understanding, patience, and push for tenacity. I deeply appreciate my brother, Ligong Ji, and my little sister, Chunmei Ji, for their continuous encouragement and help.

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BIOGRAPHY

Liwen Ji was born in Qitai County, Xinjiang Uygur Autonomous Region, P. R. China. He attended Lanzhou University for his undergraduate education and graduated with a Batchelor Degree in Materials Chemistry in July, 2001. After that, he went to Zhejiang University as a graduate student in the major of Polymer Chemistry and Physics and obtained his Master Degree in April 2004. He then found an Assistant Researcher position in Shanghai Institute of Organic Chemistry, Chinese Academy of Science and did nearly two and half years’ research work on the synthesis and characterization of functional polymer materials.

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# ABBREVIATIONS

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<td>LIBs</td>
<td>Lithium-ion batteries</td>
</tr>
<tr>
<td>Lithium</td>
<td>Li</td>
</tr>
<tr>
<td>CNFs</td>
<td>CNFs</td>
</tr>
<tr>
<td>CNTs</td>
<td>Carbon nanotubes</td>
</tr>
<tr>
<td>MWCNT</td>
<td>Multi-walled carbon nanotubes</td>
</tr>
<tr>
<td>SWCNT</td>
<td>Single-walled carbon nanotube</td>
</tr>
<tr>
<td>PAN</td>
<td>Polyacrylonitrile</td>
</tr>
<tr>
<td>PMMA</td>
<td>Poly(methyl methacrylate)</td>
</tr>
<tr>
<td>PVP</td>
<td>Poly (vinyl pyrrolidone)</td>
</tr>
<tr>
<td>PEO</td>
<td>Poly (ethylene oxide)</td>
</tr>
<tr>
<td>PVC</td>
<td>Polyvinylchloride</td>
</tr>
<tr>
<td>PI</td>
<td>Polyimide</td>
</tr>
<tr>
<td>PA</td>
<td>polyamide</td>
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<td>PE</td>
<td>Polyethylene</td>
</tr>
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<td>Polystyrene</td>
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<tr>
<td>PVB</td>
<td>Polyvinylbutyral</td>
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<tr>
<td>PVA</td>
<td>Polyvinyl alcohol</td>
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<tr>
<td>PC</td>
<td>Propylene carbonate</td>
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<tr>
<td>EC</td>
<td>Ethylene carbonate</td>
</tr>
<tr>
<td>DEC</td>
<td>Diethyl carbonate</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Description</td>
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<td>--------------</td>
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</tr>
<tr>
<td>DMC</td>
<td>Dimethyl carbonate</td>
</tr>
<tr>
<td>EMC</td>
<td>Ethyl methyl carbonate</td>
</tr>
<tr>
<td>1D</td>
<td>One dimensional</td>
</tr>
<tr>
<td>2D</td>
<td>Two dimensional</td>
</tr>
<tr>
<td>3D</td>
<td>Three dimensional</td>
</tr>
<tr>
<td>CVD</td>
<td>Chemical vapor deposition</td>
</tr>
<tr>
<td>AAO</td>
<td>Anodic aluminum oxide</td>
</tr>
<tr>
<td>PTA-Ge</td>
<td>Poly(tetraallylgermane)</td>
</tr>
<tr>
<td>TA-Ge</td>
<td>Tetraallylgermane</td>
</tr>
<tr>
<td>VLS</td>
<td>Vapor–liquid–solid</td>
</tr>
<tr>
<td>PVDF</td>
<td>Polyvinylidene fluoride</td>
</tr>
<tr>
<td>TBT</td>
<td>Tributyltin</td>
</tr>
<tr>
<td>SEI</td>
<td>Solid electrolyte interphase</td>
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<tr>
<td>CuO</td>
<td>Cupric oxide</td>
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<tr>
<td>Cu₂O</td>
<td>Cuprous oxide</td>
</tr>
<tr>
<td>NRA</td>
<td>Nanoribbons</td>
</tr>
<tr>
<td>CV</td>
<td>Cyclic voltammograms</td>
</tr>
<tr>
<td>PLD</td>
<td>Pulsed laser deposition</td>
</tr>
<tr>
<td>MPₙ</td>
<td>Metal phophides</td>
</tr>
<tr>
<td>FESEM</td>
<td>Field Emission scanning electron microscopy</td>
</tr>
<tr>
<td>TEM</td>
<td>Transmission electron microscopy</td>
</tr>
<tr>
<td>ATR-FTIR</td>
<td>Attenuated total reflection fourier transform infrared</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Description</td>
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<tr>
<td>--------------</td>
<td>-------------</td>
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<tr>
<td>DSC</td>
<td>Differential scanning calorimetry</td>
</tr>
<tr>
<td>WAXD</td>
<td>Wide-angle X-ray diffraction</td>
</tr>
<tr>
<td>TGA</td>
<td>Thermogravimetry analysis</td>
</tr>
<tr>
<td>EDS</td>
<td>Energy dispersive X-ray spectroscopy</td>
</tr>
<tr>
<td>CNWF</td>
<td>Carbonized non-woven Sn/C film</td>
</tr>
<tr>
<td>HF</td>
<td>Hydrofluoric</td>
</tr>
<tr>
<td>ZnCl₂</td>
<td>Zinc Chloride</td>
</tr>
<tr>
<td>Mn(OAc)₂</td>
<td>Manganese (II) acetate</td>
</tr>
<tr>
<td>Ni(OAc)₂·4H₂O</td>
<td>Nickel (II) Acetate tetrahydrate</td>
</tr>
<tr>
<td>Cu(OAc)₂</td>
<td>Copper (II) Acetate</td>
</tr>
<tr>
<td>LiPF₆</td>
<td>Lithium Hexafluorophosphate</td>
</tr>
<tr>
<td>CCD</td>
<td>Charge-coupled device</td>
</tr>
<tr>
<td>BET</td>
<td>Brunauer-Emmett-Teller</td>
</tr>
<tr>
<td>RF</td>
<td>Resorcinol-formaldehyde gel</td>
</tr>
<tr>
<td>BJH</td>
<td>Barret, Joyner, and Halenda</td>
</tr>
<tr>
<td>HK</td>
<td>Horvath-Kawazoe</td>
</tr>
<tr>
<td>SSA</td>
<td>Specific surface area</td>
</tr>
<tr>
<td>HTT</td>
<td>Heat-treatment temperatures</td>
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Chapter 1 Introduction

1. Overview of electrospinning process

1.1 Introduction

The synthesis and fabrication of one-dimensional (1D) nanostructures with a variety of forms, such as nanotubes, nanowires, nanobelts, and nanofibers, have gain intensive attention in recent years due to their fascinating properties and intriguing applications in many areas. Among various methods to prepare these materials, electrospinning is currently one of the most versatile and promising processes for producing continuous nanofibers for both fundamental and application-oriented research mainly due to its capability and feasibility in generating large quantities of nanofibers with well-defined surface topologies at relatively low cost. A schematic of a typical electrospinning setup is displayed in Figure 1.1. It mainly consists of a spinneret with a metallic needle, a syringe pump, a collector, and a high-voltage power supply. When the viscous solution is loaded into the syringe, it is driven to the needle tip by the syringe pump, forming a droplet at the tip. The drop experiences two major types of electrostatic forces: the electrostatic repulsion between the surface charges and the coulombic force exerted by the external electric field. Under the action of these electrostatic interactions, the liquid drop will be distorted into conical object commonly known as the Taylor cone. When the applied voltage surpasses the critical value, at which repulsive electrostatic forces over the surface tension, a fine charged jet is ejected from the tip of the Taylor cone. This electrified jet then undergoes a stretching and accelerating process, leading to the formation of a long and thin thread. As the liquid jet is continuously elongated and the
solvent is rapidly evaporated, the dry fibers are accumulated on the surface of the collector forming a non-woven mat with the fiber diameters ranging from several micrometers down to tens of nanometers.\textsuperscript{1-15}

Figure 1.1 Schematic of a basic electrospinning setup.

Electrospinning technology was firstly described in several patents in the 1930s, when Formalas disclosed an apparatus for producing polymer filament by taking advantage of the electrostatic repulsions between surface charges.\textsuperscript{3, 4, 16, 17} In the 1970s, Simm \textit{et al.} patented the production of fibers with nanoscale diameters.\textsuperscript{3} At that time, this technology have not received much more academic notices, the common application for this technology was just limited in the nonwoven nanowire industrial field.\textsuperscript{3} Interest in electrospinning gained substantial academic attention in the 1990s and after that, when several research groups revived interests in this technology by demonstrating the fabrication of thin fibers from a broad range of organic polymers. These include many kinds of synthetic and natural
polymers, polymer alloys, polymer blends, polymers containing all kinds of inorganic nanoparticles or metal salts, and so on. The scope of possibilities presented by electrospinning encompasses a multitude of new and interesting concepts, which are developed at breakneck speed. It is reflected by the skyrocketing numbers of scientific publications and patents. Electrospun nanofibers also exhibit a range of unique features and properties, such as their high surface area and complex porous structure, extremely long fiber length. These unique properties make these fibers have charming applications in various fields.

In addition to polymer nanofibers, ceramic nanofibers could also be readily obtained by thermal treatment of inorganic precursor/polymer composite nanofibers at elevated temperatures. For example, choosing poly (vinyl pyrrolidone) (PVP), poly (vinyl alcohol) (PVA), poly (L-lactide) (PLLA), poly (ethylene oxide) (PEO) and Poly(methyl methacrylate) (PMMA) as matrices to host inorganic precursors, ceramic oxides or metal nanofibers, including but not limited to SiO₂, SnO₂, TiO₂, Al₂O₃, CuO, NiO, V₂O₅, ZnO, Co₃O₄, WO₃, Au, Fe, Co, Ni, etc., have been obtained successfully.

Fibers with different micro-texture or morphology such as porous nanofibers, core/shell nanofibers, and nanofibers with hollow interiors can also be produced through modified electrospinning equipments and methods. The applications of the nanostructures include reinforced composites, membranes, smart cloths, supports for enzymes and catalysts, electronic and optical devices, and energy storage and storage systems, such as rechargeable lithium-ion batteries (LIBs), fuel cells, solar cells, and supercapacitors.
1.2 Polyacrylonitrile as a precursor to carbon fibers

Many polymers can be used as precursors for carbon fibers, e.g., polyacrylonitrile (PAN), polyvinylchloride (PVC), polyimide (PI), polyamide (PA), polyethylene (PE), polystyrene (PS), PVA, pitch, cellulose, and viscose, etc.⁴⁹-⁵⁵

Among these types of precursors used for the production of carbon fibers, PAN has been the most popular (the structure of which is shown in Figure 1.2). PAN-based carbon fibers are produced by oxidative stabilization of PAN precursor fibers in air environment followed by a carbonization process in inert gas. Briefly, the process involves the removal in gaseous of all elements other than carbon in the PAN-based filaments and then carbonizing them to form carbon.⁴²-⁴⁵,⁴⁹ PAN-based carbon fibers essentially dominate consumption by accounting for nearly 90% of carbon fiber sales worldwide compared with the pitch-based or vapor-grown fibers. The process of converting PAN to carbon is typically achieved by chemically-modifying its structure through two heat treatment steps. The first heat treatment is done at 250-300°C in air environment. During this step, PAN is involved in complicated chemical reaction processes, including cyclization, dehydrogenation, aromatization, oxidation and crosslinking, which can result in the formation of the conjugated ladder structure (Figure 1.3). The oxidative stabilization stage is one of the most complicated stages, since different chemical reactions take place and the structure of carbon fibers is also set in this stage.⁵⁶-⁵⁹ Stabilization process, which is done in air environment, changes the chemical structure of the fibers and cause them to become thermally stable and so melting will not occur in the following carbonization process.⁵⁶-⁵⁹ The most recent research results also indicate that the stabilization process plays a pivotal role in converting PAN fibers into an
infusable stable ladder polymer, and to develop crosslink between PAN molecules. The second thermal treatment step (carbonization) is aromatic growth and polymerization process, in which the stabilized fibers undergo heat treatment at enhanced temperatures in an inert gas, such as nitrogen or argon. The oxidized fibers become carbonized as they are heated up to 600-1300 °C in inert atmosphere. During this process, the non-carbon elements are removed in the forms of methane, hydrogen, hydrogen cyanide, water, carbon dioxide, and ammonia, etc (Figure 1.4). The carbonized fibers have higher density, reduced diameter, and are 40-50 % of their original weight compared to the precursor material. These carbon fibers can also be directly used after this process, or can undergo additional heat treatments up to 3000 °C to yield graphitic structures.

Both the carbon and graphite fibers are conductive and have many important applications. In our work, carbon nanofibers (CNFs) prepared from electrospun PAN precursor nanofibers (Figure 1.5) are being used as anode materials in high-performance rechargeable LIBs.

Figure 1.2 Molecular structure of PAN.
Figure 1.3 Structure changes for PAN precursor fibers during stabilization.\textsuperscript{59}

Figure 1.4 Structure changes for PAN precursor fibers during carbonization.\textsuperscript{60}

Figure 1.5 FESEM images of (A) untreated PAN nanofibers and (B) thermally treated CNFs.
1.3 Fabrication of porous CNFs

Recently, there also has been growing interest in fabricating porous carbon materials into nanofiber forms using the electrospinning technology. The surface area of CNFs can be significantly increased when the fiber structure is switched from solid to porous structure. Several research groups have tried different strategies to produce porous CNFs, one of them involves electrospinning two immiscible polymers with miscible solvents using a coaxial spinneret into core-sheath composite nanofibers and selectively removing one of the polymer components during carbonization or using additional chemical treatment to generate pore structures. Porous CNFs were also obtained by exploiting the micro-phase separation of different polymer blends or copolymers during electrospinning, followed by oxidation and carbonization processes to pyrolyze one of the components. For example, Kim et al. report the fabrication of porous, fibrous nanoscale carbon materials in the form of a web via the electrospinning of two immiscible PAN and PMMA, followed by thermal treatment at 1000 °C in an inert gas. The electrospinning process leads to the obtaining of nanosized composite organic nanofibers containing two separate components PAN and PMMA in the form of a sheet. During carbonization, the continuous PAN phase transforms into skeletons of CNFs and the discontinuous phase (PMMA) transforms into hollow pores along the fiber length (Figure 1.6).
Peng et al.\textsuperscript{63} also prepared ultrathin nanoporous CNFs through electrospinning. A binary mixture of PAN and poly(AN-co-MMA) in DMF was electrospun into submicrometer fibers. In electrospinning, the two polymers became incompatible during DMF evaporating, and the phase separation occurred, leading to microphase-separation structured fibers. After stabilization and carbonization processes, the copolymer domains were pyrolyzed, and the residual CNFs have interconnected nanopore network with dimensions of several tens of nanometers throughout the surface and the interior. Recently, Xia et al.\textsuperscript{65} demonstrated a simple and convenient method for fabricating polymeric core-sheath nanofibers and carbon nanotubes by combining electrospinning and vapor deposition polymerization. Other approaches, such as template method and chemical/physical activation, also have been used with electrospinning technique to create porous CNFs. For example, Kim et al.\textsuperscript{66} report a solution for preparing porous and nano-sized fibrous carbon in the form of thin webs with the help of ZnCl\textsubscript{2}. Specifically, ZnCl\textsubscript{2} decreases the fiber diameters from 350 to 200 nm during the electrospinning step, enhances the reaction rate catalytically in the air-stabilization process, and effectively creates suitable pores on the outer surface of the CNFs (ca. 100 nm)
during carbonization. Porous CNFs also have been fabricated by electrospinning PAN into liquid nitrogen followed by drying in vacuo\textsuperscript{11} or by backfilling a network of silica nanofibers.\textsuperscript{67}

1.4 Fabrication of composite nanofibers

Composite nanofibers, consisting of nanoscale inorganic fillers and polymer matrix, can combine both the advantages of the polymer materials such as lightweight, flexibility, and good moldability, and of inorganic materials such as high strength, heat-stability, and chemical resistance.\textsuperscript{3-5, 9, 16} As a result, these composite nanofibers can have enhanced mechanical, electrical, optical, thermal and magnetic properties without losing transparency and can be excellent candidates for many multifunctional applications that include membranes, biomedical devices, catalysts, and energy conversion and storage systems.\textsuperscript{13, 16} Composite nanofibers can be prepared directly from inorganic nanoparticulate dispersions in polymer solutions via electrospinning.\textsuperscript{1-5, 8, 9} The electrospun ultra-fine composite nanofibers are notable for small diameter, large area-to-volume ratio, and small pore size, which not only improve material properties, but also create new characteristics not observed in bulk materials.\textsuperscript{1-4, 8, 9} Because of these reasons, much progress has recently been made in the production of composite nanofibers through electrospinning. Among them, metal oxides, such as TiO\textsubscript{2},\textsuperscript{68} Al\textsubscript{2}O\textsubscript{3},\textsuperscript{12} and Co\textsubscript{3}O\textsubscript{4},\textsuperscript{69} SiO\textsubscript{2},\textsuperscript{70} represent the majority of the work reported on preparations of composite nanofibers through electrospinning.

In addition to inorganic nanoparticle-loaded composite nanofibers, the fabrication of polymer/metal salt composite nanofibers via electrospinning has also received considerable interest due to the fact that such composite nanofibers allow the fabrication of materials with
a unique blend of properties, such as the unique heat stability of metal salts and also the flexibility and good moldability of polymers. Examples include polyvinylbutyral (PVB)/Cu(NO$_3$)$_2$, PAN/PdCl$_2$, PVA/Fe(CH$_3$COO)$_2$, and many others. Figure 1.7 shows an example of thermally treated PAN/PdCl$_2$ nanofibers.

In addition, electrospun polymer/inorganic composite nanofibers can be fabricated to form carbon composite nanofiber thin films that are mechanically stable and have ultrahigh surface areas. The exciting features and properties of these materials have led to significant research efforts focusing on the preparation of composite nanofibers through electrospinning polymer solutions containing different forms of inorganic salts. These composite CNF materials are playing an increasingly important role in applications as diverse as sensors, catalysis, electrical and optical systems, energy conversion and storage systems, such as rechargeable LIBs, fuel cells, solar cells, and supercapacitors, and so on.

Figure 1.7 SEM images of thermally treated fibers from PAN/PdCl$_2$ at different resolutions.

2. Overview of rechargeable LIBs

2.1 Introduction
Rechargeable LIBs have long been considered as an attractive power source for a wide variety of applications.\textsuperscript{75-80} They have revolutionized portable electronic devices and have become the dominant power source for cell phones, digital cameras, and laptops. In addition, their popularities in defence, in aerospace and submarine also becomes more and more important. As shown in Figure 1.8, rechargeable LIBs offer energy densities 2-3 times and power densities 5-6 times higher than Ni-Cd and Pb acid batteries. LIBs are lighter, about half the weight of Ni-Cd batteries, 30-50 \% smaller in volume, yet have a life span and energy density nearly twice those of Ni-Cd batteries. LIBs recharge more quickly, with an 80 \% charge in an hour, and full charge within 2.5 hours. LIBs also do not present environmental hazards, because they contain no harmful metals, such as Pd, Cd, or Hg. In addition, LIBs have no memory effect compared with traditional Ni-Cd rechargeable batteries; memory effect refers to a change in crystalline formation from the desirable small size to a large size that leads to reversible capacity loss, which occurs because of earlier incomplete charge/discharge cycles. Because of these advantages, rechargeable LIBs cover a wide variety of applications ranging from consumer electronics (e.g., laptop computers, cell phones, and cameras) to electric vehicles (e.g., hybrid electric cars and all-electric scooters).\textsuperscript{75-80} Nowadays, rechargeable LIBs are constructed with various shapes (cylindrical, coin, or prismatic shape) by employing different electrode materials and are also the representative system for the storage of electrochemical energy.\textsuperscript{87-91} The worldwide market for rechargeable LIBs is now valued at 10 billion dollars and is still growing.\textsuperscript{87-91}
The operation of rechargeable LIBs is based on Li chemistry. Li is the lightest metal in the periodic table of elements (Figure 1.9) and as a result, they weigh less and take less space for a given energy delivery. The storage and transportation of solid-state Li in an inert environment is much easier than that of gaseous hydrogen. As a result, Li is an ideal energy carrier. In the 1970s, Li metal was first employed as negative electrode materials to assemble Li metal batteries.\textsuperscript{75, 76, 78, 82, 87} Later on, a series of intercalation compounds were developed
and demonstrated to react reversibly with Li, leading to the initiation of rechargeable LIBs.\textsuperscript{75, 76, 80, 82, 87, 88}

Figure 1.9 Periodic table of the elements.

Figure 1.10 shows the basic operating principle of rechargeable LIBs. The working principle of LIBs is based on the rocking-chair concept and it consists of a cathode and an anode, together with an electrolyte-filled separator that plays the role of allowing ion transfer but prevent the electrodes from contact with each other.

When the batteries are charged, Li ions deintercalate from the cathode and intercalate/enter the anode; while on the discharging process, Li ions intercalate the cathode through the electrolyte. During charge/discharge cycles, electrons flow between the anode
and the cathode, enabling the conversion of chemical energy and also the storage of electrochemical energy within the batteries.\textsuperscript{75, 76, 78, 80-84, 84, 85, 87-89, 92} Therefore, the performance of rechargeable LIBs strongly depends on the active materials employed for Li storage. To achieve high specific capacity, electrode materials should reversibly accommodate a large amount of Li, large contact area necessary between electrode and electrolyte and fast ionic/electronic transfer are also required to achieve high current density (namely, power capability).\textsuperscript{80, 83-89, 93-98} The chemical reactions involved in the current commercial LIBs can be briefly described as:\textsuperscript{87}

**Anode:** \[ C + xLi^+ + xe^- \xrightleftharpoons{}_{\text{charge}}^{\text{discharge}} \text{Li}_x\text{C} \]

**Cathode:** \[ \text{LiMO}_2 \xrightleftharpoons{}_{\text{charge}}^{\text{discharge}} \text{Li}_{1-x}\text{MO}_2 + x\text{Li}^+ + xe^- \]

**Overall:** \[ \text{LiMO}_2 + C \xrightleftharpoons{}_{\text{charge}}^{\text{discharge}} \text{Li}_x\text{C} + \text{Li}_{1-x}\text{MO}_2 \]

The choice of current commercial LIB anode materials, is almost exclusively limited to carbonaceous materials, whereas the cathode can be made up of Li-ion host materials possessing much more positive redox potential, such as LiCoO\textsubscript{2}, LiMn\textsubscript{2}O\textsubscript{4}, and related compounds with spinel structure, or the recently commercialized LiFePO\textsubscript{4}.\textsuperscript{78, 83, 99} Currently, both anodes and cathodes have some common design features. Typically, slurries of micron-sized particles of active materials in solutions with polymeric and conductive additives were cast onto an appropriate current collector to form electrodes. The conductive additives can ensure continuous electrical contact between active particles and also the current collector.
For typical anodic carbon materials, such as graphite, Li intercalates into the carbon layer to form Li$_x$C alloy, delivering a theoretical specific capacity of 372 mAh g$^{-1}$ (LiC$_6$) and a potential plateau lower than 0.5 V vs Li$^+$/Li. The electrochemical performance of carbon-based materials strongly depends on their crystallinity, microstructure, and surface properties. The intercalation of Li into carbon and the relation between the electrochemical intercalation of Li and the crystal structure of various carbons have been described in detail by many researchers.

Figure 1.10 Schematic operating principle of a typical rechargeable LIB.
Generally, current carbon anodes are constructed by binding active carbon materials using a polymer binder, such as polyvinylidene fluoride (PVDF) or polytetrafluoroethylene (PTFE). Non-active carbon black particles are often added to enhance the electrical conductivity. The presence of polymer binder in electrodes separates many active materials from the electrolyte, which reduces the effective electrode-electrolyte interface area and causes slow electrode reaction kinetics, especially at high current densities.\textsuperscript{79, 104, 105} Currently, the most commonly used polymer binder is PVDF, which hold the mixture together to the collector. Other important components of LIBs are electrolyte and a thin polymer separator. The former has the aim to conduct and transfer Li ions, while the later plays the role of preventing the contact of the anode and the cathode. The LIB couple could not function in an aqueous electrolyt, since its charge termination voltage is high enough to cause a strongly oxidizing environment resulting in aqueous electrolyte decomposition. However, organic liquid such as propylene carbonate (PC), ethylene carbonate (EC), diethyl carbonate (DEC), dimethyl carbonate (DMC) with large potential window containing dissolved electrolyte salts, such as LiClO$_4$, LiPF$_6$, and LiBF$_4$, are relatively stable at high voltages. The electrolyte is not consumed by the charge/discharge reactions in contrast to the case of the Pd acid batteries. Instead, the Li ions are shuttled between anode and cathode.\textsuperscript{75, 78-80, 85, 92}

Since most current electrodes are made of active powders bonded with polymer binder, it is challenging to design new anodes with very high rates using current macro-scale materials. However, an increase in the charge/discharge rate of LIBs of more than one order of magnitude is required to meet the future demands of hybrid electric vehicles and clean energy storage devices.\textsuperscript{75, 78-89, 92, 106} Therefore, further advancements in current LIBs are still
bottlenecks by the limitation in electrode materials associated with limited capacity, lack of shape flexibility, short life, and safety and environmental concerns. New active materials should have high reversible capacity, structural flexibility and stability, fast Li-ion diffusion at an enhanced rate, long cycle life, improved safety, low cost, and being environmentally benign. Recently, advances in electrochemistry, materials chemistry, solid state chemistry are leading to the applications of nanomaterials for efficient energy storage of high performance rechargeable LIBs. The nanostructured materials open up an important new avenue towards overcoming the current limits and achieving the above-mentioned goals, because of their novel properties associated with decreased size, unique morphologies (such as one dimensional (1D) wire/tube structures, two dimensional (2D) films, and three dimensional (3D) interconnected porous architectures), and defective nature compared to their bulk counterparts. Generally, the potential advantages of nanostructured active electrode materials can be summarized as follows: new reactions that are not available with their bulk counterparts, large electrode/electrolyte contact areas, leading to numerous active sites, high charge/discharge rates, and short pathway lengths for both electron and Li ion transport. In addition, nanostructures can also improve battery efficiency. As a result, improved electrochemical performance such as higher reversible capacity, longer cycling life and better rate capability can be expected accordingly.

2.2 1D carbon materials

Graphite is currently the most popular anode materials for LIBs due to its long cycle life and low cost. Nevertheless, the most Li-enriched intercalation compound of graphite only has a stoichiometry of LiC₆, resulting in less-than-desirable theoretical charge capacity (372 mAh
To increase energy and power densities as well as other electrochemical performance of rechargeable LIBs, alternative carboneous anode materials with higher Li-storage ability are really necessary. Recently, the high surface-to-volume ratio and excellent surface activities of 1D nanostructural carbon materials have stimulated great interest in their development for the next generation high performance rechargeable LIBs. The concept of using 1D nanostructural materials, such as tubes, wires, and fibers, have shown great promising.

Several years after the discovery of carbon nanotubes (CNTs), some researchers studied Li vapor interactions with CNTs, and measured the corresponding electrochemical properties. Since then, there have been numerous reports about using CNTs as anodes for rechargeable LIBs. CNTs can offer intercalation between the pseudo-graphitic layers and/or inside the central tubes. The small diameters of CNTs can impose strain on the planar bonds of the hexagon, while this strain causes de-localization of electrons and makes the structure more electronegative than regular graphitic sheets, which in turn could increase the degree of Li-ion intercalation. Usually, with the decrease of the number of graphite layers in CNTs, both electronegativity and maximum Li ion occupation increase. Li-storage capacity in CNTs results from effective diffusion of Li ions into stable sites located on the surface and/or inside individual nanotubes through endcap or sidewall openings. The sites between multi-wall carbon nanotube (MWCNT) layers or the interstitial sites of close-packed single-wall carbon nanotube (SWCNT) bundles can also storage Li, leading to relatively high Li,C capacity. There is also a curvature-induced Li condensation inside the core of the CNTs. Overall, the theoretical calculations of the reversible capacities exceeding
a LiC$_2$ stoichiometry is obtained for SWCNTs, which represents a dramatic improvement over conventional graphite.$^{107, 108, 113, 114}$

In addition to CNTs, 1D CNFs can also be used as the anodes for rechargeable LIBs. Unlike CNTs, which require a long diffusion time for the Li-ion sertion and deinsertion, the occurrence of defects, including a large number of lattice defects, surface defects along their length, and open ends in CNFs, are expected to show a significant effect on their electronic structure and LIB properties. Li ions can diffuse more easily through the surface discontinuities in the walls of CNFs to result in increased Li storage capacity at normal charge and discharge rates.$^{115, 116}$ Usually, CNFs can be synthesized through arc-discharge, template deposition, laser ablation, and catalytic chemical vapor deposition (CVD). Wei et al.$^{116}$ prepared high rate capability CNF anode materials via CVD methods. Due to the mixed features of disordered and graphitic carbon, these CNFs anodes have a specific reversible capacity of about 461 mAh/g at 0.1 C. Even at a very high charge-discharge current rate of 10 C, these CNF anodes still can deliver a reversible capacity of about 170 mAh/g with a 95% coulombic efficiency (Figure 1.11).

