ABSTRACT

LU, YAO. Centrifugal Spinning and Its Energy Storage Applications. (Under the direction of Professor Xiangwu Zhang.)

Lithium-ion batteries (LIBs) and supercapacitors are important electrochemical energy storage systems. LIBs have high specific energy density, long cycle life, good thermal stability, low self-discharge, and no memory effect. However, the low abundance of Li in the Earth’s crust and the rising cost of LIBs urge the attempts to develop alternative energy storage systems. Recently, sodium-ion batteries (SIBs) have become an attractive alternative to LIBs due to the high abundance and low cost of Na. Although the specific capacity and energy density of SIBs are not as high as LIBs, SIBs can still be promising power sources for certain applications such as large-scale, stationary grids. Supercapacitors are another important class of energy storage devices. Electric double-layer capacitors (EDLCs) are one important type of supercapacitors and they exhibit high power density, long cycle life, excellent rate capability and environmental friendliness. The potential applications of supercapacitors include memory protection in electronic circuitry, consumer portable electronic devices, and electrical hybrid vehicles.

The electrochemical performance of SIBs and EDLCs is largely dependent on the electrode materials. Therefore, development of superior electrodes is the key to achieve high-performance alternative energy storage systems. Recently, one-dimensional nano-/micro-fiber based electrodes have become promising candidates in energy storage because they possess a variety of desirable properties including large specific surface area, well-guided ionic/electronic transport, and good electrode-electrolyte contact, which contribute to enhanced electrochemical performance. Currently, most nano-/micro-fiber based electrodes are prepared via electrospinning method. However, the low production rate of this approach
hinders its practical application in the production of fibrous electrodes. Thus, it is significantly important to employ a rapid, low-cost and scalable nano-/micro-fiber production method to substitute electrospinning in industrial production.

Recently, centrifugal spinning has gained researchers’ attention. The centrifugal spinning method avoids the use of high voltage supply and can work with concentrated solutions, and most importantly, it can increase the production rate of nano-/micro-fibers to at least two orders or magnitude higher than that of electrospinning. This novel fiber fabrication approach is mostly used in tissue engineering field, and it can be potentially applied in preparing electrodes for SIBs and EDLCs. In the present work, we firstly study the influence of solution intrinsic properties and operational parameters using polyacrylonitrile as an example, and establish the processing-structure relationships for this spinning technique. We then use this novel spinning method to prepare porous carbon nanofibers (PCNFs), SnO$_2$ microfibers and lithium-substituted sodium layered transition metal oxide fibers and use them as electrodes for EDLCs and SIBs. The as-prepared PCNFs, SnO$_2$ microfibers and lithium-substituted sodium layered transition metal oxide fibers exhibit good electrochemical performance. It is therefore demonstrated that centrifugal spinning can be a promising nano-/micro-fiber preparation approach for mass production of electrode materials used in energy storage applications.
Centrifugal Spinning and Its Energy Storage Applications

by
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DEDICATION

To my wife Yujie Sun, my father Yuqiang Lu and my mother Xuping Jia, for their love and support all the time.
BIOGRAPHY

Yao Lu was born in Yangquan City, Shanxi Province, China on June 6, 1988. He is the son of Yuqiang Lu and Xuping Jia. In 2007, he attended Donghua University for his undergraduate education and received his Bachelor degree in Textile Engineering in 2011. At Donghua University, Yao Lu met his wife, Yujie Sun.

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In addition to research, Yao Lu enjoys watching movies, playing basketball and video games and collecting action figures. 
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CHAPTER 1. Introduction

1.1 Overview of Electrochemical Energy Storage and Conversion Systems

Electrochemical energy storage and conversion systems include fuel cells, batteries and electrochemical capacitors. In fuel cells and batteries, electrical energy is produced via the conversion of chemical energy by the redox reactions at the anode and cathode.\(^1\) The major difference between fuel cells and batteries is related with their energy storage and conversion locations. Fuel cells are open systems, where the anode and cathode are just the charge-transfer media and the active masses that undergo redox reaction are delivered from outside, either from a tank, for instance, fuels such as hydrogen and hydrocarbons, or from the environment such as oxygen in air. Therefore, the energy conversion and storage take place in separate compartments. In contrast, batteries are closed systems, where the anode and cathode are both the charge-transfer media and the “active masses” that take part in the redox reactions. In another word, energy conversion and storage occur in the same location for batteries.\(^1\) On the other hand, in electrochemical capacitors (or supercapacitors), energy is not delivered by redox reactions. Instead, by orientation of electrolyte ions at the interface between electrode and electrolyte, so-called electric double-layers (EDLs) are formed and released, which causes a parallel electron movement in the external wire and results in the energy delivery.\(^1\) Figure 1.1 illustrates a simplified Ragone plot of the energy storage domains for the various electrochemical energy storage and conversion systems compared to an internal combustion engine and turbines and conventional capacitors. Among various energy storage and
conversion systems, fuel cells are considered to be high-energy systems, while supercapacitors are regarded as high-power systems. Batteries have intermediate power and energy characteristics compared to fuel cells and supercapacitors. Figure 1.1 indicates that batteries have some overlaps in specific energy and power with fuel cells and supercapacitors. Figure 1.1 also demonstrates that no single electrochemical power source can match the power and energy characteristics of internal combustion engine. In order to achieve high power and high energy simultaneously compared to the combustion engines and turbines, it is necessary to combine available electrochemical power systems. In the following sections, a detailed review on energy storage systems including lithium-ion batteries (LIBs), sodium-ion batteries (SIBs), and supercapacitors is given.

Figure 1.1 Simplified Ragone plot of the energy storage domains for the various electrochemical energy conversion systems compared to an internal combustion engine and turbines and conventional capacitors.¹
1.2 Lithium-Ion Batteries

1.2.1 Introduction

Among various types of energy storage devices, rechargeable lithium-ion batteries (LIBs) have received extensive attention in recent years due to their high energy densities and power densities. Figure 1.2 compares the volumetric and gravimetric energy densities of several representative rechargeable batteries. It is seen from Figure 1.2 that LIBs can provide much higher volumetric and gravimetric energy densities compared with Nickel-metal hydride, nickel-cadmium and lead-acid batteries. In addition, LIBs also possess high operating voltage, long cycle life, low self-discharge, wide temperature window, and no memory effect. These superior properties make LIBs promising candidates for various applications including personal electronic devices such as cameras, laptops, cellphones, future electric vehicles (EVs)/hybrid electric vehicles (HEVs) and emerging smart grids.

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1.2.2 A Brief History

LIBs were firstly proposed by M. Stanley Whittingham in 1970s. In early stage, lithium metal was employed as the negative electrodes directly in LIBs. Lithium metal was selected as the negative electrode mainly because lithium is the most electropositive and the lightest element with a density of 0.534 g cm$^{-3}$. Thus, this metal makes it possible for fabrication of energy storage devices with light weight and high energy. However, using lithium directly as anode material in LIBs was found to have serious safety issue because the lithium dendrites can cause short circuit and potential explosion hazards. To solve the safety issue and improve the cycle life for LIBs, metallic lithium was substituted by lithium insertion compounds.
1991, Sony Corporation firstly commercialized LIBs. Nowadays, LIBs have become the leader in rechargeable batteries and keep increasing in market share largely due to the demand growth in portable electronic devices. In addition, LIBs have also become a candidate to power EVs. EVs can be categorized in three types based on the depth of pure electrical propulsion: light EV, plug-in hybrid EV (PHEV) and full EV. Figure 1.5 demonstrates the requirements of the three major types of EVs. It is seen from the Ragone plot that Ni-MH batteries are insufficient for full EV applications. In contrast, high-energy LIBs that have prolonged cycle life are considered to be reasonable power source for EV applications.

<table>
<thead>
<tr>
<th>Modes of operation</th>
<th>battery capacity needed, kWh</th>
<th>Energy density, Wh/kg</th>
<th>Weight of battery, Kg</th>
<th>Speed, kilometres per hour</th>
<th>Distance on one charge, kilometres</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hybrid</td>
<td>&lt;3</td>
<td>40-50 (Ni-MH)</td>
<td>60 (Ni-MH)</td>
<td>100+</td>
<td>15</td>
</tr>
<tr>
<td>Plug in Hybrid</td>
<td>5.6-18</td>
<td>90-100 (Li-ion)</td>
<td>60-200 (Li-ion)</td>
<td>100+</td>
<td>10-60</td>
</tr>
<tr>
<td>Full EV</td>
<td>35-54</td>
<td>90-100 (Li-ion)</td>
<td>450 (Li-ion)</td>
<td>&gt;100</td>
<td>150-200</td>
</tr>
</tbody>
</table>

Figure 1.3 Characterization of three types of EVs: light EC, PHEV, and full EV, in terms of performance and batteries properties. (b) Ragone plot.
1.2.3 Structure and Working Principle

Based on different configurations, LIBs can be categorized as coin, cylindrical, prismatic and flat LIBs. However, LIBs are generally composed of anode (negative electrode), cathode (positive electrode), electrolyte and separator that is used to partition the anode and cathode. Figure 1.4 depicts the schematic of the structure and operating principle for a typical LIB. A typical LIB is composed of graphite anode and LiCoO$_2$ cathode. During repeated charge and discharge process, lithium ions flow between the anode and cathode through the electrolyte. Specifically, lithium ions deintercalate from the cathode and intercalate with the anode during charge process, while during discharge, lithium ions deintercalate from the anode and intercalate with the cathode. The chemical reactions involved in a typical LIB are described as follows:\textsuperscript{9}

Negative: \[ C + x\text{Li}^+ + xe^- \xrightleftharpoons[\text{discharge}]{\text{charge}} Li_x C \]

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

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

Figure 1.5 shows a schematic diagram illustrating the relative working potential of typical anodes and cathodes for LIBs. In general, the working potentials for cathode materials are higher than 3.0 V vs Li/Li$^+$ and the working potentials for anodes are lower than 2.0 V vs Li/Li$^+$.\textsuperscript{9}
Figure 1.4 Schematic operating principle of a typical rechargeable LIBs.\textsuperscript{2}

Figure 1.5 Schematic diagram showing the relative working potential of typical electrode materials for lithium-ion batteries.\textsuperscript{10}
1.2.4 Anodes

The performance of rechargeable LIBs is dependent on active materials employed for lithium storage in the electrodes. Requirements for LIB electrode materials include high reversible capacity, fast lithium ion diffusion, good structural stability, improved safety, long cycle life, etc.\(^2\) In LIBs, anodes have the relatively low redox potential vs Li/Li\(^+\). Typical materials for LIB anodes include carbonaceous materials, lithium alloys, spinel Li\(_4\)Ti\(_5\)O\(_{12}\), transition metal oxides, etc. Carbonaceous materials are nontoxic, inexpensive and abundant. Carbonaceous materials can be generally divided into graphitic and disordered carbon, and both of them have been investigated as LIB anode materials. Currently, the most commercialized anode material for LIBs is graphite, which has a theoretical capacity of 372 mAh g\(^{-1}\) when one Li is intercalated with 6 C.\(^{11}\) Graphite has a small volumetric expansion during lithium intercalation (just over 10%), which is favorable for high reversibility and stable cycling performance.\(^{12}\) On the other hand, disordered carbon materials can demonstrate higher capacities. For example, hard carbon exhibits a high capacity of 200 to 600 mAh g\(^{-1}\) in a voltage window of 0 to 1.5 V vs Li/Li\(^+\). Soft carbon materials also show a high reversible capacity of around 300 mAh g\(^{-1}\).\(^{13,14}\)

In order to improve the specific capacity of LIB anodes, other materials have been evaluated. Alloys are an important anode candidate mainly due to their high theoretical capacities. Representative alloys used as LIB anodes include Si, Sn and Ge, which are Group IV elements in the periodic table.\(^{12,15-20}\) Among these alloys, Si has been considered to be one of the most promising anodes for LIBs because of its highest volumetric and gravimetric capacities. It has been reported Li\(_{12}\)Si\(_7\), Li\(_{14}\)Si\(_6\), Li\(_{13}\)Si\(_4\) and Li\(_{22}\)Si\(_5\) alloys can form during the
Li-Si alloying process.\textsuperscript{21} Si has the highest theoretical capacity of 4200 mAh g\textsuperscript{-1} corresponding to a fully lithiated state of Li\textsubscript{22}Si\textsubscript{5}.\textsuperscript{16} Figure 1.6 shows the first two cycles of charge-discharge curves for Si powder. Si has received extensive attention also due to its high abundancy, ranking the second most abundant element in earth’s crust. Although Si possesses high abundancy and theoretical capacity, the practical use of this material as LIB anodes is hindered by its severe structural instability caused by the large volume changes during repeated charge-discharge cycling. It has been reported that the volume change of Si during cycling can be as high as over 300\%, which leads to particle pulverization and rapid capacity fading.\textsuperscript{22} To alleviate the volume expansion and enhance the electrochemical performance of the Si-based anode materials, tremendous efforts have been made including using Si-based thin films, Si nanowires, dispersing Si into active/inactive matrix, and using different binders.\textsuperscript{23–33} In addition to nanostructure design, introducing carbon phase is another important strategy.\textsuperscript{17,34–38} The introduced carbon phase can buffer the volume change of Si, prevent the nanoparticle aggregation, and provide good electrical contact upon cycling. Therefore, the integrity of the anode material can be maintained, resulting in improved cycling stability. For instance, Fu and coworkers prepared carbon nanotube (CNT)-Si and CNT-Si-C sheets by applying chemical vapor deposition (CVD) of Si and C onto the aligned CNT sheets and obtained high capacity of over 1500 mAh g\textsuperscript{-1} in a voltage range of 0.01 to 1 V. The CNT-Si-C sheets also showed stable cycling performance at a current density of 100 mA g\textsuperscript{-1} and excellent rate capability at current densities from 50 to 800 mA g\textsuperscript{-1}. The electrochemical performance of the CNT-Si and CNT-Si-C are given in Figure 1.7.
Figure 1.6 Voltage profiles of Si powder electrodes for the first and second discharge/charge cycles. \(^{21}\)

Figure 1.7 Electrochemical characteristics of CNT–Si and CNT–Si–C sheets. Performance of CNT–Si. Galvanostatic charge-discharge profiles (a), differential capacity curves (b), and cycle performance at 50 mA/g in the potential range of 0.01–1.0 V (c). Performance of CNT–Si–C. Cycle performance at 100 mA/g (d) and rate capability cycled at different current densities (e) in the potential window of 0.01–1.0 V. \(^{34}\)
Spinel Li₄Ti₅O₁₂ (LTO) has attracted great attention in recent LIB anode research owing to its excellent lithium ion insertion and extraction reversibility. Unlike conventional carbon anodes, Li₄Ti₅O₁₂ can store up to three lithium ions in the spinel structure with negligible volume change.³⁹,⁴⁰ The lithium intercalation process can be described as follows:

\[
\text{Li}_4\text{Ti}_5\text{O}_{12} + 3\text{Li}^+ + 3\text{e}^- \rightarrow \text{Li}_7\text{Ti}_5\text{O}_{12}
\]

The advantages of LTO includes excellent cycling performance, stable voltage plateau and low cost of precursors.⁴⁰ The spinel LTO structure provides a very flat voltage plateau at around 1.55 V vs Li/Li⁺. During the lithium insertion and extraction processes, a SEI film is usually formed at a potential below 0.8 V vs Li/Li⁺, which results in the consumption of active lithium ions and the reduction of specific capacity. However, the working potential of LTO is significantly higher than the reduction potential for most organic electrolytes. Therefore, the formation of SEI films in LTO anodes can be avoided.⁴⁰ The major drawbacks of LTO are its low theoretical capacity and poor electronic conductivity. Efforts to overcome the poor electronic conductivity are mainly focused on designing nanostructured LTO materials with improved kinetics, coating LTO with carbon materials to enhance the conductivity, and doping LTO with other metal ions.³⁹,⁴¹–⁵² For example, Jung and coworkers prepared spherical, high tap density, carbon-coated LTO powders via a spray-drying method with subsequent pitch coating.⁴⁰ The carbon layer was found to be uniformly coated on the LTO particles without forming any crystalline changes. The introduced carbon coating improved the electrical conductivity of LTO significantly and made the surface carbon modified LTO an efficient, high-rate LIB anode. The LTO electrode with 3.25% carbon coating exhibited ultra-high rate capability and even at 100C (17.5 A g⁻¹), the electrode can maintain a capacity of about 90
mAh g\(^{-1}\). The comparison of structure and electrochemical performance of LTO particles with and without carbon coating is given in Figure 1.8, and the rate capabilities of the carbon-free and carbon-coated LTO electrodes are shown in Figure 1.9.

Figure 1.8 SEM images of (a) carbon-free and (b) carbon-coated LTO powders. (c) High-resolution TEM image of the carbon-coated LTO. (d) Initial charge and discharge curves of carbon-free and of two different carbon-coated LTO electrodes at a rate of 0.1 C.\(^{40}\)
Figure 1.9 Rate capability of carbon-free and carbon-coated (1.14 and 3.25 wt.%) Li₄Ti₅O₁₂ electrodes at rates ranging from 1 C (175 mA g⁻¹) to 100 C (17.5 A g⁻¹). The charging rate was 1 C.⁵³

Various metal oxides can be used as anodes for LIBs, and these metal oxides can be classified into three groups depending on their reaction mechanisms. The first group is based on Li alloy reaction mechanism and a representative example is SnO₂.⁵⁴ The second mechanism is insertion/extraction reaction, which involves the insertion and extraction of Li into and from the transition metal oxide lattice. A typical example is TiO₂.⁵⁵ The last group of metal oxides react with Li based on conversion reaction that involves the formation and decomposition of Li₂O, accompanied by the reduction and oxidation of metal nanoparticles.
Metal oxides with this reaction mechanism include Fe$_2$O$_3$, Fe$_3$O$_4$, Co$_3$O$_4$, MnO$_x$, etc. The metal oxide anodes can often demonstrate high reversible capacities between 500 and 1000 mAh g$^{-1}$, however, some of the oxides suffer from large volume change and others exhibit low electrical conductivity. Thus, designing nanostructured electrodes and introducing carbon phase are two major approaches to enhance the electrochemical performance of metal oxide-based LIB anodes.

### 1.2.5 Cathodes

Compared with anode materials, cathode materials for LIBs usually show lower specific capacities. To match the anodes and meet the requirements for next-generation LIBs, cathode materials with superior electrochemical performance need to be developed. Candidate materials for LIB cathodes can be classified into three major groups according to their structures, namely layered, spinel and olivine compounds.

Layered compounds for LIB cathodes (LiMO$_2$) are composed of one or multiple ions from Co, Ni, Mn or other transition metals. The ideal structure of layered compound LiMO$_2$ is depicted in Figure 1.10. The oxygen anions (omitted for clarity) form a close-packed lattice with cations located in the 6-coordinated octahedral crystal site. The MO$_2$ slabs and Li layers are alternatively stacked. LiCoO$_2$ has been commercialized as a LIB cathode material for 20 years, and currently, more than 70% of LIBs in mobile phones and notebook PCs are using LiCoO$_2$ as the cathode due to its high operating potential (3.75 V versus graphite) and high electrode density (3.3-3.6 g/cm$^3$). However, this material can only deliver a capacity of about 140 mAh g$^{-1}$, corresponding to half of its theoretical capacity. Such limited capacity can be
ascribed to the intrinsic structural instability when more than half of the Li ions are extracted from the material.\textsuperscript{61} In addition, Co is toxic and expensive, which causes environmental issues and raises the cost of LIBs. Hence, extensive research have been carried out to replace Co by other transition metal ions such as Mn and Ni to improve the electrochemical performance. For example, LiNi\textsubscript{1/3}Co\textsubscript{1/3}Mn\textsubscript{1/3}O\textsubscript{2}, the solid solution of LiNiO\textsubscript{2}, LiCoO\textsubscript{2}, and LiMnO\textsubscript{2}, has been extensively investigated recently.\textsuperscript{62–66} The typical capacity values for LiNi\textsubscript{1/3}Co\textsubscript{1/3}Mn\textsubscript{1/3}O\textsubscript{2} in these studies are in the range of 140 to 180 mAh g\textsuperscript{-1}.

Figure 1.10 Crystal structure of layered LiMO\textsubscript{2} (blue: transition metal ions; red: Li ions).\textsuperscript{61}

To further increase the capacity of layered compound cathodes, Thackeray and others developed a strategy to prepare a species of high-capacity LIB cathodes with a structure of Li\textsubscript{2}MnO\textsubscript{3}-LiMO\textsubscript{2}, where M = Mn, Ni and Co.\textsuperscript{67–74} In this solid solution system, Li\textsubscript{2}MnO\textsubscript{3} acts as a structural component, which in the sense of a true intercalation electrode is inactive electrochemically to lithium insertion and extraction. By dispersing Li\textsubscript{2}MnO\textsubscript{3} into the cathodes, the electrochemically active LiMO\textsubscript{2} component matrix can be stabilized, resulting in superior electrochemical performance.\textsuperscript{74} These Li-rich cathodes can achieve high specific capacities
over 250 mAh g\(^{-1}\). For instance, Thackeray prepared a specific composition of 0.3Li\(_2\)MnO\(_3\)·0.7LiMn\(_{0.5}\)Ni\(_{0.5}\)O\(_2\), and this cathode material showed an initial discharge capacity of 290 mAh g\(^{-1}\). Figure 1.11a illustrates the first two cycles of charge-discharge curves of this cathode material.