Figure 1.11 Charge-discharge curves for CNFs at (A) 0.1 and (B) 10 C rates.$^{116}$
Recently, Qian et al. synthesized and characterized CNFs using CVD methods and studied their electrochemical properties. These prepared CNFs exhibit diameters of about 80 nm and lengths ranging from several micrometers to tens of micrometers. The characterization results indicate that these as-prepared CNFs possess low graphitic crystallinity and show a relatively high capacity of about 220 mAh/g and good reversibility with little hysteresis in the insertion/deintercalation reactions of Li ions. Using anodic aluminum oxide (AAO) membrane templates during liquid phase carbonization, CNFs can also be prepared at elevated temperatures. These materials exhibit inferior reversible capacity, indicating that the presence of loops at the edge of graphene layers impedes the deep Li intercalation. The research also shows that narrower CNFs have improved rate capability but increased irreversible initial capacity, due to the decreased ionic diffusion length as well as easier platelet exfoliation and the formation of solid electrolyte interface phase (SEI) films related to the reduced diameters.

Recently, Su et al. prepared CNT-encapsulated CNFs (CNFs/CNTs) using a template-free synthetic method. The authors also investigated the electrochemical performance of CNF/CNT anodes in preliminary Li insertion/extraction experiments. CNFs/CNTs possess much better porous structure than pristine CNFs and can deliver a high Li storage capacity. After 120 cycles, the reversible capacity of the anode materials can still stay at around 410 mAh/g, which is much larger than the corresponding value of CNT-based anodes. The CNF/CNT anodes also have a high rate capability. For example, when the current rate is 1C, the reversible capacity can remain greater than 300mAh/g after 50 cycles (Figure 1.12). The superior electrochemical performance of these materials can be attributed to the steric
hindrance effect of their unique structure, which suppresses the diffusion of the large electrolyte molecules. Some other nanostructured carbon-based anodes, such as carbon nanobeads with an onion texture, are also reported.

2.3 Porous carbon materials

Recently, porous carbon materials have attracted much attention as promising materials for Li storage. Porous carbonaceous materials with different pore size, ranging from nanometer to micrometer scale (microprone: < 2 nm, mesopore: 2-50 nm, and macropore: > 50 nm) have been prepared and electrochemically investigated. These porous carbons have been demonstrated to show a prominently larger capacity than traditional graphitic carbons, although in many cases a relatively high irreversibility is also accompanied. For example, high-surface-area microporous carbon materials were synthesized and electrochemically analyzed by Takeuchi and co-workers using template method. The as-prepared carbons with microporous structure display high irreversible capacities and significant voltage hysteresis. In addition, these materials also show fast capacity fade over merely a few cycles.
In the template method, both the textures and surface properties of the as-synthesized products strongly depend on the templates employed. Textures and surface properties undoubtedly affect the electrochemical activity of electrode materials, and hence detailed investigations on the thermodynamics and kinetics of reversible Li storage and other electrochemical behaviors are needed. Moreover, micropores might hinder the electrolyte
penetration and ionic diffusion to some extent and thus may be unfavorable to attain high rate capability.\textsuperscript{87}

Mesoporous carbons have been more extensively studied with respect to their application as anode materials for LIBs. Jiang \textit{et al}.\textsuperscript{87, 123} synthesizes ordered 3D mesoporous carbons by using mesoporous silica as a template. These materials present uniform pore size of 7.4 nm, BET surface area of 750 m\textsuperscript{2}/g. These mesoporous carbons were used as anode materials for rechargeable LIBs and it was found that they can deliver a charge capacity of 616 mAh/g and a reversible capacity of 131 mAh/g at first charge/discharge cycle. They also show almost constant resistance and Li-ion diffusion coefficient when the potential is lower than a critical value. Zhou and co-workers also prepared ordered mesoporous carbon that was synthesized using silica SBA-15 as template.\textsuperscript{111} This ordered mesoporous carbon possesses 3D ordered hexagonal structure with uniform pore size, high surface area, and large pore volume. The resultant mesoporous carbon anodes exhibit a very high reversible Li-storage capacity of about 1100 mAh/g at the first cycle. In addition, after the first cycle, both charge and discharge capacities keep a stable form. These materials also have good rate capability. As shown in Figure 1.13, they display a Li extraction potential in the range of 0.1–0.5 V, and deliver a charge capacity of 3100 mA h g\textsuperscript{−1} at the first cycle, corresponding to a lithiated composition of Li\textsubscript{8.4}C\textsubscript{6}. A reversible capacity of 850–1100 mAh g\textsuperscript{−1} was also obtained (Li\textsubscript{3}C\textsubscript{6}). The increased electrode capacity can be ascribed to the short ion-transport pathway from the external electrolyte to the interior surface, the minimized ion-transport resistance, and the localized graphitic structures around the pores.\textsuperscript{87}
Recently, several research groups also reported the synthesis of ordered 3D macroporous carbons using colloid PMMA and inverse silica opal as the template. The as-prepared materials also exhibited high initial charge capacity, excellent cycle performance, and enhanced rate capability at lower critical potential.

For example, Stein et al. prepared macroporous CNFs with well-interconnected pore and wall structures using PMMA colloid-crystal templates. When used as anodes for LIBs, these macroporous CNFs exhibit high rate performance and good cycling performance with about 83% reversible capacity retention after thirty cycles. The excellent electrochemical performance reveals that 3D macroporous carbons may have the following benefits: (1) short diffusion pathway for both mobile electrons and Li-ions, (2) large amount of active sites for charge transfer reactions among the exterior surface of anode, (3) reasonable electrical conductivity provided by the well interconnected walls, and (4) minimized mechanical stress.
between CNFs for buffering the volume expansion and contraction during Li alloy-dealloy processes. However, the porous carbon materials are certainly not a panacea. One inherent disadvantage of porous structures is the low volumetric energy density and large irreversible capacity. Coating with other high-specific-capacity components offers a promising strategy for relieving this hurdle.\textsuperscript{87, 111, 124, 125}

2.4 Metal oxides composites

Transition-metal oxides, such as SnO\textsubscript{2}, Fe\textsubscript{2}O\textsubscript{3}, Fe\textsubscript{3}O\textsubscript{4}, Co\textsubscript{3}O\textsubscript{4}, TiO\textsubscript{2}, MnO\textsubscript{x}, NiO, and CuO, etc. can adopt a large variety of structural geometries with an electronic structure that may exhibit metallic, semiconductor, or insulator characteristics, endowing them with diverse chemical and physical properties.\textsuperscript{93, 126} Recently, they have been investigated as attractive active materials for rechargeable LIBs and are found to have high reversible capacities. In addition, the Li reactivity mechanism of these materials differs from the classical Li insertion/deinsertion or Li-alloying processes,\textsuperscript{126} and it involves the formation and decomposition of Li\textsubscript{2}O, accompanying the reduction and oxidation of metal nanoparticles, respectively.\textsuperscript{87, 126-133} The concept of using 1D nanostructured materials, such as wires, tubes and fibers, have been demonstrated with SnO\textsubscript{2},\textsuperscript{134} Co\textsubscript{3}O\textsubscript{4},\textsuperscript{135} Fe\textsubscript{3}O\textsubscript{4},\textsuperscript{136} TiO\textsubscript{2},\textsuperscript{137} CuO,\textsuperscript{138} and NiO,\textsuperscript{139} etc, and anodes using these material-based anodes have shown excellent electrochemical performance compared with their bulk counterparts because of their high surface areas and quantum confinement effects, which can enhance charge transport and also act as building blocks in energy and electronic devices.\textsuperscript{80, 81, 84-87, 106, 140} Nevertheless, electrodes based on pure metal oxide nanoparticles suffer from poor cycling performance owing to severe agglomerations, leading to increased diffusion lengths, as well as mechanical
instabilities, cracking and even breaking caused by the large volume changes that occur during the insertion and extraction processes. One of the most promising ways to solve these problems is to disperse nanosized metal oxide particles into a carbon matrix, where carbon acts as both structural buffer and electrode-active material during the Li insertion/extraction processes. The techniques to prepare carbon/metal oxides nanocomposite structures are really important since the resultant nanocomposites can combine the high Li-storage ability of transitional metal oxides and the excellent cycling performance of carbon matrices, and exhibit excellent overall electrochemical performance when used as anodes for rechargeable LIBs.

2.4.1 Tin-based oxide

Tin oxides (SnO$_2$) has been attracted since the late 1990s because of their large theoretical capacity for Li insertion and safety benefit for avoiding the formation of hazardous Li dendrites. Much research has been devoted to using Li-reactive SnO$_2$ as anodes for rechargeable LIBs. On the first charge process, Li bonds to the oxygen in SnO$_2$, forming Sn and Li$_2$O. Then the Sn alloys up to the theoretical limit of Li$_{4.4}$Sn, corresponding to the theoretical reversible capacity of about 783 mAh g$^{-1}$. However, the pure SnO$_2$-based anodes have several critical problems for their commercial application. The first problem is that the anode cyclability strongly depends on the grain size, cut-off voltage, and charge rate. For example, the high cut-off voltage causes deterioration in capacity retention due to the large volume change and destruction of the Li$_2$O matrix, which holds the reduced Sn particles upon Li intercalation. As a result, fracturing and the loss of contact among the grains lead to the destruction of the electrode conduction, and hence
increase the internal resistance of the batteries. The second problem is the large irreversible capacity of about 700 mAh g\(^{-1}\), and the cycle performance is also poor due to the severe volume changes that occur during Li uptake and release processes.\(^{87, 89, 149-151}\) The large irreversible capacity of SnO\(_2\) is associated with both the formation of Li\(_2\)O and the surface reactions of Li-Sn compounds with the electrolyte solution. Much attention has been paid to improve the cycling performance of SnO\(_2\).\(^{87}\) Preparation of porous structural SnO\(_2\) and nanocomposite SnO\(_2\) materials, including nanotubules, are promising methods.\(^{87}\)

When SnO\(_2\) particles contain porous structures, the pores can play the role of a structure buffer for the large volume changes upon cycling. As a result, porous SnO\(_2\) shows no clear particle aggregation, high reversible capacity, and suppressed volume change. These electrochemical performance improvements can be attributed to the ability of mesoporous Sn to expand and contract with less structural degradation.\(^{87, 109, 152}\) Recently, using KIT-6 and SBA-15 SiO\(_2\) templates, Cho et al.\(^{152}\) prepared mesoporous SnO\(_2\) with a pore size of 3.8 nm and a BET surface area of about 160 m\(^3\)/g. These SnO\(_2\)-based anode materials for LIBs can deliver a reversible capacity of 800 mAh/g at the current rate of 0.2 C (400 mA/g). In addition, the capacity retention of porous SnO\(_2\) is 98\% after 50 cycles. It is believed that the improved cycle performance is due to the porous structures, which can act as a buffer to accommodate the volume expansion and extraction upon charge/discharge processes. The research also revealed that the reversible capacity can be kept at about 734 mAh/g at 10 C rate, indicating the good rate capability of these porous SnO\(_2\). However, a drawback of the porous SnO\(_2\) was the large irreversible capacity due to the high surface area.\(^{152}\) Hyeon et al. also synthesized hollow SnO\(_2\) microspheres using the simple heat treatment of SnCl\(_4\)-5H\(_2\)O.
and resorcinol-formaldehyde (RF) gel. These hollow \( SnO_2 \) spheres exhibit high discharge capacity of 952 mAh/g. In addition, these materials still have a very large irreversible capacity of about 648 mAh/g at the first cycle.\(^{153} \)

In addition to porous structure, \( SnO_2 \)/carbon nanostructured composites also display high reversible Li storage capacity and other good solid electrochemical performance. This is because \( SnO_2 \) can be uniformly dispersed in the carbon matrix, which reduces particle aggregation during Li-ion insertion and extraction reactions. The prominent improvement of the electrochemical performance of the \( SnO_2 \)/carbon composite materials stemmed from the synergistical combination of good stability of conductive carbon matrices and high Li-storage capacity of \( SnO_2 \) nanoparticles.\(^{87, 149, 154, 155} \) Recently, Zhao and co-workers reported an ordered, nanostructured \( SnO_2 \)/carbon composite, which displayed better cycling performance than that of nanosized counterparts without carbon matrix.\(^{130} \) These prepared hybrid materials delivered an initial charge capacity of 1347 mAh g\(^{-1} \) and a subsequent capacity of more than 500 mAh g\(^{-1} \) (Figure 1.14). The superiority of the \( SnO_2 \)/carbon composite nanostructures can be ascribed to three factors: (1) small grain size of \( SnO_2 \) confined within the nanospaces of porous carbon matrix forbids the formation of two-phase Li-Sn alloys, (2) 3D interconnected carbon framework hinders particle aggregation, and (3) electronically conducting structure ensures good electrical contacts.\(^{87, 147} \) Some other \( SnO_2 \)/carbon composite, including carbon-\( SnO_2 \) nanocolloids,\(^{156} \) \( SnO_2 \)/carbon composite hollow nanospheres,\(^{157} \) \( SnO_2 \)/carbon nanoparticle composites,\(^{159} \) carbon nanotube sheets uniformly loaded with \( SnO_2 \) nanoparticles,\(^{160} \) and 3-D delaminated \( SnO_2 \)/graphene
nanoporous anodes. Recently, porous SnO$_2$ nanotubes with coaxially grown carbon nanotube overlayers are also been reported.

More recently, heterostructured nanowires or composites based on SnO$_2$ and other metal oxides have also been reported. Because of the combined effect of different components, these materials also show promising electrochemical performance. Electrochemical performances of SnO$_2$-based nanotubes, nanowires, and nanopowders, nanorod, nanostructured thin films, and hollow core–shell mesospheres has also been reported.

![Graph](image)

Figure 1.14 Capacity versus cycle number for the cell with different Sn-based materials as anode at current density of 0.5 mA cm$^{-2}$.

2.4.2 Iron-based oxides

Among various kinds of transition metal oxides, such as Fe$_2$O$_3$ and Fe$_3$O$_4$ nanoparticles, owing to their low cost and non-toxicity, are also promising anode materials for rechargeable LIBs. However, pure iron oxide-based anodes still suffer from poor cycling performance resulting from the large volume change and the unstable SEI on the surface during the Li
insertion/extraction processes. Preparing porous nanostructural materials or incorporating these iron oxides into carbon matrices were reported to be effective methods to elevate these problems and improve the electrochemical performance.

Larchar et al. have reported that about 0.5 moles Li can be reversibly intercalated into $\alpha$-Fe$_2$O$_3$ in a large potential range. However, when reacted with Li to a potential of 0.9 V vs Li/Li$^+$, 2.0 moles of Li can be intercalated, but that Li cannot be extracted by the charging process without damaging the crystal structure of the nanoparticles. On deep discharge process, till 0.005 V, about 8.5 moles Li can have a reaction with $\alpha$-Fe$_2$O$_3$ nanoparticles. The formation of Fe$^0$ from Fe$^{3+}$ yields a theoretical capacity of 1007 mA h g$^{-1}$. Reverse extraction of Li from the Li$_2$O matrix seems to be thermodynamically unattainable. However, nanosized electrode materials with a small particle size and a large proportion of surface atoms should possess high surface energy and enhanced electrochemical activity, making the back reaction possible. Studies by Larcher et al. and Morales et al. on $\alpha$-Fe$_2$O$_3$ nanoparticles and by Chen et al. on $\alpha$-Fe$_2$O$_3$ nanotubes have clearly indicated that the morphology of nanometer-sized $\alpha$-Fe$_2$O$_3$ structures plays a significant role in the reactivity towards Li, and have shown that 4 moles of Li are cyclable in the potential range of 0.005–3.0 V, but capacity degradation occurs in all cases on long-term cycling. Recently, Chowdari et al. also used a thermal treatment method to prepare nanoflake $\alpha$-Fe$_2$O$_3$, which exhibits a stable reversible capacity of about 700 mAh/g, corresponding to 4.1 moles Li intercalated to per mole of $\alpha$-Fe$_2$O$_3$, and a very small irreversible capacity after 15 cycles. These results further prove that Li ions can be released by conversion reaction of nanometersized Fe$^0$ particles...
with Li$_2$O. Similar reactions mechanism has been proposed in the cases of other nanostructured transition metal oxides, such as NiO, CuO, Co$_3$O$_4$, and MnO$_2$.\textsuperscript{87, 126, 174, 176}

Zhang \textit{et al.}\textsuperscript{177} also fabricated fiberlike Fe$_2$O$_3$ macroporous nanomaterials by in-situ synthesis of Fe$_2$O$_3$ nanoparticles in regenerated cellulose fibers, followed by the removal of cellulose matrix via calcination. Due to their increased surface area and porosity, these Fe$_2$O$_3$ nanomaterials can have a discharge capacity of 2750 mAh/g at the first cycle when used as alternative anode materials for LIBs (Figure 1.15A). This value can still be kept at about 1235, 1102, and 927 mAh/g at the 5$^{th}$, 10$^{th}$, and 20$^{th}$ cycle, respectively (Figure 1.15 B). After 50 cycles, the electrode capacity decreased to about 27% of the initial value (732 mAh/g), which is still much larger than popular graphite-based anodes.

![Figure 1.15 Discharge curves at the first cycles (A) and cycle performance (B) of the electrode made of α-Fe$_2$O$_3$ samples. The discharging current density was 100 mA/g.\textsuperscript{177}](image)

Recently, Yang \textit{et al.}\textsuperscript{178} synthesized carbon-encapsulated Fe$_2$O$_3$ hollow nanoparticles and pure Fe$_2$O$_3$ hollow nanoparticles from carbon encapsulated Fe$_2$O$_3$ nanoparticle by controlled oxideation in air environment. When used as anode materials for LIBs, these prepared
carbon-encapsulated porous Fe$_2$O$_3$ nanoparticles deliver a high reversible capacity of about 700 mAh/g after 60 cycles and also exhibit superior cycling performance. This excellent electrochemical performance can be assigned to the encapsulation of carbon and the hollow interior space. The carbon shell can act as a buffer to accommodate the large volume changes of Fe$_2$O$_3$ nanoparticles upon uptake/release processes of Li-ion. In addition, the large electronic conductivity of carbon can also ensure good electronic transport during the cycling process. These unique advantages combined with the large Li-storage capacity of Fe$_2$O$_3$ nanoparticles can finally be beneficial to the performance improvement of rechargeable LIBs.

In addition to Fe$_2$O$_3$, Fe$_3$O$_4$ nanoparticles are also promising anode materials with high capacity for rechargeable LIBs. However, these nanoparticle-based anodes also have poor cycling performance due to their large volume changes during charge/discharge processes. Like Fe$_2$O$_3$, this problem can also be partially solved by intentionally mixing Fe$_3$O$_4$ with particular nanostructures or by loading Fe$_3$O$_4$ into carbon phase to fabricate Fe$_3$O$_4$/carbon composites. To further improve the performance of Fe$_3$O$_4$ as anode materials in LIBs, Fe$_3$O$_4$/carbon composite with rationally designed nanostructure is also necessary. Recently, Simon et al reported Fe$_3$O$_4$/Cu nanoarchitectured electrodes for rechargeable LIBs. The electrodes were prepared by using a two-step design: the electrochemically assisted template growth of Cu nanorods followed by electrodeposition of Fe$_3$O$_4$. The obtained nanostructured electrodes were demonstrated to show a factor of six times improvement in power density over planar electrodes. High capacity as well as excellent cycling performance and rate capability were also observed, making these conversion anodes attractive for rechargeable LIBs. In addition, large hysteresis between charge and discharge profiles was also observed,
which was suggested to derive from the high activation barrier triggering the oxidation and reduction reactions.\textsuperscript{87}

More recently, Guo \textit{et al.}\textsuperscript{136} synthesized carbon-coated Fe\textsubscript{3}O\textsubscript{4} nanospindles by partial reduction of monodispersed hematite nanospindles with carbon coatings, and investigated their electrochemical performance. The results indicated that these Fe\textsubscript{3}O\textsubscript{4}/C nanospindles show high reversible capacity of about 745 mAh g\textsuperscript{-1} at C/5 at the first cycle. Even at C/2, the capacity can still be kept at around 600 mAh g\textsuperscript{-1}. In addition, compared with bare Fe\textsubscript{3}O\textsubscript{4} and Fe\textsubscript{2}O\textsubscript{3} hematite spindles, these prepared Fe\textsubscript{3}O\textsubscript{4}/C anodes show high coulombic efficiency, as well as significantly enhanced cycling performance and improved rate capability (Figure 1.16). These improvements can be attributed to the uniform and continuous carbon coating layers, which help maintain the integrity of particles and increase the electronic conductivity of electrodes, thereby leading to the formation of uniform and thin SEI films on the surface. The results give clear evidence of the utility of carbon coatings to improve the electrochemical performance of nanostructured transition metal oxides as superior anode materials for LIBs.

Using gas-liquid interfacial route, Guo \textit{et al.}\textsuperscript{180} also synthesized water-soluble, highly dispersed Fe\textsubscript{3}O\textsubscript{4} nanoparticle/carbon composite. These materials exhibit a reversible capacity of constantly above 600 mA h/g, which is much higher than that of the conventional graphite anode, excellent retention of capacity on cycling, and improved rate performance. During Li insertion, Fe\textsubscript{3}O\textsubscript{4} is converted to Fe\textsuperscript{0} and Li\textsubscript{2}O, resulting in a volume expansion of \(\sim 180\%\), which leads to gradual lattice destruction and deteriorating performance of normal Fe\textsubscript{3}O\textsubscript{4}. At the presence of carbon matrix, the physical change of Fe\textsubscript{3}O\textsubscript{4} nanoparticles is restricted at its
local region. The carbon matrix may also act as an elastic buffer to relieve the strain associated with the volume variations during cycling, leading to excellent cycling performance.

![Diagram of discharge/charge profiles](image)

Figure 1.16 The discharge/charge profiles of (A) bare hematite spindles, (B) commercial magnetite particles, and (C) Fe₃O₄-C composites, at a current rate of C/5.¹³⁶

2.4.3 Cobalt-based oxides

Similar to iron-based oxides, cobalt-based oxides such as Co₃O₄ and CoO have shown excellent electrochemical performance based on Li conversion reactions.⁸⁸, ⁸⁹, ¹²⁶, ¹⁸¹ Intensive research has lead to the synthesis, assembly, and application of Co₃O₄ nanostructures with diverse morphologies such as nanoparticle, nanotube, nanowire, and nanorod.
Recently, a template-free method for large-area growth of self-supported Co$_3$O$_4$ nanowire arrays has been reported.$^{182}$ Each nanowire is about 500nm in diameter and about 15 mm in length (Figure 1.17 A). The Co$_3$O$_4$ nanowire arrays show superior capacity retention compared to other non-self-supported nanowires and commercial powders. After 20 cycles, the charge capacity of these Co$_3$O$_4$ nanowire arrays is 700 mAh/g, with a capacity retention of over 50 % even at a rate of 50 C. The high capacity of these nanowire arrays come from their unique hierarchical architectures (Figure 1.17 B).

![Figure 1.17 (A) SEM images of Co$_3$O$_4$ nanowire arrays growing on Ti foil. (B) Specific capacity of the Co$_3$O$_4$ nanowire arrays on Ti foil.$^{182}$](image)

Archer et al.$^{181}$ reported a one-step self-supported topotactic transformation approach for the synthesis of needle-like Co$_3$O$_4$ nanotubes. These Co$_3$O$_4$ nanotubes are shown to manifest ultrahigh capacity with improved cycle life and high rate capability. Recently, Yang et al.$^{183}$ prepared uniform porous Co$_3$O$_4$ nanotubes by the calcination of CNT-CoO$_x$ nanocables derived from Co$_4$(CO)$_{12}$ clusters on CNT templates. These as-prepared porous Co$_3$O$_4$ nanotubes have been applied in anode materials for LIBs, and exhibit superior performance. More recently, Chen et al.$^{184}$ used the template synthesis method to prepare Co$_3$O$_4$ nanotube,
nanorods, and nanoparticles by calcinating the precursor powder and ball-milling the decomposition product of Co(NO₃)₂·6H₂O. The electrochemical performance of the resultant anodes was systematically investigated using cyclic voltammetry and galvanostatic methods. The results demonstrated that the electrode properties of Co₃O₄ nanotubes are much better than those of Co₃O₄ nanorods and nanoparticles. The excellent electrochemical performance of Co₃O₄ nanotube-based anodes may be attributed to the hollow tubular structure, which presents high surface-to-volume ratio and high specific surface area, and makes the electrochemical reaction with Li more active. In addition, the defects among the tube body are favorable for the diffusion of Li ions. The hollow structure can shorten the diffusion length of Li ions and provide more active sites. In addition, fabricating mesoporous Co₃O₄ as LIB anodes are also reported by another two research groups. Although the preparation procedures of the materials are completely different, both groups obtained porous Co₃O₄ materials, and these materials show high capacity and good cycle life when used as anodes for LIBs.

Similar to Co₃O₄, the cycling performance of CoO is extremely sensitive to the degree of particle aggregation, which leads to significant capacity fading due to deteriorated electric contact between particles upon Li insertion/extraction processes. An improved cycle performance can only be obtained when CoO particles are dispersed in certain matrices. Xia et al. prepared a type of CoO-nanoparticle loaded hollow carbon spheres with high surface area by a wet-penetration method. The graphitatable hollow carbon spheres play a role of supporting material, which hampers CoO particles from agglomeration, as well as act as a host for Li-storage. These CoO/C composites exhibit a reversible discharge capacity of 580
mAh g\(^{-1}\) at a current density of 100 mA g\(^{-1}\). After 50th cycle, the capacity can still be preserved at about 540 mAh g\(^{-1}\). The improvement of the electrochemical performance could be attributed to the special texture and morphology properties of these CoO/C nanocomposites. On one hand, the hollow carbon spheres with good electronic conductivity and high surface serve as the buffer to hamper aggregration of CoO nanoparticles, and provide enough space to accommodate the large volume changes during the Li-ion insertion and extraction reactions in CoO nanoparticles.

Figure 1.18  The charge and discharge curve (A) as well as variation of discharge capacity vs. cycle number and (B) of CoO/C hybrid microspheres annealed in nitrogen atmosphere at 800 °C.\(^{188}\)

Zhang et al.\(^{188}\) report a one-pot method to synthesize CoO/C hybrid microspheres via a solvothermal approach. These CoO/C hybrid microspheres exhibited an ultrahigh initial discharge capacity of 1481.4 mAh g\(^{-1}\) at the first cycle (Figure 1.18 A). This capacity decayed to 506.2 mAh g\(^{-1}\) at the second cycle (Figure 1.18 B), a possible reason is that Co nanoparticles may be isolated by the nonconducting materials such as Li\(_2\)O or passive film
formed during the charge/discharge processes. After ten cycles, the reversible capacity is stable at about 345 mAh g\(^{-1}\).

Recently, other CoO-based nanocomposites, such as 3D Li\(_2\)O-NiO-CoO composite thin-films,\(^{189}\) and Ni-foam-supported reticular CoO-Li\(_2\)O composites,\(^{190}\) have also been reported. These materials exhibit large reversible capacity, excellent cycle life, and unique rate capability when used as anode for LIBs. It is also indicated that the Li\(_2\)O component plays a threefold role: as an oxidizer for the conversion of Co\(^{3+}\) from Co\(^{2+}\), as a structural buffer to preserve the integrities of CoO particle, and also as a prohibitor for the agglomeration of CoO phase.