Figure 1.11 Initial two charge/discharge voltage profiles and corresponding dQ/dV plots (inset) of (a) a Li/0.3Li\(_2\)MnO\(_3\)·0.7LiMn\(_{0.5}\)Ni\(_{0.5}\)O\(_2\) cell; (b) a Li/Li\(_{1.1}(\text{Mn}_{0.5}\text{Ni}_{0.5})_{0.9}\)O\(_2\) cell; and (c) a Li/Li\(_{1.048}(\text{Mn}_{0.333}\text{Ni}_{0.333}\text{Co}_{0.333})_{0.952}\)O\(_2\) cell.

As another important species of LIB cathodes, LiM\(_2\)O\(_4\) has a spinel structure, in which the oxygen framework is the same as that of LiMO\(_2\) layered structure. Metal cations still occupy the octahedral site but a quarter of them are located in the Li layer, resulting in 1/4 vacancy in the sites of transition metal layer. Li ions are located in the tetrahedral sites in Li layer that share faces with the empty octahedral sites of the transition metal layer. The vacancies in the transition metal layer allow the three-dimensional diffusion pathways for Li ions. The most representative material, LiMn\(_2\)O\(_4\), was proposed by Thackeray et al. in 1983, however, this material was found to have serious capacity fading that limits its practical applications. The capacity fading is mainly because the disproportional reaction of Mn\(^{3+}\) forms
Mn$^{2+}$ and Mn$^{4+}$, and Mn$^{2+}$ can be dissolved into the electrolyte, while new phases can be generated during repeated cycling.\textsuperscript{61} A typical solution for better cycling performance of LiMn$_2$O$_4$ is to dope the material with metal ions including Ni, Co, Fe, Al, Mg, etc.\textsuperscript{76–79} Among these substituted materials, LiNi$_{0.5}$Mn$_{1.5}$O$_4$ exhibits the best overall electrochemical performance.\textsuperscript{80–82} Liu and coauthors prepared spherical LiNi$_{0.5}$Mn$_{1.5}$O$_4$ with core-shell structure and obtained stable cycling performance with excellent rate capability.\textsuperscript{81} The electrochemical performance of the core-shell LiNi$_{0.5}$Mn$_{1.5}$O$_4$ spheres is displayed in Figure 1.12.

![Figure 1.12](image)

Figure 1.12 (a) Initial discharge curve of LiNi$_{0.5}$Mn$_{1.5}$O$_4$ at a rate of 0.1 C and room temperature; (b) cyclic voltammetry profile between 3.0 and 5.0 V at a scanning rate of 0.2 mV s$^{-1}$; (c) cycling performances at 25°C and 55°C by applying constant current of 1 C; (d) discharge capacities of LiNi$_{0.5}$Mn$_{1.5}$O$_4$ at various C rates.\textsuperscript{81}
LiMPO₄ compounds (M = Fe, Ni, Co, Mn) with olivine structure are another important group of LIB cathodes. Among all these materials, LiFePO₄ receives most attention because of its excellent electrochemical properties, non-toxicity, good thermal stability, and low cost. LiFePO₄, firstly discovered by Goodenough and coworkers in 1997⁸³, has a very flat discharge plateau at 3.4V vs Li/Li⁺. This material has a theoretical capacity of 170 mAh g⁻¹. The major disadvantages of LiFePO₄ are the low energy density limited by its operating voltage and the poor rate capability limited by its poor intrinsic electronic conductivity.⁶¹ The low voltage problem can be overcome by introducing other transition metal redox such as Ni, Co and Mn.⁸⁴,⁸⁵ The approaches employed to enhance the electronic productivity include applying conductive coating and heterogeneous doping.⁸⁶ For instance, Chen and coauthors synthesized LiFePO₄ via solid-state method and coated LiFePO₄ using guluronic acid as the carbon precursor.⁸⁷ Figure 1.13 compares the discharge curves of the as-prepared LiFePO₄ and LiFePO₄/C cathodes. By introducing carbon coating, the rate capability of LiFePO₄ was significantly improved.
Figure 1.13 The typical charge and discharge curves of (a) LiFePO$_4$ (pure) and (b) LiFePO$_4$/C cells.$^{87}$
1.3 Sodium-Ion Batteries

1.3.1 Introduction

Over the decades, LIBs have gained successful commercialization as the power source for mobile electronic devices and EVs. However, the feasibility of lithium must be considered with ever growing energy demand. Although lithium is widely distributed in the Earth’s crust, it is not regarded as an abundant element. As shown in Figure 1.14, the mean mass fraction of lithium in the Earth’s crust is only 20 ppm. Thus, there has been recent concern that the resource availability of lithium might not be sufficient to satisfy the increasing demand on LIBs. In addition, lithium recourses are geographically constrained in isolated areas, which requires large capital and long time to process the raw materials, leading to higher expenses and more costly LIB products. Therefore, there exists an immediate demand to develop alternative energy storage devices to replace LIBs.

Figure 1.14 Elemental abundance in the Earth’s crust.
Sodium is located below lithium in the periodic table. As the second lightest and smallest alkali metal next to lithium, sodium shares similar chemical properties with lithium in many aspects. The comparison between sodium and lithium in terms of their potential, cation radii, price, atomic weight and capacity is given in Table 1.1. It is seen that sodium (E = -2.7 V vs S.H.E.) has a higher reducing potential than lithium (E = -3.04 V vs S.H.E.). The cost per kW h of energy that sodium can provide is much lower than that of lithium, which could offer tremendous advantage when a huge amount of alkali metal is needed for scale-up applications. Besides, sodium ranks as the 6th most abundant element in the Earth’s crust and is also abundant in sea water and salt deposits. The wide availability and cost-effectiveness of sodium make sodium-ion batteries (SIBs) a potential alternative chemistry to LIBs and might become competitive to LIBs in certain markets. The structure components and operating principle of SIBs are essentially the same to those of LIBs except that Li ions are replaced with Na ions. As shown in Figure 1.15, a typical SIB consists of two sodium insertion materials as the positive and negative electrodes, respectively, with Na ion containing electrolyte composed of sodium salts and organic solvent. During charge and discharge processes, Na ions shuttle between the cathode and anode. It must be pointed out that the electrochemical performance of SIBs falls behind their LIB counterpart. This is mainly due to two intrinsic shortcomings related with sodium. Firstly, sodium has a lower ionization potential than lithium, which leads to lower operating voltages and therefore lower energy densities compared with LIBs. Secondly, the larger atomic weight and size of Na ions compared with Li ions results in slower diffusion within solid electrodes and often larger volume change during the charge and discharge processes. In spite of the potentially lower gravimetric energy density than
LIBs, SIBs would still be a promising option for use in electrical energy storage (EES) for renewable sources. SIBs would be especially useful in large-scale applications such as grid energy storage.

Table 1.1 Comparison between sodium and lithium.\textsuperscript{89}

<table>
<thead>
<tr>
<th></th>
<th>Sodium</th>
<th>Lithium</th>
</tr>
</thead>
<tbody>
<tr>
<td>Potential (V vs. S.H.E.)</td>
<td>-2.70</td>
<td>-3.04</td>
</tr>
<tr>
<td>Cation radii (Å)</td>
<td>0.97</td>
<td>0.68</td>
</tr>
<tr>
<td>Price (US$ per ton)</td>
<td>250–300</td>
<td>5800</td>
</tr>
<tr>
<td>Atomic weight (g)</td>
<td>23</td>
<td>6.9</td>
</tr>
<tr>
<td>Capacity (mA h g$^{-1}$)</td>
<td>1160</td>
<td>3860</td>
</tr>
</tbody>
</table>

Figure 1.15 Schematic illustration of Na-ion batteries.\textsuperscript{93}
1.3.2 Anodes

Graphite is the most commonly used anode material in LIBs. Li can be readily intercalated with graphite to form LiC$_6$, resulting in a theoretical of 372 mAh g$^{-1}$. Unfortunately, it was found that sodium can only intercalate with graphite to a negligible extent. Hence, the anode studies for SIBs have been focused on alternative materials including several other types of carbonaceous materials, alloys, metal oxides, phosphorous-based materials, etc.

Several types of carbonaceous materials have been investigated as anodes for SIBs, including petroleum coke$^{98}$, carbon black$^{99}$, hard carbon$^{100,101}$, templated carbon$^{102}$, carbon fibers$^{103,104}$, and nanostructured carbon materials.$^{105-115}$ Tirado and coauthors heat treated petroleum coke below 1000 °C and obtained a reversible capacity of about 100 mAh g$^{-1}$. Tirado’s group later showed the reversible capacity of 121 mAh g$^{-1}$ of sodium insertion in carbon black.$^{99}$ Several studies have been focused on hard carbon materials due to their large interlayer distance and disordered structure, which are favorable for sodium insertion and extraction. For example, Dahn’s group reported high gravimetric capacity of 300 mAh g$^{-1}$ for sodium insertion in hard carbon materials prepared from pyrolyzed glucose.$^{100}$ This capacity value is close to that obtained for the same type of carbon used in LIBs. By examining the voltage curves, Dahn and coworkers proposed a “house of cards” model for the sodium insertion into the hard carbon material. In this model, the insertion of sodium ions on hard carbon took place between the graphene layers of the particles and also into the pores generated during the synthesis process. Similarly, Komaba’s group prepared hard carbon by carbonization of sucrose at 1300 °C and investigated the electrochemical performance of the as-prepared hard carbon in SIBs.$^{92}$ As shown in Figure 1.17, an irreversible reduction plateau
can be observed at 0.8 V, which was assigned to the decomposition of electrolyte associated with the formation of a passivation layer on the hard carbon surface. The hard carbon material exhibited a long plateau at 0.1 V vs Na/Na$^+$, and showed a reversible capacity of 300 mAh g$^{-1}$. It is seen from the inset of Figure 1.17 that the hard carbon electrodes demonstrated good capacity retention for 50 charge-discharge cycles.

![Figure 1.16 “House of cards” model for sodium filled hard carbon.](image)

Figure 1.16 “House of cards” model for sodium filled hard carbon.\textsuperscript{100}

![Figure 1.17 Charge/discharge curves of hard carbon electrodes, derived from sucrose carbonized at 1300 °C, at a rate of 25 mA g$^{-1}$ in 1 mol dm$^{-3}$ NaClO$_4$ dissolved in PC:FEC (98:2 in vol %), and its capacity retention is also shown in the inset.](image)

Figure 1.17 Charge/discharge curves of hard carbon electrodes, derived from sucrose carbonized at 1300 °C, at a rate of 25 mA g$^{-1}$ in 1 mol dm$^{-3}$ NaClO$_4$ dissolved in PC:FEC (98:2 in vol %), and its capacity retention is also shown in the inset.\textsuperscript{93}
More recently, engineering carbon based materials using nanostructures has drawn great attention. For example, Cao and coworkers reported a high capacity SIB anode based on hollow carbon nanowires (HCNWs) synthesized via direct pyrolyzation of a self-assembled, hollow polyaniline nanowire precursor. This novel nanostructured carbon anode displayed a high reversible capacity of 251 mAh g\(^{-1}\) at a current density of 50 mA g\(^{-1}\) with excellent cycling stability over 400 cycles. The as-prepared HCNWs also demonstrated good rate capability. As shown in Figure 1.18, even at a high current density of 500 mA g\(^{-1}\) (2C), the anode still showed a high reversible capacity of 149 mAh g\(^{-1}\). The superior sodium storage properties were attributed to the short diffusion pathway in the HCNWs and the large interlayer distance between the graphitic sheets. Attempts in designing nanostructured carbon materials for SIB anodes have also been focused on preparing nitrogen-doped carbon nanofibers (CNFs). Introduction of a hetero atom into a carbon-based anode material has been proven to be effective in improving the electrochemical performance of LIB anodes. This method is also employed in SIB anodes. Typically, polypyrrole is firstly synthesized as the precursor. The polypyrrole precursor is then pyrolyzed in inert atmosphere to produce nitrogen-doped interconnected CNFs. Nitrogen doping produces extrinsic defects on the CNFs, which can enhance reactivity and electronic conductivity of the CNFs, resulting in high capacity and stable cycling behavior.
Figure 1.18 The rate performance of the hollow carbon nanowires (HCNWs) and the schematic illustration of sodium insertion/extraction.$^{105}$

The cycling performance of carbonaceous anodes is usually stable, however, their capacities are not high. Alloys are widely used as anodes in LIBs, and similarly, this group of materials can also be utilized in SIBs due to their high theoretical capacities. Among the possible candidates, tin (Sn), antimony (Sb) and their intermetallic compounds are the most studied alloys.$^{116-129}$ The theoretical capacities of Sn and Sb are 847 and 660 mAh g$^{-1}$, respectively, corresponding to Na$_{15}$Sn$_4$ and Na$_3$Sb.$^{89,100}$ The major drawback of alloy based anodes is severe particle pulverization due to the volume change during repeated charge and discharge processes. The large ionic radii of sodium ions makes the volume expansion effect
detrimental in causing irreversible structural changes to the anode materials. Continued charge-
discharge cycles compromise the anode structures and lead to rapid capacity fading. Hence,
the main solutions adopted in several studies to achieve high-performance alloy-based anodes
are making nanostructured particles and/or introducing carbon phase as a buffer for volume
change. ¹¹⁹–¹²³,¹²⁵–¹²⁸ For example, Liu and coworkers prepared spherical Sn/C nanocomposites
by an aerosol spray pyrolysis technique using SnCl₂·2H₂O and resorcinol formaldehyde resin
as the Sn and C precursors, respectively. ¹²⁶ Sn nanoparticles with diameters of 8 and 50 nm
were used during the material synthesis, and these two materials were designated as 8-Sn@C
and 50-Sn@C, respectively. The XRD patterns and TEM images of the as-prepared 50-Sn@C
and 8-Sn@C spheres are displayed in Figure 1.19. It is seen from Figure 1.19 that both 50-
Sn@C and 8-Sn@C exhibited sphere-like architecture with Sn nanoparticles (black dots)
embedded in carbon (grey sphere) matrix. The comparison of electrochemical performance
between 50-Sn@C and 8-Sn@C is illustrated in Figure 1.20a. 50-Sn@C sample showed
inferior capacities at the current densities from 200 to 4000 mA g⁻¹ with poor cycling stability
at each current density. On the other hand, 8-Sn@C can deliver a high reversible capacity of
494 mAh g⁻¹ at 200 mA g⁻¹. This material can maintain 349 mAh g⁻¹ even at a high current
density of 4000 mA g⁻¹. Figure 1.20b shows the cycling performance of 8-Sn@C at 1000 mA
ɡ⁻¹ and this material sustained a capacity of 415 mAh ɡ⁻¹ after 500 charge-discharge cycles.
The unique structure with ultrafine Sn nanoparticles embedded in the carbon framework can
alleviate effectively the expansion and contraction stresses, accommodate large volume
changes during sodium insertion and extraction, and prevent particle pulverization and
agglomeration of Sn grains upon long-term cycling. Therefore, superior electrochemical performance was achieved for this anode material.

Figure 1.19 (a) XRD patterns of the as-prepared pure metallic Sn, 50-Sn@C, and 8-Sn@C nanocomposites; (b) TEM image of 50-Sn@C; (c) TEM image of 8-Sn@C.\textsuperscript{126}

Figure 1.20 (a) Rate capability and cycling performance of the 8-Sn@C and 50-Sn@C electrodes in the voltage range of 0.01 to 2.0 V; (b) Long-term cycle stability of the 8-Sn@C electrode at a current density of 1000 mA g\textsuperscript{-1}.\textsuperscript{126}

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To solve the volume change issue of Sb-based SIB anodes, electrospinning is used to prepare Sb/C composite nanofibers.\textsuperscript{125,127} Zhu and coauthors prepared Sb/C composite nanofibers via electrospinning of precursor solutions containing SbCl\textsubscript{3} and polyacrylonitrile as Sb and C precursors, respectively, followed by thermal treatment.\textsuperscript{125} Figure 1.21 gives the SEM image of the as-prepared Sb/C nanofibers and the cycling performance of the composite nanofibers at a current density of 100 mA g\textsuperscript{−1}. In the electrode, Sb nanoparticles were well dispersed and confined into the core of the one-dimensional (1D) carbon nanofibers. The high capacity and stable cycling behavior were resulted from the strong structural integrity, which was able to withstand the sodiation/desodiation induced volume change. In addition, the unique 1D architecture and conductive network allowed the electrode to display exceptional high rate capability, making this material a good candidate for high power applications. Moreover, the intermetallic alloy of Sn and Sb has also been embedded into CNFs and evaluated as SIB anodes. The results demonstrate the effectiveness of this approach in enhancing the electrochemical performance of Sn and Sb alloy based anode materials.\textsuperscript{116,129}

Figure 1.21 SEM image of Sb/C nanofibers and cycling performance at 100 mA g\textsuperscript{−1}.\textsuperscript{125}
Metal oxides are another important group of anode materials for SIBs. Similar to the metal oxides for LIBs, these materials can also be categorized as alloy-based, insertion-type and conversion-type materials. The alloy-based metal oxides for SIB anodes mainly include Sb$_2$O$_4$, SnO and SnO$_2$.\textsuperscript{130–140} For the initial charge, these materials react with sodium to form sodium alloy. Then, the alloy continuously intercalate/deintercalate with sodium from the initial discharge. The reduction process for SnO$_2$ in a SIB can be described as:\textsuperscript{138}

$$\text{SnO}_2 + 4\text{Na}^+ + 4\text{e}^- \rightarrow \text{Sn} + 2\text{Na}_2\text{O}$$

$$4\text{Sn} + 15\text{Na}^+ + 15\text{e}^- \leftrightarrow 4\text{Na}_{15}\text{Sn}_4$$

According to this reaction, the theoretical sodium storage capacity of SnO$_2$ is 667 mAh g$^{-1}$:\textsuperscript{138} During repeated intercalation and deintercalation between Sn and Na, different alloys with various Sn/Na ratios can be formed, including NaSn$_5$, NaSn, Na$_3$Sn, Na$_9$Sn$_4$, and Na$_{15}$Sn$_4$.\textsuperscript{134,138} The main disadvantage of SnO$_2$ based SIB anodes is the same with that in LIBs, which is the huge volume change during cycling. Similar routes as used in alloy-based anodes have been adopted to tackle the volume change of SnO$_2$ based anodes. The major approach is to prepare nanocomposites of SnO$_2$ with conductive polymer (e.g., polyaniline)\textsuperscript{133} or carbonaceous materials including multi-wall carbon nanotubes (MWCNTs), graphene, and reduced graphene oxides (RGO).\textsuperscript{131,132,134,135,138,139} For instance, Su prepared SnO$_2$/graphene nanocomposite via in situ hydrothermal synthesis method. The SnO$_2$ nanocrystals were uniformly anchored on graphene nanosheets. The as-prepared SnO$_2$@graphene nanocomposites exhibited a high reversible capacity of over 600 mAh g$^{-1}$ at 20 mA g$^{-1}$ and 150 mAh g$^{-1}$ at 640 mA g$^{-1}$ with stable cycling performance for 100 cycles. The nanocomposites demonstrated good rate
capability within a current density range of 20–640 mA g⁻¹. The electrochemical performance of the nanocomposites is plotted in Figure 1.22.