2.4.4 Copper-based oxides

Cupric oxide (CuO),\(^{191}\) and cuprous oxide (Cu\(_2\)O)\(^{126,192}\) are well-known materials of p-type semiconductors, and have been employed as anode materials for rechargeable LIBs because of their nontoxic nature and affordable price. Similar to other transitional metal oxides, pure CuO and Cu\(_2\)O based anodes suffer from large volume changes during the Li uptake/release processes, which leads to severe mechanical strains and very rapid capacity loss. In this context, two similar methods can be used to improve the cycle life of these materials: one is to use nanostructures and another is to prepare active/inactive nanocomposites. The former method benefits from the accommodation of the strain upon Li uptake/release processes,\(^{88,89}\) while the latter can be ascribed to the inactive confining buffer.\(^{193}\)

Theoretically, the capacity of CuO is 674 mAh/g assuming a reversible stoichiometric 2e transfer. However, Tarascon \textit{et al}\(^{194,195}\) has verified that CuO is reduced to Cu nanograins
during discharge through an intermediate Cu$_2$O phase. This suggested that the reduced metallic Cu mainly re-oxidizes to form Cu$_2$O instead of CuO during the charge process, therefore, CuO has a reduced theoretical capacity of only 375 mA h/g. Similar capacity results have been demonstrated by other research groups. Wu et al. prepared hierarchical CuO spheres with radiating nanoplates, which can exhibit a total charge capacity of about 800 mAh/g at the first cycle; however, the discharge capacity is only about 250 mAh/g, indicating that the reaction is highly irreversible. Recently, Sun et al. fabricated CuO nanoribbon (NRA) array electrode. The electrochemical results show that the CuO NRA electrode can deliver a reversible capacity as high as 608 mAh g$^{-1}$ up to 275 cycles (Figure 1.19). The excellent cycleability, the high capacity retention and the high rate-capability of the CuO NRA electrode are attributed to its peculiar nanostructure with large surface area, numerous interspaces of the CuO nanoribbons, and also the solid adhesion of the active material to Cu current collector.

Figure 1.19 (A) Discharge-charge curves and (B) capacity and coulombic efficiency vs. cycle number of CuO NRA electrode.

Wang et al. prepared CuO nanowires by a wet-chemical method. These CuO nanowires exhibit good electrochemical performances, such as high reversible capacity (720
mAh/g) and superior cycling performance (the capacity keeps up 650 mAh/g over 100 cycles) because of their polycrystalline microstructures. Gao et al.\textsuperscript{200} found that polycrystalline CuO nanorods could attain higher specific capacity than the theoretical value of the single crystalline CuO (674 mAh/g).\textsuperscript{201} Although nano-structured CuO, which could enhance electrochemical activity of the electrode and provide larger contact area between active material and electrolyte, was supposed to exhibit better electrochemical properties than conventional electrode materials, the initial coulombic efficiency and cycling stability at high rates are still disappointing.\textsuperscript{200} From this aspect, CuO nanocomposites were prepared to improve the overall electrochemical performance of CuO-based anodes. For example, Tu et al.\textsuperscript{202} prepared nanoflower-like CuO/Ni film by an electrodeposition method to improve electrochemical performance of CuO based anodes. Since the metallic Ni can act as both conductor and catalyst, the CuO/Ni film exhibits higher initial coulombic efficiency (72.1%) and better capacity retention (96.3% of the 2nd cycle) than pure CuO film at the current density of 0.1 mA cm\textsuperscript{−2}. Other nanocomposites, such as CuO/graphite composites\textsuperscript{203} and CuO/carbon nanotubes,\textsuperscript{204} are also prepared, and their electrochemical performances were evaluated.

Cu\textsubscript{2}O was also studied as anode materials with high capacity and good capacity retention because it is nontoxic and also abundant in nature.\textsuperscript{205, 206} Results from charge-discharge and CV experiments reveal that the morphology and crystallinity of Cu\textsubscript{2}O play important roles in determining the electrochemical performance.\textsuperscript{206} In addition, Cu\textsubscript{2}O-based nanocomposites, such as Cu\textsubscript{2}O/graphite,\textsuperscript{207} core-shell Cu\textsubscript{2}O/Cu composite,\textsuperscript{208} and Cu\textsubscript{2}O–Li\textsubscript{2}O,\textsuperscript{209} have been reported. Recently, Pan et al.\textsuperscript{210} deposited porous Cu\textsubscript{2}O/CuO nanocomposite films on nickel
foam substrates via chemical bath deposition. The films also show excellent electrochemical performances.

2.4.5 Manganese-based oxide

Manganese oxides possess diverse layered or tunneled structures and are often used as cathodes for LIBs. Yet the natural abundance of manganese oxide and its environmental compatibility are so advantageous that it should not be neglected as anode material in various energy storage systems. However, the potential application of manganese oxide-based anodes in practical rechargeable LIBs is limited due to their poor electrical conductivity and large volume expansion during repeated Li cycling processes. Recently, Wu et al.\textsuperscript{131, 176} electrochemically synthesized manganese oxide electrodes composed of interconnected nanowires from manganese acetate solution at room temperature without any template and catalyst. SEM results show that these nanowires are uniformly distributed and their sizes are of about 12-18 nm in diameter; the diameter decreases to about 8-12 nm after annealing at 300 °C. The XRD patterns show that samples prepared at 100 and 300 °C are formed by $\gamma$-manganese oxide hydroxide ($\gamma$-Mn(O$_x$OH)$_2$), while samples prepared at 500 °C resemble are mainly manganese oxide (Mn$_2$O$_3$). When used as anodes for rechargeable LIBs, the reversible capacity after annealing at 100 °C is about 600 mAh g$^{-1}$. After annealing at 300 °C, the synthesized anode materials show much larger capacity than traditional graphite materials, the electrodes’ reversible capacity reaches 800 mAh g$^{-1}$, and the specific capacity remains nearly constant even after 100 cycles. Results further show that electrodes annealed at 500 °C not only remain rechargeable, but also contain a higher capacity, the reversible capacity after annealing at 500 °C is about 970 mAh g$^{-1}$. Nevertheless, a problem with these anode
materials is their large irreversible capacity at the first cycle, which is even more than 1000 mAh/g (Figure 1.20). However, this irreversible capacity is very low after the first cycle and the coulomic efficiency is nearly 100%. The second charge curve differs considerably from that of the first one because there have been some drastic, Li-driven, and structural or textural changes after the first cycle. The large irreversible capacity occurring only in the first cycle may be caused by decomposition reactions of the electrolyte and formation of the SEI films onto the surface of the manganese oxide electrodes.

Tirado et al.\textsuperscript{211} prepared MnO submicron particles with an average size of 200 nm and a rounded shape through calcination of MnCO\textsubscript{3}. The resultant MnO particles are proved to be promising anode materials for recharge LIBs. Nanocrystalline MnO thin film has been prepared by a pulsed laser deposition (PLD) method.\textsuperscript{212} The reversible Li storage capacity of the MnO thin film electrodes at 0.125 C is over 472 mAh g\textsuperscript{-1} and can be retained more than 90% after 25 cycles. At a rate of 6 C, 55% of the capacity at 0.125 C rate can be obtained for both charge and discharge cycles. These as-prepared MnO thin film electrodes also show the lowest values of overpotential for both charge and discharge among transition metal oxides. All these properties make MnO promising high-capacity anode materials for rechargeable LIBs. Other Mn oxide-based anodes, such as MnO\textsubscript{126},\textsuperscript{213} and Mn\textsubscript{3}O\textsubscript{4} nanofibers\textsuperscript{214} have also been reported.
Although the nanostructured morphology of Mn oxide-based anodes can help overcome the large volume change upon Li uptake/release processes, the low conductivity of the nanostructured materials is still an existing issue. Recently, Ajayan et al.\textsuperscript{215} prepared coaxial nanotubes with MnO$_2$ nanotubes in the outer shell and highly conducting CNTs in the inner core by a combination of simple vacuum infiltration and CVD techniques. The coaxial electrode configuration have: (i) improved electronic conductivity due to the presence of CNT, (ii) homogeneous electrochemical accessibility and high ionic conductivity by avoiding agglomerative binder and other conductive additives, (iii) well-directed 1D conductive paths due to perfect coaxial alignment, and (iv) a dual Li storage mechanism (insertion/deinsertion in the case of CNTs and formation and decomposition of Li$_2$O in the
case of MnO$_2$ nanotubes). As a result, these MnO$_2$/CNT hybrid coaxial nanotubes have enhanced reversible capacity compared to template-grown MnO$_2$ nanotubes (Figure 1.21). In addition, limited substitution of Mn by Co or Zn in Mn$_3$O$_4$\textsuperscript{216, 217} can also dramatically increase the electrochemical performance.

![Figure 1.21 Electrochemical properties of MnO$_2$/CNT hybrid coaxial nanotubes as positive electrodes in Li-ion batteries.](image)

2.4.6 Titanium-based oxides

TiO$_2$ nanowires and nanotubes have also been demonstrated to be attractive anode materials. Bruce \textit{et al.}\textsuperscript{218} used TiO$_2$ nanowires as an improved anode material to prepare full LIBs, and these prepared LIBs demonstrate the superior capacity compared to similar batteries constructed using Li$_4$Ti$_5$O$_12$ (225 mAh g$^{-1}$ compared to 150 mAh g$^{-1}$ at C/5) (Figure 1.22). Recently, Zhou \textit{et al.}\textsuperscript{219} reported the preparation of TiO$_2$ nanotubes with mesoporous
walls within AAO membranes. Such nanostructure provides pathways for both electrons and Li ions, which are essential for a high rate rechargeable LIBs.

Figure 1.22 A) The second cycle charge-discharge profiles of the mesoporous titania nanotube in the potential range from 1.2 to 3.0 V (versus Li⁺/Li) with the current densities of 1, 10, and 40 A g⁻¹ based on active TiO₂. B) The performance cycle of charge and discharge capacities of mesoporous TiO₂ nanotube at the current densities of 1, 10, and 40 A g⁻¹.

2.4.7 Nickel-based oxides

NiO can also be used as anode material for rechargeable LIBs. However, the reversible capacity is lower and the cycling performance is worse than those of other transition metal oxides, such as CoO and Co₃O₄. To improve the electrochemical properties of NiO, one effective way is to prepare nanostuctured materials since the nanoparticles structure facilitates the transportation of Li ions by offering a shorter solid-state diffusion length. However, the most critical problem for NiO nanomaterials is the aggregation of NiO nanoparticles, which results in poor cycling performance. There are other factors that affect
the cycling performance, such as pulverization of the active particles during charge and
discharge, and poor conductivity of the active materials. To avoid the above-mentioned
problems, it is necessary to prepare net-structured NiO/C\textsuperscript{220} and/or other nanocomposite
structures, including NiO/Ni\textsuperscript{221} and spherical NiO/C.\textsuperscript{222} These nanocomposite based-anodes
also show improved electrochemical performance, such as larger reversible and better cycle
performance (Figure 1.23). These electrochemical performance improvements are attributed
to the carbon matrix, which can enhance the conductivity of NiO, suppress the aggregation of
active particles, and increase the structure stability during cycling.

![Figure 1.23 Galvanostatic Li-insertion/extraction curves of (a) NiO and (b) NiO/C at a rate of 0.1–4C.\textsuperscript{222}](image)

2.5 Metals and metal alloys

Many metal or semiconductor nanoparticles, such as Si, Ge, Sn, Sb, Al, Bi, Mg, Pb, Zn,
and Cd, etc. have been revealed to be capable of accommodating Li with both much larger
Li-storage capacities and also much smaller irreversible capacities compared with those of
carbonaceous materials.\textsuperscript{89, 108, 144, 145, 223-225} However, these pure metal-based anodes exhibit
significant volume changes that occur during Li alloying/dealloying processes, which cause
severe cracking and crumbling of the electrodes and the subsequent loss of electrical contact between the single particles, resulting in severe capacity fading.\textsuperscript{226}

There are mainly several methods to reduce the large volume changes and preserve the integrity of the electrodes. The first approach involves preparing nanostructured materials since nano-scale materials have been proved to be able to absorb the large volume expansion/contraction and preserve the integrity of the electrodes. Another approach is to introduce a second component to form composites or alloys. For example, metals particles can be coated with carbon or dispersed in the carbon matrix.\textsuperscript{89} Here, carbon matrix acts as a buffer for the volume changes of metals and an electrical connector with the current collector. Similarly, the metal particles can also form alloy with a second ductile active/inactive metal M, where M is an electrochemically active or inactive transition metal. Li alloy-dealloy induces dissociation of the starting material into an active component that can react with Li to form Li-M alloy and an inactive part. The main role of the second metal M in the alloy is to provide a matrix that can absorb the massive volume expansion and contraction upon Li alloying and dealloying, respectively. As a result, the mechanical integrity between the electrochemical active particles and also with the current collector can be effectively maintained. In addition, the second metal M can also enhance the electronic conductivity of the electrode, which is more effective than the insulating Li$_2$O-based matrix formed in the cases of the metal oxides. In the alloy, if M is electrochemically inactive, its content should be high enough to retain the cycling stability, but a high M content can also lead to a significant decrease of reversible capacity.\textsuperscript{89} To ensure much better cycling stability, a better intermetallic M-M should be electrochemically active-active composites, such as
electroplated multiphase, because the different phases have different potentials for the onset of the Li alloying reaction. At the same time, these two different phases can act as the buffer for each other to overcome the large volume expansion/extraction upon Li uptake/release process.

Among various metal or semiconductor nanoparticles, Si seems to be the most attractive high-capacity anode material for rechargeable LIBs as it exhibits a low discharge potential and has the highest known theoretical Li intercalation capacity of approximately 4200 mAh g\(^{-1}\), which is more than ten folds higher than the theoretical value of commercial graphite (372 mAh g\(^{-1}\)), corresponding to the fully lithiated composition of Li\(_{4.4}\)Si. However, the large capacity fading and pulverization due to enormous volume changes during repeated Li insertion and extraction processes have limited their practical applications.

Tremendous efforts have been made to improve the cyclability of the Si-based anodes through improving the microstructural stability and the structural integrity of the Si particles. One generally accepted strategy is to generate nanoscale materials with designed structures since nanostructured electrodes can accommodate the large volume change of Si during charge and discharge processes, keeping the integrity of the electrode. Indeed, there is also increasing evidence showing that tailored nanostructure materials can significantly improve the electrochemical performance compared to their bulk counterparts because a well-designed nanostructure can accommodate the large strain without pulverization, provide good electronic contact and conduction, and display short Li insertion distances and improved material durability. Another alternative strategy to improve the overall electrochemical properties of Si is to prepare composite materials containing well dispersed
Si particles by introducing a second phase component as the host matrix. In this case, carbon has shown to be an ideal candidate as a host matrix because carbon can buffer the volume changes of Si particles and help maintain good electrical contact during Li insertion and extraction. Recent work has also demonstrated that anodes made of Si/carbon (Si/C) composites can combine the advantageous properties of carbon (long cycle life) and Si (high Li-storage capacity) to improve the overall electrochemical performance of the LIB anodes (Figure 1.24). Recently, Park et al. synthesized Si–Ni alloy and graphite composite by arc-melting followed by high-energy mechanical milling. The alloy particles consist of an electrochemically active Si phase with an inactive phases, such as NiSi₂ and NiSi, distributed uniformly on the surface of the graphite. The inactive phases can accommodate the large volume changes of Si during cycling of the composite. The cycle life of the composite increases with increase in Si content.

![Figure 1.24 Charge–discharge plots of: (A) a nanocrystalline Si electrode, and (B) a carbon-coated Si nanocomposite electrode with 44 wt% Si content.](image)

Several Si-based Li-active metal alloys have also been prepared and their electrochemical performance was evaluated. For example, Cho et al. prepared well-dispersed Si₇₀Sn₃₀
nanoalloys coated with carbon by vacuum annealing butyl-capped analogues at 900 °C. The resultant anodes showed a reversible capacity of 2032 mAh g⁻¹ and capacity retention of 97% after 60 cycles.

In addition to Si, Sn nanostructures or Sn nanoparticle-loaded carbon composite anodes have also been prepared and exhibit very promising electrochemical performance. Recent research results indicated that the Sn nanoparticles dispersed in electrical conducting carbon matrix demonstrate reversible capacity of 500 mAh g⁻¹ up to 200 cycles (Figure 1.25).

Figure 1.25 Cycling response at a 0.8 C rate (A), and voltage profiles at a 0.8 C rate (B) of a Sn–C composite electrode in an electrochemical cell having Li metal as a counter electrode and a LiPF₆-EC:DMC electrolyte.

Lee et al. also reported a simple procedure to fabricate a rambutan-like Sn/C nanocomposites consisting of Sn-containing carbon mesospheres, CNTs with completely filled or partially-filled metallic Sn interiors, and carbon encapsulated Sn nanopears. The Rambutan-like Sn/carbon nanocomposite electrodes has good cycling performance. The improved electrochemical performance of Sn in the nanocomposites can be attributed to the unique Sn/C structure, which prevents the aggregation of nanosized metallic Sn and the presence of one-dimensional carbon nanotube “hair-like” structures, which may enhance the
electrical connectivity and integration of the active electrode materials. In addition, Sn nanoparticle-encapsulated in hollow carbon spheres have also been reported, and these materials show significantly improved cycling stability, compared to pure Sn nanoparticle-based anodes.\textsuperscript{238-240} For example, Oh \textit{et al.}\textsuperscript{240} encapsulated nanosized Sn metal particles into spherical hollow carbon. The spherical hollow carbon plays several important roles in this preparation. First, the hollow carbon acts as a barrier to prevent the aggregation between Sn particles. Second, the hollow carbon provides a void space where Sn metal particles can experience volume change without collapsing the carbon shell. Third, the hollow carbon itself is an active material for additional Li storage. Finally, the carbon particles are spherical in shape, which provides a high packing density in practical LIBs to allow a high volumetric energy density. As a result, these Sn/C porous composite anodes exhibit enhanced electrochemical performance.

Recently, Wan \textit{et al.}\textsuperscript{239} prepared Sn nanoparticle-encapsulated elastic hollow carbon spheres (TNHCs) (74 wt % Sn and 26 wt % carbon). When the volume ratio of the Sn nanoparticles and the void space encapsulated is about 1:3, the hollow carbon spheres can accommodate the large volume expansion during Li-insertion, and thus prevents the pulverization of the electrodes. As a result, this type of Sn-based nanocomposites have high specific capacity of >800 mAh g\textsuperscript{-1} in the initial 10 cycles, and >550 mAh g\textsuperscript{-1} after the 100th cycle, as well as excellent cycling performance (Figure 1.26).
Cho et al.\textsuperscript{241} reported that branched Sn\textsubscript{78}Ge\textsubscript{22}/carbon core-shell nanowires can be prepared by the thermal annealing of butyl-capped Sn\textsubscript{78}Ge\textsubscript{22} clusters at 600 °C in vacuum. The first discharge and charge capacities are 1250 and 1107 mA h/g, respectively, showing a Coulombic efficiency of 88%. Such a one-dimensional core-shell design exploits the benefits of Sn\textsubscript{78}Ge\textsubscript{22} nanowires to produce an exceptional high rate Li reactivity (93% Coulombic efficiency at 8C rate) as well as excellent capacity retention after extended cycles (capacity retention of 94%) (Figure 1.27).
Ge is another promising material for LIB anode as it was reported to show a theoretical capacity of 1600 mAh/g and to exhibit a high diffusivity of Li. Nevertheless, electrodes based on pure Ge suffer from poor cycling performance due to the particle agglomeration, which leads to increased diffusion lengths, and the mechanical instabilities caused by the volume changes occurring during the Li insertion/deinsertion, which electrically isolate the particles from the current collector.
Cui et al.\textsuperscript{225} prepared a novel nanostructured n-C/Ge material with Ge nanoparticles dispersed in carbon matrix by the solid-state pyrolysis of poly(tetraallylgermane) (PTA-Ge) thermally polymerized from tetraallylgermane (TA-Ge) in a sealed tube at 700 °C. The composites exhibit high charge (discharge) capacities of 1190 (923) mAh/g at the first cycle at the current density of 150 mA/g. A highly stable and reversible capacity of about 900 mAh/g was achieved in these C/Ge nanocomposite anodes. Further electrochemical measurements indicated that the reversible capacity was still about 613 mAh/g when the applied current density is increased to 900 mA/g (Figure 1.28), indicating that the rate capability was improved significantly.\textsuperscript{225} The high performance of Li storage is probably due to the unique nanostructure of C/Ge nanocomposites. Recently, the same authors\textsuperscript{244} also prepared novel Ge/CNT nanocomposites through a pyrolysis technique. The composites
exhibit a reversible capacity of about 750 mAhg\(^{-1}\) at about 75 mAgr\(^{-1}\) current density and an improved rate performance, compared with that of CNTs processed as the same condition.

2.6 Metal phosphides

Preparing metal phosphides (MP\(_n\)) is also an alternative strategy to avoid the problems of poor reversible capacity and high volume changes of metal oxide and metal anodes in rechargeable LIBs. The high degree of electron delocalization of the MP\(_n\) lead to a low oxidation state of the metal and also a strong covalent character of the M-pnictogen bond.\(^{245}\) As a result, MP\(_n\) shows an overall lower intercalation potential compared to the counterpart oxides. MP\(_n\) with small particle size can deliver very large reversible capacity and good high-rate cycling stability when used as the anode for LIBs.\(^{246-248}\)

2.7 1D nanowire-based anodes

Recently, there have been reports on 1D metallic nanowires as anode materials for LIBs. Compared to 0D nanoparticles, 1D nanowires have been proven to have improved capacity retention and rate capabilities. To promote faster Li reaction with the nanostructured electrode, self-supported nanowire arrays directly grown on a current-collecting substrate represent an attractive architecture for LIB electrodes.\(^{89, 97, 249-251}\) In this architecture, each nanowire has independent contact with the substrate from the bottom. The open space between neighboring nanowires allows an easy diffusion of the electrolyte into the inner region of the electrode, where all nanowires can participate in the electrochemical reactions. This nanoengineered structure leads to reduced internal resistance and improved high-power performance.
More recently, Si$^{97}$ and Ge$^{251}$ nanowire electrodes have been directly fabricated on metallic current-collector substrates with the purpose of providing direct electrical contact without carbon-coating process. Cui et al.$^{97, 251}$ synthesized carbon-free and free-standing Si and Ge nanowires through vapor–liquid–solid (VLS) growth from SiH$_4$ or GeH$_4$, and these nanowires have good performance during cycling with Li.

![Figure 1.29 Schematic of morphological changes that occur in Si during electrochemical cycling (A) Si films and particles, (B) Si nanowires.$^{97}$](image)

Compared to composite anodes consisting of binder and carbon black, these nanowires have the advantage of significantly large surface areas, which can direct contact the current collector, minimize mechanical stress between the nanowires, buffer large volume expansion
and shrinkage during Li alloy–dealloy process, and provide short Li insertion distances (Figure 1.29). As a result, these metallic nanowire-based electrodes were found to have excellent electrochemical performance during cycling with Li. For example, both Si and Ge nanowires show capacity retention up to 10 cycles at lower rates (Figure 1.30). After cycling, both Si and Ge nanowires remain intact and are also not pulverized. The Si nanowire electrodes can have charge (discharge) capacities of about 4277 mAh/g (3124 mAh/g) at the first cycle. These values change to 3541 and 3193 mAh/g at the second cycle. Both charge and discharge capacities remained nearly constant for the subsequent cycles, with little fading up to 10 cycles. In addition, these Si nanowires also displayed high capacities at higher current rates; for example, even at 1 C current rate, the capacities still remain larger than 2100 mAh/g, which is more than five times greater than the theoretical value of graphite. The Ge nanowire electrodes can also deliver an initial discharge capacity of 1141 mAh/g, which is stable over 20 cycles at the C/20 rate. High power rates were also observed up to 2 C with coulombic efficiency larger than 99%. The above-mentioned examples indicate that the structural and morphological characteristics as well as the fabrication of carbon-based composite materials are beneficial to their electrochemical performance of rechargeable LIBs.

Recently, the same group also prepared crystalline-amorphous core/shell Si nanowire and carbon/Si core/shell nanowire-based anodes. Crystalline-amorphous core-shell nanowires were grown directly on stainless steel current collectors by a simple one-step synthesis. Amorphous Si shells instead of crystalline Si cores can be selected to be electrochemically active due to the difference of their lithiation potentials. Therefore, crystalline Si cores function as a stable mechanical support and an efficient electrical
conducting pathway while amorphous shells store Li. These core-shell nanowires have high charge storage capacity (∼1000 mAh/g) with ∼90% capacity retention over 100 cycles. They also show excellent electrochemical performance at high charging and discharging rates. Amorphous Si was coated onto CNFs to form a core-shell structure and the resulted core-shell nanowires showed great promise as anode material. Since carbon has a much smaller capacity compared to Si, the carbon core experiences less structural stress or damage during Li cyclings and can function as a mechanical support and an efficient electron conducting pathway. These nanowires have a high charge storage capacity of ∼2000 mAh/g and also good cycling life. They also have a high coulombic efficiency of 90% for the first cycle and 98-99.6% for the following cycles.

![Figure 1.30 Capacity versus cycle number for (A) the Si nanowires and (B) Ge nanowires at the C/20 current rate.](image)

2.8. Electrospun CNFs or composite CNFs

Among various 1D nanofibrous materials, electrospun nanofibers have gained special consideration because electrospinning is a relative simple, inexpensive way to fabricate fibers
at micron or nanoscale. Electrospun nanofibers of Li-active materials have shown improved
electrochemical behavior and can be used in energy storage and conversation devices,
especially as the anodes in rechargeable LIBs. For example, Kim et al. fabricated CNFs
by electrospinning and subsequent thermal treatments at different temperatures.

![Charge-discharge curves for nanofiber webs thermally treated at different temperature (2nd cycle at 30 mA g\(^{-1}\) current density).](image)

Figure 1.31 Charge-discharge curves for nanofiber webs thermally treated at different
temperature (2\(^{nd}\) cycle at 30 mA g\(^{-1}\) current density).

CNFs prepared at 1000 °C deliver the largest reversible capacity of about 500 mAh g\(^{-1}\) at
the first cycle (Figure 1.31). In addition, the conductivity, electrical and mechanical stability,
and structural integrity of the CNF anodes eliminate the need for non-active materials, which
may improve the total capacity of the anodes. CNF anodes experience small (~10%) volume
changes during Li insertion. A binder is more appropriate for materials with large structural
changes. As a result, these nanofibers can be used as anodes without binders (e.g. PVDF)
or conductive additives (e.g. carbon black) However, these CNF-derived anodes display
large irreversible capacity and poor rate capability with increasing current rates as shown in Figure 1.32.

![Graph](image)

**Figure 1.32 Variation of reversible capacities (rate capability) for nanofiber webs thermally treated at different current densities.**

Recently, Chen’s group also electrospun PAN with cobalt and iron precursors and carbonized the fibers to form CNFs containing Co$_3$O$_4$ and Fe$_3$O$_4$ nanoparticles. Unlike the previous study on PAN-derived CNFs, the authors used PVDF as a binder. The binder helps to maintain the contact of the composite anodes with current collectors after the fragmentation of active materials, which improve the resultant electrochemical performances. These composite CNF anodes deliver high reversible capacities of about 1100 mAh g$^{-1}$ and 1550 mAh g$^{-1}$, respectively, at the first cycle. The increased capacities are attributed to the ability of the nanoparticles to form alloys with Li. Despite the improvement, SEM analysis of the Fe$_3$O$_4$/C fiber mats after cycling revealed drastic structural changes. As shown in Figure 1.33, The Fe$_3$O$_4$/C composite nanofibers display a smooth and regular surface morphology before the electrochemical testing. After 80 cycles’ charge/discharge reactions, the composite
fibers show swollen and fragmented morphology.\textsuperscript{255} The large mushroom structures along with cracks, crumbling, and pulverization are also clear shown. These phenomena can be explained as a result of the insertion of Li into Fe\textsubscript{3}O\textsubscript{4}, which increases the volume by up to 80\% and break down the carbon matrix. Although the morphology changes after charge/discharge cycles, these composite CNF anodes exhibit high reversible capacity, good cycling performance and excellent rate capability (Figure 1.34). The addition of Fe\textsubscript{3}O\textsubscript{4} in the composite plays an important role in increasing the effective surface area, enhancing the electronic conductivity, and improving the wettability of the electrode. The superior electrochemical properties of these composite nanofibers indicate that they may find promising applications in high-performance rechargeable LIBs.

![Figure 1.33 SEM images of Fe\textsubscript{3}O\textsubscript{4}/C composite nanofibers, (A) before and (B) after 80 cycles.\textsuperscript{255}](image)

More recently, Yu et al.\textsuperscript{256} fabricated Sn/C composite structure, namely Sn/carbon encapsulated in bamboo-like hollow CNFs by the pyrolysis of tributyltin (TBT) (core)/PAN (sheath) nanofibers through a coaxial electrospinning method. As a potential anode material
for LIBs, this composite displays a high reversible capacity of 737 mAh g\(^{-1}\) after 200 cycles at the rate of 0.5 C. It also exhibits a reversible discharge capacity as high as 480 mAh g\(^{-1}\) when cycled at 5 C (Figure 1.35). Sn/carbon encapsulated in hollow CNF structure has high Sn content (close to 70 wt% Sn and 30 wt% carbon) but still provides appropriate void space to accommodate to the large volume change and to prevent the pulverization of Sn nanoparticles.

Kang et al.\(^{257}\) also prepared Sn/C non-woven films by electrospinning and carbonization treatment. The resultant nanocomposites contain amorphous carbon and homogeneously-dispersed Sn nanoparticles. These nanocomposites can deliver charge and discharge capacities of about 816 and 421 mAh/g, respectively, and after 20 cycles, the reversible
capacity can still be kept at about 382 mAh/g, which means 96.7 % coulomic efficiency (Figure 1.36).

Figure 1.35 A) Voltage profiles of a Sn/C composite electrode at a cycling rate of 0.1 C; B) Capacity–cycle number curves of a Sn/C composite electrode and a commercial Sn nanopowder electrode at a cycling rate of 0.5 C; C) Discharge capacity of a Sn/C composite electrode as a function of discharge rate (1–5 C).²⁵⁶

Figure 1.36 Galvanostatic discharge-charge experiments (A), and cycle performance (B) of the non-woven Sn/C films (CNWFs).²⁵⁷
Chapter 2 Research Objectives

The objective of this work is to fabricate porous and composite CNFs and explore their potential applications as anode materials for rechargeable LIBs (Figure 2.1). The main research work includes:

(I) Fabrication of porous CNFs and their applications as anode materials for rechargeable LIBs.

The total surface area and activity can be significantly increased by introducing porous structure to the nanofibers. Compared with other carbon materials, porous CNFs have notable properties such as extremely high length-to-diameter ratio, nano-scale diameter, and ultrahigh specific surface area. Although porous CNFs have been produced by several groups, the fundamental understanding of their structure formation has not been obtained and, so far, it is still difficult to control the structure, especially the pore size and the distribution of these nanofibers. As a result, the technological impact of investigating the processing-structure relationship of porous CNFs would be significant and needs further exploration.

Current carbon anodes are constructed by binding active carbon materials using a polymer binder, such as PVDF or PTFE. Non-active carbon black particles are often added to enhance the electrical conductivity. The presence of polymer binder in electrodes separates many active materials from the electrolyte, which reduces the effective electrode-electrolyte interface area and causes slow electrode reaction kinetics, especially at high current densities. Porous CNFs are typically in the form of electron-conducting nonwoven webs, providing good mechanical stability. Hence, they can be directly used as anodes for LIBs without
adding non-active materials (e.g., polymer binder and conducting carbon black). The elimination of non-active materials leads to high energy and power densities, long cycle life, and improved safety of rechargeable LIBs. In addition, the fully-interconnected three-dimensional network pore structure in CNFs facilitates easy access of Li ions to the inner sites of anodes, which dramatically reduces Li ion diffusion distance and improves electron transfer rate. As a result, LIBs using porous CNFs as anodes offer advantages, such as improved energy and power densities, fast-charging capability, long cycle life, and low cost.

In this work, we use three different methods to prepare porous CNFs, the results are discussed in Chapters 4, 5 and 6, respectively.

(II) Fabrication of Li-active nanoparticle-loaded CNFs and their applications as anodes for rechargeable LIBs.

Incorporating Li-active semiconductor or metal oxide nanoparticles in 1D porous CNFs can combine the advantages of both metal or metal oxide nanoparticles, which can alloy a large amount of Li, and porous CNFs, which have highly-developed surface area and porosity that facilitate easy access of Li ions to the entire inner sites of anodes, dramatically decrease Li ion diffuse distance, and induce high rates of electron transfer. Most important of all, these composite fibers can facilitate strain relaxation, prevent nanoparticle aggregation, and provide extra space needed for the huge volume changes of the Li-active nanoparticles involved upon Li insertion. As a result, these nanofibers have enhanced Li storage capacities, improved the rate performance and good capacity retention abilities. In this work, Si- and manganese oxide-loaded nonporous/porous CNFs are fabricated, and results are discussed in Chapters 7, 8 and 9.
(III) Fabrication of Li-inactive nanoparticle-loaded CNFs and their applications as anodes for rechargeable LIBs.

Transitional metal Ni and Cu nanoparticles are less active or inactive with Li; however, an appropriate amount of these metals can create a conducting matrix that promotes electrical contact of the electrodes and leads to better endurance of high current densities upon charge/discharge cycling when used as inert fillers in electrodes. Nanoscale transition metal particles also show the potential to stabilize the SEI film during the charge process, leading to reduced irreversible capacities. As a result, the incorporation of Ni and Cu metal nanoparticles in CNFs can increase the electronic conductivity of the composite materials, reduce the initial irreversible capacity, and improve the coulombic efficiency and cycling performance of anodes at high current densities. Hence, incorporating transition metal particles into LIB electrodes has great beneficial impact on the battery performance. In this work, transitional metal Ni and Cu particle-loaded CNFs are fabricated and their electrochemical performance are also evaluated in Chapters 10 and 11.

Figure 2.1 Preparation and application of porous and composite CNFs.
Chapter 3 Overall Experimental Section

1. Chemicals

PAN, PLLA, Zinc Chloride (ZnCl₂) salt (99.995 %, power, anhydrous), manganese (II) acetate (Mn(OAc)₂) salt (99.995 %), Nickel (II) acetate tetrahydrate (Ni(OAc)₂·4H₂O) salt (99.998 %), Copper (II) acetate (Cu(OAc)₂) salt (98 %), Li ribbon and solvent N, N-dimethylformamide (DMF) were purchased from Aldrich Chemical Company Inc (USA). Si nanoparticles (particle size ≥ 70 nm) were purchased from Nanostructured & Amorphous Materials, Inc. Copper foil (thickness is 25 µm) was purchased from Lyon Industries. Li hexafluorophosphate (LiPF₆) (power, sealed under argon), ethylene carbonate (EC) (100 %, sealed under argon), ethyl methyl carbonate (EMC) (100 %, sealed under argon), separator, spring, gasket, cases, cap, spacer were purchased from Ferro Corporation (USA). Fumed SiO₂ nanoparticles were supplied by Degussa (Germany) and Separion S240 P25 (25 µm) was purchased from Degussa AG. All were used as-received without further purification.

2. Nanofiber preparations

A variable high voltage power supply (Gamma ES40P-20W/DAM) was used to apply a spinning voltage. Electrospinning solutions were loaded in a 10 ml syringe to which a stainless steel capillary metal-hub needle was attached. The inside diameter of the metal needle was 0.30 mm. The positive electrode of the high voltage power supply was connected to the needle tip. The grounded electrode was connected to a metallic collector covered with an aluminum foil. The tip-collector distance and flow rate were fixed at 15 cm and 0.5 ml/h,
respectively. Under the high voltage, a polymer jet was ejected and accelerated toward the counter electrode, during which the solvent was rapidly evaporated. Dry nanofibers were accumulated on the collection screen and collected as a fibrous mat.

The carbonization of PAN precursor nanofiber webs was performed in an atmosphere-controlled furnace (Model 7AM-C12, LUCIFER, Pennsylvania). Firstly, the electrospun nanofibers were heated to 280 °C at 5 °C/min in air environment, and this temperature was maintained for several hours. In this process, thermoplastic PAN was converted to a non-plastic cyclic or ladder compound. The temperature was then increased from 280 °C to higher temperatures with a heating rate of 2 °C/min in an inert atmosphere (i.e., industrial-level nitrogen or high-purity argon) and held for several hours in order to complete the carbonization process.

3. Nanofiber characterizations

The morphology and diameter of nanofibers were evaluated using scanning electron microscopy (JEOL 6400F FESEM at 20 kV) and FEI XL30 SEM. Electrospun samples were coated with Au/Pd layers of approximately 100 Å thickness by a K-550X sputter coater to reduce charging. The morphology and diameter of porous CNFs were also characterized using ultra-high resolution microscopy electron microscopy (Hitachi S-5500) at 2.0 kV. Transmission electron microscopy (TEM) with an accelerating voltage of 120 kV (FEI Tecnai G² Twin and Hitachi HF-2000 TEM) was also used to study the structure of nanofibers collected and carbonized on 200-mesh Si nitride (Si₃N₄) membrane window grids or 200 mesh carbon coated Cu grids.
Attenuated Total Reflection Fourier Transform Infrared (ATR-FTIR) spectra were collected from a FTIR spectrometer (Nicolet 560) in the wavenumber range of 4000 - 400 cm\(^{-1}\) at room temperature. At least 32 scans were conducted to achieve an adequate signal-to-noise ratio.

Thermal properties of electrospun fibers were measured using differential scanning calorimetry (DSC) from 25 to 400 °C at a 10 °C/min in a nitrogen environment (Perkin Elmer Diamond Series DSC with Intracooler). Thermo-gravimetric analysis (TGA) was used to determine the weight loss of PAN composite nanofibers (after solvent evaporation) at a heating rate of 10 °C/min from 25 – 800 °C in an air environment (TA Instruments Hi-Res TGA 2950).

Wide-angle X-ray diffraction (WAXD) analysis was performed with Philips XLF ATPS XRD 1000 with OMNI Instruments Inc. customized automount and a Cu tube (\(\lambda = 1.5405 \text{ Å}\)). The operating voltage and current were 40.0 kV and 60.0 mA, respectively. A crystal-monochromated collection system was used to acquire the diffractograms at 0.02 degree intervals at a rate of 1 s per step. Peak positions were determined by the APD 1700 (Version 4) software.

Raman spectra were obtained using a Horiba Jobin Yvon LabRam Aramis Microscope. Radiation of 514.5 nm from a HeCd Laser at 10 mW was used to excite the samples under ambient conditions and results were recorded with a Renishaw Image Microscope System 1000 using a charge-coupled device (CCD) multi-channel detector at a 2.0 cm\(^{-1}\) resolution. The spectra were averaged over three scans to improve the signal-to-noise ratio and the data were corrected for the spectral response of the instrument.
Surface area analysis was carried out using the Brunauer-Emmett-Teller (BET) nitrogen adsorption method.\textsuperscript{11,13,17} Samples were degassed under flowing ultra high pure grade nitrogen for two hours at a temperature of 100 °C. Nitrogen gas adsorption measurements were taken at 0.05, 0.1, 0.15, 0.2, and 0.25 of saturation pressure using a Micromeritics Gemini 2360 instrument capable of measuring surface area of 0.01 m$^2$/g and higher. The free space in the analysis tube was measured by the helium method, and the five pressure points were used to calculate the BET surface area.

4. Electrochemical evaluations

Electrochemical performance evaluations were performed using 2032 coin-type cells. The relatively thin, mechanically tough electrospun CNFs were prepared by a simple punching process after carbonization, and were attached onto copper foil (thickness is 25 µm, Lyon industries), and directly used as the working electrode. Li ribbon (thickness is 0.38 mm, Aldrich) and Separion S240 P25 (thickness is about 10 µm, Degussa) were used counter electrode and separator, respectively. The working electrode, separator, spring, gasket, cases, cap and spacer were placed in an oven at about 120 °C overnight under vacuum. Electrolyte used was 1 M LiPF$_6$, dissolved in 1/1 (V/V) EC/ EMC (Ferro Corp.). The cells were assembled in a high-purity argon-filled glove box using a pressure crimper. Charge (Li insertion) and discharge (Li extraction) were conducted using an Arbin automatic battery cycler at different current densities between cut-off potentials of 0.01 and 2.8 V with different current densities. Electrochemical impedance spectra (EIS) were obtained using a Gamry reference 600 Potentiostat/Galvanostat/ZRA in a 10.0 mV AC voltage signal and 100 kHz - 10 mHz frequency.
Chapter 4 Fabrication of Porous CNFs and Their Applications as Anode Materials for High-Performance Rechargeable LIBs: Approach I

Three approaches were used in the research work to fabricate porous CNFs. The first approach utilized SiO$_2$ nanoparticles as the pore generator to create porous structure in CNFs. SiO$_2$ nanoparticles were first dispersed in PAN precursors and electrospun into composite nanofibers. These composite nanofibers were then carbonized to form SiO$_2$-loaded CNFs. Porous CNFs were obtained by removing SiO$_2$ nanoparticles from the composite nanofibers. The second approach utilized ZnCl$_2$ salt as the pore generator, which can help create small pores in PAN-based CNFs during the carbonization step. The third approach utilized PLLA as the pore generator, which was highly degraded during the carbonization process. This chapter discusses the results using the first approach. The second and the third approach will be discussed in Chapters 5 and 6.

1. Experimental
1.1 Chemicals

PAN (Mw = 150,000), HF acid and DMF were purchased from Aldrich Chemical Company Inc (USA). Fumed SiO$_2$ nanoparticles were supplied by Degussa (Germany). All were used as-received without further purification.

1.2 Nanofiber preparation

DMF solutions of 7 wt % PAN containing various amounts of SiO$_2$ nanoparticles (0, 5, 10, and 20 wt %) were prepared at 60 °C through strong mechanical stirring for at least 24
hours. A variable high voltage power supply (Gamma ES40P-20W/DAM) was used to provide a high voltage (21 kV) for the electrospinning of as-prepared solutions. The positive electrode of the high voltage power supply was connected to the needle tip. The grounded electrode was connected to a metallic collector wrapped with an aluminum foil. Dry fibers were accumulated on the aluminum foil and collected as a fibrous mat. The flow rate and tip-collector distance were fixed at 0.8 ml h\(^{-1}\) and 15 cm, respectively.

The carbonization of SiO\(_2\)/PAN composite nanofiber webs was performed in an electric heat-treating furnace (Lucifer furnaces, Int.). Firstly, the electrospun SiO\(_2\)/PAN composite nanofibers were stabilized in an air atmosphere at 280 °C for 2.5 h (heating rate was 5 °C min\(^{-1}\)). Samples were then carbonized as the temperature was increased from 280 °C to 700 °C or 1000 °C with a heating rate of 2 °C min\(^{-1}\) in a nitrogen atmosphere. They were held at the final temperature for 1 hour. The as-prepared SiO\(_2\)/carbon composite nanofibers were placed in a HF acid solution (Aldrich, 35 wt %) for 24h to remove SiO\(_2\),\(^{70}\) followed by washing with deionized water several times.

1.3 Nanofiber characterization

The morphology and diameter of both nonporous and porous CNFs were evaluated using scanning electron microscopy (SEM, JEOL 6400F FESEM at 5 kV). The structural variations were identified by wide angle X-ray diffraction (WAXD, Philips X'Pert PRO MRD HR X-Ray Diffraction System, Cu k\(_\alpha\), \(\lambda = 1.5405\) Å) and Raman spectra (Horiba Jobin Yvon LabRam Aramis Microscope, 633 nm HeNe Laser). Surface area analysis was carried out using the BET nitrogen adsorption method (Micromeritics Gemini 2360).
1.4 Electrochemical evaluations

The EIS was performed using a Gamry reference 600 Potentiostat/Galvanostat/ZRA in a 10.0 mV AC voltage signal in the 100 kHz-10 mHz frequency ranging in automatic sweep mode from high to low frequency. Galvanostatic charge-discharge experiments were carried out using 2032 coin-type cells (Hohsen Corp.). The thin, circular, flexible and mechanically tough CNF mats were attached onto the copper foil (Lyon industries, 0.025 mm thick) to form the working electrode. Separion S240 P25 (Degussa AG, 25 µm) was used as the separator. The working electrode, separator, cap, spring, spacer, gasket and cases (Hohsen Corp.) were placed in a vacuum oven at above 100 °C for 16 h. A Li ribbon (Aldrich, 0.38mm thick) was used as the counter electrode. The electrolyte used was 1 M LiPF₆, dissolved in EC/EMC (1 to 1 ratio by volume, Ferro Corp.). After the coin cells were assembled, they were sealed by a pressure crimper inside a high purity argon-filled glove box. Charge (Li insertion) and discharge (Li extraction) were conducted using an Arbin automatic battery cycler at 50 mA g⁻¹ current density over the range of 0.01 to 2.5 V.

2. Results and discussion
2.1 Morphology and structure characterization

Figure 38 shows SEM images of both nonporous and porous CNFs carbonized at 700 °C. It can be seen that CNFs made from pure PAN precursors have relatively smooth and regular surface morphology (Figure 4.1A). With the increase of SiO₂ contents in SiO₂/PAN precursors, the surface morphology of the resultant CNFs becomes rough, undulate, and irregular. Additionally, porous structures appeared after the HF treatment (Figs. 4.1B-D).
In order to investigate the effect of carbonization temperature, nanofibers were also carbonized at 1000 °C.

CNFs prepared from pure PAN precursors at 1000 °C also display smooth surface structure (Figure 4.2A). The morphology of CNFs from PAN/5 wt % SiO₂ precursor appears slightly uneven and shows ridges on the surface after HF treatment (Figure 4.2B). CNFs made from PAN/10 % SiO₂ (Figure 4.2C) and PAN/20 % SiO₂ precursors (Figure 4.2D) display distinct porous structures after HF treatment. In addition, all of the CNFs prepared at 1000 °C have a continuous sponge-like morphology which is not shown in those prepared at 700 °C. These results indicate that carbonization temperature has significant influence on the surface morphology of the resultant fibers, which may be caused by variation in weight loss and density change at different carbonization temperatures.⁴⁹
Figure 4.1  SEM images of nonporous CNFs made from pure PAN (A), and porous CNFs made from SiO2/PAN precursors with different SiO2 contents: (B) 5, (C) 10, and (D) 20 wt %. Carbonization Temperature: 700 °C.

Nitrogen adsorption measurements were performed at 77K to track the surface area and the pore size of nonporous and porous CNFs prepared at 700 °C, and the results are summarized in Table 4.1. It can be seen that CNFs made from SiO2/PAN precursors (5, 10, and 20 wt % SiO2) have mesoporous structure and exhibit specific surface areas of 31.7 – 91.8 m² g⁻¹. This is higher than the surface area (26.1 m² g⁻¹) of nonporous CNFs prepared from pure PAN precursor (0 wt % SiO2). In addition, both micropore and mesopore volumes increase with increasing SiO2 content in SiO2/PAN precursors.
Figure 4.2  SEM images of nonporous CNFs made from pure PAN (A), and porous CNFs made from SiO$_2$/PAN precursors with different SiO$_2$ contents: (B) 5, (C) 10, and (D) 20 wt %. Carbonization Temperature: 1000 °C.

In order to understand the carbon structure of these CNFs, nanofiber samples were studied using WAXD and Raman spectroscopy, respectively (Figures. 4.3 and 4.4). In WAXD results (Figure 4.3), the peak near 2θ = 25°, corresponding to the (002) layers of the graphite, sharpens with the increase of the surface area and the pore volume. Raising the carbonization temperature also leads to a sharper peak at 2θ = 25°. This is due to the structural development from disordered to graphitic carbon as a result of higher treatment temperature.$^{64, 64}$ In addition, CNFs prepared at 1000 °C present a (100) peak near 2θ = 45°, which also indicates there is partially graphitized carbon in these nanofibers.$^{258}$
Table 4.1 Surface and pore parameters of CNFs prepared from SiO$_2$/PAN precursors at 700 °C.

<table>
<thead>
<tr>
<th>SiO$_2$ content (wt %)</th>
<th>SSA$^{[a]}$ [m$^2$ g$^{-1}$]</th>
<th>TPV$^{[b]}$ [cm$^3$ g$^{-1}$]</th>
<th>$V_{meso}^{[c]}$ [cm$^3$ g$^{-1}$]</th>
<th>$V_{micro}^{[d]}$ [cm$^3$ g$^{-1}$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>26.1</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>5</td>
<td>31.7</td>
<td>0.062</td>
<td>0.052</td>
<td>0.009</td>
</tr>
<tr>
<td>10</td>
<td>41.0</td>
<td>0.115</td>
<td>0.103</td>
<td>0.011</td>
</tr>
<tr>
<td>20</td>
<td>91.8</td>
<td>0.176</td>
<td>0.149</td>
<td>0.026</td>
</tr>
</tbody>
</table>

$^{[a]}$ Specific surface area (SSA) was calculated by the BET method.

$^{[b]}$ TPV: total pore volume.

$^{[c]}$ $V_{meso}$: mesopore (2 - 50 nm) volume calculated by the Barret, Joyner, and Halenda (BJH) method based on the Kelvin equation.

$^{[d]}$ $V_{micro}$: micropore (< 2 nm) volume calculated by the Horvath-Kawazoe (HK) method.

The Raman spectra (Figure 4.4) show a well-known D-band at around 1350 cm$^{-1}$ and G-band at 1600 cm$^{-1}$. The ratio of the integrated intensity of D peak to G peak, denoted by $R_I = I_D/I_G$, increases slightly with the increase of porous structure at both carbonization temperatures (Table 4.2). Since the peak at 1350 cm$^{-1}$ is attributed to defects and disordered portions of carbons and the peak at 1600 cm$^{-1}$ is indicative of ordered graphitic crystallites of carbon,$^{49, 64, 258}$ these results indicate that the prepared CNFs are mainly hard (non-graphitizted) carbons containing turbostratically disordered graphene sheets.$^{49, 64, 258}$
Figure 4.3 WAXD patterns of CNFs carbonized at 700 °C (A) and 1000 °C (B), respectively. CNF types: nonporous CNFs made from pure PAN (a), and porous CNFs made from SiO$_2$/PAN precursors with different SiO$_2$ contents: (b) 5, (c) 10, and (d) 20 wt %.

Figure 4.4 Raman spectra of CNFs carbonized at 700 °C (A) and 1000 °C (B), respectively. CNF types: nonporous CNFs made from pure PAN (a), and porous CNFs made from SiO$_2$/PAN precursors with different SiO$_2$ contents: (b) 5, (c) 10, and (d) 20 wt %.
Further, porous CNFs have more disordered non-graphitizable structures compared with nonporous CNFs. When the carbonization temperature increases from 700 to 1000 °C, D-band peak at 1350 cm\(^{-1}\) decreases slightly and the G-band peak at 1600 cm\(^{-1}\) increases, indicating that the carbon becomes more ordered and graphitic at increased carbonization temperature. These results also prove the structural development of CNFs from disordered to graphitic carbon with the increase of thermal treatment temperature.

Table 4.2 \(R_f\) values of nonporous and porous CNFs prepared at different heat-treatment temperatures (HTT). CNFs types: nonporous CNFs made from pure PAN (a), and porous CNFs made from SiO2/PAN precursors with different SiO2 contents: (b) 5, (c) 10, and (d) 20 wt %.

<table>
<thead>
<tr>
<th>HTT (°C)</th>
<th>(a)</th>
<th>(b)</th>
<th>(c)</th>
<th>(d)</th>
</tr>
</thead>
<tbody>
<tr>
<td>700</td>
<td>4.14</td>
<td>4.79</td>
<td>-</td>
<td>5.17</td>
</tr>
<tr>
<td>1000</td>
<td>3.16</td>
<td>3.33</td>
<td>3.50</td>
<td>3.58</td>
</tr>
</tbody>
</table>

2.2 Electrochemical performances

Porous CNFs are collected in the form of nonwoven porous mats and can be directly used as anodes in LIBs without adding polymer binders or carbon black conductors. The elimination of non-active materials ensures the high-rate electron conduction and has the potential to increase the electrode capacities. In addition, anodes made of porous CNFs have large surface areas, which permit high Li-ion flux across the interface and reduce Li-ion diffusion distance, further improving the electrochemical performances. In the present study,
we compared both EIS and galvanostatic charge-discharge phenomena of nonporous and porous CNF anodes.

Figure 4.5 displays the impedance spectra of both nonporous and porous CNF anodes carbonized at 700 and 1000 °C. All these anodes show one high-frequency semicircle that is usually taken to be a result of the interfacial charge-transfer impedance\textsuperscript{231, 255, 259}, and a straight line in the low-frequency ranges, which indicates the impedance due to the Li diffusion in electrodes.\textsuperscript{259} As shown in Figure 4.5, porous CNF anodes have smaller interfacial impedances than nonporous CNF anodes, which indicate that the presence of porous structure in the anodes facilitates the charge transfer at the electrode-electrolyte interface due to the increased electrode surface area.\textsuperscript{259} CNFs prepared at 1000 °C (as shown in Figure 4.5B) have smaller charge-transfer interfacial impedance compared with those prepared at 700 °C (Figure 4.5A).

Figure 4.5 EIS for CNF anodes prepared from SiO\textsubscript{2}/PAN precursors, thermally treated at 700 (A) and 1000 °C (B), respectively. CNF types: nonporous CNFs made from pure PAN (a), and porous CNFs made from SiO\textsubscript{2}/PAN precursors with different SiO\textsubscript{2} contents: (b) 5, (c) 10, and (d) 20 wt %.
Galvanostatic charge-discharge experiments were carried out at a current density of 50 mA g\(^{-1}\) to evaluate the electrochemical performance of porous CNF anodes in comparison with nonporous CNF anodes.

Figure 4.6 Charge-discharge curves (A, B, and C), and cycling performance (D) of CNF anodes at a constant current density of 50 mA g\(^{-1}\). CNF types: nonporous CNFs made from pure PAN (a), and porous CNFs made from SiO\(_2\)/PAN precursors with different SiO\(_2\) contents: (b) 5, (c) 10, and (d) 20 wt %. Carbonization Temperature: 700 °C.

Figure 4.6 shows the voltage profiles and cycling performance of both nonporous and porous CNF anodes prepared at 700 °C within a voltage window 0.01 - 2.5 V. From Figure 4.6A, it is apparent that, compared with nonporous CNF anode, porous CNF anodes have
larger Li storage capacities. For example, porous CNF anodes prepared from SiO₂/PAN precursors with different SiO₂ contents (5, 10, and 20 wt %) have charge capacities of 910, 1010, and 1100 mA h g⁻¹ at the first cycle, respectively. Their reversible capacities are all around 567 mA h g⁻¹ at the same cycle (Figure 4.6A). The charge and reversible capacities for nonporous CNF anode are 960 and 510 mA h g⁻¹, respectively (Figure 4.6A). At the second cycle (Figure 4.6B), porous CNF anodes maintain relatively high reversible capacities of 473, 484, and 484 mA h g⁻¹, respectively, while the reversible capacity for nonporous nanofibers reduces to 440 mA h g⁻¹. The reversible capacity for porous CNF anodes made from 20% SiO₂/PAN precursor decreases by 20 % to 454 mA h g⁻¹ at the tenth cycle (Figure 4.6C), which is still much larger than the corresponding value of nonporous CNFs (400 mA h g⁻¹, decreased by 22 % at the tenth cycle) as well as the theoretical value (372 mA h g⁻¹) of graphite, the most used anode material in current LIBs.⁴⁹, ⁷⁹, ¹⁰⁰, ¹⁰¹ Figure 4.6D shows the cycling performance of these electrodes. The results indicate that CNF anodes prepared at 700 °C have relatively good capacity retention, and porous CNF anodes always have larger discharge capacities than both nonporous CNFs and graphite as cycle number increases.

Figure 4.7 shows the voltage profiles and cycling performance of both nonporous and porous CNF anodes carbonized at 1000 °C. Figure 4.7A demonstrates that the CNF anodes prepared at 1000 °C display similar voltage profiles as those prepared at 700 °C, i.e., storage capacity increases with surface area. For example, for porous CNF anodes made from SiO₂/PAN precursors with different SiO₂ contents (5, 10, 20 wt %), the first cycle charge capacities are 1100, 1400, and 1900 mA h g⁻¹, and their reversible capacities are 368, 464, and 593 mA h g⁻¹, respectively. The charge and reversible capacities for nonporous CNFs are
just 780 and 300 mA h g\(^{-1}\), respectively (Figure 4.7A). At the second cycle (Figure 4.7B), porous CNF anodes provide reversible capacities of 300, 370, and 470 mA h g\(^{-1}\), respectively, while this value for nonporous nanofibers is 260 mA h g\(^{-1}\). At the tenth cycle, the reversible capacity of porous CNF anodes made from 20 % SiO\(_2\)/PAN precursor decreases by 36 %, and holds a value at about 380 mA h g\(^{-1}\) (Figure 4.7C), which is similar to the 372 mA h g\(^{-1}\) theoretical value for the pure graphite, but much larger than the value for nonporous nanofiber anode (200 mA h g\(^{-1}\)).