Figure 1.22 a) 1st and 2nd cycles discharge and charge profiles of bare graphene, bare SnO₂, and SnO₂@graphene nanocomposites at 20 mA g⁻¹ current density. (b) Cycling performance of bare graphene, bare SnO₂, and SnO₂@graphene nanocomposites at 20 mA g⁻¹ current density. (c) Cycling performance of SnO₂@graphene nanocomposites at current densities of 40, 80, 160, 320, and 640 mA g⁻¹. (d) Rate performance of SnO₂@graphene nanocomposites at varied current densities. (b–d) are recorded from the 2nd cycle.¹³⁹
Insertion-type anodes for SIBs are mainly Ti-based materials, including TiO$_2$, Na$_2$Ti$_3$O$_7$, Na$_2$Ti$_6$O$_{13}$, Li$_4$Ti$_5$O$_{12}$, and P2-type Na$_{0.66}$[Li$_{0.22}$Ti$_{0.78}$]O$_2$.\textsuperscript{141,142,142–151} The specific capacities of these materials are less than 300 mAh g$^{-1}$ due to the limited number of storage sites in their crystalline structures.\textsuperscript{88} Other metal oxides that are reported to have conversion reaction with sodium and show high capacities include Fe$_3$O$_4$ and Co$_3$O$_4$.\textsuperscript{152–154} Other types of potential anodes for SIBs including NASICON-type NaTi$_2$(PO$_4$)$_3$ and phosphorus-based materials.\textsuperscript{155,156}

### 1.3.3 Cathodes

Potential cathode materials for SIBs mainly include transition metal oxides, phosphates and fluorophosphates, metal fluorides and sulfides, sulfates, metal hexacyanoferrates, etc. Among these materials, transition metal oxides receive the most research attention recently. The transition metal oxides for SIB cathodes generally have a layered structure, which can be categorized as P2-type or O3-type compounds. This species of materials are easy to synthesize with controllable stoichiometry and show high electrochemical reactivity.\textsuperscript{157} The layered structure is built by sheets of edge-shared MO$_6$ octahedra, wherein sodium ions are located between MO$_6$ sheets. The A$_x$MO$_2$ compounds were firstly specified by Delmas and coworkers.\textsuperscript{90,91,93,158} They described the stacking arrangements of alkali ions between layers. O or P represents octahedral or trigonal prismatic coordination environment of alkali ions; while the number 3 or 2 indicates the number of transition metal (TM) layers in a repeated stacking unit. The stacking types of O3 and P2 phases are given in Figure 1.23. O3 and P2 type layered oxides are usually synthesized via solid-state reactions, co-precipitation routes, and hydrothermal methods.\textsuperscript{157}
Figure 1.23 The stacking types of (a) O3 and (b) P2 phases in A$_x$MO$_{2+y}$. In particular, in the P2-structure, there are two different sites for Na ions. One occupies the 2d site sharing the edges with the MO$_6$ octahedra whereas the other occupies the 2b site sharing two faces with the MO$_6$ octahedra.$^{158}$

O3-type sodium transition metal oxides can be written as NaMO$_2$, where M is one or multiple transition metals from Ni, Co, Mn, Fe, Cr, V, Ti, etc.$^{159-165}$ O3-type sodium layered transition metal oxides are characteristic in their stable cycling performance, whereas their capacity are moderate. For example, Yu and coworkers prepared O3-type NaTi$_{0.5}$Ni$_{0.5}$O$_2$ and
this material exhibited a reversible discharge capacity of 100 mAh g\(^{-1}\) at 20 mA g\(^{-1}\) and 85 mAh g\(^{-1}\) at 100 mA g\(^{-1}\). A stable cycling performance was observed in a voltage range of 2.0-4.7 V: this cathode showed a high capacity retention of 93\% after 100 cycles at 20 mA g\(^{-1}\) and 75\% after 300 cycles at 100 mA g\(^{-1}\).\(^{159}\) The excellent cycling performance was attributed to the structural stability of the O3-type electrode material during the sodium ion insertion and extraction processes. In another study, Komaba and coauthors synthesized NaNi\(_{0.5}\)Mn\(_{0.5}\)O\(_2\) via a co-precipitation approach and the cathode materials showed a reversible capacity of 120 and 105 mAh g\(^{-1}\), respectively, at 48 and 240 mA g\(^{-1}\).\(^{163}\) This cathode material can sustain over 75\% of its initial capacities at both current densities, indicating good cycling stability.

In contrast, P2-type sodium layered transition metal oxides exhibit in higher reversible capacities.\(^{166–170,170–179}\) Remarkably, Yabuuchi and Komaba prepared NaFe\(_{1/2}\)Mn\(_{1/2}\)O\(_2\) and Na\(_{2/3}\)Fe\(_{1/2}\)Mn\(_{1/2}\)O\(_2\) by solid-state reaction method and these two cathode materials showed reversible capacities of 125 and 190 mAh g\(^{-1}\), respectively at a current density of 12 mA g\(^{-1}\).\(^{178}\) The electrochemical performance of these two cathodes are illustrated in Figure 1.24. In this study, the authors also estimated the energy density of the P2- Na\(_{2/3}\)Fe\(_{1/2}\)Mn\(_{1/2}\)O\(_2\) and found it to be around 520 mWh g\(^{-1}\), which is comparable to that of LiFePO\(_4\) (about 530 mWh g\(^{-1}\) vs Li). Moreover, the estimated density of Na\(_{2/3}\)Fe\(_{1/2}\)Mn\(_{1/2}\)O\(_2\) was 4.1 g cm\(^{-3}\), which is higher than that of LiFePO\(_4\) (3.6 g cm\(^{-3}\)). The submicrometer-sized primary particles of Na\(_{2/3}\)Fe\(_{1/2}\)Mn\(_{1/2}\)O\(_2\) were electrochemically active without further carbon coating. These superior characteristics are preferable for the improvement in the energy density of the electrode materials in SIBs. Furthermore, aluminum and copper collectors are used respectively in LIB cathodes and anodes, while in SIBs, both cathodes and anodes can use aluminum collectors because sodium
cannot form alloy with aluminum. Therefore, if $P2-Na_{2/3}Fe_{1/2}Mn_{1/2}O_2$ cathode is combined with hard carbon or other anode materials using aluminum as current collectors, it could be possible to fabricate 3 V-class rechargeable batteries consisting of only abundant elements in the Earth’s crust without metallic sodium, lithium, cobalt and nickel. This study is a milestone in developing next-generation, high capacity, high energy density SIBs to substitute present LIBs.

Figure 1.24 Galvanostatic charge/discharge curves for Na/NaFe$_{1/2}$Mn$_{1/2}$O$_2$ (a) and Na/Na$_{2/3}$Fe$_{1/2}$Mn$_{1/2}$O$_2$ (b) cells at a rate of 12 mA g$^{-1}$ in the voltage range of 1.5 and 4.3V. (c) Comparison of the discharge capacity retention of the sodium cells. (d) Rate capability of a Na/Na$_{2/3}$Fe$_{1/2}$Mn$_{1/2}$O$_2$ cell.  

Yabuuchi and Komaba’s study demonstrated a novel high capacity, high energy density cathode material for SIBs. However, the high capacity showed significant decaying trend in
less than 30 cycles. Thus, the capacity retention of this material needs to be further improved. Nanosized materials have a short sodium ion diffusion pathway, relatively less volume change during cycling, and more contact sites between the electrode and electrolyte due to their high specific area, all of which could lead to enhanced overall electrochemical performance.\(^{179}\)

Active nanoparticles tend to aggregate due to their high surface energy, which can cause limited contact with the conducting components and result in poor battery performance. The nanoparticle aggregation phenomenon could be mitigated by utilizing 1D nanostructures, which can facilitate better electrode-electrolyte contact. Therefore, Zhu and coworkers prepared Na\(_{2/3}\)Fe\(_{1/2}\)Mn\(_{1/2}\)O\(_2\) nanofibers via electrospinning of precursor fibers followed by thermal treatment in air. The as-spun Na\(_{2/3}\)Fe\(_{1/2}\)Mn\(_{1/2}\)O\(_2\) nanofibers showed improved cycling stability compared to the nanoparticle rival. The charge-discharge curves and cycling performance of Na\(_{2/3}\)Fe\(_{1/2}\)Mn\(_{1/2}\)O\(_2\) nanofibers and nanoparticles are demonstrated in Figure 1.25. It is seen that at 0.1 C (26 mA g\(^{-1}\)), the Na\(_{2/3}\)Fe\(_{1/2}\)Mn\(_{1/2}\)O\(_2\) nanofibers and nanoparticles showed initial discharge capacities of 195 and 179 mAh g\(^{-1}\), respectively. After cycling at 0.1 C for 80 cycles, the nanofibers maintained a capacity of 167 mAh g\(^{-1}\), corresponding to a capacity retention of 86%. In contrast, the nanoparticles exhibited a discharge capacity of 113 mAh g\(^{-1}\), corresponding to a capacity retention of 61%. It is therefore demonstrated that the cyclability of Na\(_{2/3}\)Fe\(_{1/2}\)Mn\(_{1/2}\)O\(_2\) has been significantly improved with the 1D fibrous nanostructure.
Figure 1.25 (a) Charge–discharge curves of Na$_{2/3}$Fe$_{1/2}$Mn$_{1/2}$O$_2$ nanofibers and nanoparticles at the initial and 80th cycles at the 0.1 C current rate; (b) corresponding cycling stability.$^{179}$

More recently, Hasa and coauthors evaluated a new P2-type sodium layered transition metal oxide with a composition of Na$_{0.5}$[Ni$_{0.23}$Fe$_{0.13}$Mn$_{0.63}$]O$_2$. This work also focused on the synthesis of SIB cathodes with naturally abundant, environmental friendly and potentially low cost elements such as iron and manganese. The charge-discharge curves and associated cycling performance are displayed in Figure 1.26. This cathode material exhibited a discharge capacity of 200 mAh g$^{-1}$ at the lowest current and 150 mAh g$^{-1}$ at the highest current. At each current density, stable cycling performance was obtained after charged and discharged for over 70 cycles. It was also proposed that further improvement of the capacity and capacity retention could be achieved by reducing the active material size.$^{167}$
Figure 1.26 Performance of a Na/PC, NaPF$_6$ 1 M/Na$_{0.5}$[Ni$_{0.23}$Fe$_{0.13}$Mn$_{0.63}$]O$_2$ cell upon galvanostatic charge–discharge cycles within the 4.6–1.5 V voltage range at 20 °C ± 2 °C. The cycling behavior (a, c, e) and the voltage profiles (b, d, f) are reported at various current rates (a, b: 15 mA g$^{-1}$; c, d: 50 mA g$^{-1}$; f, e: 100 mA g$^{-1}$).$^{167}$
Interestingly, in both P2 and O3 type SIB cathodes, Li substitution appears to be an effective method to improve the electrochemical performance.\textsuperscript{180–186} For example, P2-Na\textsubscript{1.0}Li\textsubscript{0.2}Ni\textsubscript{0.25}Mn\textsubscript{0.75}O\textsubscript{6} delivered a reversible capacity of 100 mAh g\textsuperscript{-1} in a potential window of 2.0–4.2 V, and showed almost no capacity fading in 50 cycles.\textsuperscript{184} P2-Na\textsubscript{0.80}[Li\textsubscript{0.12}Ni\textsubscript{0.22}Mn\textsubscript{0.66}]O\textsubscript{2} exhibited a discharge capacity of 118 mAh g\textsuperscript{-1} within a voltage range of 2.0–4.4 V and showed a capacity retention of 91% over 50 cycles.\textsuperscript{185} Oh and coworkers prepared O3-type Na[Li\textsubscript{0.05}(Ni\textsubscript{0.25}Fe\textsubscript{0.25}Mn\textsubscript{0.5})\textsubscript{0.95}]O\textsubscript{2} cathode and the Li-substituted cathode demonstrated high discharge capacities of 180 mAh g\textsuperscript{-1} at 0.1C, 131 mAh g\textsuperscript{-1} at 1C and 96 mAh g\textsuperscript{-1} at 5C.\textsuperscript{180} Guo prepared a layered composite with P2 and O3 integration (Na\textsubscript{0.66}Li\textsubscript{0.18}Mn\textsubscript{0.71}Ni\textsubscript{0.21}Co\textsubscript{0.08}O\textsubscript{2+δ}), and this composite cathode showed a high specific capacity of 200 mAh g\textsuperscript{-1} at 0.1C. It also demonstrates a good rate capability (134 mAh g\textsuperscript{-1} at 1C) and decent cycling stability with a capacity retention of 84% over 50 cycles.\textsuperscript{181} The significantly enhanced electrochemical performance of the Li-substituted Na layered transition metal oxide fibers is largely contributed by the Li stabilizing effect in the transition metal layers of the materials. It is commonly believed that the substituted Li ions share the adjacent transition metal sites with Mn and Ni ions, which results in minimal anti site disorder. In this way, the added Li in the cathode materials is expected to stabilize the transition metal layer and counter the movement of Ni into the Na layer during repeated Na intercalation and deintercalation.\textsuperscript{181,184,186} Therefore, the substituted Li in the structure can help prevent phase transformation and mitigate structural degradation during cycling, resulting in improved electrochemical performance.
Other candidate materials for SIB cathodes include phosphates and fluorophosphates such as NaFePO$_4$, Na$_3$V$_2$(PO$_4$)$_3$, NaVPO$_4$F, NaFePO$_4$F, etc.\textsuperscript{187–193} This group of cathode materials usually show reversible capacities below 120 mAh g\(^{-1}\). Metal sulfides, sulfates, and metal hexacyanoferrates such as FeS$_2$, NaFeSO$_4$F, Na$_2$Fe$_2$(SO$_4$)$_3$, and iron-nickel hexacyanoferrate, can also be used as potential cathodes in SIBs. Unfortunately, the reversible capacities of these materials are generally limited below 100 mAh g\(^{-1}\).\textsuperscript{194–197} Hence, they are not reviewed in details here.

1.4 Supercapacitors

1.4.1 Introduction

Supercapacitors, or ultracapacitors, electrochemical capacitors, are considered to be promising candidates for alternative energy storage due to their high rate capability, long cycle life, high power supply, simple principles, environmental friendliness, low maintenance cost, etc.\textsuperscript{198–200} As shown in Figure 1.1, batteries have high energy density but suffer from low power density, whereas conventional capacitors show high power density but low energy density. Supercapacitors, on the other hand, are able to bridge the gap between batteries and conventional capacitors. The potential applications of supercapacitors include memory protection in electronic circuitry, consumer portable electronic devices, and electrical hybrid vehicles.\textsuperscript{1,198,199}

A supercapacitor is a charge-discharge device that has similar structure to that of a battery. As shown in Figure 1.27, a supercapacitor is composed of two electrodes, electrolyte solution and a separator that can isolate the two electrodes electrically. It is seen from Figure 1.27 that
charges can be stored and separated at the interface between the electrolyte and the conductive solid particles, for example, carbon or metal oxide particles. Electrodes are the major components in supercapacitors. In general, supercapacitors are constructed with electrode materials with high surface area and high porosity.\textsuperscript{200}

Figure 1.27 Schematic representation of a supercapacitor cell.\textsuperscript{201}
Based on different types of energy storage mechanisms, supercapacitors can be categorized into two classes: electrochemical double-layer capacitors (EDLCs) and pseudocapacitors. In EDLCs, the electrodes are not electrochemically active. Energy is stored via the adsorption of both anions and cations and the charge transfer process is non-faradic, i.e. electron transfer across the electrode material does not take place and therefore, the charge accumulation is purely electrostatic. On the other hand, in pseudocapacitors, energy storage is achieved through fast surface redox reactions between the electrolyte and the electroactive species on the surface of the electrode. Electron transfer results in charge accumulation in the pseudocapacitors and such charge transfer process is in nature faradic.\textsuperscript{199,200,202,203}

In EDLCs, the electrode-electrolyte interface is treated as a capacitor with an electrical double-layer (EDL) capacitance, which can be estimated using the following equation:\textsuperscript{201,202}

\[ C = \frac{\varepsilon_r \varepsilon_0}{d} A \]  

Where \( \varepsilon_r \) is the electrolyte dielectric constant, \( \varepsilon_0 \) the permittivity of a vacuum, \( A \) the specific surface area of the electrode accessible to the electrolyte ions, and the \( d \) the effective thickness of the EDL (the Debye length). In pseudocapacitors, the pseudocapacitance arises due to the thermodynamic consideration between the charge acceptance (\( \Delta q \)) and the change in voltage (\( \Delta v \)). The derivative \( d\Delta q/d\Delta v \) is associated with the pseudocapacitance.\textsuperscript{201}

1.4.2 Electrode Materials for EDLCs

Carbon materials are widely investigated and are considered to be the ideal candidate for supercapacitors due to their high specific surface area, good electronic conductivity, high
chemical stability, abundance, non-toxicity, easy processing, wide operating temperature range, and low cost.\textsuperscript{199,200,202} The capacitance in EDLCs is realized via the build-up of charges in the layers or the EDL formed at the interface between the electrolyte and the high-surface area electrodes. In general, porous carbon materials are the most suitable materials for use in EDLC electrodes. A variety of carbon materials have been studied as electrode materials for EDLCs, such as activated carbon (AC)\textsuperscript{204,205}, templated carbon\textsuperscript{206,207}, carbon nanotubes (CNTs)\textsuperscript{208–210}, carbon aerogels\textsuperscript{211,212}, carbide-derived carbons\textsuperscript{213,214}, graphene-based materials,\textsuperscript{198,215–217} and carbon nanofibers (CNFs)\textsuperscript{218–235}.

Among the carbon materials, ACs are the most widely used electrodes in EDLCs. Generally, ACs are prepared from physical (thermal) or chemical activation of different types of carbonaceous materials. Physical activation involves high temperature treatments from 700 to 1200 °C with oxidizing gases such as air or CO\textsubscript{2}. On the other hand, chemical activation is usually carried out at lower temperatures (400 to 700 °C ) in the presence of potassium hydroxide, sodium hydroxide, zinc chloride, phosphoric acid, etc.\textsuperscript{202} For example, He and coworkers produced ACs via microwave-assisted heat treatment of petroleum coke with KOH as the activation agent.\textsuperscript{204} The authors evaluated the influence of the activation time on the specific surface area and the capacitive behavior of the resultant ACs. It was reported that the ACs produced with 35 min of activation time showed the highest specific surface area of 2312 m\textsuperscript{2} g\textsuperscript{−1}. The ACs exhibited a high specific capacitance of 342.8 F g\textsuperscript{−1} at a scan rate of 50 mA g\textsuperscript{−1}. This material also remained 245.6 F g\textsuperscript{−1} after 800 cycles with an energy density of 8.0 Wh kg\textsuperscript{−1} retained. It is therefore demonstrated that microwave-assisted heat treatment can be an effective method in preparation of AC electrodes for EDLCs. Although ACs have been used
in commercial supercapacitors, their applications are still restricted because the control of pore size distribution and porous structure is challenging. Therefore, future studies can be focused on designing ACs with narrowed pore size distribution with an interconnected porous structure and shortened pore width, as well as controlled surface chemistry.

CNTs are another important group of EDLC electrode candidates. The unique porous structure, superior electrical conductivity and excellent mechanical and thermal stability together make CNTs attractive for EDLCs.\(^{202,236}\) Moreover, CNTs are ideal electrodes for high-power supercapacitors due to their excellent electrical conductivity and readily accessible surface area. In addition, their superior mechanical properties with open tubular network can provide good support for other active materials such as MnO\(_2\).\(^{237,238}\) Recently, Kaempgen and coworkers fabricated flexible, thin film supercapacitors based on printable materials.\(^{210}\) The active electrodes were synthesized from sprayed networks of single-walled carbon nanotubes (SWCNTs) serving as electrode materials and charge collectors simultaneously. A printable aqueous gel electrolyte was used as the organic liquid electrolyte in the supercapacitors. Figure 1.28 illustrates the SEM image of the as-deposited SWCNT networks and a photograph showing the as-assembled thin film supercapacitor based on SWCNT films on PET as electrodes and a PVA/H\(_3\)PO\(_4\) based polymer electrolyte as both electrolyte and separator. As a comparison, organic electrolyte (LiPF\(_6\)/EC:DEC) and paper filter membrane were also used. The thin film supercapacitors demonstrated high energy (6 Wh kg\(^{-1}\)) and power densities (23 and 70 kW kg\(^{-1}\), respectively for aqueous gel electrolyte and organic electrolyte), which is comparable to the performance of SWCNT based supercapacitors fabricated by other approaches. The results underline the potential of using printable materials in next-generation
energy storage applications. Although CNTs show excellent capacitive performance, the energy density is relatively low compared with ACs. The low energy density of CNTs, which is resulted from their relatively small surface area (generally less than 500 m² g⁻¹), remains an obstacle for their practical applications in supercapacitors. In addition, the present difficulty in purification and high cost of production still hamper the practical applications.

Figure 1.28 (a) Scanning electron microscopy image of as-deposited SWCNT networks. (b) Thin film supercapacitor using sprayed SWCNT films on PET as electrodes and a PVA/H₃PO₄ based polymer electrolyte as both electrolyte and separator.²¹⁰

Recently, graphene based materials have received plenty of attention as a potential candidate in EDLCs due to its unusual characteristics. It is composed of pure carbon in a single layered, two-dimensional structure and such structure offers very large surface area, which
makes it favorable to be used as electrode materials in EDLCs. Theoretically, the parallel plates can provide extensive channels that enable various electrolytes to easily access the surface of each graphene sheet with low diffusion resistance. Due to the high electrical conductivity of graphene, conductive additives can be avoided in EDLCs and thus the energy density of the cells could be improved. In addition, the two-dimensional layered structure with high aspect ratio provides graphene with excellent mechanical flexibility, allowing it to be assembled in freestanding film electrodes with sufficient structural robustness. Therefore, graphene based materials are extensively investigated as freestanding electrodes in EDLCs. For example, Park et al. prepared functionalized reduced graphene oxide (RGO) films via functionalization of graphene with Nafion using a supramolecular assembly method. As shown in Figure 1.29A, the all-solid-state flexible EDLC was fabricated by assembling functionalized RGO films as the electrodes, and solvent-cast Nafion electrolyte membrane as the electrolyte and separator. It was proposed that the tight integration of Nafion not only prevented the re-stacking of graphene sheets, but also enhanced the interfacial wettability between the electrolyte and the electrodes. As a result, the interconnected functionalized RGO networks formed continuous transport pathways for rapid ion transport. The specific capacitance achieved in this study was 118.5 F g\(^{-1}\), which is much higher than the reported value (62.3 F g\(^{-1}\)). The EDLC also showed superior rate capability: with current densities from 1 to 30 A g\(^{-1}\), the EDLC maintained 90% of the capacitance at 30 A g\(^{-1}\). In addition, excellent flexibility was observed by bending the EDLC with high tensile strain during the operation. Figures 1.29D and E demonstrate that after bending at a radius of 2.2 mm, the rectangular shapes of cyclic voltammograms of the electrode
material remained almost unchanged, indicating superior mechanical stability in this all-solid-state EDLC.