![Figure 4.7 Charge-discharge curves (A, B, and C), and cycling performance (D) of CNF anodes at a constant current density of 50 mA g\(^{-1}\). CNF types: nonporous CNFs made from pure PAN (a), and porous CNFs made from SiO\(_2\)/PAN precursors with different SiO\(_2\) contents: (b) 5, (c) 10, and (d) 20 wt %. Carbonization Temperature: 1000 °C.](image-url)
In addition, the cycle performance shown in Figure 4.7D indicates that CNF anodes prepared at 1000 °C show relatively fast capacity fading during the initial several cycles, but they retain relatively stable capacities after three cycles.

It should be noted that porous CNF anodes prepared at both temperatures (700 and 1000 °C) always have larger capacities than nonporous nanofibers. It was reported that the quality of Li intercalation and deintercalation strongly depends on the crystalline phase, microstructure, and micromorphology of the carbonaceous materials. The exact mechanism of Li-ion transport within porous textures is very complex because many factors, such as tortuosity, connectivity, size distribution, shape of the pores, as well as the nature of electrolyte and the solid-liquid interface. There are several models for excess Li storage observed in carbonaceous materials, including the formation of Li multi-layers on graphene sheets. It was also reported that metallic Li clusters can form in microporosity. Micropores surrounded by small graphite stacking blocks are assumed to be able to trap Li in a metallic Li cluster.

Owing to their large surface area for faradaic reaction, short distance for charge diffusion, low resistance for electron conduction, as well as the added freedom for the volume change accompanying Li-ion intercalation, porous CNF anodes offer high Li-storage capacity, fast charge-discharge kinetics, and good cyclic stability. In addition, the large void space can effectively alleviate the electrode pulverization problem and benefit the achievement of large capacity. From the Raman spectra, it can be seen that with the increase of pore volume, the structural development of defects and proportion of disordered carbon sections increases. Compared with the ordered lattice in graphite, these defective structures store more
Li, which also benefits the improvement of the electrochemical performance of LIBs.\textsuperscript{79, 103, 261} The increased capacity in these disordered carbon materials may also be derived from the adsorption of Li on the internal surfaces of nanopores formed by small graphene sheets arranged in a “house of cards” configuration.\textsuperscript{261}

3. Summary

It is demonstrated that porous CNFs can be prepared by the carbonization of electrospun SiO$_2$/PAN composite nanofiber, followed by removing SiO$_2$ nanoparticles with HF acid. The characterization results show that porous CNF anodes have magnified surface areas and surface defects. These materials can be used directly as anodes in LIBs without adding any polymer binder or nonactive carbon black. Electrochemical performance testing indicates that porous CNF anodes have large capacities and good cyclability, which are caused by their large surface area for charge transfer, short distance for charge diffusion and electron conduction, and added freedom for the volume change that accompanies Li-ion intercalation. In addition, CNF anodes prepared at 1000 °C exhibit larger first cycle irreversible capacities, but poorer capacity retention than those prepared at 700 °C.
Chapter 5 Fabrication of Porous CNFs and Their Applications as Anode Materials for Rechargeable LIBs: Approach II

In addition to SiO₂ nanoparticles, inorganic salts can also be used to create porous structure in CNFs. In this chapter, ZnCl₂ salt was added to PAN precursor and electrospun into ZnCl₂-added PAN nanofibers. During the carbonization, ZnCl₂ helped create porous structure through an activation process and porous CNFs were obtained.

1. Experimental

1.1 Chemicals

PAN (Mw = 150,000), ZnCl₂ salt (99.995 %, power, anhydrous) and solvent DMF were purchased from Aldrich Chemical Company Inc (USA). LiPF₆ (power, sealed under argon), EC (100 %, sealed under argon), EMC (100 %, sealed under argon) were purchased from Ferro Corporation (USA). All these reagents were used without further purification. DMF solutions of PAN (7 wt %) containing various amount of ZnCl₂ (0, 5, 10, and 15 wt %) were prepared at 60 °C. Mechanical stirring was applied for at least 24 hours in order to obtain homogeneously-distributed solutions.

1.2 Nanofiber preparations

A variable high voltage power supply (Gamma ES40P-20W/DAM) was used to provide a high voltage (around 14 kV) for electrospinning with 0.5 ml h⁻¹ flow rate and 15 cm needle-to-collector distance. The electrospun ZnCl₂/PAN composite nanofibers were firstly stabilized in an air environment at 280 °C for 2.5 h (heating rate was 5 °C min⁻¹) and then
carbonized and activated at 700 °C for 1 h in nitrogen atmosphere (heating rate was 2 °C min⁻¹). Finally, these porous CNFs were washed with hydrochloric acid solution (18 wt%) three times at 80 °C and deionized water over three times at 80 °C to remove the residual Zn-containing compounds and chloride ions.

1.3 Nanofiber characterizations

The morphology of ZnCl₂/PAN composite nanofibers were evaluated using SEM (JEOL 6400F FESEM at 20 kV). The morphology of porous CNFs were characterized using ultra-high resolution SEM (Hitachi S-5500) at 2.0 kV. Both activated and unporous CNFs were characterized Raman spectra (Horiba Jobin Yvon LabRam Aramis Microscope, 633 nm HeNe Laser). Surface area analysis was carried out using the BET nitrogen adsorption method (Micromeritics Gemini 2360).

1.4 Electrochemical evaluations

Electrochemical Performance was investigated using a 2032 button coin cell (Hohsen Corp.). Thin, circular, flexible, and mechanically-tough CNFs were attached onto copper current collector to be directly used as working electrodes. A Li ribbon (thickness of 0.38mm) was used as the counter electrode. The electrolyte used was 1 M LiPF₆, dissolved in 50/50 (V/V) EC/EMC. Coin cells were assembled in a high pure argon-filled glove box. Charge (Li insertion) and discharge (Li extraction) were conducted using an Arbin automatic battery cycler at three different current densities between cut-off potentials of 0.01 and 2.5 V. EIS was performed using a Gamry reference 600 Potentiostat/Galvanostat/ZRA over the
frequency range in a 10.0 mV AC voltage signal and 100 kHz - 10 mHz frequency range in automatic sweep mode from high to low frequency.

2. Results and discussion

2.1 Morphology and structure characterization

SEM images of ZnCl$_2$/PAN nanofibers (Figure 5.1A-D) show relative smooth and taut surface structure. The average nanofiber diameter decreases with the increase of ZnCl$_2$ content, but the diameter distribution of nanofibers with 15 wt % ZnCl$_2$ becomes heterogeneous and a small number of bead-like irregularities appear. The reason for decreasing fiber diameter is that the increased net charge density caused by the higher ZnCl$_2$ content leads to greater electrostatic repulsion, which results in thinner fibers with larger surface areas.

SEM images of CNFs are displayed in Figure 5.1E-H. Compared with corresponding ZnCl$_2$/PAN precursors, CNFs still keep smooth and regular outer surface, long and straight cylindrical fibrous structure, and homogeneous diameter distribution without collapsing or disrupting morphology. In addition, with the increase of ZnCl$_2$ content in ZnCl$_2$/PAN precursors, the CNF diameter decreases slightly.
Figure 5.1 SEM images of ZnCl$_2$/PAN precursor nanofibers (A, B, C, and D) and the corresponding CNFs (E, F, G, and H). ZnCl$_2$ contents in ZnCl$_2$/PAN precursors: (A, E) 0, (B, F) 5, (C, G) 10, and (D, H) 15 wt %. 
Table 5.1 Surface structural parameters of CNFs.

<table>
<thead>
<tr>
<th>ZnCl₂ (%)</th>
<th>SSA [a] [m²g⁻¹]</th>
<th>TPV [b] [cm³g⁻¹]</th>
<th>Vₘeso [c] [cm³g⁻¹]</th>
<th>Vₘicro [d] [cm³g⁻¹]</th>
<th>Wₘeso [e] [nm]</th>
<th>Wₘicro [f] [nm]</th>
<th>APS [g] [nm]</th>
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<td>0.05</td>
<td>8.1</td>
<td>0.05</td>
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<td>0.04</td>
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<td>0.05</td>
<td>0.24</td>
<td>3.8</td>
<td>0.24</td>
<td>2.1</td>
</tr>
</tbody>
</table>


Surface properties of CNFs were studied using N₂ absorption isotherms at 77k⁶⁴ and are summarized in Table 5.1. The results show that the BET specific surface area, total pore volume, micropore volume, and mesopore volume of CNFs increase with the increase content of ZnCl₂ in ZnCl₂/PAN precursors, which indicates that the evolution of the porous structure in CNFs is caused by the presence of ZnCl₂ during carbonization. From Table 1, it is also seen that the pore sizes of porous CNFs made from ZnCl₂/PAN precursors are relatively small, and most pores are smaller than 1.7 nm. This is probably why those pores cannot be seen in SEM images in Figure 5.1.
Raman spectra (Figure 5.2) of CNFs are consistent with typical disordered carbon materials.49, 64 The strong peak centered at near 1350 cm$^{-1}$ (D line) can be explained as defect-induced structures in the graphene layers of carbon materials, while the peak centered at near 1600 cm$^{-1}$ (G line) is indicative of the high-frequency $E_{2g}$ first-order graphitic crystallites49, 64. With the increase content of ZnCl$_2$ in ZnCl$_2$/PAN precursors, the Raman spectra of resultant CNFs show a decreased intensity of G peak and an increased intensity ratio of D peak to G peak. These results demonstrated that ZnCl$_2$ activated CNFs promotes the presence of defects and disordered sections.64

2.2 Electrochemical performance
The charge-discharge curves of CNF anodes are shown in Figure 5.3A-B at 50 mA g\(^{-1}\) with a potential window from 0.01 to 2.5 V. Porous CNF anodes exhibit specific charge capacities of about 860, 880, and 970 mA h g\(^{-1}\) at the first cycle, and their reversible capacities are about 518, 533 and 515 mA h g\(^{-1}\), respectively (Figure 5.3A). The corresponding values for nonporous CNF anode (i.e., that prepared from pure PAN precursor with 0 % ZnCl\(_2\)) are 860 and 410 mA h g\(^{-1}\), respectively, and they are smaller than those activated ones. At the second cycle (Figure 5.3B), porous CNF anodes maintain relatively stable reversible capacities (483, 482, and 483 mA h g\(^{-1}\), respectively). However, the reversible capacity of nonporous counterpart reduces to 389 mA h g\(^{-1}\). Figure 5.3C shows the cycling performance of these CNF anodes. It is seen that porous CNF anodes keep relatively stable capacities after three cycles and always have larger capacities than the nonporous one.

Porous CNF anodes also have good electrochemical performance at high current densities. The variations of reversible capacity with different current densities (i.e., rate capability) are shown in Figure 5.3D. At 75 mA g\(^{-1}\), porous CNF anode made from PAN/15 wt % ZnCl\(_2\) precursor has a high discharge capacity of 400 mAh g\(^{-1}\) at the tenth cycle; conversely, nonporous CNF anode only has a capacity of 260 mAh g\(^{-1}\). Although the discharge capacity of this porous CNF anode reduces slightly at the tenth cycle (385 mAh g\(^{-1}\)) at 100 mA g\(^{-1}\), it is still slightly larger than the theoretical value of graphite (372 mAh g\(^{-1}\)) and also the capacity (210 mAh g\(^{-1}\)) of nonporous one.
Figure 5.3 (A) First-cycle charge-discharge curve at 50 mA g\(^{-1}\), (B) Second-cycle charge-discharge curve at 50 mA g\(^{-1}\), (C) Cycling performance at 50 mA g\(^{-1}\), (D) Rate capability at the tenth cycle, and (E) EIS for CNF anodes. ZnCl\(_2\) contents in ZnCl\(_2\)/PAN precursors: (a) 0, (b) 5, (c) 10, and (d) 15 wt %.

BET data (Table 5.1) show that porous CNFs have large surface areas and small pores. The large surface areas in porous CNF anodes are readily accessible to electrolyte, and as a
result, they reduce the electronic and ionic transport length, which facilitates rapid charging and discharging at high current densities.\textsuperscript{87, 106} Small pores in porous CNFs provide additional room for Li insertion during charge. From Raman spectra results, it is also seen that, compared with nonporous carbon, porous CNFs have more disordered microstructure, which is able to provide extra space for the storage of Li.\textsuperscript{79, 100, 101, 103, 261} As a result, porous CNF anodes have relatively large capacities and high rate capability.

EIS curves, which can identify the fundamental mechanism of the Li ion phase-transfer at the electrode-electrolyte interface,\textsuperscript{231, 255, 259} were obtained for CNF anodes and are shown in Figure 5.3E. All anodes show one depressed semicircle of the interfacial impedance in the high-frequency range, which is attributed to the parallel combination of interface film resistance ($R_I$) associated with the SEI film on the electrode surface and the charge transfer impedance ($R_{ct}$), and an inclined line in low frequencies, which is designated to the diffusion of Li ions into the electrode active materials.\textsuperscript{231, 255} From Figure 47E, it is seen that porous CNF anodes have smaller interfacial resistance than nonporous one. In addition, the interfacial impedance decreases slightly with the increase of ZnCl\textsubscript{2} content in ZnCl\textsubscript{2}/PAN precursors. Therefore, instead of increasing the interfacial resistances, the large surface areas and small pores in porous CNF anodes leads to the reduction of these values, which is beneficial for improving the anode kinetics.

3. Summary

The combination of electrospinning, carbonization, and activation processes lead to porous CNF anodes that have large capacities, good cycling stability, and high rate capacity, owning to their large surface area for faradaic reaction, short distance for mass and charge
diffusion, as well as added freedom for volume change accompanying Li insertion. The present results suggest that salt-porous CNFs are promising anode materials for high-performance rechargeable LIBs.
Chapter 6 Fabrication of Porous CNFs and Their Applications as Anode Materials for Rechargeable LIBs: Approach III

In this Chapter, a blend of PAN and PLLA in solvent DMF was used to prepare CNFs via electrospinning and subsequent thermal treatments. PAN and PLLA were firstly electrospun into bicomponent nanofibers, and the further thermal treatment procedure allowed the elimination of PLLA during the carbonization of PAN, thereby creating porous CNFs without the necessity of any chemical treatments. These porous CNFs were used as anodes for LIBs without adding any binder or other additives. Compared with conventional graphite anode, porous CNFs show clear advantages in electrochemical behaviors in terms of high reversible capacity and relatively stable cycle performance.

1. Experimental

1.1 Chemicals

PAN, PLLA and solvent DMF were purchased from Aldrich. First, 8 wt % DMF solution of PAN/PLLA (9:1) was prepared at 60 °C. Strong mechanical stirring was applied for at least 24 hours in order to obtain homogeneous solution. In comparison, 8 wt % DMF solution of pure PAN was also prepared. A variable high-voltage power supply (Gamma ES40P-20W/DAM) was used to provide a high-voltage of around 17 kV for electrospinning. The positive electrode of the high voltage power supply was connected to the needle tip. The flow rate and tip-collector distance were fixed at 0.5 ml h\(^{-1}\) and 15 cm, respectively. The grounded electrode was connected to a metallic collector wrapped with aluminum foil. Dry fibers were accumulated on the collection screen and collected as a fibrous mat.
1.2 Nanofiber preparations

Electrospun PAN/PLLA (9:1) nanofibers were stabilized in an air environment at 280 °C for 5.5 hours (heating rate was 5 °C min⁻¹). In this process, the thermoplastic PAN was converted to a nonplastic cyclic or ladder compound, while PLLA phase decomposes. The stabilized samples were then carbonized at 800 °C for 1 hour (heating rate was 2 °C min⁻¹) to generate porous CNFs. For comparison, nonporous CNFs were also prepared from electrospun PAN nanofibers.

1.3 Nanofiber characterizations

The morphology and diameter of electrospun PAN and PAN/PLLA (9:1) nanofibers were evaluated using FESEM (JEOL 6400F Field Emission SEM at 5 kV). ATR-FTIR spectra were collected from a FTIR spectrometer (Nicolet 560). Thermal properties of electrospun fibers were evaluated using DSC from 25 to 400 °C at a heating rate of 10 °C min⁻¹ in a nitrogen environment (Perkin Elmer Diamond Series DSC with Intracooler). The morphology and diameters of nonporous and porous CNFs were characterized using ultra-high resolution SEM (Hitachi S-5500) at 2.0 kV. TEM (FEI Tecnai G² Twin) with an accelerating voltage of 120 kV was also used to study the structure of porous CNFs. The structural variations of porous CNFs were also identified by WAXD (Philips X'Pert PRO MRD HR X-Ray Diffraction System, Cu kα, λ = 1.5405 Å) and Raman spectra (Horiba Jobin Yvon LabRam Aramis Microscope, 633 nm HeNe Laser). Surface area analysis was carried out using the BET nitrogen adsorption method (Micromeritics Gemini 2360).
1.4 Electrochemical evaluations

The EIS of both nonporous and porous CNFs were obtained using a Gamry reference 600 Potentiostat/Galvanostat/ZRA in a 10.0 mV AC voltage signal in the 100 kHz-10 mHz frequency range in automatic sweep mode from high to low frequency. Electrochemical charge/discharge performance of nonporous and porous CNFs was evaluated using 2032 button coin cells (Hohsen Corp.). CNFs were attached onto copper foil to be directly used as the working electrode. Li ribbon (0.38mm thick, Aldrich) was used as the counter electrode. Separion S240 P25 (Degussa AG, 25 µm) was used as the separator. The electrolyte used was 1 M LiPF₆, dissolved in 1/1 (V/V) EC/EMC (Ferro Corp.). Coin cells were assembled in a high-pure argon-filled glove box. Charge (Li insertion) and discharge (Li extraction) were conducted using an Arbin automatic battery cycler at a constant current density of 50 mA g⁻¹ between cut-off potentials of 0.01 and 2.8 V. The surface morphology of both nonporous and porous CNF anodes after 50 charge/discharge cycles was also examined with analytical UHR FE-SEM (SU-70) at 5 kV.

2. Results and discussion
2.1 Morphology and structure characterization

Their SEM images and diameter distributions are displayed in Figure 6.1. It is seen that pure PAN nanofibers show a relatively taut and regular surface structure, long fibrous morphology, and also a homogeneously distributed diameter in the range of 200 to 300 nm (with an average value of 250 nm). However, in the presence of PLLA, the surface morphology of PAN/PLLA bicomponent nanofibers becomes irregular, and beads or fibers
with so-called ‘beads on a string’ morphology are also clearly shown.\textsuperscript{264} In addition, the nanofiber diameter decreases slightly. It is known that solution properties, such as conductivity, viscosity, and surface tension, influence the electrospinning process and the resultant nanofiber structure.\textsuperscript{1, 3, 4, 16, 18} The addition of the PLLA component changes both the conductivity and viscosity of the electrospinning solution,\textsuperscript{265} and hence alters the balance among solution properties during electrospinning, which in turn leads to the morphology change of electrospun PAN/PLLA bicomponent nanofibers.\textsuperscript{266}

Figure 6.1 SEM images and diameter distributions of (A, B, and C) pure PAN and (D, E, and F) PAN/PLLA (9:1) nanofibers.

ATR-FTIR spectra recorded in the spectral range of 3800 - 700 cm\textsuperscript{-1} were presented in Figure 6.2 Compared with pure PAN nanofibers, PAN/PLLA (9:1) bicomponent nanofibers show a typical ester peak by lactide at 1750 cm\textsuperscript{-1}, which comes from the PLLA component.
Moreover, the partial transformation of the ester groups in carboxyls brings about the small spectral change at about 1200 cm⁻¹, where the C–O stretching vibration resonates.

Figure 6.3 shows the DSC thermograms of PAN and PAN/PLLA (9:1) nanofibers. Pure PAN nanofibers exhibit a relatively large and sharp exothermic peak at about 290 °C, which is caused by the three exothermic reactions (i.e., dehydrogenation, instantaneous cyclization, and crosslinking reactions) of PAN during the heat-treatment process.²⁶⁶ In the presence of PLLA component, the exothermic peak shifts to a higher temperature, and the peak also becomes a little broader compared to that of pure PAN nanofibers. In addition, the peak intensity, which indicates the total heat of reactions, decreases in PAN/PLLA (9:1) bicomponent nanofibers. The broadening of the exothermic peak in the presence of PLLA suggests that PLLA modifies the activity of the free radicals involved in the complex chemical reactions. The reduced reaction heat is caused by the interactions between PAN and PLLA, which decrease the formation of free radicals on the nitrile groups and subsequently their recombination reactions. The shifting of the peak to a higher temperature is also attributed to the inhibiting effect of PLLA on the free radical formation.²⁶⁵, ²⁶⁶
Porous CNFs can be prepared by thermally treating PAN/PLLA (9:1) bicomponent nanofibers. During that treatment, the PLLA component can be decomposed without producing carbon residues\textsuperscript{263}, while the PAN phase transfers into a carbon structure\textsuperscript{262}. The decomposition of PLLA leads to the formation of pores in CNFs. However, without the presence of PLLA, nonporous CNFs are formed.
Figure 6.3 DSC thermograms of (a) PAN and (b) PAN/PLLA (9:1) nanofibers.

Figure 6.4 shows SEM images of nonporous and porous CNFs made from pure PAN and PAN/PLLA (9:1) nanofibers, respectively. The micrographs indicate that CNFs made from pure PAN have a smooth surface morphology, while CNFs made from PAN/PLLA (9:1) bicomponent nanofibers exhibit an uneven and wrinkled “molecular sponge” surface morphology. In addition, there are large variations in the fiber diameter of porous CNFs. The pore structure of porous CNFs can be more clearly seen in TEM images. Figure 6.5 shows TEM images of porous CNFs made from PAN/PLLA (9:1) bicomponent nanofibers. The largely irregular and undulate surface morphology with elongated indents and clear ridges along the fiber surface indicate the presence of relatively large pores (meso-pores with the diameter in the range of 2-50 nm). However, the presence of smaller pores (micro-pores with
the diameter less than 2 nm) need be studied using other techniques such as the BET nitrogen adsorption method.64

Figure 6.4 SEM images of (A, B) nonporous and (C, D) porous CNFs made from PAN and PAN/PLLA (9:1) nanofibers, respectively.

Table 6.1 shows the surface and pore structural parameters of nonporous and porous CNFs, which were obtained by the BET method.64 Porous CNFs with pores or rough surface morphology made from PAN/PLLA bicomponent nanofibers have a BET surface area of 235 m² g⁻¹ and a total pore volume of about 0.114 cm³ g⁻¹. In addition, porous CNFs have both micro- and meso-pores, with about 75 % of pore volume coming from micro-pores (< 2.0 nm). These micro-pores cannot be seen directly from SEM or TEM images obtained in this
work. However, the nonporous CNFs with smooth and long fibrous morphology made from pure PAN only has smaller surface area of about $33.9 \text{ m}^2 \text{ g}^{-1}$. In addition, there is no clear pore structures among this fibers. From these BET results, it is clear that pores or undulate and wrinkled surface morphology is important for the increasing of surface area. These results are consisted with our former research results, that is surface area are strongly influenced by Micro-, and meso-porosity developed on the uneven and rough outer surface of nanofibers.\textsuperscript{265}

Figure 6.5 TEM images of porous CNFs made from PAN/PLLA (9:1) nanofibers.
The structure of porous CNFs was also studied using WAXD and Raman spectroscopy, respectively. The WAXD pattern (Figure 6.6) shows a sharpening peak near $2\theta = 25.0^\circ$ and an unobvious peak near $2\theta = 45.2^\circ$, corresponding to (002) and (100) layers of the graphitic structure, respectively.\textsuperscript{49, 64} Figure 6.7 shows the Raman spectra of porous CNFs. The strong peak centered near 1350 cm\(^{-1}\) (D line) can be explained as structure defects and disorder-induced features of the carbon, while another relatively small peak centered near 1600 cm\(^{-1}\) (G line) is indicative of the high-frequency $E_{2g}$ first-order graphitic crystallites of the carbon. The presence of both D and G bands is consistent with WAXD patterns and indicates that porous CNFs contain turbostratically disordered graphene sheets.\textsuperscript{49, 64}

Table 6.1 Structural parameters of nonporous and porous CNFs made from PAN and PAN/PLA (9:1) nanofibers, respectively.

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<th>SSA\textsuperscript{[a]} [m(^2) g(^{-1})]</th>
<th>TPV\textsuperscript{[b]} [cm(^3) g(^{-1})]</th>
<th>$V_{\text{meso}}$\textsuperscript{[c]} [cm(^3) g(^{-1})]</th>
<th>$V_{\text{micro}}$\textsuperscript{[d]} [cm(^3) g(^{-1})]</th>
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<tr>
<td>Nonporous CNFs</td>
<td>33.9</td>
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<td>-</td>
<td>-</td>
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<tr>
<td>Porous CNFs</td>
<td>235</td>
<td>0.114</td>
<td>0.028</td>
<td>0.086</td>
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\textsuperscript{[a]} Specific surface area (SSA) was calculated by the Brunauer-Emmett-Teller (BET) method.

\textsuperscript{[b]} TPV is the total pore volume.

\textsuperscript{[c]} $V_{\text{meso}}$ is the mesopore (2-50 nm) volume calculated by the Barret, Joyner, and Halenda (BJH) method based on the Kelvin equation.

\textsuperscript{[d]} $V_{\text{micro}}$ is the micropore (< 2 nm) volume calculated by the Horvath-Kawazoe (HK) method.

2.2 Electrochemical performance

Porous CNFs are typically collected in the form of nonwoven porous mats and can be directly used as anodes in LIBs without adding any polymer binder or other additives. The elimination of non-active additives ensures the high-rate electron conduction and has the
potential to improve the electrochemical properties. In addition, anodes made of porous CNFs have more accessible sites, shorter transport distances for both electrons and Li ions as well as larger electrode-electrolyte contact areas resulting from their large surface areas. All these structural features benefit the improvement of electrochemical performance of porous CNF anodes. In the present study, we investigated both EIS and galvanostatic charge-discharge phenomena of porous CNF anodes.

Figure 6.6 WAXD of porous CNFs made from PAN/PLLA (9:1) nanofibers.
Figure 6.7 Raman spectra of porous CNFs made from PAN/PLLA (9:1) nanofibers.

Figure 6.8 displays EIS of both nonporous and porous CNF anodes carbonized at 800 °C. The impedance spectra of both anodes consist of one semicircle in the high frequency range, which is usually taken to be the charge-transfer processes on the electrode-electrolyte interface, and a straight line in the low frequency range, which indicates the impedance due to the Li diffusion and accumulation processes in the working electrode. As shown in Figure 6.8, porous CNF anode has smaller interfacial impedance than nonporous CNF anode, indicating that the porous structure facilitates the charge transfer at the electrode-electrolyte interface.
Figure 6.8 EIS of nonporous and porous CNF anodes made from PAN and PAN/PLLA (9:1) nanofibers, respectively.

Galvanostatic charge-discharge experiments were carried out at a current density of 50 mA g\(^{-1}\) within a voltage window of 0.01 - 2.80 V to evaluate the electrochemical performance of the porous CNF anode. Figure 6.9 show the voltage profiles of the porous CNF anodeS at different cycles. When Li ions insert into the anode in the first charge, there are two sloping voltage ranges (2.80 - 0.75 V and 0.75 - 0.01 V vs. Li\(^+\)/Li) that can be discerned. The first slope is attributed to the decomposition of the electrolyte and the formation of the SEI film, while the potential slope in 0.75-0.01 V corresponds to the insertion of Li ions into the porous CNF anode.
Figure 6.9 Charge-discharge curves of porous CNF anode made from PAN/PLLA (9:1) nanofibers at a constant current density of 50 mA g\(^{-1}\).

From Figure 6.9, it is also apparent that porous CNF anode has a large Li storage capacity. For example, the charge and discharge capacities are about 858 and 566 mAh g\(^{-1}\), respectively, at the first cycle. A large irreversible capacity of about 292 mAh g\(^{-1}\) can also be seen at the first cycle, and this leads to a relatively low coulombic efficiency of about 66%. This irreversible capacity may be caused by the reductive decomposition of electrolyte solution and the subsequent formation of the SEI film.\(^{49, 231}\) However, the coulombic efficiency increases to nearly 100% at the second and the sequential cycles, indicating that the newly-formed interface is stable during cycling. In addition, the reversible capacity of the porous CNF anode at the second cycle is about 491 mA h g\(^{-1}\), which indicates a relatively high capacity retention of 87% from the first cycle. At 25th and 50th cycles, the reversible capacities are still 449 and 435 mAh g\(^{-1}\), respectively, indicating a slow capacity fading after
the second cycle. All these reversible capacities are much larger than the 372 mAh g\(^{-1}\) theoretical value of graphite - the conventional anode material.

Figure 6.10 shows the cycling performance of both nonporous and porous CNF anodes. The results further demonstrate that porous CNF anode delivers good cycle stability and large reversible capacity, which is always larger than that of nonporous CNF anode at least in the first 50 cycles.

![Figure 6.10 Cycling performance of nonporous and porous CNF anodes made from PAN and PAN/PLLA (9:1) nanofibers, respectively.](image)

Owing to their large surface area for faradaic reaction, short distance for charge diffusion, low resistance for electron conduction, as well as the added pore space for the volume change accompanying Li-ion intercalation, porous CNFs offer high Li storage capacity, fast charge-discharge kinetics, and good cyclic stability.\(^{80-84, 86, 87, 106}\) Raman spectrum demonstrated that porous CNFs consist of disordered carbon sections with developed structural defects. Compared with ordered lattices in graphite, these structural defects make porous CNFs store
more Li, and benefit the improvement of the electrochemical performance of LIBs.

Figure 6.11 SEM images of (A, B) nonporous and (C, D) porous CNF anodes made from PAN and PAN/PLLA (9:1) nanofibers, respectively, after 50 charge/discharge cycles at a constant current density of 50 mA g⁻¹.

We also examined the morphology changes of both nonporous and porous CNF anodes after electrochemical cycling. SEM images of both anodes after 50 cycles at 50 mA g⁻¹ current density are displayed in Figure 6.11. It is seen that nonporous CNFs show a large amount of sponge-like particles, which are loosely agglomerated on the fiber surface. These particles are formed during electrochemical cycling and indicate the limited structural stability of nonporous CNFs. However, porous CNFs still exhibit a highly convoluted and
wrinkled morphology. Although porous CNFs also have some small particles on fiber surface, the comparison between Figures 6.4 and 6.11 shows that the structural change of porous CNFs caused by the charge/discharge cycling is significantly smaller than that of nonporous CNFs. Therefore, the pore structure in porous CNFs can help the anode better withstand the volume expansion and shrinkage during Li insertion and extraction processes. As a result, the integrity of porous CNF anodes can be retained during charge/discharge cycles.

3. Summary

It is demonstrated that porous CNFs can be generated by thermally treating electrospun PAN/PLLA bicomponent nanofibers. During the thermal treatments, PAN serves as the carbon precursor, while PLLA acts as the pore generator. The resultant porous CNFs have a relatively large surface area of about 235 m² g⁻¹ and can be directly used as anodes for LIBs without adding any binder and other additives. A satisfactory cycling performance was achieved with specific capacities of about 566 mAh g⁻¹ at the first cycle and 435 mAh g⁻¹ at the 50th cycle, respectively, which are much larger than the theoretical value of conventional graphite anode and also greater than those of nonporous CNF anode. The good electrochemical performance of the porous CNF anode may be due to the unique structural features such as numerous active sites for charge transfer reaction, short diffusion pathway for both Li ions and electrons as well as reasonable electrical conductivity provided by the good contact between neighboring nanofibers. Therefore, porous CNFs with large reversible capacity and stable cycling performance are promising anode material for high-performance rechargeable LIBs. The future work should focus on performing galvanostatic charge-
discharge experiments at higher current densities in order to explore the relationship between specific discharge capacity and current density (rate capability) of these porous CNF anodes.
Chapter 7 Fabrication of Li-Active Manganese Oxide-Loaded Porous CNFs and Their Applications as Anodes for Rechargeable LIBs.

Confining Li-active nanoparticles to porous CNFs can combines key advantages of both components: Li-active nanoparticles, which possess large Li-storage capacity properties, and porous carbon matrices, which exhibit highly-developed internal surface area, good mechanical stability, and high electrical conductivity. In this Chapter, Li-active Mn oxide nanoparticle-loaded porous CNFs (MnO\textsubscript{x}/CNFs) and the electrochemical performance of the resultant nanofibers were evaluated.

1. Experimental

1.1 Chemicals

PAN (\(M_w = 150,000\)), Mn(OAc)\textsubscript{2} (99.995 %) and solvent DMF were purchased from Aldrich (USA). DMF solutions of PAN (8 wt %) containing different amount of Mn(OAc)\textsubscript{2} (15, 30, and 50 wt %) were prepared at 60 °C. Mechanical stirring was applied for at least 24 h in order to obtain homogeneous solutions.

1.2 Nanofiber preparations

A high voltage power supply (Gamma ES40P-20W/DAM) was used to provide a high voltage at around 21 kV for electrospinning. Dry fibers were accumulated on the collection screen and collected as a fibrous mat. The electrospun Mn(OAc)\textsubscript{2}/PAN nanofibers were firstly stabilized in air environment at 280 °C for 5 h (heating rate: 5 °C min\textsuperscript{-1}), and then carbonized at 700 °C for 1 h in argon atmosphere (heating rate: 2 °C min\textsuperscript{-1}).
1.3 Nanofiber characterizations

The morphology and diameter of Mn(OAc)$_2$/PAN and MnO$_x$/CNFs were evaluated using FESEM (JEOL 6400F FESEM at 20 kV). The morphology and structure variations of MnO$_x$/CNFs were also characterized using TEM (Hitachi HF-2000 TEM at 200 kV) and X-ray diffraction (Philips X’Pert PRO MRD HR X-Ray Diffraction System).

1.4 Electrochemical evaluations

Electrochemical evaluations were performed using 2032 coin-type cells. MnO$_x$/CNFs attached onto copper foil (Lyon industries), Li ribbon (Aldrich), and Separion S240 P25 (Degussa) were directly used as the working electrode, counter electrode, and separator, respectively. The electrolyte used was 1 M LiPF$_6$, dissolved in 1/1 (V/V) EC/EMC (Ferro Corp.). Charge and discharge were conducted using an Arbin automatic battery cycler at different current densities between cut-off potentials of 0.01 and 2.8 V.

2. Results and discussion

2.1 Morphology and structure characterization

Figure 7.1A-C shows SEM images of electrospun Mn(OAc)$_2$/PAN nanofibers with different Mn(OAc)$_2$ contents (15, 30, and 50 wt %). All nanofibers exhibit a long and straight morphology with relatively uniform diameters ranging from 200 to 300 nm. Defects, such as beads or fibers with so-called ‘beads on a string’ morphology, can seldom be observed. After the thermal treatment as described in the Experimental section, the surface morphology of nanofibers (Figure 7.1D-F) becomes more irregular and the porous structure can be clearly seen. In order to further identify the structures of these carbonized nanofibers, TEM images
are also shown in Figure 7.1G-L. It can be seen that MnO\(_x\) particles with an average diameter of 10 nm are well-dispersed along porous CNFs.

The WAXD patterns obtained from MnO\(_x\)/CNFs are presented in Figure 7.2. For comparison, the spectrum of pure CNFs made from PAN precursor is also given. Pure CNFs only show a characteristic diffusion peak at \(2\theta = 25.0^\circ\) (002), which indicates the amorphous structure of typical carbon materials.\(^{49, 64}\) MnO\(_x\)/CNFs from the 15 wt % Mn(OAc)\(_2\)/PAN precursor shows diffusion peaks at \(2\theta = 18.0^\circ, 32.3^\circ, 37.9^\circ,\) and \(56.0^\circ\), which are assigned to scattering from 101, 103, 004, and 303 lattice planes of Mn\(_3\)O\(_4\) crystals.\(^{131, 267}\) MnO\(_x\)/CNFs from 30 wt % Mn(OAc)\(_2\)/PAN precursor shows diffusion peaks at \(34.9^\circ, 40.1^\circ,\) and \(58.7^\circ\), which can be assigned to 111, 200, and 220 planes of MnO.\(^{268}\) MnO\(_x\)/CNFs from 50 % Mn(OAc)\(_2\)/PAN precursors show some characteristic diffraction peaks of both Mn\(_3\)O\(_4\) and MnO. Therefore, during the thermal treatment, Mn(OAc)\(_2\) precursor transforms to Mn\(_3\)O\(_4\) and/or MnO,\(^{269}\) while PAN is carbonized. At the same time, the large density change, which induces the liberation of heteroatoms and the densification of carbon atoms, may finally cause the formation of the porous structure.
Figure 7.1 SEM images (A, B, and C) of Mn(OAc)$_2$/PAN nanofibers, and SEM (D, E, and F) and TEM images (G, H, I, J, K, L) of MnO$_x$/CNFs made from Mn(OAc)$_2$/PAN precursors. Mn(OAc)$_2$ contents in Mn(OAc)$_2$/PAN precursors: (A, D, G, and J) 15, (B, E, H, and K) 30, and (C, F, I, and L) 50 wt %.
Figure 7.2 WAXD patterns of MnO\textsubscript{x}/CNFs made from Mn(OAc)\textsubscript{2}/PAN precursors with different Mn(OAc)\textsubscript{2} contents: (a) 0, (b) 15, (c) 30, and (d) 50 wt %.

2.2 Electrochemical performance

In order to study the electrochemical performance of MnO\textsubscript{x}/CNFs, LIB anodes were prepared by attaching these nanofibers directly onto the current collector without adding any binder or conductor. Figure 7.3A-D shows the charge-discharge curves of different MnO\textsubscript{x}/CNF anodes between 0.01 and 2.8 V at a galvanostatic charge/discharge current of 50mA g\textsuperscript{-1}. For comparison, the charge/discharge curves of pure CNF anode are also given. During the first cycle (Figure 7.3A), the charge (Li insertion) curves of the anodes consist of three regions: 1) a rapid voltage drop to about 0.75-0.8 V; 2) a voltage plateau; and 3) a relatively slow voltage decrease to 0.01 V. The first region can be attributed to the
decomposition of the electrolyte and the formation of SEI film and other inactive materials.\textsuperscript{131} The second and third regions are related to the insertion of Li into the MnO\textsubscript{x}/CNFs. Typically, the charge capacity of the first region is irreversible, but the capacities of the second and third regions are reversible if the anode material can withstand the volume change during charge/discharge.\textsuperscript{131} From Figure 7.3A, it can also be seen that, at the first cycle, pure CNF anode shows charge and discharge capacities of about 784 and 542 mAh g\textsuperscript{-1}, respectively, corresponding to a coulombic efficiency of 69.1 %. However, MnO\textsubscript{x}/CNF anodes from Mn(OAc)\textsubscript{2}/PAN precursors (15, 30, and 50 wt \%) deliver higher charge (954, 976, and 1155 mAh g\textsuperscript{-1}) and discharge capacities (614, 694, and 785 mAh g\textsuperscript{-1}), corresponding to coulombic efficiencies of 64.4, 71.1, and 68.0 \%, respectively. After the first cycle, all anodes show insignificant irreversible capacities (Figure 7.3B-D). However, both charge and discharge capacities of MnO\textsubscript{x}/CNF anodes are still much larger than those of pure CNF anode. For example, at the second cycle (Figure 7.3B), pure CNF anode has charge and discharge capacities of 499 and 478 mAh g\textsuperscript{-1}, respectively, with a coulombic efficiency of 95.8 \%. While MnO\textsubscript{x}/CNF anodes (15, 30, and 50 wt \% Mn(OAc)\textsubscript{2} in precursor) show larger charge (597, 645, and 753 mAh g\textsuperscript{-1}) and discharge capacities (586, 645, 714 mAh g\textsuperscript{-1}), corresponding to coulombic efficiencies of 98.2, 100, and 94.8 \%, respectively.
Figure 7.3 Charge-discharge curves (A, B, C, and D) and cycling performance (E) at 50 mA g\(^{-1}\) current density, and rate capability (F) at the 50th cycle for MnO\(_x\)/CNF anodes. Mn(OAc)\(_2\) contents in Mn(OAc)\(_2\)/PAN precursors: (a) 0, (b) 15, (c) 30, and (d) 50 wt %.

Figure 7.3E compares the cycling stability of MnO\(_x\)/CNF anodes with pure CNF anode at a galvanostatic charge/discharge current density of 50 mA g\(^{-1}\) between 0.01-2.8 V. It is seen...
that although the discharge capacities decrease in the first few cycles, anodes exhibit small capacity loss after the initial few cycles and always have much larger capacities than pure CNF anode. At 50th cycle, MnOx/CNF anodes (15, 30, and 50 wt % Mn(OAc)2 in precursor) still remain relatively large reversible capacities of 560, 542, and 597 mAh g⁻¹, i.e., 91.5, 78.1, and 76.1 % capacity retention, respectively, while pure CNF anode has a much lower reversible capacity of about 396 mAh g⁻¹, corresponding to a capacity retention of 73.0 %.

In order to study the rate capability of MnOx/CNF anodes, discharge capacities are shown as a function of current density in Figure 7.3F. It is seen that MnOx/CNF anodes remain relatively high reversible capacities even at high current densities. It should be noticed that MnOx/CNF anodes from 50 wt % Mn(OAc)2/PAN precursor shows largest reversible capacity at 100 mA g⁻¹ current density at the 50th cycle compared with the value at other current density. The further research and characterizations need to be carried out to identify this interesting phenomenon.

The good electrochemical performance of MnOx/CNF anodes is a result of the combined advantages of MnOx and carbon matrices as well as the unique feature of porous nanofiber geometries. Both MnOx and carbon matrices can be used as active anode materials. During cycling, MnOx can accept a large amount of Li ion insertion, leading to high capacities, while the carbon matrices have good cycling performance and can also act as a buffer to alleviate the volume expansion of MnOx, thus preserving the integrity of the electrode. As a result, the merits of carbon (long cycle life) and MnOx (high Li-storage capacity) can be combined. In addition, the unique fiber structure of these MnOx/CNF anodes can minimize solid-state transport distance of both Li ions and electrons, and their high surface area permits a high
contact area with the electrolyte, thereby leading to a high Li-ion flux across the interface. The porous volume in nanofibers can also provide extra space for volume changes. As a result, favorable electrochemical behaviors, such as large reversible capacity, stable cycling performance, and high rate performance, are obtained in MnO$_x$/CNF anodes.$^{87, 88, 106, 260}$

3. Summary

The present study provides a novel route to fabricate MnO$_x$/CNFs using the electrospinning technique. The morphological and structural characterizations indicate that nano-sized MnO$_x$ particles are formed among porous CNFs. These porous MnO$_x$/CNFs are directly used as anodes for rechargeable LIBs without adding any binder or conductor. The electrochemical results indicate that these MnO$_x$/CNFs have high reversible capacity, long cycle life, and good rate capability because of the combinative effects of nano-sized MnO$_x$ and carbon matrices as well as the unique morphology and structural features of porous nanofibers. Future work includes pursuing the possibilities of extending this novel strategy to incorporate other nano-sized transition-metal oxide, such as CuO, Fe$_3$O$_4$, NiO, CoO or SnO$_2$, into porous CNFs for use as anodes in LIBs.
Chapter 8 Fabrication of Li-Active Si Nanoparticle-Loaded Solid CNFs as Anodes for Rechargeable LIBs

Among all known anode materials, Si has the highest theoretical capacity (more than 4000 mAh g\(^{-1}\)), which is at least 10-fold greater than the theoretical value of graphite.\(^{97, 230, 231}\) However, the high capacity of Si is difficult to be realized in practice because Si anodes suffer from pulverization-induced capacity fading that is caused by the huge specific-volume changes during repeated Li uptake and removal reactions.\(^{97, 230, 231}\) One generally accepted strategy to alleviate this problem is to generate nanoscale Si particles that can tolerate some volume changes during electrode reactions. However, this method can only partially accommodate the volume change, and the resulting anode materials still have limited cycle life.\(^{230, 231}\) Another alternative strategy is to prepare various composite materials containing well-dispersed Si particles in host matrices. Among various hosts, carbon materials show advantages because they can buffer the volume changes of Si particles and provide good electrical contact during Li insertion and extraction.\(^{270-275}\) Therefore, dispersing Si nanoparticles into carbon matrices is a promising approach to combine the advantageous properties of carbon (long cycle life) and Si (high Li-storage capacity) to improve the overall electrochemical performance of LIBs.

This Chapter presents a relatively simple and low-cost approach to prepare Si/carbon composite nanofibers (Si/CNFs) by a judicious combination of electrospinning and subsequent thermal treatments.\(^{49, 64, 258}\) These Si/CNFwebs can be directly used as anodes in rechargeable LIBs without introducing additional binding or conductive materials.
Alternatively, binding materials can also be used with chopped Si/CNFs to make anodes in order to reduce free space between nanofibers. In addition to combining the advantages of Si nanoparticles and carbon matrices, these Si/CNFs have other unique characteristics, such as long fiber length for efficiently transporting charge carriers, large surface-to-volume ratio for increasing Li insertion kinetics, and enhanced electrical and mechanical properties for improving the stability and safety of the batteries. As a result, improved electrochemical performance has been achieved for LIB anodes in terms of large reversible capacity (about 1800 mAh g\(^{-1}\)), good cycling performance, and high rate capability.

1. Experimental

1.1 Chemicals

PAN (Mw = 150,000) and solvent DMF were purchased from Aldrich (USA). Si nanoparticles (particle size \(\geq 70\) nm) were purchased from Nanostructured & Amorphous Materials, Inc. All these reagents were used without further purification.

1.2. Nanofiber preparations

DMF solutions of PAN (8 wt %) containing various amounts of Si nanoparticles (15, 30, and 50 wt %) were prepared at 60 °C. Mechanical stirring was applied for at least 24 hours in order to obtain homogeneously-distributed solutions. A variable high-voltage power supply (Gamma ES40P-20W/DAM) was used to provide a high voltage (around 21 kV) for electrospinning. The flow rate used was 0.75 ml h\(^{-1}\) and the needle-to-collector distance was 15 cm. Electrospun Si/PAN composite nanofibers were firstly stabilized in air environment at
280 °C for 5 hours (heating rate was 5 °C min\(^{-1}\)) and then carbonized at 700 °C for 1 hour in nitrogen atmosphere (heating rate was 2 °C min\(^{-1}\)) to form Si/CNFs.

1.3 Nanofiber characterization

The morphology and diameter of both Si/PAN composite nanofibers and Si/CNFs were evaluated using scanning electron microscopy (SEM, JEOL 6400F FESEM at 5 kV). The structural variations were identified by wide angle X-ray diffraction (WAXD, Philips X’Pert PRO MRD HR X-Ray Diffraction System, Cu k\(\alpha\), \(\lambda = 1.5405\) Å) and Raman spectra (Horiba Jobin Yvon LabRam Aramis Microscope, 633 nm HeNe Laser), respectively.

1.4 Electrochemical evaluations

Galvanostatic charge-discharge experiments were carried out using 2032 coin cells (Hohsen Corp.). Thin, circular, flexible, and mechanically-tough Si/CNFs were attached onto copper current collector to be directly used as the working electrode. The electrode density and active material load density of the nanofiber electrodes are about 0.6 g cm\(^{-3}\) and 1.1 mg cm\(^{-2}\), respectively. A Li ribbon (thickness of 0.38mm) was used as the counter electrode. The electrolyte used was 1 M LiPF\(_6\), dissolved in 1/1 (V/V) EC/ EMC. Coin cells were assembled in a high-pure argon-filled glove box. Charge (Li insertion) and discharge (Li extraction) were conducted using an Arbin automatic battery cycler at several different current densities between cut-off potentials of 0.01 and 2.8 V. In order to investigate the effect of electrode reactions on the nanofiber structure, the morphology of Si/CNFs was also examined with analytical UHR FE-SEM (SU-70) at 5 kV after 50 charge/discharge cycles.
2. Results and discussion

2.1 Morphology and structure characterization

Figure 8.1 illustrates SEM images of electrospun Si/PAN composite nanofibers. When Si content is low (15 wt %), Si nanoparticles have a relatively homogeneous distribution along PAN nanofibers (Figure 8.1A-B). With the increase of Si content, some Si nanoparticles begin to agglomerate and form clusters (Figure 8.1C-F). Si/CNFs are produced by thermally treating electrospun Si/PAN composite nanofibers in air (stabilization at 280 °C) and subsequently in nitrogen (carbonization at 700 °C). Figure 8.2 displays SEM images of as-prepared Si/CNFs. Compared with the corresponding Si/PAN precursor nanofibers shown in Figure 8.1, Si/CNFs are less straight and more Si nanoparticles are exposure on fiber surface.

XRD measurements were conducted in order to examine the evolution of Si nanoparticle structure in CNFs. Figure 8.3 shows the evolution of the XRD patterns of Si/CNFs. It is seen that pure CNFs exhibit a diffraction peak at 2θ = 25.0°, which is corresponding to the (002) layers of the graphite. However, that peak is weak and broad, indicating the nanofibers are largely formed by disordered carbon. Si/CNFs present diffraction peaks at 2θ of about 28.4°, 47.4°, 56.2°, 69.2°, 76.5° and 88.1°, which are ascribed to the (111), (220), (311), (400), (331) and (422) planes of Si crystals in nanofibers, respectively. In addition, with the increasing of Si content in Si/PAN precursor, the intensities of diffraction peaks increase.
Figure 8.1 SEM images of Si/PAN composite nanofibers with different Si contents: (A, B) 15, (C, D) 30, and (E, F) 50 wt %.
Figure 8.2 SEM images of Si/CNFs prepared from Si/PAN precursors with different Si contents: (A, B) 15, (C, D) 30, and (E, F) 50 wt %.

The structure variation of Si/CNFs was also studied using Raman spectroscopy, which is able to provide information related to the bonding and order in carbon materials.\textsuperscript{49, 64} Figure 8.4 shows Raman spectra of both CNFs and Si/CNFs. It is seen that all nanofibers exhibit two
strong peaks. The peak centered near 1350 cm\(^{-1}\) (D band) can be explained as structure defect- and disorder-induced features in the graphene layers of carbon materials, while the peak centered near 1600 cm\(^{-1}\) (G band) is indicative of the high-frequency \(E_{2g}\) first-order graphitic crystallites of the carbon\(^{49, 64, 258}\). The presence of the strong D band suggests that the carbon component in these composite nanofibers has low crystallinity and graphitization and is typical of disordered graphitic material with two Raman bands\(^{49, 64, 258}\).

Figure 8.3 WAXD patterns of Si/CNFs prepared from Si/PAN precursors with different Si contents: (a) 0, (b) 15, (c) 30, and (d) 50 wt %. 

![WAXD patterns](image-url)
2.2 Electrochemical evaluation

In order to understand the electrochemical performance of Si/CNF anodes, galvanostatic charge-discharge tests were carried out between 0.01 and 2.8 V at a constant current density of 50 mA g$^{-1}$, and the results are shown in Figure 6.5. For comparison, pure Si anodes were prepared using the traditional method, i.e., mixing Si nanoparticles (80 wt %) with polyvinylidene fluoride binder (10 wt %) and carbon black conductor (10 wt %), and their typical charge and discharge curves are also shown in Figure 8.5. As shown in Fig. 8.5A, during the charge of Si anodes, a potential plateau appears at about 0.2 V vs. Li/Li$^+$, and the charge capacity is about 3300 mAh g$^{-1}$. However, the high Li packing density results in a large volume change on insertion, which causes anode cracking and pulverization. As a result, the discharge capacity is only 113 mAh g$^{-1}$.\textsuperscript{230, 231} In subsequent cyclings, no appreciable capacities can be detected. However, Si/CNF anodes show relatively large capacities that can be retained during cycling. For example, Si/CNF anodes made from 15 wt % Si/PAN...
precursor exhibit a specific charge capacity of about 1157 mAh g\(^{-1}\) and discharge capacity of 886 mAh g\(^{-1}\) at the first cycle, corresponding to a coulombic efficiency of 76.3 % (Figure 8.5B). A coulombic efficiency of less than 100 % at the first cycle is mainly ascribed to the electrolyte decomposition, which leads to the formation of the SEI.\(^49\) At the second cycle, the charge/discharge capacities are 871 and 861 mAh g\(^{-1}\), respectively, and the coulombic efficiency is about 99 %. These anodes still remain a relatively high charge capacity of 452 mAh g\(^{-1}\) at the 50\(^{th}\) cycle (about 51 % retention of the initial value), which is much greater than the theoretical value of commercial graphite (372 mAh g\(^{-1}\)).\(^49, 79, 100, 101\) These results indicate that the combinative effects of Si phase (high Li-storage capacity) and carbon matrices (long cycle life) can be utilized to improve electrochemical performance of LIB anodes.\(^270, 271, 281-286\)
Figure 8.5 Charge-discharge curves of Si anode (A), and Si/C nanofiber anodes (B, C, and D) at a constant current density of 50 mA g\(^{-1}\). Si/CNFs were prepared from Si/PAN precursors with different Si contents: (B) 15, (C) 30, and (D) 50 wt %.

From Figure 8.5C, it is seen that Si/CNF anodes made from 30 wt % Si/PAN precursor deliver a charge capacity of 1541 mAh g\(^{-1}\) and discharge capacity of 1281 mAh g\(^{-1}\) at the first cycle, corresponding to a coulombic efficiency of 83.1%. At the second cycle, the charge/discharge capacities are 1228 and 1225 mAh g\(^{-1}\), respectively. However, their
discharge capacity decreases to 318 mAh g⁻¹ at 50th cycle with capacity retention of 24.8%. Si/CNF anodes made from 50 wt % Si/PAN precursor have the largest initial charge and discharge capacities (1913 and 1613 mAh g⁻¹, respectively) in the first cycle, corresponding to a coulombic efficiency of 84.3%. At second cycle, they still keep a large discharge capacity of 1609 mAh g⁻¹ with a coulombic efficiency of 96.2%. But this value reduces rapidly to 134 mAh g⁻¹ at 50th cycle (Figure 8.5D), corresponding to low capacity retention of 8.3%. These results indicate that at very high Si contents (such as 50 wt %), the large volume change of Si nanoparticles still leads to Si pulverization and capacity fading during the continuous insertion/extraction of Li.

Figure 8.6 shows the cycling stabilities of Si/CNF anodes at different charge/discharge current densities: 50, 100, 150, and 200 mA g⁻¹. It is seen that Si/CNF anodes exhibit relatively good cycling stability when the Si content in Si/PAN precursor is 15 wt %. For example, these Si/CNF anodes have relatively high first-cycle capacities (886, 855, 733, and 690 mAh g⁻¹, respectively) at current densities of 50, 100, 150, and 200 mA g⁻¹. At 50th cycle, these values change to 452, 512, 405, and 467 mAh g⁻¹, and the capacity retentions are 51.1, 59.9, 55.3, and 67.7 %, respectively. Compared to pure Si anodes (Fig. 8.5A), this improvement in capacity retention is significant. However, the cycle stability deteriorates rapidly when the Si content in Si/PAN precursor increases to 30 and 50 wt %. For example, Si/CNF made from 50 wt % Si/PAN precursor show first-cycle capacities of 1613, 1459, 1434, and 1188 mAh g⁻¹, respectively, at current densities of 50, 100, 150, and 200 mA g⁻¹. At 50th cycle, these values decrease to 134, 103, 107, and 146 mAh g⁻¹, and the reversible capacity retentions are 8.3, 7.1, 7.5, and 12.3 %, respectively.
Figure 8.6 Cycling performance of Si/CNFs anodes at different current densities (A) 50, (B) 100, (C) 150, and (D) 200 mA g⁻¹. Si/CNFs were prepared from Si/PAN precursors with different Si contents: (a) 15, (b) 30, and (c) 50 wt %.