Figure 1.29 Photograph and schematic diagram of an all-solid-state flexible-RGO-supercapacitor. (B, C) SEM images of the surface and cross-section of RGO films. (D) Photos of a flexible-RGO-supercapacitor before and after bending. (E) Cyclic voltammograms at a 100 mV s\(^{-1}\) scan rate of a flexible- RGO-supercapacitor before and after bending.\(^\text{215}\)
Among the diverse carbonaceous materials for EDLC electrodes, CNFs have been extensively studied because their one-dimensional fibrous architecture can provide shortened electron transportation pathways, contribute to high ion-accessible surface sites and facilitates the electrolyte penetration from perpendicular to longitudinal directions with respect to the fibers.\textsuperscript{228,234} Therefore, CNFs can be potential alternatives to commercially available ACs in EDLCs with high capacitance and high rate capability. In addition, CNFs are flexible and can form binder-less and conductive-additive-free electrodes with sufficient mechanical stability, which can further increase the energy density of EDLCs. Currently, the studies of using CNFs in EDLCs are mainly focused on preparing CNFs from a variety of polymer precursors.\textsuperscript{218,219,222,224,227,230} To increase the specific surface area of CNFs, attempts have been made on using activation process\textsuperscript{220,221,228} and introducing pore generators into the precursors.\textsuperscript{223,235} Moreover, introducing surface functional groups or heteroatoms on the surface of carbonaceous materials becomes an effective approach in enhancing the electrodes’ capacitance.\textsuperscript{232,233} For instance, Chen and coworkers prepared nitrogen-doped CNFs via in situ polymerization of polypyrrole on CNFs with subsequent heat treatment in N\textsubscript{2} at various temperatures.\textsuperscript{233} Figure 1.30 depicts the schematic illustration of the preparation for N-CNFS. Figures 1.31 a and b show representative cyclic voltammograms and charge-discharge curves of N-CNFS prepared at 900 °C. It is seen from Figures 1.31 c and d that the N-CNFS prepared at 900 °C demonstrated significantly reduced electrochemical impedance and improved capacitance compared with CNFs and N-CNFS carbonized at other temperatures.
Figure 1.30 Schematic illustration for the fabrication processes of nitrogen-doped CNFs.\textsuperscript{233}

Figure 1.31 Electrochemical performance measured in a three-electrode system. (a) Cyclic voltammograms of N-CNPs-900 at different scan rates and (b) charge-discharge curves of N-CNPs-900 at different current densities. (c) Specific capacitances of CNFs-900, CNFs@Ppy, N-CNPs-500, N-CNPs-700, N-CNPs-900, and N-CNPs-1100 at different current densities. (d) Electrochemical impedance spectra (inset: magnified 0-4 $\Omega$ region) under the influence of an AC voltage of 5 mV.\textsuperscript{233}
1.4.3 Electrode Materials for Pseudocapacitors

In contrast to EDLCs, pseudocapacitors store energy via a Faradic process with rapid and reversible redox reactions occurred at the interface between the electrode and the electrolyte. In general, the electrode materials for pseudocapacitors mainly include conducting polymers, such as polyaniline, polypyrrole, and polythiophene; and metal oxides, such as RuO$_2$, MnO$_2$, V$_2$O$_5$, SnO$_2$, etc. Electrodes for pseudocapacitors can exhibit much higher capacitance than EDLCs, however, their rate capability and long-term cycling stability are usually inferior compared to EDLCs. Consequently, these materials are often combined with carbonaceous materials to obtain high capacitance with stable cyclability and good rate performance.

1.5 Brief Introduction on Electrospinning

Electrospinning is a simple, non-mechanical and versatile approach for the preparation of nanofibers from various materials including polymers, ceramics and composites. Figure 1.32 illustrates a schematic of a basic electrospinning setup. A typical single-nozzle electrospinning setup is comprised of a syringe, a metal nozzle, a high voltage power supply, and a metallic collector. Prior to electrospinning, the electrospinning solution is firstly fed into the syringe, and then a high voltage is applied between the syringe and the metallic collector. As the high voltage is applied, the electrically-charged fluid begins to elongate and generate a conical droplet, known as “Taylor cone”. When the voltage reaches a critical value, where electrostatic force can overcome the surface tension of the spinning solution, a liquid jet is ejected from the nozzle tip and then undergoes a stretching-and-whipping process,
accompanied by fast evaporation of solvent. During this process, the jet undergoes a diameter reduction from hundreds of micrometers to as small as tens of nanometers, forming a long and thin threads. Eventually, dried nanofibers are deposited on the surface of the metallic collector, forming a nonwoven mat.

Figure 1.32 Schematic of a typical single-nozzle electrospinning setup.$^{242}$

The morphology and diameter of electrospun nanofibers can be tuned by a number of parameters including: (a) solution intrinsic properties such as viscosity, surface tension and electric conductivity, polymer molecular weight, and solution concentration; (b) operational conditions including applied electric field strength, nozzle-collector distance, nozzle diameter, flow rate of the feeding solution, and motion of collector.$^{241,243-248}$ The thickness of the nanofiber mat can be adjusted by changing the duration of the electrospinning process.$^{249}$ It is
also possible to engineer electrospun nanofiber mats with a wide range of porosity values with careful design and control.\textsuperscript{250}

1.6 Centrifugal Spinning

Nanofibers are an important class of materials and can be employed in a variety of applications, such as tissue engineering, protective clothing, filtration, battery separators, energy storage, etc.\textsuperscript{240,241,249,251} So far, electrospinning is the most widely used approach for preparing nanofibers. However, the wide-spread commercial use of electrospinning in nanofiber production is largely limited by its low production rate. Most other nanofiber production methods, including bicomponent fiber spinning, phase separation, melt-blowing, self-assembly and template synthesis\textsuperscript{252–256}, are complicated and can only be used to generate nanofibers from limited types of polymers, which hinders their practical applications.\textsuperscript{253,254,256}

Hence, a novel nanofiber production technology must be developed to eliminate the limitations encountered by the above-mentioned approaches and such new technology can potentially address the mass production of nanofibers required by the industry. In this section, a brief history about centrifugal spinning will be given, followed by the discussion on the fiber formation process during centrifugal spinning, the centrifugal spinning system, and the possible types of fibers that can be prepared via this novel spinning technology. This section will also address the processing-structure-performance relationships and discuss potential applications of the centrifugally-spun fibers.
1.6.1 A Brief History

Centrifugal spinning is not an entirely new technology to the industry. For instance, this technology has been utilized extensively in the production of glass fibers (which is also known as glass wool or fiberglass) for over half a century. The resultant glass fibers have diameters greater than 1 μm and are used for filtration and thermal insulation purposes. The spinning head, which is a metal container with a thousand of holes evenly distributed around the sidewall, is one of the major components in the system. A stream of molten glass is loaded into the spinning head, and then a high speed rotation (2000 to 3000 rpm) is applied to the spinning head. During this course, high temperature of about 900–1100 °C is maintained for the spinning head to keep the glass at its liquid state. During the high speed rotational movement, the centrifugal force generated at high rotational speed makes the molten glass to flow through the fine holes of the spinning head, producing fine glass streams. The glass streams then come out from the side wall and are attenuated by high velocity gas, broken into glass fibers with less than 1 μm diameter and several centimeters in length. A binder is sprayed onto the glass fibers when they are produced. The produced glass fibers move through a “forming hood” positioned beneath the spinning head, and are then collected on a conveyor belt in the form of a mat. The conveyor belt carries the glass fiber mat through a curing oven, which helps dry and cure the binder. Eventually, the glass fiber mats are cut into desirable widths and lengths for various end applications. Although the centrifugal spinning of glass fibers is mainly performed in industry, it is seen that the concept of using centrifugal spinning to prepare various fibers has seeded in this industrial practice.
Centrifugal spinning has been commonly used in the fiberglass industry for long, however, the use of this technology to prepare polymer fibers, especially polymer nanofibers, is relatively new. In 1990s, companies such as BASF Aktiengesellschaft, Owens Corning Fiberglas Technologu, and Akzo Nobel NV, have attempted to produce polymer fibers using centrifugal spinning technology and have issued patents on spinning heads that can spin fibers from polymers. More recently, FibeRio Technology Corporation successfully commercialized large-scale centrifugal spinning facilities (Cyclone FE 1.1 M/S and Cyclone FS 1.1) for mass production of polymer nanofibers. FibeRio’s centrifugal spinning facilities were designed based on a patented technology called Forcespinning®-The Force For Nanofibers®, which was developed by Lozano and coworkers at the University of Texas at Pan American. The Forcespinning® technology uses high-speed rotational spinning heads and is capable of producing nanofibers from different polymers.

Centrifugal spinning technology has also drawn the attention in academia. In 2008, Weitz and coworkers reported a so-called “unexpected finding of nanoscale fibers with a diameter down to 25 nm that emerge from a polymer solution during a standard spin-coating process.” To spin poly(methyl methacrylate) (PMMA) nanofibers, a 5 wt. % PMMA solution in chlorobenzene was firstly dripped onto the center of a rotating chuck of a spin-coater. Then, a high rotating speed of 3,000 rpm was imitated. Finally, PMMA nanofibers with diameter of around 25 nm were obtained. It has been reported that the fiber forming process relies on the competition between the centrifugal force and the solution surface tension.

In 2010, Lozano and coworkers designed a three-plate spinning head, which allows the rotation at much higher speed (Figure 1.33A). Equipped with such a spinning head, the
Forcespinning® system was able to rotate within a rotational speed ranging from 3,000 to 5,000 rpm and produced polyethylene oxide (PEO) nanofibers with diameters up to 300 nm (Figure 1.33B). This spinning head design finally resulted in the Forcespinning® technology used by FibeRio Technology Corporation, as discussed previously. Since 2010, more and more academic researchers have reported their work on preparing nanofibers via centrifugal spinning, and the total amount of journal articles on centrifugal spinning is around 30.\textsuperscript{257–287}

Figure 1.33  (A) Schematic of a three-plate spinning head system, and (B) SEM image of PEO nanofibers prepared using the spinning head system shown in (A).\textsuperscript{259}

1.6.2 Fiber Formation during Centrifugal Spinning

A basic bench-top centrifugal spinning device is shown in Figure 1.34A. During the centrifugal spinning process, the solution is fed into the rotating spinning head, which has multiple nozzles around the sidewall. After the rotational speed increases to a crucial value, at which the centrifugal force can overcome the surface tension of the spinning fluid, liquid jets are generated at the nozzles. Figure 1.34B illustrates the path of a liquid jet after it is ejected from the nozzle. The nanofibers are formed by the elongation of liquid jets under the combined
centrifugal force and air frictional force. In addition, other forces including rheological force, gradational force, and surface tension, might also have influences on the nanofiber formation. The elongated jets are deposited onto the collectors, and after the solvent is evaporated, a nonwoven mat of nanofibers is formed. The most important feature and significant advantage of centrifugal spinning technology is its high production rate. The average production rate for a simple two-nozzle setup is approximately 50 g/hour, which is at least two orders of magnitude higher than that of a typical, one-nozzle electrospinning device. Similar production rate values have been reported by Lozano and coworkers\textsuperscript{288} in their Forcespinning\textsuperscript{®} facility. Such a high production rate might not be necessary for academia, but it is certainly a game changer in industry. The high production rate demonstrates that centrifugal spinning can be a low-cost, scalable method for mass production of nanofibers.

Figure 1.34  (A) Schematic of a basic bench-top centrifugal spinning setup, and (B) the path of a liquid jet ejected from the nozzle tip during centrifugal spinning.
To understand the nanofiber formation process during centrifugal spinning process, researchers have performed simulation and modeling studies and brought valuable visions. For instance, Badrossamay and coworkers\textsuperscript{289} reported a scaling framework complemented via a semi-analytic and numerical method and used it to characterize the regimes of nanofiber formation. They proposed a theoretical model for fiber radius as a function of parameters including solution viscosity, angular speed, orifice radius and orifice-collector distance. This model is meaningful in controlling the morphological quality of nanofibers prepared by centrifugal spinning. In another study, Hlod and coworkers\textsuperscript{260} described the centrifugal spinning process as a thin jet of viscous Newtonian fluid flowing between the rotor and coagulator upon the two inertial body force (centrifugal force and Coriolis force) for producing fibers after hitting the collector. In this model, the vertical movement due to gravity was neglected and the jet flew in two dimensions in the horizontal frame. The researchers investigated the specific boundary conditions depending on the balance between the inertia and viscosity in the momentum transfer through the thin jet cross-section and discovered that there were two probable regimes during the spinning, namely viscous-inertial, where viscosity dominates near the nozzle and inertia dominates near the collector, and inertial, where inertia dominates in the momentum transfer through the jet cross-section. Two scenarios where the centrifugal spinning process can’t happen were also described, either because of the lack of a steady-jet solution or the jet wrapping the rotor.
1.6.3 Centrifugal Spinning System

A typical centrifugal spinning system has two major components, namely rotating spinning head and nanofiber collecting system. In this section, several spinning head designs and fiber collection setups are discussed.

1.6.3.1 Rotating Spinning Head

A simple spinning head design is shown in Figure 1.35A. In this design, two identical syringes are connected to the rotor. Before spinning, same amount of spinning fluids are loaded into the syringes. When high speed rotation is applied, two liquid jets are generated simultaneously from the needle tips under centrifugal force. The main technical difficulty for this design is to maintain balance between the weights of the two syringes that contain the spinning fluids. Lozano and coworkers developed a three-plate spinning head, which has a single reservoir to keep the spinning fluids and can sustain balanced rotation during the spinning, as shown in Figure 1.33A. For most recently reported work, cylinder-shape spinning head design is used. Figure 1.35B displays a typical cylinder-shape spinning head design. In this specific design, two nozzles perforated through the cylinder wall are placed opposite to each other. Such spinning head design not only allows nanofiber preparation from polymer solutions, but can also produce nanofibers from polymer melts, if necessary parts such as inductive heating coils or other heating elements are installed. In addition, multiple nozzles can be introduced if the production rate needs to be further improved. Moreover, other types of spinning heads can be used, and the possible shapes include but are not limited to spheroid, oblate spheroid and trapezoid.
1.6.3.2 Fiber Collecting System

Several different nanofiber collection systems can be employed in centrifugal spinning system. In the design illustrated in Figure 1.36A, nanofibers are deposited on the surface of the inner wall of a circular collector made of metal or plastic. The diameter of the circular collector is important, because it determines the nozzle-collector distance and can affect the structure of resultant nanofibers. This kind of design is suitable for batch production of nanofibers, which is usually seen in lab-scale setups.

For industrial applications, the nanofiber collection systems need to be able to collect as-spun nanofibers continuously. This can be realized by employing a moving substrate, which is
placed under the spinning head. (Figure 1.36B) The gravity of the as-spun nanofibers helps the disposition of nanofibers onto the moving substrate, producing continuous nonwoven nanofiber mats. To improve distribution and packing density of the nanofiber nonwovens, suction force (Figure 1.36B) and air jets (Figure 1.36C) can be introduced. If suction force is introduced, porous substrates such as paper, textile fabrics, or other porous membranes are necessary for the nanofiber collection. Figure 1.36D demonstrates a yarn collector. In this design, nanofibers are collected in a water bath. Continuous nanofiber yarns are collected with the help of a rotating roller.

Figure 1.36 Schematics of (A) gravity-assisted nanofiber nonwoven collector, (B) suction force-assisted nanofiber nonwoven collector, (C) air jet-assisted nanofiber nonwoven collector, and (D) water bath-assisted nanofiber yarn collector.
1.6.4 Types of Centrifugally-Spun Fibers

So far, centrifugal spinning technology is mainly applied in producing nanofibers from polymer materials. However, nanofibers made from other types of materials can also be produced by centrifugal spinning of various precursor solutions combined with subsequent thermal treatments.

1.6.4.1 Polymer Fibers

Polymer nanofibers can be centrifugally-spun from polymer solutions or melts. Several studies have reported fabrication of nano-/micro-fibers via centrifugal spinning from various polymer solutions, such as PMMA, PEO, polylactic acid (PLA), polyacrylic acid (PAA), polystyrene (PS), polyvinylidene fluoride (PVDF), polycaprolactone (PCL), polycrylonitrile (PAN), polystyrene (PS), polyvinylidene fluoride (PVB), and polyamide 6 (PA6). Figure 1.37A demonstrates an SEM image of nanofibers generated from a 5 wt. % PEO aqueous solution at 12,000 rpm. These PEO nanofibers exhibit smooth surface with an average fiber diameter of 500 nm. The nanofibers obtained from centrifugal spinning process also show some alignments along the radial direction with respect to the spinning head, and this can possibly lead to reasonable strength of the fibrous mat, which might be needed for certain applications.

So far, most centrifugal spinning research are focused on preparing nanofiber from polymer solutions, however, it is possible to generate nanofibers from polymer melts using the same approach. For example, Huttunen and Kellomaki produced fibers from polylactide melts using a cotton-candy machine in 2011. The cotton-candy machine operates...
in a similar fashion to that of the centrifugal spinning device. However, the resultant fibers show large diameter due to large nozzles size and low rotational speed. Therefore, the polylactide fibers obtained in this study have diameters over 1μm. Recently, Lozano’s group and Ellison’s group prepared polypropylene (PP) and poly(butylene terephthalate) (PBT) nanofibers, respectively, using Forcespinning system. Figure 1.37B shows the nanofibers prepared from PP melts at 12,000 rpm and 225 °C. During the polymer melt centrifugal spinning, harmful solvent is avoided, which helps protect the production personnel and the environment. Moreover, the absence of solvent during nanofiber production also makes this approach more attractive because structures created by solvent-free process are easier to register for many commercial products, especially for medical applications.

1.6.4.2 Carbon Fibers

Carbon nanofibers (CNFs) are usually synthesized by spinning of precursor fibers, such as PAN, pitch, polyimide, etc., followed by thermal treatment with proper conditions. For instance, CNFs can be prepared by electrospinning of the precursor fibers combined with a two-step thermal treatment including stabilization in air and carbonization in inert gas atmosphere. However, the precursor fibers can also be produced by centrifugal spinning. In Chapter 4, we will discuss the preparation of porous carbon nanofibers (PCNFs) via the carbonization of centrifugally-spun PAN/PMMA precursor fibers at high temperatures in argon gas. Figure 1.37C shows a representative SEM image of the as-prepared PCNFs. During the carbonization, PAN was converted into carbon while PMMA was eliminated and resulted in porous structure. The as-prepared PCNFs are lightweight and show large surface area, good
conductivity, excellent adsorptive capacity and strong affinity for bacteria or other microorganisms. Consequently, the PCNFs can find their applications in semiconductors, aerospace, energy conversion and storage, etc. The application in supercapacitors will also be discussed in Chapter 4.

1.6.4.3 Ceramic Fibers

Similar to CNFs, ceramic nanofibers can be prepared by the annealing of precursor fibers prepared via centrifugal spinning. For example, Liu and coworkers prepared TiO$_2$ nanofibers from titanium tetrachloride precursor. Prior to centrifugal spinning, acetylacetone was added as a chelating agent to help conversion of titanium tetrachloride into spinnable polyacetylacetonatotitanium. The as-spun precursor fibers were annealed at 700 °C to obtain TiO$_2$ nanofibers. A SEM image of the TiO$_2$ nanofibers is shown in Figure 1.37D. Similarly, Ren and coworkers have produced silica micro-/nanofibers and silica nanotubes using polyvinylpyrrolidone (PVP) and tetraethyl orthosilicate (TEOS) as precursors.
Figure 1.37 SEM images of (A) PEO nanofibers produced by centrifugal spinning of aqueous solution, (B) PP nanofibers produced by centrifugal spinning of polymer melt, (C) carbon nanofibers produced by carbonization of centrifugally-spun PAN/PMMA precursor, and (D) TiO₂ nanofibers produced by calcination of centrifugally-spun titanium tetrachloride precursor.

1.6.5 Processing-Structure Relationship of Centrifugal Spinning

To make centrifugal spinning a useful process for scalable production of nanofibers, the processing-structure relationships must be established. The morphology of the centrifugally-spun nanofibers is dependent on a variety of parameters: (a) intrinsic properties of the spinning
fluids such as viscosity, surface tension, molecular weight, molecular structure, solution concentration, solvent type and structure, additive; and (b) operational conditions including rotational speed, nozzle diameter, spinning head diameter, nozzle-collector distance. The effects of the intrinsic properties of the spinning fluids and the operational conditions on the morphology and properties of the centrifugally-spun nanofibers are investigated and detailed discussed in Chapter 3.

1.6.5.1 Fluid Properties

There are many fluid properties that can influence the structure of centrifugally-spun nanofibers. For polymer solutions, the most important solution properties include surface tension, viscosity, molecular weight and structure, solution concentration, solvent type, additive, etc. However, not all of the above-mentioned solution properties are equally important in determining nanofiber structure. Among them, viscosity and surface tension are two dominant factors in deciding fiber formation, and other factors affect the process by altering these two solution properties. Analogously, in centrifugal spinning of polymer melts, parameters such as viscosity, surface tension, molecular weight and structure, and additive, can affect the nanofiber structure synergistically. However, viscosity and surface tension are the key factors. The viscosity of polymer melts can be controlled by selectively adjusting the molecular weight and structure and processing temperature. In contrast, the most convenient way to adjust the viscosity of polymer solutions is to control the solution concentration. Surface tension plays an important role in nanofiber production. In conventional spinning techniques, surface tension, a driving force for the bead formation and it tends to transform liquid jet to spheres by
restricting the surface area. During centrifugal spinning process, three different forces including surface tension, centrifugal force and rheological force interplay and co-determine the structure of the resultant nanofibers. Specifically, centrifugal force is prone to draw liquid jets and enlarge their surface area, while rheological force resists rapid transformations in shape and therefore, assists the formation of smooth nanofibers. To adjust surface tension, molecular weight and structure and solvent type can be adjusted. It is also feasible to control surface tension by introducing additives and using mixing solvents with different surface tensions.

1.6.5.2 Operational Conditions

There are many operational conditions that can affect the nanofiber structure, such as rotating speed, nozzle diameter, spinning head diameter, nozzle-collector distance, etc. Rotating speed of the spinning head can directly affect the centrifugal force and air frictional force and is one of the most dominating operational conditions. During centrifugal spinning process, centrifugal force and air frictional force together elongate liquid jets into nanofibers. When the spinning fluid is placed in a rotating nozzle tip, the centrifugal force \( F_{\text{centri}} \) exerted on the liquid can be described by:

\[
F_{\text{centri}} = m\omega^2 D/2
\]  

(2)

where \( m \) is the mass of the fluid, \( \omega \) the rotating speed of the spinning head, and \( D \) the diameter of the spinning head. In order to eject liquid jets from the nozzle tip, the rotating speed must accelerate to a crucial value, at which enough centrifugal force is produced to overcome the
surface tension of the fluid. Therefore, to prepare nanofibers, it is critical to find the crucial rotating speed.

As the liquid jet ejects from the nozzle, the frictional force applied on the jet can be still calculated by Equation 2. However, it should be noted that $\omega$ needs to be changed to the rotating speed of the jet while $D$ becomes the diameter of the path of the jet. In the same time, the air frictional force ($F_{\text{fri}}$) can be calculated by:

$$F_{\text{fri}} = \pi C \rho A \omega^2 D^2 / 2$$

(3)

where $C$ is a numerical drag coefficient, $\rho$ the air density, $A$ the cross-sectional area of the jet, $\omega$ the rotating speed of the jet, and $D$ the diameter of the path of the jet.

During the course for the jet to travel from the nozzle to the collector, the rotating speed decreases gradually. However, higher rotating speed of the spinning head always results in a higher rotating speed of the liquid jet after traveling for a certain distance. Thus, with the increase in the spinning head, the centrifugal force and air frictional force exerted on the liquid jet also increase, resulting a greater stretching of the jet and finer fibers. However, if the rotating speed is too high, thick fibers might be obtained mainly because the flight time for the jet to elongate is not sufficient. In addition, high rotating speed comes with larger mass throughput of the liquid jet, which also leads to larger fiber diameter. Therefore, it is critically important to find the optimal rotating speed that is suitable to generate the finest fibers.

The spinning head diameter is another critical parameter in deciding fiber structure. According to Equation 2, considering the rotating speed as a constant, the centrifugal force will increase with the increase in spinning head diameter. Thus, it is easier to eject liquid jets from a larger spinning head. Moreover, a larger spinning head is helpful for producing thinner
fibers by applying greater elongation for the liquid jets. However, in reality, the loading capability of the motor must be taken into consideration and therefore, the diameter of the spinning head cannot be too large. Otherwise, the balance of the motor during high-speed rotation will be difficult to maintain.

The nozzle diameter is another important factor to control the nanofiber structure. The nozzle size mainly controls the mass throughput of the ejected liquid jet. Smaller nozzle diameter basically limits the mass throughput and therefore, yields fibers with smaller diameter. However, the nozzle diameter can’t be too small; otherwise, it becomes difficult for the liquid jets to eject.

The nozzle-collector distance has a direct effect on the travel time for the ejected liquid jets. A minimum nozzle-collector distance is required so that the jet has sufficient time for solvent evaporation before arrives at the collector. Moreover, a longer distance provides lengthened flight course, which is favorable to obtain thinner fibers. However, compared with other operational conditions, this factor is less significant in determining fiber diameter.

1.6.6 Application of Centrifugally-Spun Fibers

Nanofibers prepared via centrifugal spinning can generally be used in the same applications as those fabricated by electrospinning. So far, the most studied application of centrifugally-spun polymer nanofibers is tissue engineering. For instance, Badrossamay and coworkers prepared PLA nanofiber scaffold by centrifugal spinning. In order to assess the feasibility of using the PLA nanofibers as tissue engineering scaffolds, they seeded chemically dissociated neonatal rat ventricular myocytes on the fibrous constructs.
They found that the myocytes were bound to and aligned with the nanofibers spontaneously. Moreover, the multicellular constructs self-organized along the PLA nanofibers, forming anisotropic muscle with elongated and aligned myocytes and ordered myofibrils. This work suggests that centrifugal spinning is a simple but facile approach to fabricate anisotropic and biodegradable nanofiber scaffolds.

In another study, Ren and coworkers\textsuperscript{271} applied centrifugal spinning in the fabrication of tissue engineering scaffold from PVP and poly-L-lactide (PLLA) composite fibers. These two polymer components showed phase separation phenomenon during the centrifugal spinning process. After the composite fibers were prepared, PVP was etched from the binary system and the hydrophilicity of the fibrous materials were adjusted. Pores and surface roughness were created, and these are preferable for cell attachment and proliferation. The researchers used human dermal fibroblasts to simulate partial skin graft and demonstrated that the porous PLLA nanofibers prepared by centrifugal spinning are promising tissue engineering scaffolds with improved cell attachment and growth.

Although most current studies on the applications of centrifugally-spun nanofibers are focused on tissue engineering, it can be expected that centrifugally-spun nanofibers, similar to electrospun nanofibers, can be applied in filtration, composites, protective clothing, aerospace, semiconductors, and energy conversion and storage. Recently, centrifugally-spun fibers have been used in composites.\textsuperscript{272,273} More recently, centrifugally-spun fibers are started to be employed in energy storage applications such as electrode materials and battery separators.\textsuperscript{275,278,284} In the present work, we firstly evaluate the influences of various solution properties and operational parameters on the fiber structure (Chapter 3), and then focus on
using centrifugally-spun fibers as energy storage materials. Centrifugally-spun PCNFs, SnO$_2$ microfibers and lithium-substituted sodium layered transition metal oxide fibers are used respectively as electrodes for EDLCs, anodes and cathodes for SIBs, and the results are discussed in Chapter 4, 5 and 6 respectively.
CHAPTER 2. Research Objectives

Nanofibers are an important class of material that is useful in numerous applications, including tissue engineering, filtration, composites, protective clothing, energy storage, etc. Currently, the most commonly-used approach for nanofibers is electrospinning. Other nanofiber preparation approaches include phase separation, self-assembly and template synthesis. However, these methods are complex and the material choices are limited. Although electrospinning is versatile and popular in academia, the wide-spread industrial use is limited mainly due to its poor safety, low production rate and high cost. To meet the demand for large quantities of nano-/micro-sized fibrous materials, it is important to establish a novel fiber production system that can eliminate the limitations encountered by the above-mentioned methods. To address this, an alternative fiber production process, centrifugal spinning, has been proposed recently. This novel technology can produce fine fibers from various materials in a high-speed and low-cost fashion. The first objective of this work is to develop a lab-scale centrifugal spinning system with adjustable operational parameters and investigate the processing-structure-performance relationships.

Recently, one-dimensional (1D) structured, nano-/micro-sized electrode materials have become attractive candidates in energy storage field because the 1D nano-/micro-structures, including nanobelts, nanowires, nanotubes and nanofibers, have a variety of unique properties such as large specific surface area, well-guided ionic/electronic transport, and good electrode-electrolyte contact, which contribute to enhanced electrochemical performance. Currently, electrospinning is one of the most widely used methods to prepare the 1D electrode materials.
Therefore, the second objective of this work is to use centrifugal spinning to replace electrospinning in the electrode material preparation, and produce centrifugally-spun nanofibers and microfibers for effective energy storage.

(I) Parameter Study and Characterization of Centrifugally-Spun Polyacrylonitrile Nanofibers

To investigate centrifugal spinning as an alternative spinning technology for electrospinning, a lab-scale centrifugal spinning system was established. It is important to understand the processing-structure relationships of centrifugal spinning process. Therefore, the goal of this work is to use polyacrylonitrile (PAN) as an example polymer to study the influence of various solution intrinsic properties and operational parameters on the resultant fiber morphology and properties. The obtained processing-structure relationships can be helpful for the subsequent preparation of carbon and ceramic fibers and their applications in energy storage. The results of this work are discussed in Chapter 3.

(II) Centrifugally-Spun Porous Carbon Fibers as Binder-Free Electrodes for Electric Double-Layer Capacitors

Good conductivity and large surface area are two key factors to construct high-performance electric double-layer capacitors (EDLCs). Carbon nanofibers (CNFs), as an important carbonaceous material candidate for EDLCs, have drawn extensive attention because their 1D nano-sized architecture provides both high ion-accessible sites and shortened electron pathways. If more pores can be introduced in CNFs, the resultant porous CNFs (PCNFs) can potentially have larger specific surface area and enhanced capacitance. CNFs are usually prepared by electrospinning of precursor fibers with subsequent thermal treatment. On
the contrary, centrifugal spinning is mostly used in preparation of polymer fibers, and there is no report on using centrifugal spinning to produce carbon fibers. Hence, the purpose of this work is to prepare PCNFs from the polyacrylonitrile/poly(methyl methacrylate) precursor fibers with various weight ratios at different temperatures, and investigate the influence of carbonization temperatures and porous structures on the electrochemical performance of the EDLCs. The results are discussed in Chapter 4.

(III) Centrifugally-Spun SnO$_2$ Microfibers Composed of Interconnected Nanoparticles as Anode for Sodium-Ion Batteries

SnO$_2$ is a potential anode material for sodium-ion batteries (SIBs). Recently, several studies reported using SnO$_2$ as SIB anodes, however, the anodes prepared in these studies were mostly composed of SnO$_2$ nanoparticles and carbonaceous materials. Although the electrochemical properties achieved in these work are superior, the methods were usually complicated. Moreover, it is important to evaluate the electrochemical performance of solely SnO$_2$ without any carbonaceous additives so that the influence of adding these materials could be clearly understood. Currently, centrifugal spinning has mostly used in the synthesis of polymer fibers, and there is no report on preparing SnO$_2$ fibers via this novel method. The aim of this study is to prepare SnO$_2$ microfiber electrode through centrifugal spinning and compare its different morphology, structure and electrochemical performance with traditional electrode in particle form and the commercially available material. The detailed results are discussed in Chapter 5.

(IV) Lithium-Substituted Sodium Layered Transition Metal Oxide Fibers as Cathodes for Sodium-Ion Batteries
Na layered transition metal oxides are promising cathode candidates for sodium-ion batteries. These materials possess high specific capacities, however, their capacity retention and rate capabilities are usually poor due to structural instability. It has been reported that partial substitution of transition metals with lithium in the transition metal layer can effectively enhance the structural stability. Therefore, the electrochemical performance, including cycling stability and rate capability can be improved. The first aim of this study is to develop a new cathode material with a specific composition of Na$_{1.2}$Ni$_{0.15}$Mn$_{0.55}$Co$_{0.1}$O$_2$, and then investigate the effect of different amounts of partial lithium substitution on the electrochemical performance of the new cathode materials. The 1D fibrous structured electrode can provide many advantages compared with the particle electrodes, and therefore, the second purpose of this study is to compare the morphology and performance between the fiber and particle materials. The detailed results are discussed in Chapter 6.
CHAPTER 3. Parameter Study and Characterization of Centrifugally-Spun Polyacrylonitrile Nanofibers

Abstract

Electrospinning is currently the most popular method for producing polymer nanofibers. However, the low production rate and safety concern limit the practical use of electrospinning as a cost-effective nanofiber fabrication approach. Herein, we present a novel and simple centrifugal spinning technology that extrudes nanofibers from polymer solutions by using a high-speed rotary and perforated spinneret. Polyacrylonitrile (PAN) nanofibers were prepared by selectively varying parameters that can affect solution intrinsic properties and operational conditions. The resultant PAN nanofibers were characterized by SEM, and XRD. The correlation between fiber morphology and processing conditions was established. Results demonstrated that the fiber morphology can be easily manipulated by controlling the spinning parameters and the centrifugal spinning process is a facile approach for fabricating polymer nanofibers in a large-scale and low-cost fashion.

Keywords: Nanofibers, centrifugal spinning, electrospinning, polyacrylonitrile, diameter, crystallinity
3.1 Introduction

Being an important material class with fiber diameters ranging from less than 100 nm to 1000 nm, nanofibers are of great interests owing to their unique structure and properties. As a result of their high surface to volume ratio, extremely long fiber length, and superior mechanical strength, nanofibers can be potentially applied in fields such as filtration, medicine, textile, composite, energy, etc.\textsuperscript{293–297} In the last decade, study on nanofiber production and applications becomes a hot topic in both academic and industrial world. The beneficial and practical applications of nanofibers also give rise to an urgent and insistent demand of producing high-quality nanofibers in a low-cost and large-scale fashion.

The state-of-the-art nanofiber production techniques include phase separation, template synthesis, self-assembly and electrospinning.\textsuperscript{241,253,254,298} Except for the electrospinning technique, all the other abovementioned nanofiber production approaches have restricted applications due to the complexity of fiber fabrication procedures and limited material choices. Resulting from the simple working principle and relatively wide material choice, electrospinning is probably the most studied nanofiber production method by far. Although it is popular and versatile, electrospinning is not the ideal solution for producing nanofibers. First and foremost, the low production rate of electrospinning highly hampers its use for mass production of nanofibers. Moreover, electrospinning is sensitive to solution conductivity and environmental factors. Last but not least, the application of high-voltage electric field and the inevitable use of solvents lead to potentially increased production cost and safety concern. Thus, advanced technologies should be developed to overcome the disadvantages of electrospinning.
Aiming to eliminate the limitations encountered by the electrospinning process, researchers are sparing no effort to explore the possibility of producing nanofibers in simple, low-cost and large-scale ways. Recently, several studies demonstrated the successful fabrication of micro/nanofibers through centrifugal spinning of polymers, such as polyethylene oxide\textsuperscript{259,264,268}, polyvinylidene fluoride\textsuperscript{266}, polymethyl methacrylate\textsuperscript{258}, and polycaprolactone\textsuperscript{269}. For example, Ellison’s group reported that polybutylene terephthalate fibers centrifugally-spun from polymer melts showed high crystallinity and enhanced molecular orientation.\textsuperscript{270} Ravandi and co-workers proposed an electro-centrifuge spinning system that synthesized nanofibers with enhanced quality, fineness and production rate.\textsuperscript{299} Most other works associated with centrifugal spinning focused on the exploration of its potential applications and one of the most studied applications for centrifugally-spun nanofibers is probably tissue engineering. Parker and co-workers developed a rotary jet spinning device and applied the as-spun polylactic acid nanofibers in scaffold applications.\textsuperscript{265} In another study, poly(L-lactic acid) fibrous tissue scaffolds with controlled nanoscale surface roughness were fabricated via the centrifugal jet spinning process.\textsuperscript{271} Similarly, another research by Wang and co-workers implemented commercial cotton candy machine to prepare a fiber matrix of poly-lactic-co-glycolic acid and polystyrene, and its application in scaffold for cell culture was assessed.\textsuperscript{263} Amalorpava Mary and co-workers also evaluated the possibility of using centrifugally-spun polycaprolactone and polyvinyl pyrrolidone nanofiber blends as drug delivery vehicle.\textsuperscript{300}

In this work, a centrifugal spinning system has been fabricated to facilitate the large-scale and low-cost production of fibers with diameters ranging from micro-scale to nano-scale
(Figure 3.1). The centrifugal spinning system consists of a spinneret, which is located in the center of the spinning platform and contains two small nozzles; several rod collectors, which are radially positioned in the outer perimeter; a DC motor, which is used to rotate the spinneret; and a speed controller, which is for adjusting the rotational speed of the spinneret. Two flexible air foils are placed below the spinneret to generate air turbulence and accommodate the fiber collection. This centrifugal spinning system is simple and is capable of eliminating the limitations of electrospinning process.

![Schematic of the centrifugal spinning system.](image)

During centrifugal spinning, a polymer solution is fed into the spinneret, which is rotated at high speeds. When the rotational speed reaches a critical value, the centrifugal force
overcomes the surface tension of the solution and ejects a liquid jet from each nozzle. The jet then undergoes a stretching process, accompanied by rapid evaporation of the solvent, and is eventually deposited on the rod collectors forming dried nanofibers. Since the centrifugal spinning process does not use high-voltage electric field, it alleviates the related safety concern. In addition, the high rotational speed allows fast and scalable fiber fabrication, which can dramatically improve the production rate by two to three orders of magnitude and reduce the production cost when compared with the electrospinning process. Moreover, the centrifugal spinning process enables the fabrication of nanofibers from polymer solutions with much higher concentrations than the electrospinning process, which also reduces the production cost by using less solvent.

Polyacrylonitrile (PAN) is a well-known polymer with good stability and mechanical properties. PAN nanofibers can be potentially applied into multiple fields including tissue engineering, sensing, composites, battery separators, and precursors for producing carbon nanofibers. Among the various applications, the most important role of PAN nanofibers is the precursor for producing carbon nanofibers due to its high carbon yield and flexibility for tailoring the structures of resultant carbon nanofibers. Therefore, the mass production of high-quality PAN nanofibers is urgently demanded. In this study, we hypothesized the feasibility of producing PAN nanofibers with the newly-developed and facile centrifugal spinning system. In centrifugal spinning process, the morphology of nanofibers mainly depends on solution intrinsic properties and operational parameters. Hence, solution intrinsic properties including viscosity and surface tension were measured and critical polymer concentration for centrifugal spinning was determined. Operational parameters, such as
rotational speed, nozzle diameter and nozzle-collector distance, were varied and their effects on the nanofiber morphology were evaluated. The morphology of resultant nanofibers was characterized using scanning electron microscopy (SEM); and the structural analysis was performed using X-ray diffraction (XRD). In order to fully understand this new process and take good control for the morphology of resultant products, the fundamental processing-structure correlations were studied and established.

3.2 Experimental

3.2.1 PAN Solution Preparation and Property Measurement

Polyacrylonitrile (PAN, homopolymer, Mw = 150,000) was purchased from Pfaltz&Bauer Inc. N, N-dimethylformamide (DMF, Aldrich) was selected as the solvent to dissolve PAN polymer. A series of PAN solutions with concentrations ranging from 0 (only solvent) to 15 wt. % were prepared by mechanically stirring at 60 °C for 24 hours.

To understand the effects of solution intrinsic properties on the morphology of as-spun PAN nanofibers, the viscosities and surface tensions of PAN solutions were measured prior to centrifugal spinning. During the viscosity measurements, PAN solutions ranging from 0 to 15 wt. % were loaded into the viscometer (ATS Rheosystem) fitted with a plate spindle (40 mm in diameter and 0.4 mm in gap distance) and the viscosities were recorded under steady-state shear stress from 0.003 Pa to 10 Pa at room temperature. The raw data were analyzed to obtain solution viscosities at the Newtonian region and the zero-shear viscosities ($\eta_0$) were determined over this region. The polymer contribution to the $\eta_0$ was studied by defining the specific viscosity ($\eta_{sp}$):
\[ \eta_{sp} = \frac{\eta_0 - \eta_s}{\eta_s} \]  

(1)

where \( \eta_s \) is solvent viscosity.

The surface tension measurements of the PAN solutions from 0\% to 15\% were performed on a tensiometer (Fisher Scientific Surface Tensiometer 20).

### 3.2.2 Nanofiber Preparation

The centrifugal spinning system was powered by a DC motor (115 volts, Grainger) and the rotational speed was controlled by a speed controller (DART CONTROLS 253G-200C). In this study, the rotational speed of the motor was controlled in the range of 2000 rpm to 4000 rpm. The spinneret had a cylindrical shape with 2 cm in height and 1.5 cm in radius. Teflon spinnerets with different nozzle diameters (0.4 mm, 0.8 mm, and 1 mm) and fixed wall thickness (3 mm) were used. The distance between the nozzle tip and the rod collector was adjustable from 10 cm to 30 cm. PAN nanofibers with controlled morphology were fabricated by selectively adjusting polymer solution concentration, rotational speed, nozzle diameter, and nozzle-collector distance. All the spinning operations were conducted at room temperature. In this work, the solvent DMF has a relatively slow evaporation rate. In the large-scale production of PAN nanofibers, the evaporation rate could be enhanced by using a low-boiling point solvent or introducing a strong exhausting system.

### 3.2.3 Nanofiber Characterization

The morphology of collected PAN nanofibers was characterized by field emission scanning electron microscope (FESEM-JEOL 6400F SEM at 5 kV). Prior to testing, the
centrifugally-spun samples were coated with Au/Pd (60/40) to reduce charging with a Hummer II sputter coater. The fiber diameter distributions were analyzed using Revolution 1.6.0 software.