It should be noted that the cycling stabilities of these nanofibers are still not high enough for some applications. However, the cycling performance can be enhanced by optimizing the material structures, such as reducing Si particle diameter, improving particle distribution, and decreasing the fiber diameter, etc.
In addition to the improved cycling stability, Si/CNF anodes from 15 wt % Si/PAN precursor also have good rate capabilities. From Figure 8.6, it is seen that these Si/CNF anodes exhibit no large degradation of capacity with the increase of current density. These results further confirm that at relatively low Si content, the combination force between Si and carbon can hinder the aggregation and separation of Si nanoparticles during Li insertion/extraction processes. From Raman spectra, it is found that the carbon component in Si/CNFs is largely in the amorphous form. Compared with ordered lattice in graphite, the defective structures in amorphous carbon store more Li (e.g., the pure CNF-based anode exhibits a relatively small reversible capacity of about 450 mAh g\textsuperscript{-1} at the first cycle),\textsuperscript{49} which also benefits the improvement of the electrochemical performance of LIBs.\textsuperscript{79, 100, 103}

In order to understand the impact of charge/discharge cycling on the nanofiber structure, SEM images of Si/CNF anodes were taken after 50 cycles and shown in Fig. 8.7. It is seen that, after 50 cycles, Si/CNFs made from 15 wt % Si/PAN precursor still keep regular fibrous structure and relatively homogeneous morphology, indicating that the CNF matrix can trap Si nanoparticles firmly and circumvent Si nanoparticles from aggregating during cycling. In addition, the close contact between Si nanoparticles and carbon matrix ensures a good electronic conduction and short Li insertion distances. As a result, the special structure of composite nanofibers leads to the combination of the advantageous properties of carbon (long cycle life) and Si (high Li-storage capacity), which in turn improves the overall electrochemical performance of the resultant nanofiber anodes.\textsuperscript{80, 81, 83, 84, 86-89, 97, 106, 232, 260} However, from Figure 8.7, it is also seen that Si/CNFs made from PAN solutions containing 30 and 50 wt % Si precursors experience relatively large morphology changes after 50 cycles.
Si nanoparticles in these nanofibers aggregate, which reduces the buffering effect of CNF matrices and leads to the large capacity fading of the anodes shown in Figure 8.6.\textsuperscript{230, 231}

Figure 8.7 SEM images of Si/CNF anodes after 50 cycles charge/discharge at a constant current density of 50 mA g\textsuperscript{-1}. Si/CNFs were prepared from Si/PAN precursors with different Si contents: (A, B) 15, (C, D) 30, and (E, F) 50 wt %. 

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3. Summary

A new and inexpensive method has been introduced to fabricate Si/CNFs for energy storage by electrospinning and subsequently thermal treatments. It is found that if the Si content is not too high (e.g., 15 wt %), Si nanoparticles can have a good dispersion in CNFs. In this case, the huge volume change of Si nanoparticles during Li insertion/extraction can be alleviated by the CNF matrix. Hence, the combinative effects of both carbon (excellent electronic conductivity) and Si nanoparticle (super-high Li storage) provide these composite nanofiber anodes with good electrochemical performance in terms of large discharge capacity (much greater than the theoretical value of graphite), improved capacity retention, and good rate capability. However, at higher Si contents (30 and 50 wt %), Si nanoparticles are easy to agglomerate in CNFs, which causes large morphology change and pronounced capacity fading during charge/discharge cycles. However, it should be noticed that compared with pure Si anodes, Si/CNF anodes with high Si contents still have better electrochemical performance. It can be envisaged that the electrochemical performance of these Si/CNF anodes can be further improved by homogeneously dispersing smaller Si nanoparticles within CNFs.
Chapter 9 Fabrication of Li-Active Si Nanoparticle-Loaded Porous CNFs as Anodes for Rechargeable LIBs

Dispersing Si nanoparticles into CNFs with porous structures may also be an effective means to prevent severe pulverization of Si and finally achieve satisfactory electrochemical performance for LIBs. The 1D porous carbon matrix can hinder Si particle aggregation, provide continuous long-distance electron transport pathway, support numerous active sites for charge-transfer reactions, and eliminate the need for binding or conducting additive. In addition, these porous composite materials have large surface area combined with extra pore volume, which permits a high contact area between electrode and electrolyte, reduces the distance for Li-ion transport, and increases the rate of Li insertion/extraction. As a result, these materials can have improved reversible capacity, enhanced cycling performance, and elevated rate capability.

This Chapter presents a relatively novel, simple and environmentally benign strategy to prepare porous Si/carbon composite nanofibers (Si/CNFs) by a judicious combination of electrospinning and subsequent thermal treatment. After a careful analysis of the structural features, we directly utilized these Si/CNF composites as anodes for rechargeable LIBs without introducing additional polymer binder or conductive material. These novel materials can not only combine the merits of both Si and carbon, but also present many unique characteristics, such as long length for efficiently transporting charge carriers, large surface-to-volume ratio for increasing Li-storage capacity, large pore volume for providing...
extra room for volume expansion that accompanies Li-ion intercalation and discharge, and enhanced electrical and mechanical properties for improving the stability and safety of the batteries. As a result, we achieved dramatically improved electrochemical performance for LIB anodes in terms of high reversible Li-storage capacity (about 1600 mAh g\(^{-1}\)), relatively good cycling performance, and high rate capability. These excellent electrochemical properties combined with the low cost, high efficiency, and improved durability of these materials may have a significant impact in making Si-based anode materials commercially viable in the near future.

1. Experimental

1.1 Chemicals

PAN, PLLA and solvent DMF were purchased from Aldrich (USA). Si nanoparticles were purchased from Nanostructured & Amorphous Materials, Inc. Dispersion of 30 wt % Si nanoparticles in 8 wt % DMF solution of PAN/PLA blends (85/15) was prepared at 60 °C. Strongly mechanical stirring combined with ultrasonic treatment (FS20H Sonicator, Fisher Scientific) was applied for at least 72 hours in order to obtain a homogeneous dispersion. In comparison, dispersion of 30 wt % Si nanoparticles in 8 wt % DMF solution of pure PAN was also prepared.

1.2 Nanofiber preparations

Electrospinning was carried out with 0.75 ml h\(^{-1}\) flow rate, 15 cm needle-to-collector distance, and 21 kV voltage. Electrospun Si/PAN/PLLA nanofibers were firstly stabilized in air at 280 °C for 8 h (heating rate was 5 °C min\(^{-1}\)) and then carbonized at 700 °C for 1 h in
argon (heating rate was 2 °C min⁻¹) to obtain Si/CNFs [named Si/CNFs (85/15)]. For comparison, Si/CNFs [named Si/CNFs (100/0)] were also prepared from electrospun Si/PAN nanofibers.

1.3 Nanofiber characterizations

The morphology and diameter of Si/PAN and Si/PAN/PLLA composite nanofibers were evaluated using SEM (JEOL 6400F Field Emission SEM at 5 kV). Their corresponding carbonized nanofibers were also studied with analytical UHR FE-SEM (SU-70) at 5 kV. ATR-FTIR spectra were collected from a FTIR spectrometer (Nicolet 560) in the wavenumber range of 3800 - 700 cm⁻¹ at room temperature. Thermal properties of electrospun nanofibers were evaluated using DSC from 25 to 400 °C at a heating rate of 10 °C min⁻¹ in a nitrogen atmosphere (Perkin Elmer Diamond Series DSC with Intracooler). TGA was also used to determine the weight loss of composite nanofibers (after solvent evaporation) at 10 °C min⁻¹ heating rate from 25 to 800 °C in air environment (TA Instruments Hi-Res TGA 2950). The structural variations of Si/CNFs were identified by WAXD (Philips X’Pert PRO MRD HR X-Ray Diffraction System, Cu kα, λ = 1.5405 Å) and Raman spectra (Horiba Jobin Yvon LabRam Aramis Microscope, 633 nm HeNe Laser). Surface area analysis was carried out using the BET nitrogen adsorption method (Micromeritics Gemini 2360).

1.4 Electrochemical evaluations

Electrochemical performance evaluations were performed using 2032 coin-type cells. Si/CNF membranes attached onto copper foil (Lyon industries), Li ribbon (Aldrich), and
Separion S240 P25 (Degussa) were used as the working electrode, counter electrode, and separator, respectively. Electrolyte used was 1 M LiPF$_6$, dissolved in 1/1 (V/V) EC/EMC (Ferro Corp.). Charge (Li insertion) and discharge (Li extraction) were conducted using an Arbin automatic battery cycler at different current densities between cut-off potentials of 0.01 and 2.8 V. The surface morphology of Si/CNFs after electrochemical measurement was also examined with analytical UHR FE-SEM (SU-70) at 5 kV.

2. Results and discussion

2.1 Morphology and structure characterization

Figure 9.1 shows typical SEM images of electrospun Si/PAN (Figure 9.1A-C) and Si/PAN/PLLA (Figure 9.1D-F) composite nanofibers. In both types of nanofibers, agglomerates formed by Si nanoparticles can be seen from fiber surface. Bead-like irregularities or fibers with ‘beads on a string’ morphology also appear in nanofibers. Compared with Si/PAN composite nanofibers, Si/PAN/PLLA composite nanofibers have slightly smaller diameters because the presence of conductive PLLA phase increases conductivity of the electrospinning solution and leads to the thinner fiber diameter.287

ATR-FTIR spectra of pure PAN, Si/PAN and Si/PAN/PLLA nanofibers were illustrated in Figure 9.2. All three types of nanofibers exhibit peaks at 2930, 2240, and 1470 cm$^{-1}$ due to stretching vibration of methylene (–CH$_2$–), stretching vibration of nitrile groups (–CN–), and bending vibration of methylene, respectively, but the intensities of these peaks in Si/PAN/PLLA composite nanofibers are significantly lower than those in PAN and Si/PAN nanofibers. In addition, compared with pure PAN and Si/PAN nanofibers, Si/PAN/PLLA
composite nanofibers show a typical ester peak by lactide at 1750 cm\(^{-1}\) and a characteristic C-O-C stretch vibration at 1200 cm\(^{-1}\).\(^{265,266}\)

Thermal properties of electrospun nanofibers were performed using DSC and TGA. Figure 9.3 shows the DSC thermograms of PAN, Si/PAN, and Si/PAN/PLLA composite nanofibers. Pure PAN nanofibers exhibit a relatively large and sharp exothermic peak at about 287 °C,\(^{287}\) indicating that complicated and multiple chemical reactions, such as cyclization, crosslinking and dehydrogenation, etc. take place during thermal treatment processes.
Figure 9.1 SEM images of (A, B, C) Si/PAN, and (D, E, F) Si/PAN/PLLA composite nanofibers.
Figure 9.2 ATR-FTIR spectra of (a) pure PAN, (b) Si/PAN, and (c) Si/PAN/PLLA nanofibers.

Figure 9.3 DSC thermograms of (a) pure PAN, (b) Si/PAN, and (c) Si/PAN/PLLA nanofibers.
The exothermic peak of Si/PAN composite nanofibers shifts to a slightly higher temperature (293 °C). However, the exothermic peak of Si/PAN/PLLA nanofibers shifts to a much higher temperature (313 °C), and at the same time, the peak area intensity, i.e., total heat of reaction, of these nanofibers is lower than those of pure PAN and Si/PAN nanofibers. The increased peak temperature and the reduced reaction heat are caused by the interactions between PAN and PLLA, which inhibit the formation of free radicals on the nitrile groups and subsequently their re-combinations.287

TGA thermograms of PAN, Si/PAN and Si/PAN/PLLA nanofibers were performed in air environment. As shown in Figure 9.4, the major weight loss of all three types of nanofibers starts at around 310 °C. Pure PAN nanofibers show nearly 100 % weight loss after reaching 800 °C while both Si/PAN and Si/PAN/PLLA composite nanofibers give about 26 wt % residual, which is ascribed to the remaining Si from precursors.

PAN, Si/PAN and Si/PAN/PLLA nanofibers were thermally treated in argon, during which PAN transfers to carbon, but PLLA decompose completely without leaving any residual.287 Figure 9.5 exhibits SEM images of Si/CNFs (100/0) and Si/CNFs (85/15), which were prepared from Si/PAN and Si/PAN/PLLA precursor nanofibers, respectively. The micrographs indicate that both Si/CNFs (100/0) and Si/CNFs (85/15) have uneven, coggd and wrinkled surface morphology. Si nanoparticles also agglomerate and form clusters among exterior surfaces of the fibers.
Figure 9.4 TGA thermograms of (a) pure PAN, (b) Si/PAN, and (c) Si/PAN/PLLA nanofibers.

Figure 9.5 SEM images of (A, B) Si/CNFs (100/0) and (C, D) Si/CNFs (85/15).
In addition, compared with Si/CNFs (100/0), Si/CNFs (85/15) have smaller fiber diameters. In order to further investigate the surface area and pore structure of Si/CNFs, nitrogen adsorption studies were carried out. The BET method was employed, along with various other theories, to determine specific surface areas, and meso- and micropore volumes and widths (Table 9.1). The results indicate that both Si/CNFs (100/0) and Si/CNFs (85/15) have large surface areas and pore volumes.

Table 9.1 Surface parameters of Si/CNFs.

<table>
<thead>
<tr>
<th>PAN/PLLA [wt %]</th>
<th>SSA[a] [m² g⁻¹]</th>
<th>TPV[b] [cm³ g⁻¹]</th>
<th>V_meso [c] [cm³ g⁻¹]</th>
<th>V_micro [d] [cm³ g⁻¹]</th>
<th>W_meso [e] [nm]</th>
<th>W_micro [f] [nm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>100/0</td>
<td>175.80</td>
<td>0.24</td>
<td>0.09</td>
<td>0.15</td>
<td>9.2</td>
<td>0.15</td>
</tr>
<tr>
<td>85/15</td>
<td>188.43</td>
<td>0.23</td>
<td>0.08</td>
<td>0.15</td>
<td>8.2</td>
<td>0.15</td>
</tr>
</tbody>
</table>

[a] Specific surface area (SSA) was calculated by the BET method.
[b] TPV indicates total pore volume.
[c] V_meso is the mesopore (2 - 50 nm) volume calculated by the BJH method based on the Kelvin equation.
[d] V_micro is the micropore (< 2 nm) volume calculated by the HK method.
[e] W_meso: average mesopore width calculated using the BJH method.

WAXD patterns and Raman spectra were conducted to evaluate the structure variations of Si/CNFs. Figure 9.6 depicted WAXD patterns of the Si/CNFs along with pure PAN-based CNFs. Typically, pure CNFs only exhibit a diffraction peak at 2θ = 25.0°, which is corresponding to the (002) graphite layers.49, 64, 258 Both Si/CNFs (100/0) and Si/CNFs (85/15)
have apparent diffraction peaks at 28.4°, 47.3°, 56.1°, 69.3°, 76.5° and 88.1°, which are assigned to the (111), (220), (311), (400), (331) and (422) planes of Si, respectively. In addition, compared with Si/CNFs (100/0), a significant increase in the diffraction peak intensity is observed in Si/CNFs (85/15). This is because that Si/CNFs (85/15) are prepared from carbonizing 30 wt % Si/PAN/PLLA precursor and the completely degradation of PLLA during the thermal treatment provide Si/CNFs (85/15) with higher Si content than Si/CNFs (100/0) prepared from 30 wt % Si/PAN precursor.

Figure 9.6 WAXD patterns of (a) pure CNFs, (b) Si/CNFs (100/0), and (C) Si/CNFs (85/15).

The Raman spectra in Figure 9.7 show defect and disordered carbon induced D-band at about 1300 cm⁻¹ and E₂g₂ graphitic mode based G-band at around 1600 cm⁻¹. The presence of both D and G bands combined with the absence of (100) and (004) planes of graphite crystal in WAXD results indicate that the carbon in both CNFs and Si/CNFs is formed mainly by turbostratically disordered graphene sheets.
Figure 9.7 Raman spectra of (a) pure CNFs, (b) Si/CNFs (100/0), and (C) Si/CNFs (85/15).

2.2 Electrochemical performance

Galvanostatic charge-discharge experiments were carried out at a current density of 50 mA g\(^{-1}\) within a voltage window 0.01 - 2.8 V to evaluate the electrochemical performance of Si/CNF-based anodes. For comparison, pure Si-based anodes were also prepared. The voltage profiles are shown in Figure 9.8. It is seen that, at the first cycle, pure Si-based anodes have a large charge capacity of about 3300 mAh g\(^{-1}\), but the discharge capacity is only 130 mAh g\(^{-1}\) (Figure 9.8A). Both capacities fade to nearly zero in the sequential cycles. However, compared with pure Si, Si/CNF anodes have much larger reversible capacities, which are relatively stable during cycling. In addition, Si/CNFs (85/15) have larger Li storage capacities than Si/CNFs (100/0). For example, at the first cycle, the Si/CNFs (100/0) exhibit charge and discharge capacities of about 1541 and 1281 mAh g\(^{-1}\), respectively, corresponding to a coulombic efficiency of 83.1 % (Figure 9.8B). At the same time, Si/CNFs
(85/15) exhibit charge and discharge capacities of 1900 and 1550 mAh g\(^{-1}\), respectively, corresponding to a coulombic efficiency of 81.6% (Figure 9.8C). In addition, during the first charge process, the voltage of the Si/CNFs (100/0) rapidly drops to about 0.55-0.6V with a small plateau, followed by a sloping line smoothly downshifting to 0.01 V. In case of Si/CNFs (85/15), this small plateau appears at the range of 0.7-0.75 V. These classical plateaus are well-known as the result of the decomposition of electrolyte solution and the formation of SEI, which covers the anode surfaces and hinders the electrolyte from further decomposing.\(^{142, 232, 270-273, 284, 286}\)

From Figure 9.8, it is seen that these plateaus nearly disappeared after the first cycle, resulting in coulombic efficiencies of nearly 98% at the following cycles. In addition, the discharge capacity of Si/CNFs (100/0) at the second cycle is about 1225 mAh g\(^{-1}\) (Figure 9.8B), which indicates about a 95.6% retention of the capacity (1281 mAh g\(^{-1}\)) of the first cycle, whereas the discharge capacity of Si/CNFs (85/15) at the second cycle is about 1528 mAh g\(^{-1}\) (Figure 9.8C), corresponding to a 98.6% retention from the first cycle. This indicates that the capacity of Si/CNFs (100/0) fades faster than that of Si/CNFs (85/15). The enhanced cycling performance of Si/CNFs (85/15) compared to Si/CNFs (100/0) is further exhibited at sequential cycles. For examples, at twentieth and fortieth cycles, Si/CNFs (85/15) still have relatively high discharge capacities of about 1075 and 726 mAh g\(^{-1}\), respectively (Figure 9.8C), indicating about 69.4 and 46.8% capacity retentions from the first cycle. However, at twentieth and fortieth cycles, the discharge capacities of Si/CNFs (100/0) are about 720 and 400 mAh g\(^{-1}\), respectively (Figure 9.8B), indicating faster capacity fading (56.2 and 31.2% capacity retentions from the first cycle). Figure 9.9 further compares the
charge/discharge cycling performance of Si/CNFs (100/0) and Si/CNFs (85/15). The results demonstrate that Si/CNFs (85/15) always deliver larger capacities than Si/CNFs (100/0) upon cycling.

Figure 9.8 Charge-discharge curves of (A) pure Si anode, (B) Si/CNFs (100/0), and (C) Si/CNFs (85/15) at a constant current density of 50 mA g\(^{-1}\).

Figure 9.10 summarizes the capacities of Si/CNFs (100/0) and Si/CNFs (85/15) at current densities of 50, 100, 200, 300 and 500 mA g\(^{-1}\). It is seen that both types of Si/CNFs have small degradation in capacity when current density increases. However, the Si/CNFs (85/15) always have larger reversible capacities.
The improvement of electrochemical performance for Si/CNFs (85/15) can be ascribed to their unique structure with a variety of favorable properties.\textsuperscript{80, 81, 83, 84, 86-89, 97, 106, 232} Firstly, Si nanoparticles are dispersed in carbon matrix, which plays the role of a structural buffer for hampering the large volume changes during Li insertion and extraction processes, enabling good electrical contact among Si nanoparticles upon cycling, and as a result, the stress formed during the electrochemical cycling can be overcome and the integrity of the electrode can be maintained after cycles.\textsuperscript{97, 232, 273-275, 282} Therefore, Si/CNFs (85/15) combine both the advantages of Si, such as high theoretical specific capacity and low discharge potential, and carbon matrix, such as long cycle life. The cooperative effect between Si and carbon also makes Si/CNFs have good capacity retention, high rate capability, and safe operation over many charge/discharge cycles. In addition, compared with regular Si- or carbon-based electrodes, Si/CNFs have larger accessible surface area that provides additionally active sites for Li-ion diffusion and a reduced distance for the transport of both Li ions and electrons; and at the same time, the relatively large Si content in Si/CNFs (85/15) also plays an important role in increasing the capacity of the resultant anodes.

Many Si-based electrodes completely lose their structural integrity after cycling. In order to understand the impact of charge/discharge cycling on the electrode microstructures of Si/CNFs (100/0) and Si/CNFs (85/15), SEM images of these nanofibers were taken after 40 cycles and shown in Figure 9.11. In Si/CNFs (100/0) (Figure 9.11A-B), the fibrous structure is no longer obvious, indicating the buffering effect of carbon matrix is not strong enough to hinder the large volume change of Si in these nanofibers. However, the fibrous structure of Si/CNFs (85/15) is largely maintained although the agglomerates of Si nanoparticles become
severer after cycling (Figure 9.11C-D). As a result, compared with Si/CNFs (100/0), the carbon matrix in Si/CNFs (85/15) has better ability in buffering the volume changes and accommodating large strain of Si nanoparticles during Li insertion and extraction.

Figure 9.9 Cycling performance of Si/CNFs (100/0) and Si/CNFs (85/15) at a constant current density of 50 mA g\(^{-1}\).

Figure 9.10 Reversible capacity vs. current density (rate capability) of Si/CNFs (100/0) and Si/CNFs (85/15) at different current densities.

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Figure 9.11 SEM images of (A, B) Si/CNFs (100/0), and (C, D) Si/CNFs (85/15) after 40 charge/discharge cycles at a constant current density of 50 mA g$^{-1}$.

Figure 9.12 further shows the morphologies of Si/CNFs (85/15) after 40 cycles at a much higher current density of 500 mA g$^{-1}$. It is clearly shown that the fibrous structure is maintained after 40 cycles at this high current density. As a result, the special nanofiber structure of these Si/CNFs can combine the advantageous properties of carbon (long cycle life) and Si (high Li-storage capacity) to improve the overall electrochemical performance of LIB anodes.$^{80, 81, 83, 84, 86-89, 97, 106, 232}$ In addition, Si nanoparticles closely encapsulated within the carbon matrix have good electronic contacts and short Li$^+$ insertion distances.$^{80-84, 86-89, 97, 106, 232}$ All these factors lead to enhanced electrochemical performance of Si/CNFs (85/15).
3. Summary

Si/CNFs were fabricated by electrospinning and thermal treatment processes. These Si/CNFs exhibit large surface areas and pore volumes, and display high reversible capacity, improved cyclic retention, and acceptable rate capability when used as anode materials for LIBs. The good electrochemical performance of Si/CNFs is a result of the cooperative effects of Si filler and carbon matrix as well as the unique one-dimensional nano-fibrous structure with large surface area and high length/diameter ratio.
Pure CNF-based anodes are currently extensively studied due to their good cyclability and low, flat potential. However, these anodes have relatively low capacity and also suffer from large initial irreversible capacity and poor rate capability because of the formation of the SEI film and relatively slow electrochemical reactions. Li-inactive transition metal Ni nanoparticles confined to CNFs are an exciting, yet relatively unstudied, class of materials and may have the potential to improve the construction of LIB anodes and enhance both the coulomic efficiency and rate performance. The high electric conductivity of Li-inactive transition metal Ni nanoparticles leads to better endurance of high current densities upon charge/discharge cycling when used as inert filler in electrodes. Nanoscale Li-inactive transition metal Ni nanoparticles also show the potential to stabilize the SEI film during the charge process, leading to reduced irreversible capacities. In addition, Ni nanoparticles can also act as a catalyst to facilitate Li$_2$O decomposition and enhance the coulombic efficiency of the CNF anodes. As a result, the incorporation of Ni metal nanoparticles in CNFs can increase the electronic conductivity of the composite materials, reduce the initial irreversible capacity, improve the coulombic efficiency and cycling performance of anodes at high current densities. Hence, incorporating Li-inactive transition metal particles into LIB electrodes has great beneficial impact on the battery performance.
In this Chapter, low cost and non-toxic Li-inactive Ni nanoparticles confined to CNFs (Ni/CNFs) are prepared by carbonizing electrospun Ni(OAc)$_2$·4H$_2$O/PAN precursor at elevated temperatures. These Ni/CNFs exhibit promising electrochemical performance such as high reversible capacity, low irreversible capacity, slow fading after prolonged cycling, and excellent rate capacity upon increased currents when used as anodes for rechargeable LIBs without adding any binder or conducting additive (Figure 10.1).

![Figure 10.1 Schematic diagram of preparing Ni/CNFs as anodes for LIBs.](image)

1. Experimental

1.1 Chemicals

PAN, Ni(OAc)$_2$·4H$_2$O and solvent DMF were purchased from Aldrich (USA). A DMF solution of 10 wt % PAN with 30 wt % Ni(OAc)$_2$·4H$_2$O was prepared at 60 °C, with mechanical stirring for at least 72 hours.

1.2 Nanofiber preparations

The electrospinning of precursor nanofibers was carried with 0.5 ml h$^{-1}$ flow rate, 15 cm needle-to-collector distance, and 12.5 kV applied voltage. The electrospun Ni(OAc)$_2$·4H$_2$O/PAN composite nanofibers were first stabilized in an air environment at 280
°C for 6 h (heating rate was 5 °C min⁻¹) and then carbonized at 600 °C for 8 h in argon atmosphere (heating rate was 2 °C min⁻¹) to form Ni/CNFs. For comparison, pure CNFs were also prepared from electrospun PAN nanofibers.

1.3 Nanofiber characterizations

The morphology and diameter of Ni(OAc)₂·4H₂O/PAN precursor nanofibers, and their stabilized and carbonized nanofibers were evaluated using SEM (JEOL 6400F Field Emission SEM at 5 kV) and TEM (Hitachi HF-2000 TEM at 200 kV). The structural variations of these prepared nanofibers were also identified by WAXD (Philips X’Pert PRO MRD HR X-Ray Diffraction System) and Raman spectroscopy (Horiba Jobin Yvon LabRam Aramis Microscope, 633 nm HeNe Laser).

1.4 Electrochemical evaluations

Electrochemical performance was evaluated using 2032 button coin cells (Hohsen Corp.). Ni/CNFs were attached onto copper foils to be directly used as the working electrode. Li ribbon (0.38mm thick, Aldrich) was used as the counter electrode. Separion S240 P25 (Degussa AG, 25 µm) was used as the separator. The electrolyte used was 1 M LiPF₆, dissolved in 1/1 (V/V) EC/ EMC (Ferro Corp.). Coin cells were assembled in a high-purity argon-filled glove box. Charge (Li insertion) and discharge (Li extraction) were conducted using an Arbin automatic battery cycler at several different current densities between cut-off potentials of 0.01 and 2.80 V.
2. Results and discussion

2.1 Morphology and structure characterization

Shown in Figure 10.2 are SEM images of Ni(OAc)$_2$·4H$_2$O/PAN precursor nanofibers and their stabilized and carbonized products. Ni(OAc)$_2$·4H$_2$O/PAN precursor nanofibers exhibit smooth surface morphology, uniform diameter, and straight fiber structure (Figures 10.2A and B). After stabilization in air environment, the fibers still have even and regular surface morphology and homogeneous diameter distribution, although some fibers are not so taut (Figures 10.2C and D). SEM micrographs of carbonized nanofibers show spherical particles on CNFs (Figures 10.2E and F), indicating that Ni is formed during the high-temperature carbonization process. Metallic Ni is formed because Ni ions are reduced by carbon created during the thermal treatments. The average size of Ni particles is about 20 nm. The presence of Ni nanoparticles can also be further observed from the high-resolution TEM images (Figures 10.3E and F) and the corresponding EDS as shown in Figure 10.4. However, both PAN/Ni(OAc)$_2$·4H$_2$O precursor nanofibers (Figure 10.3A and B) and the corresponding stabilized products (Figure 10.3C and D) do not contain Ni nanoparticles.

The crystallinity and phase composition of the precursor, stabilized, and carbonized nanofibers are investigated using wide-angle X-ray diffraction (WAXD) (Figure 10.5A). WAXD profiles of the precursor and stabilized nanofibers do not show any obvious diffraction peak, but that of carbonized nanofibers exhibit diffraction peaks at 2θ of about 44.4°, 51.9°, and 76.4°, which are ascribed to the (111), (200), and (220) Ni crystal planes, indicating the formation of cubic crystalline Ni.$^{292-295}$ A diffraction peak at 2θ = 25.0°, which
is corresponding to the (002) layers of the graphite, is also found for carbonized nanofibers.49,
64, 287, 288

Figure 10.2 SEM images of (A, B) PAN/Ni(OAc)$_2$·4H$_2$O precursor, (C, D) stabilized, and (E, F) carbonized composite nanofibers.

Figure 10.2 SEM images of (A, B) PAN/Ni(OAc)$_2$·4H$_2$O precursor, (C, D) stabilized, and (E, F) carbonized composite nanofibers.
Figure 10.3 TEM images of (A, B) PAN/Ni(OAc)$_2$·4H$_2$O precursor, (C, D) stabilized, (E, F) carbonized composite nanofibers.
Figure 10.4 EDS spectrum of carbonized composite nanofibers.