X-ray diffraction analysis was conducted with Rigaku Smartlab X-ray diffraction system using Cu Kα radiation (λ = 1.544 Å). The samples were scanned in a 2θ range of 10°–60°, with 2θ step-scan interval of 0.1°. Characteristic peaks were analyzed and the degrees of crystallinity were estimated with MDI Jade 5.0 software.

3.3 Results and Discussion

3.3.1 Solution Intrinsic Properties

Solution intrinsic properties play vital role in determining the morphology and structure of centrifugally-spun nanofibers. Many solution properties can influence the structure and morphology of nanofibers, such as rheological behavior, surface tension, polymer molecular weight, solution concentration, solvent type and additive. However, not all the parameters are fundamental or independent. In general, polymer molecular weight, solvent type, solution concentration and additive together affect the process of fiber formation by changing the rheological behavior and surface tension of the spinning solution. Therefore, this work focuses on the most important parameters, i.e., rheological behavior and surface tension. The compositions and properties of PAN solutions with different concentrations are shown in Table 3.1.
Table 3.1 Compositions and properties of PAN solutions studied in this work.

<table>
<thead>
<tr>
<th>Solution Concentration (wt. %)</th>
<th>η₀ (mPa·s)</th>
<th>ηₚ</th>
<th>Surface Tension (mN/m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.9</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>2</td>
<td>2.1</td>
<td>1.3</td>
<td>37.5</td>
</tr>
<tr>
<td>4</td>
<td>9.5</td>
<td>9.6</td>
<td>38</td>
</tr>
<tr>
<td>6</td>
<td>47</td>
<td>51.2</td>
<td>38.7</td>
</tr>
<tr>
<td>8</td>
<td>167</td>
<td>185</td>
<td>38.7</td>
</tr>
<tr>
<td>10</td>
<td>478</td>
<td>530</td>
<td>39</td>
</tr>
<tr>
<td>12</td>
<td>1198</td>
<td>1330</td>
<td>40</td>
</tr>
<tr>
<td>13</td>
<td>2233</td>
<td>2480</td>
<td>40.7</td>
</tr>
<tr>
<td>14</td>
<td>3165</td>
<td>3516</td>
<td>42</td>
</tr>
<tr>
<td>15</td>
<td>4079</td>
<td>4531</td>
<td>43.7</td>
</tr>
</tbody>
</table>

The rheological behavior, especially solution viscosity, is very important in determining the fiber morphology. The viscosity of a polymer solution can be interpreted by the extent of polymer chain entanglement. During centrifugal spinning, a critical solution concentration must be exceeded to form nanofibers. This critical concentration is called entanglement concentration ($c^*$), which denotes the polymer chain entanglement density. When the polymer solution is too dilute ($c \ll c^*$, semi-dilute unentangled regime), there is almost no polymer chain entanglement, therefore, nanofibers are very difficult to form due to the insufficient chain overlap. When the concentration increases to close to the critical value ($c < c^*$, semi-dilute entangled regime), fibers can be formed but the chain entanglement is still insufficient to avoid the formation of beads during fiber spinning. When the solution concentration is greater than the entanglement concentration ($c > c^*$, concentrated regime), chain entanglement is sufficient to produce uniform and continuous bead-free fibers. In order to determine the critical
concentration that features with sufficient polymer chain entanglement, specific viscosity of each PAN solution was calculated based on the zero-shear viscosity (Table 3.1). It is seen that the specific viscosity of PAN solutions increases with increase in polymer concentration. To identify the critical concentration, the specific viscosity was plotted against polymer concentration in Figure 3.2 for PAN solutions. The changes in the slopes defined the semi-dilute unentangled, semi-dilute entangled, and concentrated regimes. The critical concentration \( (c^*) \), \textit{i.e.}, the onset of the concentrated regime, is 10 wt. %.

Figure 3.2 Specific viscosity versus polymer concentration profile for PAN solutions. Changes in the slope denoted the onset of the semidilute unentangled, semidilute entangled, and concentrated regimes. The \( c^* \) was found to be 10 wt. %.
In addition to rheological behavior, the fiber morphology is also dependent on the surface tension of polymer solutions. Generally, the surface tension of a polymer solution inhibits the spinning process because it results in jet instability.\textsuperscript{10} In addition, surface tension tends to convert the liquid jet into spherical droplets to reduce the surface area. In centrifugal spinning process, the surface tension is overcome by the centrifugal force, which tends to stretch and elongate the liquid jet and increase the surface area. As shown in Table 3.1, the surface tension of PAN solutions increases when the polymer concentration increases. However, as compared with the rapidly-changing viscosity, the increase in surface tension is relatively small when the solution concentration increases.

3.3.2 Effect of Solution Properties

To understand the correlation between solution intrinsic properties and fiber morphology, PAN nanofibers from different polymer concentrations were fabricated at constant operational conditions of rotational speed, nozzle diameter and nozzle-collector distance. The average production rate of this novel approach was found to be around 50 g/hour, which is at least two orders of magnitude higher than that of a typical lab-scale electrospinning process,\textsuperscript{310} suggesting centrifugal spinning process is a potentially large-scale and low-cost approach for mass production of polymer nanofibers. The centrifugally-spun PAN products were collected and characterized under SEM and the fiber diameter distributions were analyzed. It is found that when polymer concentration is lower than 6 wt. %, no fibers were formed due to high surface tensions and insufficient chain entanglements \textit{(i.e.,} low viscosities). When the concentration increased to 8 wt. %, both beads and fibers started to be formed since the polymer
solution entered the semi-dilute entangled regime. Figure 3.3 shows the beads and fibers centrifugally-spun from 8 wt. % PAN solution. The formation of beads was due to the high surface tension. In addition, the amount of fibers formed was small since the chain entanglement was still limited in the semi-dilute entangled regime.

![Figure 3.3 SEM images of PAN nanofibers centrifugally-spun from 8 wt. % solution at 4000 rpm using 0.4 mm nozzle and 10 cm nozzle-collector distance under different magnifications: (a) 1000 ×, and (b) 5000 ×.](image)

Figure 3.3 SEM images of PAN nanofibers centrifugally-spun from 8 wt. % solution at 4000 rpm using 0.4 mm nozzle and 10 cm nozzle-collector distance under different magnifications: (a) 1000 ×, and (b) 5000 ×.

The polymer solution entered the concentration entangled regime when the solution concentration reached 10 wt. %. Figure 3.4 shows the SEM images and corresponding fiber distributions of PAN nanofibers spun from solutions with higher concentrations, i.e., from 10 to 15 wt. %. It is seen that large amount of fibers were formed with few beads. The average fiber diameters of PAN nanofibers spun from 10, 12, 13, 14, 15 wt. % solutions were 406, 458, 440, 665, 1077 nm, respectively. This indicates that when the polymer concentration further increased to 10 % and above, although the surface tension increased slightly, the significantly
enhanced solution viscosity and chain entanglement stabilized the jet and led to continuous fiber formation without bead generation. This experimental observation agrees well with the critical polymer concentration that was defined in Figure 3.2.

These data demonstrate that the nanofiber formation is a function of the polymer concentration where an optimal range of solution concentration increases the probability of polymer chain entanglement, resisting bead formation and resulting in fine fibers. It should be also noted that once the polymer concentration is beyond such an optimal range, for example, at 15 wt. %, the highly-viscous solution often exhibits longer stress relaxation time, which limits the evaporation of solvents and resists jet fracturing, elongation and thinning. Consequently, the increase in solution concentration and viscosity leads to larger fiber diameter, and thick fibers with average fiber diameter over 1µm could be produced.
Figure 3.4 SEM images and fiber diameter distributions of PAN nanofibers centrifugally-spun at 4000 rpm using 0.4 mm nozzle and 10 cm nozzle-collector distance with different solution concentrations: (a, b) 10 wt. %, (c, d) 12 wt. %, (e, f) 13 wt. %, (g, h) 14 wt. %, and (i, j) 15 wt. %.
3.3.3 Effect of Rotational Speed

The centrifugal spinning process utilizes centrifugal force to overcome the surface tension of polymer solutions. During the spinning, the centrifugal force accelerates a slender liquid stream where polymer chain elongation and solvent evaporation occur simultaneously. Therefore, higher centrifugal force can induce greater extension and thinning for polymer jets, which in turn result in finer fiber diameters. The centrifugal force experienced by the liquid jets increases with the increasing angular speed, which can be translated into the rotational speed of the spinneret.

To establish the correlation between fiber morphology and rotational speed, the 13 wt. % PAN solution was centrifugally spun into nanofibers by using different rotational speeds. The SEM images and fiber diameter distributions of the resultant PAN nanofibers are shown in Figure 3.5. It is seen that the nanofibers have smooth morphology with no beads observed. The average fiber diameter decreased from 663, 541, to 440 nm, respectively, when the rotational speed increased from 2000, 3000, to 4000 rpm. When the rotational speed increased, the centrifugal force exerted on the solution per volume increased significantly while the surface tension remained the same. Hence, reduced fiber diameter was obtained when the rotational speed was increased.
Figure 3.5 SEM images and fiber diameter distributions of PAN nanofibers centrifugally-spun from 13 wt. % solution using 0.4 mm nozzle and 10 cm nozzle-collector distance at different rotational speeds: (a, b) 2000 rpm, (c, d) 3000 rpm, and (e, f) 4000 rpm.
3.3.4 Effect of Nozzle Diameter

Fiber morphology can also be influenced by other operational parameters such as nozzle diameter. Instead of directly affecting the centrifugal force that is applied on solution jet, changing the nozzle diameter can alternate the nanofiber structure by controlling the mass throughput of the liquid jet. A decrease in nozzle diameter typically leads to smaller mass throughput, which in turn restricts the fiber diameter. Three spinnerets with nozzle diameters of 0.4, 0.8, and 1.0 mm, respectively, were used to study the relationship between fiber morphology and nozzle diameter. The SEM images of the resultant nanofibers are presented in Figure 3.6. The average fiber diameter decreased from 895, 807, to 665 nm when nozzle diameter decreased from 1.0, 0.8, to 0.4 mm. These data suggests that to fabricate thinner fibers, smaller nozzle diameter is desired.
Figure 3.6 SEM images and fiber diameter distributions of PAN nanofibers centrifugally-spun from 14 wt. % solution at 4000 rpm using 10 cm nozzle-collector distance with different nozzle diameters: (a, b) 0.4 mm, (c, d) 0.8 mm, and (e, f) 1.0 mm.
3.3.5 Effect of Nozzle-Collector Distance

As discussed in previous sections, the centrifugal spinning process is also closely related with the evaporation rate of the solvent. Thus, varying the nozzle-collector distance can affect the fiber morphology by changing the flight time of the liquid jet. In centrifugal spinning, there exists a minimum nozzle-collector distance that allows the adequate time for most of the solvent to evaporate before arriving at the rod collectors. If longer nozzle-collector distance is applied, the liquid jet can have a longer distance to travel, which may favor the formation of reduced fiber diameter. In this work, the effect of nozzle-collector distance on fiber morphology was studied by varying the nozzle-collector distance from 10, 20, to 30 cm. The SEM images of the resultant fibers are given in Figure 3.7. The average fiber diameters were 665, 658 and 647 nm, respectively, when the nozzle-collector distances were 10, 20 and 30 cm. It is apparent that the average fiber diameter did not change significantly when the nozzle-collector distance increased. This indicates that a nozzle-collector distance of 10 cm is already sufficient for the evaporation of the solvent so that further increase in distance only decreases the fiber diameter slightly.
Figure 3.7 SEM images and fiber diameter distributions of PAN nanofibers centrifugally-spun from 14 wt. % solution at 4000 rpm using 0.4 mm nozzle diameter with different nozzle-collector distances: (a, b) 10 cm, (c, d) 20 cm, and (e, f) 30 cm.
3.3.6 X-Ray Diffraction of PAN Nanofibers

XRD patterns of PAN nanofibers centrifugally-spun under different solution concentrations, rotational speeds, nozzle diameters and nozzle-collector distances are displayed in Figure 3.8. For comparison, the X-ray diffraction pattern of PAN powder is also shown in Figure 3.8a. All the patterns show typical diffraction peaks at $2\theta = 17^o$ and $29^o$, respectively, corresponding to $(1 0 0)$ and $(1 1 0)$ planes of PAN.$^{311}$

The degree of crystallinity ($X_c$) was estimated by MDI Jade 5.0 software using:

$$X_c = \frac{\sum I_c}{\sum I_a + \sum I_c}$$  \hspace{1cm} (2)

where $I_c$ is the diffracted intensity of the crystalline region, and $I_a$ the diffracted intensity of the amorphous region. The estimated degree of crystallinity of PAN powder was 32.7 % while PAN nanofibers centrifugally-spun at different conditions showed higher degrees of crystallinity than that of the PAN powder. The centrifugal spinning process enhanced the degree of crystallinity because of the stretching effect caused by the centrifugal force. During centrifugal spinning, the nanofibers were extruded through small nozzles under a large centrifugal force. This centrifugal force created tensile stress which can partially align the molecules and such molecular alignment promoted the crystallization.

When the rotational speed was 4000 rpm, the degrees of crystallinity of nanofibers prepared from solutions of 10, 12, 13, 14 and 15 wt. % were 74.5, 73.8, 71.2, 54.5 and 53.4 %, respectively. The degree of crystallinity decreased with the increase in solution concentration because higher-concentration solution tended to contain more polymer chain entanglements, which made the fibers difficult to crystallize if the centrifugal force exerted remained
unchanged. For nanofibers centrifugally-spun from 13 wt. % PAN solution, the degree of crystallinity of nanofibers increased from 62.7, 70.0, to 71.2 % when the rotational speed increased from 2000, 3000, to 4000 rpm, respectively. This is mainly because the higher rotational speed led to larger centrifugal force, which stretched the polymer chains to a greater extent and helped achieve higher degree of crystallinity. When comparing the effect of nozzle diameter on the degree of crystallinity, it is found that with the degree of crystallinity decreased from 54.5, 37.1, to 34.2 %, respectively, when the nozzle diameter increased from 0.4, 0.8, to 1.0 mm. This is because the increased nozzle diameter allowed larger mass throughput of polymer, which in turn led to reduced crystallinity. In addition, the degree of crystallinity increased from 54.5, 61.6, to 62.1 % when the nozzle-collector distance increased from 10, 20, to 30 cm. This observation suggests that increased distance facilitates longer flight time for polymer and accommodates its crystallization process.
Figure 3.8 XRD patterns of PAN nanofibers showing the influences of different parameters: (a) concentration, (b) rotational speed, (c) nozzle diameter, and (d) nozzle-collector distance.

Using PAN as an example, this study successfully establishes a correlation between fiber morphology and processing parameters of centrifugal spinning process, which is fundamental and helpful for researchers to fabricate other types of polymer nanofibers through this simple and facile approach. As PAN is the most important precursor for carbon nanofibers, the knowledge acquired in this research can also be extended to the preparation of carbon nanofibers and related materials and their potential applications in composites, filtration, and energy storage fields.
3.4 Conclusions

A facile and effective centrifugal spinning system was developed to generate continuous PAN nanofibers by using a high-speed rotary spinneret. Compared with traditional nanofiber production methods, centrifugal spinning process has several surpassing advantages: the apparatus is simple to implement, no electric field is needed, fiber formation is independent of solution conductivity, the technology can operate with high-concentration solutions, the production rate is high, and the cost is low. To harness this technology, solution intrinsic properties including polymer concentration, surface tension and rheological behavior were studied in detail. The effects of different influencing parameters such as solution concentration, rotational speed, nozzle diameter and nozzle-collector distance were correlated with fiber morphology. Results show that the morphology of the nanofibers can be easily manipulated by selectively controlling solution intrinsic properties and operational parameters. As a result, centrifugal spinning technology is a promising approach for nanofiber production in a low-cost and large-scale fashion.

Abstract

Carbon nanofibers (CNFs), among various carbonaceous candidates for electric double-layer capacitor (EDLC) electrodes, draw extensive attention because their one-dimensional architecture offers both shortened electron pathways and high ion-accessible sites. Creating porous structures on CNFs yields larger surface area and enhanced capacitive performance. Herein, porous carbon nanofibers (PCNFs) were synthesized via centrifugal spinning of polyacrylonitrile (PAN)/poly(methyl methacrylate) (PMMA) solutions combined with thermal treatment and were used as binder-free EDLC electrodes. Three precursor fibers with PAN/PMMA weight ratios of 9/1, 7/3 and 5/5 were prepared and carbonized at 700, 800, and 900 °C, respectively. The highest specific capacitance obtained was 144 F g⁻¹ at 0.1 A g⁻¹ with a rate capability of 74 % from 0.1 to 2 A g⁻¹ by PCNFs prepared with PAN/PMMA weight ratio of 7/3 at 900 °C. These PCNFs also showed stable cycling performance. The present work demonstrates that PCNFs are promising EDLC electrode candidate and centrifugal spinning offers a simple, cost-effective strategy to produce PCNFs.

Keywords: Carbon nanofiber; binder-less electrode; centrifugal spinning; capacitor; energy storage
4.1 Introduction

Ever-growing concerns over environmental issues and fossil fuel depletion continue to invoke researchers’ interest in developing alternative energy conversion and storage systems.\textsuperscript{17,296,312} Possessing extremely rapid charge/discharge capability, considerably high power density, and satisfactorily long cycle life, supercapacitors have gained extensive attention and can be potentially applied in a vast number of commercial and industrial devices including portable electronics, electric vehicles/hybrid electric vehicles, memory backup systems, and industrial power and energy management.\textsuperscript{200,202,312} Electric double-layer capacitors (EDLCs) are one important type of supercapacitors, where the storage of energy is realized through the reversible adsorption/desorption of electrolyte ions onto the conductive electrodes that have large specific surface area.\textsuperscript{313} In this context, high-surface area carbonaceous materials such as activated carbon\textsuperscript{204}, templated carbon\textsuperscript{206}, carbide-derived carbon\textsuperscript{213}, graphene\textsuperscript{216}, carbon aerogel\textsuperscript{212}, carbon nanotube\textsuperscript{210} and carbon nanofibers have ignited significant investigations world-wide not only because of their superior conductivity and large specific surface area, but also due to their abundance, low cost, ease of processing, good mechanical strength, and high chemical stability.\textsuperscript{202,228,236,314}

Among the diverse carbonaceous materials for EDLC electrodes, carbon nanofibers (CNFs) have been extensively studied because their one-dimensional architecture not only offers shortened pathways for electron transportation, but also contributes to high ion-accessible surface sites and facilitates the electrolyte penetration from perpendicular to longitudinal directions with respect to the fibers.\textsuperscript{228,234} Consequently, CNFs are extraordinarily
desirable for EDLCs with high capacitance and high rate capability simultaneously. Moreover, CNFs are flexible and they self-assemble to form mats or papers that can be directly tailored to binder-free electrodes without the addition of other conductive agents and polymeric binding agents, reducing the mass of electrochemically inactive components and sustaining the high specific capacitance with sufficiently high conductivity. In order to further improve the capacitive performance of CNFs, endeavors have been made in making porous carbon nanofibers (PCNFs) by activation process\textsuperscript{220,228} or introducing pore generators\textsuperscript{223,235} into precursor fibers. The PCNFs prepared by using sacrificial materials to form porous architectures exhibit large specific surface area and show enhanced capacitive performance.

So far, carbon nanofibers for EDLC electrodes have been mostly fabricated through the electrospinning of precursor polymer fibers and subsequent heat-treatment. Electrospinning technique is versatile in tuning fiber structure and morphology, however, it cannot meet the increasing demand of mass production of CNFs due to its low production rate, safety concern and high cost.\textsuperscript{265,269,315} Recently, centrifugal spinning has been developed as an alternative approach to fabricate nanofibers in a large-scale, low-cost fashion.\textsuperscript{315} In this work, centrifugal spinning was employed in synthesizing polyacrylonitrile (PAN)/poly(methyl methacrylate) (PMMA) precursor fibers with different weight ratios, and different thermal treatment conditions were used to carbonize the precursor fibers, during which PAN was converted to carbon while PMMA was decomposed to generate small open pores in the resultant carbon nanofiber matrix. By adjusting the relative content of PMMA, the pore generator, the influence of specific surface area on the capacitance of the resultant PCNFs was evaluated. The effect of
conductivity on the capacitive performance was assessed by comparing PCNFs carbonized at different temperatures. The precursor fibers were characterized using scanning electron microscopy (SEM) and Fourier transform infrared spectroscopy (FTIR); the PCNFs were characterized by SEM, transmission electron microscope (TEM), and BET surface analysis; the electrochemical performance of PCNFs prepared from different PAN/PMMA ratios and carbonization temperatures were investigated by cyclic voltammetry (CV) and galvanostatic charge/discharge tests. Results demonstrated that PCNFs prepared by centrifugal spinning of PAN/PMMA binary precursors could be promising EDLC electrode material and this method would also be of potential interest for researchers who are searching for alternative approach in fabricating CNF-based materials for other applications.

4.2 Experimental

4.2.1 Chemicals

Polyacrylonitrile (PAN, Pfaltz & Bauer Inc., 150,000 g mol\(^{-1}\)), poly(methyl methacrylate) (PMMA, 120,000 g mol\(^{-1}\), Sigma-Aldrich) and N, N-dimethylformide (DMF, Sigma-Aldrich) were used as received.