Figure 10.5 (A) WAXD patterns of (a) Ni(OAc)$_2$·4H$_2$O/PAN precursor, (b) stabilized, and (c) carbonized composite nanofibers, and (B) Raman spectra of carbonized composite nanofibers.

In addition, the large intensity ratio (> 4) of D peak to G peak in Raman spectra (Figure 10.5B) indicates the presence of a large amount of disordered structures or defects in the carbon matrix of Ni/CNF composites. $^{49, 64, 287, 288}$
2.2 Electrochemical performance

Galvanostatic discharge-charge experiments were carried out to evaluate the electrochemical performance of Ni/CNFs (Figure 10.6). The charge (Li insertion)/discharge (Li extraction) curves of Ni/CNFs were obtained in 1 M LiPF_6 in EC/EMC (1/1 in volume) electrolyte solution at a constant current density of 50 mA g\(^{-1}\) with a potential window from 0.01 V to 2.8 V (Figure 10.6A). It is seen that, during the first charge process, the voltage decreases steeply to about 1.3 V and then decreases slowly until a total charge capacity of 1020 mAh g\(^{-1}\) is reached. The first discharge profile of Ni/CNFs reveals a slight polarization at around 0.75 V, followed by a smoothly increasing curve\(^{296}\). The first discharge capacity is about 795 mAh g\(^{-1}\). A relatively small irreversible capacity of 225 mAh g\(^{-1}\) is obtained at the first cycle and it can be ascribed to the formation of SEI film\(^{202,221,290,291,296}\). At the second charge/discharge cycle, these Ni/CNFs have a reversible capacity of about 725 mAh g\(^{-1}\), which indicates a relatively high capacity retention of 91.2 % from the first cycle. At the 20th and 50th cycles, the reversible capacities are about 565 and 540 mAh g\(^{-1}\) (71.1 and 67.9 % retention from the first cycle), respectively, indicating relatively larger reversible capacity and slower capacity fading compared with pure CNF anodes (Figure 10.7A).

Figure 10.6B shows the cycling performance of Ni/CNFs. For comparison, the theoretical capacity of graphite\(^{49,79,100,101}\) is also shown. For Ni/CNFs, a satisfactory cycling performance can be observed after the tenth cycle. This stable and reversible capacity is much larger than the theoretical capacity (372 mAh g\(^{-1}\)) of commercial graphite, other reported pure CNF-based anodes\(^{287,288}\) and also our results of electrospun CNF anodes in Figure 10.7B.
Figure 10.6 Charge-discharge capacities (A) and cycling performance (B) of Ni/CNF anodes at a constant current density of 50 mA g\(^{-1}\), (C) reversible capacity vs. current density (rate capability) of Ni/CNFs, (D) cycling performance of Ni/CNF anodes at different current densities.
Figure 10.7 Charge-discharge capacities (A) and cycling performance (B) of electrospun CNF anodes at a constant current density of 50 mA g\(^{-1}\), (C) reversible capacity vs. current density (rate capability) of CNFs.

The Li storage characteristics of Ni/CNF anodes at high current densities (i.e., rate capability) were also investigated. Figure 10.6C shows the relationship between reversible capacity (the second cycle) and current density. It is seen that Ni/CNF anodes show an improved rate capability as compared to commercial graphite\(^{79,100,101}\). For example, even at very high current densities of 500 and 1000 mA g\(^{-1}\), Ni/CNFs have reversible capacities of
about 378 and 353 mAh g\(^{-1}\), respectively, which are still comparable to the theoretical specific capacity of graphite,\cite{78, 79, 100, 101} and also much larger than pure CNF anodes (Figure 10.7C). In addition, at larger current densities (300, 500 and 1000 mA g\(^{-1}\)), these Ni/CNFs can still maintain relatively good cycle performance (Figure 10.6D).

It should be noticed that compared with the electrochemical performance of some Ni/Metal oxide (MO\(_x\)) nanocomposite anodes,\cite{233, 234, 290, 291} the performance of Ni/CNF anodes are somewhat lower since pure carbon matrix exhibits smaller Li-storage capacity than MO\(_x\). However, during the preparation of Ni/CNF anode materials, a relatively low cost and convenient electrospinning process was adopted, and this process avoids complicated oxidative and reductive treatments. In addition Ni/CNFs can be used directly as anodes without using any additional polymer binders and conductive additives. Thus, Ni/CNF materials are still promising candidates as the anodes for the next-generation LIBs.

Ni/CNFs show high reversible capacity, improved cyclability, and good rate capability because their unique nanocomposite structure and surface properties help combine two types of dissimilar materials into one incorporated entity for Li storage. In order to obtain high electrochemical performance, electrode materials should possess the properties of high Li storage, high electronic conductivity, and high surface area. In Ni/CNFs, the high surface area not only provides large numbers of active sites for Li to insert into nanofibers, but also leads to enhanced Li storage kinetics, such as shorter transport distances for both electrons and Li ions, and higher charge/discharge rates. The CNF matrix can preserve the integrity of the electrode upon charge/discharge processes, leading to long cycle life. The incorporated Ni nanoparticles can create defects and disordered structures in carbon matrix, which further
increase the Li-storage ability of the anodes. In addition, the high electronic conductivity of Ni nanoparticles can lead to stable electronic pathways and reduce the polarization to improve the both the cycling stability and rate performance. As a result, good electrochemical performance, including large reversible capacity, reduced irreversible capacity, elevated cycle performance, and improved rate capacity, is obtained.

3. Summary

Ni nanoparticles were dispersed among CNFs by direct electrospinning and carbonization processes, and the resultant Ni/CNFs are promising anode materials for high-performance LIBs. The incorporation of Li-inactive metal into CNFs raises many possibilities in achieving further performance enhancements. Future work will seek to further elucidate the origins of the performance enhancements from the incorporation of Ni, as well as investigate the effects of other Li-inactive metals.
In addition to Ni nanoparticle, other Li-inactive metals, such as Cu, have also great impact on the electrochemical performance of rechargeable LIBs because they can create a conducting pathway in electrodes to enhance the electrical contact.\textsuperscript{297, 298, 299}

In this Chapter, Li-inactive Cu nanoparticle-loaded CNFs (Cu/CNFs) were fabricated by electrospinning Cu(OAc)\textsubscript{2}/PAN nanofibers, followed by thermal stabilization in air environment and carbonization in argon atmosphere. These Cu/CNFs exhibit enhanced surface-to-volume ratio, numerous active sites, facile electronic/ionic transfer, and reduced transport pathway for both electrons and Li ions. In addition, Li-inactive metallic Cu can help increase the electrode conductivity, enhance the coulombic efficiency, and improve the cycling performance of the final electrodes.\textsuperscript{202, 300-302} As a result, Li-inactive Cu nanoparticle-loaded CNFs are demonstrated to be promising LIB anode materials with large reversible capacities and good cycle performance.

1. Experimental

1.1 Chemicals

PAN (Mw = 150,000), Cu(OAc)\textsubscript{2} salt (98 \%) and solvent DMF were purchased from Aldrich. All these reagents were used without further purification. DMF solution of 8 wt \% PAN containing 50 wt \% Cu(OAc)\textsubscript{2} was prepared at room temperature. Mechanical stirring was applied for at least 72 hours in order to obtain a homogeneous solution.
1.2 Nanofiber preparations

A variable high voltage power supply (Gamma ES40P-20W/DAM) was used to provide a high voltage (around 10.5 kV) for electrospinning with 0.5 ml h⁻¹ flow rate and 15 cm needle-to-collector distance. The electrospun Cu(OAc)₂/PAN nanofibers were firstly stabilized in an air environment at 280 °C for 5.5 h (heating rate was 5 °C min⁻¹) and then carbonized at 600 °C for 8 h in argon atmosphere (heating rate was 2 °C min⁻¹).

1.3 Nanofiber characterizations

The morphology and diameter of Cu(OAc)₂/PAN precursor nanofibers and their stabilized and carbonized products were evaluated using FESEM (JEOL 6400F FESEM at 5 kV) and TEM (Hitachi HF-2000 TEM at 200 kV). The structural variations of these nanofibers were identified by WAXD (Philips X’Pert PRO MRD HR X-Ray Diffraction System, Cu ka, λ = 1.5405 Å). Finally, the stabilized and carbonized nanofibers were examined using Raman spectra (Horiba Jobin Yvon LabRam Aramis Microscope, 633 nm HeNe Laser).

1.4 Electrochemical evaluations

EIS was performed using a Gamry reference 600 Potentiostat/Galvanostat/ZRA over the frequency range of 100 kHz - 10 mHz in a 10.0 mV AC voltage signal in automatic sweep mode from high to low frequency. Electrochemical performance was also evaluated using 2032 coin-type cells (Hohsen Corp.). Cu/CNFs attached onto copper foils were directly used as the working electrode. Li ribbon (0.38mm thick, Aldrich) was used as the counter electrode. Separion S240 P25 (Degussa AG, 25 μm) was used as the separator. The
electrolyte used was 1 M LiPF$_6$, dissolved in 1/1 (V/V) EC/EMC (Ferro Corp.). Coin cells were assembled in a high-purity argon-filled glove box. Charge (Li insertion) and discharge (Li extraction) were conducted using an Arbin automatic battery cycler at different current densities between cut-off potentials of 0.01 and 2.8 V. Finally, the surface morphologies of Cu/CNF anodes after 50 charge/discharge cycles at 50 and 100 mA g$^{-1}$ current densities were also examined with JEOL 6400F FESEM at 5 kV.

2. Results and discussion

2.1 Morphology and structure characterization

Figure 11.1 shows the FESEM images of Cu(OAc)$_2$/PAN precursor nanofibers and their stabilized and carbonized composites. As shown in Figure 11.1 A-B, Cu(OAc)$_2$/PAN precursor nanofibers have relatively smooth, regular, and long fibrous morphologies and also a relatively homogeneous diameter distribution.$^{73}$ Compared to Cu(OAc)$_2$/PAN precursor, the surface of stabilized nanofibers (Figure 11.1 C-D) is slightly undulated and rougher. Figure 11.1E-F exhibits SEM images of the carbonized nanofibers. The micrographs indicate that the straight fibrous morphology and netlike structure are maintained after carbonization. However, the carbonized nanofibers have reduced average diameter, which may be ascribed to the complex chemical reactions (such as dehydration, dehydrogenation, and cyclization, etc.) during the process of carbonization.$^{64, 66, 287}$

TEM studies of Cu(OAc)$_2$/PAN precursor nanofibers and their stabilized and carbonized products were also conducted and representative images are shown in Figure 11.2. The TEM images are consistent with the above-mentioned SEM results, i.e., all fibers exhibit straight surface morphology. The diameter of nanofibers increases after stabilization, but decreases
after carbonization. In addition, the corresponding energy dispersive X-ray spectrum (EDS) as shown in Figure 11.3 indicates the existence of Cu element in carbonized nanofibers.

Figure 11.1 SEM images of (A, B) Cu(OAc)$_2$/PAN precursor, (C, D) stabilized, and (E, F) carbonized composite nanofibers.
Figure 11.2 TEM images of (A, B) Cu(OAc)$_2$/PAN precursor, (C, D) stabilized, and (E, F) carbonized composite nanofibers.
The crystallinity and phase composition of Cu(OAc)$_2$/PAN precursor nanofibers and their stabilized and carbonized products are investigated using WAXD, and the results are shown in Figure 11.4. The WAXD pattern of carbonized nanofibers shows the classical peak of carbon at near $2\theta = 25^\circ$, corresponding to the (002) graphite layers; however, this peak is weak, indicating a low crystallinity of the carbon matrix. In addition, Bragg’s diffractions at $2\theta$ of 43.6$^\circ$, 50.5$^\circ$ and 74.5$^\circ$, representing (111), (200) and (220) planes of fcc crystal structures of metallic Cu, are also present in carbonized nanofibers, indicating that the Cu salt has been reduced to metallic Cu. From Figure 11.4, it is also seen that Cu(OAc)$_2$/PAN precursor and thermally stabilized fibers show no clear diffraction peaks at these positions. Therefore, the reduction of Cu occurs during the carbonization step.

Figure 11.3 EDS spectrum of carbonized composite nanofibers.

The Raman spectra (Figure 11.5) of Cu/CNFs display broad absorption bands at around 1600 cm$^{-1}$ (G-line) and 1350 cm$^{-1}$ (D-line), which are assigned to the E$_{2g}$ mode involving two
adjacent C atoms in a graphene sheet and the disorder/defect-induced carbon structures, respectively.\textsuperscript{287, 288} The large intensity ratio (> 3.5) of D peak to G peak indicates the formation of a large amount of disordered carbon structures in the carbon matrix of Cu/CNFs.

The prepared Cu/CNFs were directly placed on a Cu foil to be used as the anode in rechargeable LIBs without introducing additional polymer binder or conductive additive. In

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{waxd.png}
\caption{WAXD patterns of (a) Cu(OAc)$_2$/PAN precursor, (b) stabilized, and (c) carbonized composite nanofibers.}
\end{figure}

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{raman.png}
\caption{Raman spectra of Cu/CNFs made from Cu(OAc)$_2$/PAN precursor.}
\end{figure}
order to identify the adhesion between Cu/CNFs and the Cu foil and the Li-ion phase-transfer kinetics at electrode-electrolyte interface, EIS measurement was carried out and a typical impedance spectrum is shown in Figure 11.6. It is seen that Cu/CNFs present a depressed semicircle and a linear portion, which can be assigned to electrode-electrolyte interfacial impedance and Li diffusion, respectively.\textsuperscript{287,288} No apparent resistance can be found for the interface between Cu-CNFs and Cu foil, indicating a good electronic contact between Cu-CNFs and Cu foil.

![Figure 11.6 EIS of Cu/CNFs made from Cu(OAc)$_2$/PAN precursor.](image)

2.2 Electrochemical performance

The charge-discharge curves and cycling performance under a constant current density of 50 mA g\textsuperscript{-1} with a potential window from 0.01 V to 2.8 V are shown in Figure 11.7. At the first cycle, the Cu/CNFs have a large Li storage capacity of about 870 mAh g\textsuperscript{-1} and the corresponding discharge capacity is nearly 617 mAh g\textsuperscript{-1}. The initial irreversible capacity loss
of approximately 253 mAh g⁻¹ could mainly originate from the formation of the SEI film, on the surface of the Cu/CNFs. At the second cycle, the discharge capacity reduces to about 537 mAh g⁻¹, indicating an 87.3 % retention of the initial value. At 20th and 50th cycles, the capacities keep around at 425 mAh g⁻¹ (Figure 11.7A), which is still much larger than the 372 mAh g⁻¹ theoretical value for graphite. Figure 11.7B shows the cycle performance of Cu/CNFs at 50 mA g⁻¹ current density. It is seen that Cu/CNFs keep relatively constant capacities after 10 cycles.

Cells contacting Cu/CNFs as the anode were also cycled between 0.01 V to 2.8 V at a higher current density: 100 mA g⁻¹. The charge/discharge profiles and the cycle performance curve are displayed in Figure 11.8. During the first charge process, there is a flat plateau at about 0.9 V, which may be linked with the irreversible reaction due to the formation of the SEI film, and then the voltage smoothly downshifts to 0.01V. The total Li⁺ storage capacity is about 870 mAh g⁻¹. A discharge capacity of about 563 mAh g⁻¹ is found at the first cycle (Figure 11.8A). From Figure 11.8B, it is seen that the charge/discharge capacities at the second cycle are 539 and 508 mAh g⁻¹, respectively, giving a coulombic efficiency up to 94.2 %. At 50th cycle, the discharge capacity stays about 410 mAh g⁻¹, indicating a capacity fading of 2.0 % per cycle at 100 mA g⁻¹. This discharge capacity is much larger than the corresponding value of commercial graphite at this current density.
Figure 11.7 Charge-discharge capacities (A) and cycling performance (B) of Cu/CNFs at a constant current density of 50 mA g$^{-1}$. 

Figure 11.8 Charge-discharge capacities (A) and cycling performance (B) of Cu/CNFs at a constant current density of 100 mA g$^{-1}$. 

The improved capacities and enhanced cycle performance of Cu/CNFs may be attributed to their unique architecture and composition. Metallic Cu may suppress the electrolyte reduction and cointercalation of solvated Li ions. As a result, the presence of Cu phase can help maintain stable charge transfer resistance, thus keeping stable electrochemical kinetics during repeated charge/discharge processes.$^{202,208}$ At the same time, because of the existence
of metallic Cu, the carbon matrix in Cu/CNFs becomes mainly amorphous, as shown in Raman spectrum. Carbon with amorphous structure can have relatively large Li-storage ability, which can also finally increase the reversible capacity of the LIBs. In addition, the fibrous nanostructure provides sufficient open space between neighboring nanofibers and allows an easy diffusion of liquid electrolyte into the inner sites of the electrode, where the active material can participate in the electrochemical reactions. As a result, Cu/CNFs have improved electrochemical performance, such as high capacity and improved cycle stability.

Figure 11.9A summarizes the second-cycle discharge capacities of Cu/CNFs at different current densities (rate capacity). When the current density increases to 200 mA g⁻¹, Cu/CNFs can main a relatively high discharge capacity of about 383 mAh g⁻¹, which is still comparable to the theoretical value of graphite. At larger current density (300 mA g⁻¹), the reversible capacity decreases greatly (295 mAh g⁻¹). However, further cycling tests indicate that Cu/CNFs can still maintain good cycle performance at these high current densities (Figure 11.9B).
After Li intercalation, Cu/CNFs were examined using SEM. Figure 11.10 shows SEM images of Li-intercalated nanofibers after 50 charge/discharge cycles at 50 mA g$^{-1}$. It is seen that nanofibers still maintain long fiber structure with comparable diameters. However, the nanofiber morphology becomes slightly convoluted and wrinkled. In addition, some nanoparticles with the size of 10 nm are observed on the surface of nanofibers, which may be due to the volume expansion associated with the charge/discharge process.$^{97, 168}$ However, from Figure 11.9, it can be concluded that the nanofiber structure of Cu/CNFs can help relieve the stresses associated with the volume changes during cycling and this contributes to the improvement of both reversible capacity and cycling performance.
The morphology and structure of cycled Cu/CNFs at 100 mA g\(^{-1}\) are also studied with SEM. Figure 11.11 reveals the images after 50 electrochemical cycles. It is seen that the fibrous morphology still remain after 50 cycles.
3. Summary

A new strategy has been developed for the facile fabrication of Cu/CNF composites for direct use as LIB anodes by the simple and effective electrospinning approach and subsequent thermal treatments. The prepared Cu/CNFs show promising electrochemical properties in terms of relatively high reversible capacity and good cycle performance. In addition, Cu/CNFs still can maintain morphological stability and structural integrity after 50 electrochemical charge/discharge cycles. By adjusting a number of fabrication conditions, such as the content or type of Cu salts, and the carbonization temperature, etc., the electrochemical properties of these nanofibers may be further improved. In addition, this fabrication route can be extended to nanofibers of other types of metal or metal alloy as well, and the generated nanofibers can also be potentially used in other energy storage and conversion devices.
Chapter 12 Summary and Conclusions

The development of sustainable, clean, and renewable energy technologies is recognized to be an economically as well as environmentally sound alternative to address the worldwide critical energy issue that is heading the list of top urgent global problems facing our society. Among various energy storage and conversion systems, high-performance rechargeable lithium-ion batteries (LIBs), which have high energy density, long cycle life, and flexible design, appear as one of the most promising energy storage devices.

In recent years, particular attention has been given to the design and synthesis of high-capacity alternative nanostructured electrode materials since innovative and nano-scale materials have proven to be critical to next-generation LIBs. Novel nanomaterials can provide a viable route to improve the electrochemical performance of rechargeable LIBs to power our modern lifestyles. Nanostructured carbon materials with varieties of forms, such as carbon nanotubes (CNTs), carbon nanocomposites (CNCs), and carbon nanofibers (CNFs), have been employed to construct anodes for LIBs through a large number of synthetic and fabrication methods. Among them, the judicious combination of electrospinning and carbonization is potentially an efficient, simple, and inexpensive way to fabricate CNF anodes for LIBs.

Electrospinning is an industry-viable technology which provides straightforward and relatively cheap fabrication strategies for the unification of organic and inorganic materials to produce one-dimensional (1D) polymer matrix-based composite fibers at the nano- and meso-scale levels. The resultant composite nanofibers combine complementary strengths from two
different chemical realms, and are promising material candidates for numerous practical applications (including LIBs) because of their large specific surface area, long fiber length, nano-scale fiber diameter, and unique functionalities. In addition to polymer matrix-based composite nanofibers, carbon matrix-based composite nanofibers (i.e., composite CNFs) can be fabricated by the carbonization of electrospun polymer composite nanofibers containing inorganic precursors. Due to their high surface area, large pore volume, and good chemical resistance, these composite CNFs also have many potential applications including anodes for rechargeable LIBs, catalyst supports, electrodes for supercapacitors, and others.

Our first research topic focused on fabricating porous CNFs via electrospinning and carbonization processes and exploring their potential applications as anode materials for high-performance LIBs. In order to increase the reversible capacity of the anodes and provide the electrodes with the ability to have good capacity retention, high rate capability, and safe operation over many charge-discharge cycles, we also prepared Li-active particle-loaded composite CNF anodes and evaluated their electrochemical performance. In addition, Li-inactive metal nanoparticle-loaded composite CNFs were prepared and their electrochemical performance was evaluated. The research in this dissertation can be divided into the following three parts:

(I) Fabrication of porous CNFs and their applications as anode materials for rechargeable LIBs.

Three approaches were used to fabricate porous CNFs. The first approach utilized SiO₂ nanoparticles as the pore generator to create porous structure in CNFs. The second approach utilized ZnCl₂ salt as the pore generator, which can create small pores in PAN-based CNFs
during the carbonization step. The third approach utilized poly(L-lactide) (PLLA) as pore generator, which is degradable during the carbonization of electrospun polyacrylonitrile (PAN)/PLLA bicomponent nanofibers. All three approaches have different pore generation mechanisms. Compared with other carbon materials, porous CNFs have notable properties such as extremely high length-to-diameter ratio, nano-scale diameter, and ultrahigh specific surface area. As a result, porous CNFs present the opportunity to be used as energy-storage materials for rechargeable LIBs with high-capacity, fast-charging capability, and long-cycle life.

In our experiments, porous CNFs are typically in the form of electron-conducting nonwoven webs, providing good mechanical stability. Hence, they can be directly used as anodes for LIBs without adding non-active materials (e.g., polymer binder and conducting carbon black). The elimination of non-active materials leads to high energy and power densities, long cycle life, and improved safety of LIBs. In addition, the fully-interconnected three-dimensional porous structure in CNFs facilitates the easy access of Li ions to the inner sites of anodes and improves electron transfer rate. As a result, LIBs using porous CNFs as anodes offer advantages such as improved energy and power densities, fast charging capability, long cycle life, and low cost.

(II) Fabrication of Li-active nanoparticle-loaded CNFs and their applications as anodes for rechargeable LIBs.

Si and MnO\textsubscript{x} nanoparticles can store a large amount of Li by forming alloys through Li insertion reactions and hence are suitable for use as high-capacity anode materials in LIBs; however, they suffer from particle aggregation and low mechanical stability, which cause
deterioration in capacity retention due to the large volume change and structural destruction during Li insertion/extraction reactions. Consequently, severe fracturing and the loss of electrical integrity lead to the destruction of the electrode conduction, which in turn causes poor cycle performance. In our experiments, these Li-active nanoparticles (Si and MnOx) were dispersed into active CNFs via electrospinning and carbonization processes. The resultant composite CNFs combine the advantages of both Li-active nanoparticles, which storage a large amount of Li, and CNFs, which have highly developed internal surface area and porosity that facilitate the easy access of Li ions to the entire inner sites of anodes, dramatically decrease Li-ion diffuse distance, and induce high rates of electron transfer. Most important of all, these composite CNFs can facilitate strain relaxation, prevent nanoparticle aggregation, and provide extra space needed for the huge volume changes of the Li-active nanoparticles involved upon Li insertion. As a result, these composite CNFs have enhanced Li-storage capacities, improved rate capability, and good capacity retention abilities. Accordingly, Li-active nanoparticle-loaded CNFs are excellent candidates as anodes in rechargeable LIBs.

(III) Fabrication of Li-inactive nanoparticle-loaded CNFs and their application as anodes for rechargeable LIBs.

Transitional metal Ni and Cu nanoparticles are less active or inactive with Li. However, an appropriate amount of these metals in electrodes can create a conducting matrix that maintains electrical contact of the electrodes and leads to better endurance of high current densities during charge/discharge cycling. These nanoscale transition metal particles also show the potential to stabilize the SEI film during the charge process, leading to reduced
irreversible capacities. As a result, the incorporation of Ni and Cu metal nanoparticles in CNFs can increase the electronic conductivity of the composite materials, reduce the initial irreversible capacity, and improve both the coulombic efficiency and cycling performance of anodes at high current densities. Hence, incorporating Li-inactive nanoparticles into LIB electrodes has great beneficial impact on the battery performance.

In this research, two kinds of Li-inactive nanoparticle-loaded CNFs (i.e., Ni/CNFs and Cu/CNFs) were fabricated by electrospinning their precursor salts and PAN nanofibers, followed by thermal treatments in argon atmosphere. These Li-inactive nanoparticle-loaded CNFs exhibit enhanced surface-to-volume ratio, numerous active sites, facile electronic/ionic transfer, and reduced transport pathway for both the mobile electrons and Li ions. As a result, promising electrochemical performance, such as high reversible capacity, low irreversible capacity, slow fading after prolonged cycling, and excellent rate capacity upon increased currents, was obtained when these Li-inactive metal nanoparticle-loaded CNFs were used as anodes for rechargeable LIBs.
Chapter 13 Recommendation Work

The recommended future work can include but not limited to:

(1) Carry out cycle voltammogram (CV) measurements to identify the microstructure changes and the reactions on the electrode surfaces.

   CV is one of the most versatile electroanalytical techniques for the research of electroactive species. The electrochemical properties of the electrospun composite CNFs as anodes in rechargeable LIBs can be investigated by CV. From the information of the peaks in CV curves in anodic and cathodic processing, we can induce the reduction and oxidation processes and the irreversible reactions of the electrodes with the electrolyte. Through a detailed exploration of these phenomena, we can finally delete or decrease undesired by-reactions among the electrodes and the electrolyte, and improve the overall electrochemical performance of materials.

(2) Prepare Sn or SnO$_2$-loaded CNF anodes and evaluate their electrochemical performance in LIBs.

   Just as mentioned in Chapter 1. Introduction, Sn or SnO$_2$ are charming anode materials for high-performance rechargeable LIBs because they can deliver theoretical capacities of about 994 and 783 mAh/g, respectively, which are much higher to that of graphite. However, the practical use of pure Sn or SnO$_2$-based anodes is always hindered by the severe volume expansion and shrinkage among Li-ion uptake/release processes, leading to poor cycleability. If Sn or SnO$_2$ can be embedded into CNFs, the CNF matrix can play the role of buffer to elevate or absorb the large volume changes of anodes.
among charge/discharge processes, and preserve the integrities of the electrodes, thereby improving the overall electrochemical performance, especially the cycle life.

(3) Fabricate hollow Si/CNF materials to further the electrochemical performance of the Si/C composite anodes.

As showing in our experiments (Chapters 8 and 9), through the judicious combination of electrospinning and carbonization, we obtain Si-loaded solid CNFs and Si-loaded porous CNFs. Compared with pure Si-based anodes, these Si/CNFs have greatly improved electrochemical performance. In addition, the SEM characterizations also indicate that these Si/C nanocomposites can keep clear nano-fibrous morphology and also structure integrities even after tens of cycles. However, the capacity fading is still serious, especially at high current rates. Si-based composites with a hollow structure can preserve the electrical pathways and keep the integrities of the electrodes during cycling, because the hollow structure offers a “buffer zone” to compensate the volume fluctuation of the reactants.

(4) Insert CNTs into CNF matrices to prepare CNT/CNF anodes for rechargeable LIBs.

CNT-based anodes for rechargeable LIBs have been explored by several groups. Nevertheless, their weak stabilities and loose macroscopic structure, which leads to low energy density, make them difficult to have practical applications. As a result, spatially compact structures are necessary to provide improved Li-storage capacities. To fabricate CNT-loaded CNFs may be a promising way to prepare structural
compact nanocarbon materials, which may have improved electrochemical performance.
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