4.2.2 Centrifugal Spinning of PAN/PMMA Precursor Fibers

PAN/PMMA precursor fibers were prepared by centrifugal spinning of PAN/PMMA blend solutions. Firstly, PAN and PMMA were added into DMF and mechanically stirred for 12 h. Three solutions were prepared with different PAN/PMMA weight ratios of 9/1, 7/3 and 5/5 while the total polymer concentration was fixed at 16 wt. %. A lab-scale centrifugal
spinning apparatus was employed to fabricate PAN/PMMA fibers with a rotational speed of 4,000 rpm, spinneret diameter of 3 cm, and nozzle diameter of 0.4 mm. The bi-component fibers were collected on aluminum rods with a nozzle-collector distance of 10 cm.

4.2.3 Synthesis of Porous Carbon Nanofibers

PCNFs were synthesized by a two-step heat-treatment process including stabilization in air atmosphere at 280 °C for 5.5 hours with a heating rate of 5 °C min⁻¹ and subsequent carbonization in argon atmosphere at 700 °C, 800 °C or 900 °C for 1 hour with a heating rate of 2 °C min⁻¹.

4.2.4 Structural Analysis

The PAN/PMMA precursor fibers with 9/1, 7/3 and 5/5 PAN/PMMA weight ratios were analyzed using FTIR (Thermo Fisher Nexus 470 FTIR with Continuum Microscope and ORBIT/OMNI ATR’s) in a range of wavenumbers from 500 to 4,000 cm⁻¹. BET surface areas of the PCNFs were examined by BET Analyzer (Gemini VII 2390p physiosorption analyzer from Micromeritics coupled with SmartPrep 065 degassing unit).

4.2.5 Morphological Characterization

The morphology of PCNFs prepared with various PAN/PMMA weight ratios and carbonization temperatures were characterized by field emission scanning electron microscope (FESEM, JEOL JSM-6400F) in both plane view and cross-sectional view. The fiber diameter data were collected by Revolution 1.6.0 software and the fiber diameter distributions were
obtained by analyzing 100 fibers for each sample. Scanning transmission electron microscope (STEM, JEOL 2000FX) was utilized to identify the formation of porous structures along the longitudinal directions with respect to the fibers.

4.2.6 Electrochemical Evaluation

To evaluate the electrochemical capacitive performance of PCNFs, Swagelok cells were assembled by sandwiching two electrodes, which were directly punched from the carbonized fiber mats without the addition of conductive agent and polymer binder, and a glass fiber separator (Whatman GF/D glass microfiber filters) with 6 M potassium hydroxide (KOH) aqueous electrolyte. The mass of the electrodes varied from 2 to 3 mg. However, the masses of the two electrodes in a cell were kept almost the same. The assembled cells were rested for 24 hours prior to electrochemical testing. Cyclic Voltammetry (CV) test was performed using a Gamry Reference 600 Potentiostat/Galvanostat/ZRA system from 0 to 1 V with scan rates varying from 5 to 100 mV s$^{-1}$. Galvanostatic charge/discharge tests were conducted on Arbin BT2000 battery tester from 0 to 1 V at different current densities from 0.1 A g$^{-1}$ to 2 A g$^{-1}$. The cycling performance of the cells was evaluated by repeating charging and discharging for 1,000 cycles at a current density of 0.5 A g$^{-1}$. The specific capacitance of a single electrode was calculated based on the following equation:

$$C = \frac{2i\Delta t}{m\Delta V}$$

(1)
where \( C \) is the specific capacitance of the electrode in farads per gram (F g\(^{-1}\)), \( i \) the discharge current in ampere (A), \( \Delta t \) the discharge time in seconds (s), \( m \) the mass of the single electrode in grams (g), and \( \Delta V \) the voltage window (0 to 1 V) in volts (V).

### 4.3 Results and Discussion

PAN/PMMA precursor fibers were synthesized via a lab-scale centrifugal spinning apparatus. Figure 4.1 shows the schematic of the centrifugal spinning device and the preparation of PAN/PMMA fibers and PCNFs. The major components of the centrifugal spinning device include a perforated Teflon spinneret residing in the center of the spinning platform, a motor beneath the spinneret to provide high-speed rotation, a speed controller connected to the motor to tune the rotational speed, and a series of fiber collectors installed radially in the outer perimeter of the spinning platform.

![Schematic of the centrifugal spinning device and the preparation of PAN/PMMA fibers and PCNFs.](image)

Figure 4.1 Schematic of the centrifugal spinning device and the preparation of PAN/PMMA precursor fibers and PCNFs.
To prepare PAN/PMMA precursor fibers, PAN/PMMA solutions were loaded into the spinneret and the rotation was initiated. As the rotational speed increased to a critical value, where the centrifugal force overcame the solution surface tension, liquid jets were formed at the nozzles, stretched in the flight of the circular trajectory accompanied by solvent evaporation, and deposited on the collectors in the form of fiber mat. This simple centrifugal spinning process is capable of producing tens of grams of fibers per nozzle in an hour and can drastically improve the production rate compared to that of conventional electrospinning method.\textsuperscript{315}

The as-spun PAN/PMMA precursor fibers were characterized with FTIR to confirm their different relative ratios between the two components. Figure 4.2 presents the FTIR spectra of the PAN/PMMA precursor fibers in the spectral range of 4000 to 500 cm\textsuperscript{-1}. The precursor fibers with PAN/PMMA weight ratio of 9/1 demonstrate comparable intensities between the peaks at 1732 cm\textsuperscript{-1}, the characteristic peak for acrylate carboxyl group, and the peak at 2240 cm\textsuperscript{-1}, the characteristic peak for nitrile group.\textsuperscript{316,317} As the PAN/PMMA weight ratios increases to 7/3 and 5/5, the intensities of the peaks representing the acrylate carboxyl group becomes higher with respect to those of the peaks representing the nitrile groups, confirming that more PMMA was adopted into the binary system.
The intensities of the absorbance are normalized with respect to the absorption of nitrile group.

The morphology of precursor fibers with different PAN/PMMA weight ratios was investigated using SEM. Figure 4.3 displays SEM images and fiber diameter distributions of precursor fibers with PAN/PMMA weight ratios of 9/1, 7/3 and 5/5. All three precursor fibers show smooth surface without apparent bead formation. The average fiber diameter of the precursor fibers with PAN/PMMA weight ratio of 9/1 is $6.00 \times 10^3$ nm; as the PMMA relative content increases, the precursor fibers with PAN/PMMA weight ratios of 7/3 and 5/5 show remarkably reduced fiber diameters of $2.32 \times 10^3$ nm and $8.80 \times 10^2$ nm, respectively. The dramatic reduction in fiber diameter is mainly caused by the increasing relative amount of the
low-molecular weight component, PMMA, which contributes to lower solution viscosity and less polymer chain entanglement during centrifugal spinning, thereby leading to thinner fibers.

Figure 4.3 SEM images and fiber diameter distributions of precursor fibers with different PAN/PMMA weight ratios: 9/1 (a, b), 7/3 (c, d) and 5/5 (e, f).
PCNFs were prepared by the heat-treatment of PAN/PMMA precursor fibers. Recently, Kim et al. developed a procedure to fabricate PCNFs by utilizing the micro phase separation phenomenon in the PAN/PMMA binary system. In this procedure, PAN and PMMA were firstly mixed in DMF to form a stable solution and then underwent electrospinning and subsequent heat-treatment to obtain PCNFs. Due to the different surface tensions between the two polymer components, the PAN/PMMA polymer blends constructed an islands-in-sea architecture during electrospinning, where the low surface tension component (PAN) forms the continuous phase in the solution, while the high surface tension constituent (PMMA) occupies the discontinuous phase. PMMA was chosen in the study since it has low thermal stability and can be completely decomposed to generate the porous structure during carbonization process.

In this work, electrospinning technique was substituted by centrifugal spinning to build PAN/PMMA precursor fibers with the islands-in-sea structure. The preparation of PCNFs from PAN/PMMA precursors was demonstrated in Figure 4.1. During centrifugal spinning, PMMA formed discrete nanoparticles within the continuous PAN phase at the nozzle of the spinneret, and due to the stretching and elongation from the centrifugal force, the PMMA nanoparticles transformed to nanowires inside or on the surface of the PAN skeleton fibers. The PAN/PMMA precursor fibers were then stabilized in air atmosphere, where PMMA nanowires started to be partially decomposed. However, the complete elimination of PMMA nanowires was completed in the carbonization process, resulting in formation of a porous structure.
The morphology of the resultant PCNFs was investigated using SEM (both plane-view and cross-sectional view) and TEM. Since PAN/PMMA weight ratios and carbonization temperatures directly influence the specific surface area and conductivity of PCNFs, the morphology of PCNFs prepared from various PAN/PMMA weight ratios at the same carbonization temperature (900 °C) was examined and showed in Figure 4.4, respectively. The PCNFs shown in Figures 4.4 and 4.5 are all long fibers without bead formation. The PCNFs carbonized at 900 °C from the PAN/PMMA ratios of 9/1, 7/3, and 5/5 exhibit average fiber diameters of $1.73 \times 10^3$ nm, $7.50 \times 10^2$ nm, and $5.30 \times 10^2$ nm, respectively, indicating significant diameter shrinkage compared to their precursor fibers ($6.00 \times 10^3$ nm, $2.32 \times 10^3$ nm, and $8.80 \times 10^2$ nm, respectively). The morphology of PCNFs prepared from precursor fibers with PAN/PMMA weight ratio of 7/3 at different carbonization temperatures of 700 °C, 800 °C and 900 °C was shown in Figure 4.5. At a carbonization temperature of 700 °C, the average fiber diameter is $1.50 \times 10^3$ nm, however, as the carbonization temperature rises to 800 °C and 900 °C, smaller fiber diameters of $9.50 \times 10^2$ nm and $7.50 \times 10^2$ nm, respectively, are achieved.
Figure 4.4 SEM images and fiber diameter distributions of PCNFs prepared at 900 °C from precursor fibers with different PAN/PMMA weight ratios: 9/1 (a, b), 7/3 (c, d) and 5/5 (e, f).
Figure 4.5 SEM images and fiber diameter distributions of PCNFs prepared from precursor fibers with PAN/PMMA weight ratio of 7/3 at different carbonization temperatures: 700 °C (a, b), 800 °C (c, d) and 900 °C (e, f).
In order to determine the successful formation of porous structures in the PCNFs, cross-sectional SEM and TEM were implemented. Figure 4.6 presents the plane-viewed SEM, cross-sectional SEM, and TEM images of PCNFs fabricated from precursor fibers with PAN/PMMA weight ratio of 7/3 at carbonization temperature of 900 °C. The low-magnification, plane-viewed SEM image shows long fibers without much detailed surface or internal characteristics (Figure 4.6a), while the cross-sectional SEM image reveals the development of large quantities of surface roughness and internal pores (Figure 4.6b). The TEM image, as complimentary evidence in addition to the cross-sectional SEM image, further demonstrates that a multi-channel porous architecture is successfully created for PCNFs (Figure 4.6c).

Figure 4.6 Plane-viewed SEM (a), cross-sectional SEM (b), and TEM (c) images of PCNFs prepared from precursor fibers with PAN/PMMA weight ratio of 7/3 at carbonization temperature of 900 °C.

Surface parameters of PCNFs were obtained using the BET method. Table 4.1 reports the surface parameters including specific surface area and total pore volume of PCNFs prepared from different precursor fibers and carbonization temperatures. When the PAN/PMMA weight
ratio is fixed at 7/3, the specific surface area increases from 405 m$^2$ g$^{-1}$ to 444 m$^2$ g$^{-1}$ as the carbonization temperature increases from 700 °C to 900 °C; simultaneously, the total pore volume also increases from 0.171 cm$^3$ g$^{-1}$ to 0.310 cm$^3$ g$^{-1}$. When the carbonization temperature is settled at 900 °C, PCNFs prepared from precursor fibers with PAN/PMMA weight ratio of 7/3 show the largest specific surface area of 444 m$^2$ g$^{-1}$ with a total pore volume of 0.310 cm$^3$ g$^{-1}$.

Table 4.1 Surface parameters of PCNFs made from precursor fibers with various PAN/PMMA ratios at different carbonization temperatures.

<table>
<thead>
<tr>
<th>PAN/PMMA Weight Ratio</th>
<th>Carbonization Temperature / °C</th>
<th>Specific Surface Area / m$^2$ g$^{-1}$</th>
<th>Total Pore Volume / cm$^3$ g$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>700</td>
<td>405 ± 2</td>
<td>0.171</td>
</tr>
<tr>
<td>7/3</td>
<td>800</td>
<td>418 ± 2</td>
<td>0.176</td>
</tr>
<tr>
<td></td>
<td>900</td>
<td>444 ± 8</td>
<td>0.310</td>
</tr>
<tr>
<td>9/1</td>
<td>214 ± 19</td>
<td></td>
<td>0.148</td>
</tr>
<tr>
<td>7/3</td>
<td>900</td>
<td>444 ± 8</td>
<td>0.310</td>
</tr>
<tr>
<td>5/5</td>
<td>308 ± 27</td>
<td></td>
<td>0.212</td>
</tr>
</tbody>
</table>

To evaluate the electrochemical performance of the PCNFs, symmetrical cells were assembled using 6 M KOH aqueous electrolyte and glass fiber separator. Figure 4.7 illustrates the cyclic voltammograms of PCNFs prepared from precursor fibers with different PAN/PMMA weight ratios and various carbonization temperatures. The CV measurements
were carried out over the voltage window of 0 to 1V at scan rates varying from 5 mV s\(^{-1}\) to 100 mV s\(^{-1}\). All six PCNFs exhibit distorted, near-rectangular charge/discharge characteristics. Figures 4.7a, b and c compare the CV curves of PCNFs fabricated from precursor fibers (PAN/PMMA ratio = 7/3) at various carbonization temperatures of 700 °C, 800 °C, and 900 °C. PCNFs carbonized at 900 °C presents the least distortion with the curve shape closest to ideal rectangle, which represents the typical electric double-layer capacitance behavior. Moreover, when the carbonization temperature rises from 700 °C to 900 °C, the area of the CV curves at a fixed scan rate becomes larger, suggesting larger specific capacitance. Figures 4.7d, e, f demonstrate the CV curves of PCNFs fabricated from precursor fibers with PAN/PMMA weight ratios of 9/1, 7/3, and 5/5 at carbonization temperature of 900 °C. These PCNF materials all yield near-rectangular shapes at both slow and fast scan rates, indicating fast charge/discharge behavior and low electrochemical resistance. Among the three samples, PCNFs prepared from precursor fibers with PAN/PMMA weight ratio of 9/1 show the smallest CV area due to its lowest specific surface area as seen in Table 4.1, while the 7/3 and 5/5 samples demonstrate comparable CV areas, indicating that they have comparable specific capacitance.
Figure 4.7 Cyclic voltammograms of PCNFs prepared from precursor fibers with PAN/PMMA weight ratio of 7/3 at various carbonization temperatures of 700 °C (a), 800 °C (b), and 900 °C (c); cyclic voltammograms of PCNFs prepared from precursor fibers with PAN/PMMA weight ratios of 9/1 (d), 7/3 (e), and 5/5 (f) at carbonization temperature of 900 °C. The scan rate varied from 5 mV s\(^{-1}\) to 100 mV s\(^{-1}\).

To assess the specific capacitance of the PCNFs, galvanostatic charge/discharge tests were conducted. The cells were charged and discharged in a voltage range of 0 to 1V at current densities from 0.1 A g\(^{-1}\) to 2 A g\(^{-1}\). Firstly, the discharge curves of PCNFs prepared from precursor fibers with PAN/PMMA weight ratios of 7/3 at different carbonization temperatures are compared in Figures 4.8a, b and c. The discharge curves display nearly triangular shapes, representing fairly ideal EDLC behavior. However, PCNFs prepared at 700 °C shows significant IR drop at the beginning of discharge. The specific capacitances of the PCNFs were calculated according to Equation 1 based on the mass of a single electrode. PCNFs prepared...
from precursor fibers with PAN/PMMA weight ratio of 7/3 at 700 °C, 800 °C and 900 °C exhibit specific capacitances of 113 F g\(^{-1}\), 140 F g\(^{-1}\) and 141 F g\(^{-1}\), respectively, at a current density of 0.1 A g\(^{-1}\). The specific capacitance increases significantly as the carbonization temperature increases from 700 °C to 800 °C, mainly due to the evolution of the chemical structure occurred during the carbonization process. In general, as the carbonization temperature increases, the N content decreases and the C content increases.\(^{319}\) Such content changes of N and C elements are mainly caused by the growth of aromatic structure and the removal of nitrogen-containing functional groups during carbonization. The high-temperature treatment facilitates graphitization via aromatic growth and results in enhanced electrical conductivity.\(^{319}\) It has been reported that significant removal of heteroatoms of nitrogen generally takes place at around 800 ºC.\(^{320}\) As a result, PCNFs prepared at 800 ºC exhibit significantly improved electrochemical performance than PCNFs prepared at 700 ºC. After 800 ºC, the structural change is largely completed, and hence the capacitance remains relatively constant even when the carbonization temperature further increases to 900 ºC.

From Figures 4.8a, b and c, it is also seen that the specific capacitance decreases with increase in current density: the specific capacitances of PCNFs prepared at 700 ºC, 800 ºC and 900 ºC at a current density of 2 A g\(^{-1}\) decrease to 0.1 F g\(^{-1}\), 97 F g\(^{-1}\) and 100 F g\(^{-1}\), respectively. The PCNFs carbonized at 700 ºC completely lose its capacitive behavior at 2 A g\(^{-1}\) and such reduced specific capacitance is primarily rooted in the diffusion limitation between the electrolyte and the carbon electrode material.\(^{321}\) The discharge curves of PCNFs fabricated from precursor fibers with different PAN/PMMA weight ratios at carbonization temperature
of 900 °C are given in Figures 4.8d, e and f. The discharge curves are nearly linear with small IR drop at the onset of discharge. All three PCNFs carbonized at 900 °C demonstrate good capacitive performance in accordance with those found in their associated CV curves (Figures 4.7d, e and f). The specific capacitances of PCNFs obtained from precursor fibers with PAN/PMMA weight ratios of 9/1, 7/3 and 5/5 at 0.1 A g⁻¹ are 125 F g⁻¹, 141 F g⁻¹ and 144 F g⁻¹, respectively. When the current density increases to 2 A g⁻¹, these three PCNFs maintain relatively high specific capacitances of 86 F g⁻¹, 100 F g⁻¹ and 106 F g⁻¹, respectively. Although the PCNFs carbonized at 900 °C show good electric conductivity, the 9/1 sample exhibits the lowest specific capacitance among the three because of its small specific surface area of 214 m² g⁻¹. The PCNFs prepared from precursor fibers with PAN/PMMA weight ratios of 7/3 and 5/5 show comparable specific capacitance, because the former possesses larger specific surface area of 444 m² g⁻¹, while the latter exhibits better conductivity, and these two factors are both important in determining the capacitance of EDLC electrode materials.
Figure 4.8 Discharge curves of PCNFs prepared from precursor fibers with PAN/PMMA weight ratio of 7/3 at various carbonization temperatures of 700 °C (a), 800 °C (b), and 900 °C (c); discharge curves of PCNFs prepared from precursor fibers with PAN/PMMA weight ratios of 9/1 (d), 7/3 (e), and 5/5 (f) at carbonization temperature of 900 °C. The current density varied from 0.1 A g\(^{-1}\) to 2 A g\(^{-1}\).

The rate capability of the PCNFs is shown in Figures 4.9a and c while the normalized rate capability curves are given in Figures 4.9b and d. The specific capacitance of the PCNFs decreases with increase in current density. For PCNFs prepared from precursor fibers with PAN/PMMA weight ratio of 7/3 at 700 °C, 800 °C and 900 °C, the capacitance retention percentages at 2 A g\(^{-1}\) with respect to those at 0.1 A g\(^{-1}\) are 0.1%, 69% and 71%, respectively. For PCNFs synthesized from precursor fibers with PAN/PMMA weight ratios of 9/1, 7/3 and 5/5 at 900 °C, the capacitance retention percentages at 2 A g\(^{-1}\) compared to those at 0.1 A g\(^{-1}\) are 69%, 71% and 74%, respectively.
Figure 4.9 Rate capabilities and normalized rate capabilities of PCNFs prepared from precursor fibers with PAN/PMMA weight ratio of 7/3 at different carbonization temperatures (a, b); rate capabilities and normalized rate capabilities of PCNFs prepared from precursor fibers with various PAN/PMMA weight ratios at carbonization temperature of 900 °C (c, d).

EDLCs are usually used in ultrafast charge/discharge application for a considerably long time, and hence the cycling performance of EDLC electrode materials is important. Figure 4.10 plots the cycling performance of PCNFs fabricated from precursor fibers with different PAN/PMMA weight ratios at various carbonization temperatures. The cells were galvanostatically charged and discharged at a current density of 0.5 A g⁻¹ for 1,000 cycles.
Most of the PCNFs show some capacitance loss for the initial 100 cycles, and then their capacitance becomes stable for the following cycles. Stable capacitance retentions are observed for the PCNFs: 61%, 90% and 86% of the initial capacitances are retained for PCNFs prepared from precursor fibers (PAN/PMMA weight ratio = 7/3) at 700 °C, 800 °C and 900 °C, respectively; 79%, 86% and 77% are maintained for PCNFs prepared from precursor fibers with PAN/PMMA weight ratios of 9/1, 7/3 and 5/5 at 900 °C.

Figure 4.10 Cycling performance of PCNFs prepared from precursor fibers with PAN/PMMA weight ratio of 7/3 at various carbonization temperatures (a); cycling performance of PCNFs prepared from precursor fibers with different PAN/PMMA weight ratios at carbonization temperature of 900 °C (b). The current density used was 0.5 A g⁻¹.

4.4 Conclusions

PCNFs were prepared by centrifugal spinning of PAN/PMMA precursor solutions followed by two-step heat treatment and were used as binder-free electrode materials for EDLCs. The centrifugal spinning approach produced smooth and bead-free PAN/PMMA
fibers. An islands-in-sea architecture was obtained during the centrifugal spinning process due to the different surface tensions between the two components, in which PMMA, the high surface tension polymer occupied the discontinuous phase and formed nanowires on the surface of and inside the PAN phase. Upon thermal treatment, the PMMA component was completely eliminated from the system and the carbonized product was PCNFs. Electric conductivity and specific surface area are two dominant factors that determine the capacitive behavior of EDLC electrode materials, and their influences on the electrochemical performance were investigated by varying the relative weight ratios between PAN/PMMA, and the carbonization temperatures. The cyclic voltammograms and galvanostatic charge/discharge curves display near-rectangular and near-linear shapes, respectively, indicating good EDLC behavior. Among all PCNFs studied, those prepared from precursor fibers with PAN/PMMA weight ratio of 7/3 at 900 °C showed the highest specific capacitance of 144 F g⁻¹ at 0.1 A g⁻¹ with a rate capability of 74 % from current density of 0.1 A g⁻¹ to 2 A g⁻¹. PCNFs also demonstrated stable cycling performance and the highest cycling stability of 90 % over 1,000 cycles was accomplished by those prepared from precursor fibers with PAN/PMMA weight ratio of 7/3 at 800 °C. The results demonstrate that the PCNFs offer promising potential for EDLC electrode applications and centrifugal spinning offers a simple, cost-effective strategy to produce PCNFs.
CHAPTER 5. Centrifugally-Spun SnO$_2$ Microfibers Composed of Interconnected Nanoparticles as Anode for Sodium-Ion Batteries

Abstract

SnO$_2$ microfibers were synthesized by centrifugal spinning technology and were evaluated as the anode in sodium-ion batteries. The as-prepared SnO$_2$ microfibers are composed of interconnected nanoparticles with small interparticle opening. The 1-dimensiona fibrous morphology, fine particle size and open pore structure together result in reduced electrochemical impedance and enhanced electrochemical performance. The highest capacity achieved is 567 mAh g$^{-1}$ at 20 mA g$^{-1}$. At a much higher current density of 640 mA g$^{-1}$, the microfiber electrode still retains a high capacity of 158 mAh g$^{-1}$ after 50 cycles. The SnO$_2$ microfibers also demonstrate good rate performance in a current range of 20 – 640 mA g$^{-1}$. The results demonstrate that SnO$_2$ microfibers are potential anode material candidate for sodium-ion batteries and centrifugal spinning offers a feasible solution of large-scale production of fibrous electrode materials.

Keywords: Anode materials, centrifugal spinning, intercalations, sodium-ion batteries, tin dioxide microfibers
5.1 Introduction

Since the debut of Sony’s very first commercialized lithium-ion batteries (LIBs) in 1991, LIBs have vastly penetrated into human’s daily life, becoming a successful and sophisticated energy storage device.\textsuperscript{92,93} Owning to their large energy density, high output voltage, and long cycle life, LIBs have been recognized as a prime candidate to power portable electronics and furthermore, next-generation electric vehicles.\textsuperscript{36,89,93,95,322–324} Although LIBs offer superior electrochemical performance and are currently one of the most attractive energy storage systems, debates recently surfaced regarding of the limited reserve size and geographical constraint on Li resources.\textsuperscript{88,95} In contrast, Na ranks as the sixth most abundant element in the Earth crust, and is also in principle unlimited because of its availability in seawater and salt deposits.\textsuperscript{92,96} Due to Na’s low cost, wide availability and Li-like properties, the counterpart energy storage device for LIBs, sodium-ion batteries (SIBs), provides an attractive alternative chemistry and can potentially meet the requirements of electric grids for large-scale, stationary energy storage purpose.

To realize the practical application of SIBs, one crucial issue is to develop electrode materials with high Na storage capability and stable cycling performance. Many cathode candidate materials have been studied for SIBs, such as transition metal oxides (\(V_2O_5\), \(MnO_2\), \(Na_xMO_2\), where \(M = Mn\), \(Ni\), \(Co\), \(Fe\), or the combinations of these elements)\textsuperscript{160,167,178,325,326}, phosphates (\(NaFePO_4\), \(Na_3V_2(PO_4)_3\))\textsuperscript{188,327} and fluorophosphate (\(NaVPO_4F\), \(Na_2FePO_4F\))\textsuperscript{189,190}. Recently, many material candidates have been reported as SIB anodes. It should be noted that graphite, the most commercialized anode material in LIBs, was found to be incapable of intercalating Na to an appreciable extent in an electrochemically reversible fashion, providing
negligible capacity. On the contrary, many non-graphitic carbon materials have been demonstrated to be able to insert Na, including soft and hard carbon, carbon black, pitch-based carbon fibers, as well as petroleum cokes. However, the specific capacities of these materials are limited to below 300 mAh g\(^{-1}\). Alternative anode materials for SIBs include TiO\(_2\), Na\(_2\)Ti\(_3\)O\(_7\), Li\(_4\)Ti\(_5\)O\(_12\), and NaTi\(_2\)(PO\(_4\))\(_3\). These materials exhibit good cycling stability, however, their capacities are also below 300 mAh g\(^{-1}\). Recently, Na alloys (Sn, Sb, and SnSb) have become a group of attractive anode materials because of their high specific capacities. Similarly, the oxides for these alloys, for instance, SnO\(_2\), can react with Na and be reduced to Sn, and the resultant Sn can further alloy/de-alloy with Na. SnO\(_2\) has a low reaction potential for Na\(^+\) and a high theoretical capacity of 667 mAh g\(^{-1}\) in SIBs. Hence, SnO\(_2\) can be potentially used as a high-capacity anode for SIBs.

Recently, using SnO\(_2\) based materials as SIB anodes has been reported by several research groups. Su and Lu prepared pure SnO\(_2\) nanoparticles using the hydrothermal method and obtained specific capacities of over 500 mAh g\(^{-1}\) at 20 mA g\(^{-1}\) and 400 mAh g\(^{-1}\) at 50 mA g\(^{-1}\), respectively. Most other literature reports focused on the preparation of nanocomposites composed of SnO\(_2\) and conducting polymer (polyaniline) or carbonaceous materials including multi-wall carbon nanotube, graphene, and reduced graphene oxide. In these studies, high capacities with good capacity retentions were achieved due to the conductive nature and the buffering effect of the carbonaceous and conductive polymer components. For example, Su prepared a SnO\(_2\)/graphene nanocomposite and achieved specific capacity of over 500 mAh g\(^{-1}\) at 20 mA g\(^{-1}\) and 150 mAh g\(^{-1}\) at 640 mA g\(^{-1}\) with stable cycling performance for 100 cycles. The electrochemical performance obtained in these studies are
superior, however, these methods are usually complex. Moreover, it is important to investigate the electrochemical performance of solely SnO$_2$ without any carbonaceous materials so that the effect of adding these materials could be clearly understood. Herein, we incorporated a simple preparation method called centrifugal spinning, to prepare precursor fibers for SnO$_2$ microfiber anode. Centrifugal spinning is a simple but effective approach to fabricate large quantity of thin fibers in a very short time period, increasing the production rate by two orders of magnitude compared to traditional electrospinning. SnO$_2$ microfibers were then obtained by calcining the centrifugally-spun precursor fibers in air. The calcinated SnO$_2$ microfibers were composed of interconnected fine SnO$_2$ nanoparticles. The as-prepared SnO$_2$ microfibers exhibited a high discharge capacity of 567 mAh g$^{-1}$ at 20 mA g$^{-1}$. At a much larger current density of 640 mA g$^{-1}$, the SnO$_2$ microfibers still maintained a high discharge capacity of 158 mAh g$^{-1}$ after 50 charge-discharge cycles. The SnO$_2$ microfibers composed of interconnected nanoparticles also showed good rate capability in a wide current range of 20 - 640 mA g$^{-1}$. It is, therefore, demonstrated that centrifugal spinning is an effective route to produce fibrous electrode materials and centrifugally-spun SnO$_2$ microfibers are promising anode material candidate for SIBs.
5.2 Experimental

5.2.1 Material Synthesis

Polyacrylonitrile (PAN, Pfaltz & Bauer Inc., 150,000 g mol\textsuperscript{-1}), tin (II) chloride (SnCl\textsubscript{2}, 98 %, Sigma-Aldrich), N, N-dimethylformide (DMF, Sigma-Aldrich), Tin (IV) oxide (SnO\textsubscript{2}, 99.9%, Sigma-Aldrich) and alginic acid sodium salt (MP Biomedicals, LLC) were used as received.

To make SnCl\textsubscript{2}/PAN precursor solution, 13 wt. % of PAN powder was dissolved into the solvent DMF. After stirring the PAN/DMF solution for over 24 hours, SnCl\textsubscript{2} was added into the solution and stirred for additional 24 hours to obtain a homogeneous SnCl\textsubscript{2}/PAN precursor solution. The weight ratio of SnCl\textsubscript{2} with respect to PAN was 40 %. The SnCl\textsubscript{2}/PAN precursor fibers were prepared by using the centrifugal spinning method. During the process, the SnCl\textsubscript{2}/PAN precursor solution was fed into the spinneret, which had an inner diameter of 3 cm and eight 0.4 mm-diameter nozzles. Then, a 4,000 rpm rotational speed was applied to generate SnCl\textsubscript{2}/PAN precursor fibers. Multiple aluminum rods were installed 10 cm away radially from the spinneret as the fiber collectors. SnO\textsubscript{2} microfibers were synthesized by calcinating the SnCl\textsubscript{2}/PAN precursor fibers at 500 °C in air for 3 hours with a 2 °C min\textsuperscript{-1} heating rate. For comparison, SnO\textsubscript{2} particles were prepared by drying the precursor solution in an oven overnight, followed by calcination in air with the same heating protocol to the microfibers.
5.2.2 Structural Analysis

Morphological analyses of SnO\textsubscript{2} microfibers, SnO\textsubscript{2} particles and commercial SnO\textsubscript{2} were evaluated by field emission scanning electron microscope (FESEM, JEOL 6400F SEM at 5 kV). The porous structure and elemental distribution were obtained by scanning transmission electron microscope (STEM, aberration corrected STEM-FEI Titan 80-300). The crystal structures of SnO\textsubscript{2} microfibers, SnO\textsubscript{2} particles and commercial SnO\textsubscript{2} were investigated by X-ray diffraction (XRD, Rigaku Smartlab, Cu K\textalpha, \(\lambda = 1.544 \text{ Å}\)). The XRD experiments were performed with a step size of 0.02° and 2\(\theta\) range of 10-90°. The surface parameters of the samples were obtained by TriStar II 3020 instrument (V1.04, Micromeritics Instrument Corporation).

5.2.3 Electrochemical Evaluation

CR2032-type coin cells were assembled to assess the electrochemical performance of the SnO\textsubscript{2} microfibers, SnO\textsubscript{2} particles and commercial SnO\textsubscript{2}. To prepare the working electrodes, the active material (70 wt. %, SnO\textsubscript{2} microfibers, SnO\textsubscript{2} particles, or commercial SnO\textsubscript{2}) was mixed with alginic acid sodium salt (10 wt. %) dissolved in deionized water as the polymer binder and carbon black (20 wt. %) as the conductive additive. The well-mixed slurries were then casted onto copper foil, which was used as the current collector, and dried in a vacuum oven at a temperature over 100 °C for 24 hours. The working electrodes were cut from the as-prepared electrode sheets using a puncher and the diameter of the electrodes was 1/2". Na foil cut from dry Na stick was used as the counter electrode. Glass fiber separator (Whatman GF/D glass microfiber filters) was used to partition the working electrodes from the Na counter
electrode. The electrolyte used in this study composed of 1 M NaClO$_4$ salt in a mixed solvent of ethylene carbonate (EC) and dimethyl carbonate (DMC) by a volume ratio of 1:1. The cells were rested for over one day before any electrochemical tests.

Cyclic voltammetry (CV) test was conducted using a Gamry reference 600 Potentiostat/Galvanostat/ZRA system from 2.5 to 0.01 V with a scan rate of 0.1 mV s$^{-1}$. Galvanostatic charge/discharge tests were carried out using an Arbin BT2000 battery cycler. The voltage window in the present study was from 2.5 to 0.01 V vs Na$^+$/Na. The current densities varied from 20 to 640 mA g$^{-1}$. To assess the cycling stability of SnO$_2$ microfibers, SnO$_2$ particles and commercial SnO$_2$, the assemble cells were repeatedly charged and discharged for 50 cycles at 20 and 640 mA g$^{-1}$. Rate capabilities were evaluated at current densities varying from 20 to 640 mA g$^{-1}$.

5.3 Results and Discussion

SnCl$_2$/PAN precursor fibers were fabricated using a lab-scale centrifugal spinning process and the major components of the system are sketched in Figure 5.1a. The centrifugal spinning system is mainly composed of a spinneret connected with a motor and the rotational speed of the motor can be adjusted by a DC motor controller. Prior to centrifugal spinning, SnCl$_2$/PAN precursor solution was loaded into the top opening of the spinneret. High-speed rotation was then applied and when the rotational speed reached a critical point, where the surface tension of the solution was overcome by the centrifugal force, liquid jets were formed at the fine nozzles around the spinneret. The liquid jets were then stretched during the circular trajectory movement, while the solvent evaporated. Eventually, precursor fibers were collected on the
aluminum rods, which were settled at a 10 cm distance to the spinneret. Two leather pieces were installed with the spinneret to provide lifting air, helping fibers be collected in the upper region of the centrifugal spinning platform, producing a freestanding fibrous mat that was easy to be removed. Centrifugal spinning technology enables rapid fiber fabrication process: compared with other spinning methods such as electrospinning, this spinning method can generate fibers weighed tens of grams per nozzle in one hour, which dramatically increases the production rate and can potentially meet industrial demand of mass production for micro/nanofibers. Figure 5.1b demonstrates schematically the SnCl$_2$/PAN precursor fibers as-prepared by the centrifugal spinning process. In this work, the SnCl$_2$/PAN precursor fibers were further calcinated at 500 °C in air for 3 hours to produce the SnO$_2$ microfibers comprised of interconnected nanoparticles, as shown in Figure 5.1c.

Figure 5.1 Schematic illustration of (a) centrifugal spinning setup, (b) a centrifugally-spun SnCl$_2$/PAN precursor fiber, and (c) a SnO$_2$ microfiber composed of interconnected nanoparticles.
Figure 5.2 depicts the XRD patterns of SnO$_2$ microfibers, SnO$_2$ particles and commercial SnO$_2$. The patterns for all the three samples show characteristic diffraction peaks of SnO$_2$ at 2-theta angles of 26.6°, 33.9°, 37.9°, 51.8°, 54.8°, 61.9°, 64.7°, 65.9°, and 78.7°, which correspond to the (1 1 0), (1 0 1), (2 0 0), (2 1 1), (2 2 0), (3 1 0), (1 1 2), (3 0 1), and (3 2 1) planes of crystalized SnO$_2$ (PDF#41-1445), respectively. No impurities can be found for both SnO$_2$ microfibers and SnO$_2$ particles, indicating that the calcinating process of SnCl$_2$/PAN precursor in air at 500 °C is able to completely eliminate the polymer components and ensure the fully oxidation of Sn precursor to phase-pure SnO$_2$ microfibers or particles.

Figure 5.2 X-ray diffraction patterns of SnO$_2$ microfibers (a), SnO$_2$ particles (b), commercial SnO$_2$ (c) and SnO$_2$ (PDF#41-1445) (d).
The morphology of SnO$_2$ microfibers, SnO$_2$ particles and commercial SnO$_2$ was examined by SEM. Figure 5.3 displays the SEM images of SnO$_2$ particles and commercial SnO$_2$ at different magnifications. It is seen from Figure 5.3a that the SnO$_2$ particles generated by directly calcinating SnCl$_2$/PAN precursor exhibit very large particle size averaging 20 µm. Such large particle size is mainly due to the self-aggregation tendency of nanoparticles, which have high surface energy, especially at high temperatures. During the calcinating process, fine SnO$_2$ nanoparticles were firstly formed with an average particle size of 150 nm (Figures 5.3c). However, as the SnO$_2$ nanoparticles were kept at the calcination temperature for 3 hours, fine SnO$_2$ nanoparticles began to aggregate, merging into large plates composed of densely packed structure. It is seen from Figure 5.3 b and d that the commercial SnO$_2$ also show particle aggregation and the primary particle size falls in the range of 80 to 300 nm. The aggregation of nanoparticles limits the contact between the electrode materials and the conductive additives and electrolyte. Consequently, such particle aggregation usually results in declined battery performance.
Figures 5.3 SEM images of SnO$_2$ particles (a, c) and commercial SnO$_2$ (b, d) at different magnifications.

Figures 5.4a and b illustrate the SEM images of precursor fibers. It is seen that the SnCl$_2$/PAN precursor fibers exhibit smooth surface, and they assemble to form a continuous fibrous mat with a 3D interlaced structure. The average precursor fiber diameter is 5 µm. After the calcinating process, the as-spun SnCl$_2$/PAN precursor fibers were converted to SnO$_2$ microfibers, accompanied by a significant fiber diameter shrinkage from 5 µm to 2 µm, as shown in Figures 5.4c and d. A closer examination of the as-prepared SnO$_2$ microfibers from
the enlarged side-view and the cross-sectional view is shown in Figures 5.4e and f, respectively. The SnO$_2$ microfibers are composed of numerous fine, interconnected SnO$_2$ nanoparticles with a particle size of about 10 nm. Moreover, small voids or pores are formed between the interconnected nanoparticles during the formation of SnO$_2$ microfibers, and such open space can allow active nanoparticles to expand during charge/discharge without falling off the microfiber structure, which could potentially lead to an improved cycling performance. The 1D architecture of the SnO$_2$ microfibers not only reduces the size of the electrode materials, but also effectively mitigates particle self-aggregation. In addition, the fibrous structure could also facilitate enhanced contact between the electrolyte and the electrode material, which could contribute to improved rate performance.
Figure 5.4 SEM images of SnCl₂/PAN precursor fibers (a, b), SnO₂ microfibers (c, d), and enlarged side view (e) and cross-sectional view (f) of a SnO₂ microfiber.
The surface parameters of SnO₂ microfibers, SnO₂ particles and commercial SnO₂, including surface area, total pore volume and average pore width are given in Table 1. Table 1 demonstrates that the BET surface areas of the SnO₂ microfibers, SnO₂ particles and commercial SnO₂ are 56.2, 12.3 and 7.25 m² g⁻¹, respectively. The enlarged specific surface area of SnO₂ microfibers indicates the existence of voids and pores between the interconnected nanoparticles. The total pore volumes of SnO₂ microfibers, SnO₂ particles and commercial SnO₂ are 0.271, 0.0393 and 0.0296 cm³ g⁻¹, respectively, while their average pore widths are 16.0, 10.2 and 16.3 nm, respectively.

Table 5.1 Surface parameters of SnO₂ microfibers, SnO₂ particles and commercial SnO₂.

<table>
<thead>
<tr>
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<th>BET surface area (m² g⁻¹)</th>
<th>Total pore volume (cm³ g⁻¹)</th>
<th>Average pore width (nm)</th>
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</thead>
<tbody>
<tr>
<td>SnO₂ microfibers</td>
<td>56.2</td>
<td>0.271</td>
<td>16.0</td>
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<tr>
<td>SnO₂ particles</td>
<td>12.3</td>
<td>0.0393</td>
<td>10.2</td>
</tr>
<tr>
<td>Commercial SnO₂</td>
<td>7.25</td>
<td>0.0296</td>
<td>16.3</td>
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The fiber structure was further examined by STEM with EDX to investigate the porous nature and elemental distribution. Figures 5.5a and b show TEM image and STEM image, respectively, of a piece of an as-prepared SnO₂ microfiber. It is seen from these images that small pores can be observed although the SnO₂ primary particles appeared to be closely packed. EDX elemental distributions of Sn-O, Sn and O are given in Figures 5.5c, d and e, respectively. The EDX elemental mappings suggest that Sn and O are uniformly distributed along the SnO₂ microfiber.
Figure 5.5 TEM image (a) and corresponding STEM image (b) of a piece of SnO$_2$ microfiber with elemental mappings of Sn-O (c), Sn (d), and O (e).

To evaluate the electrochemical performance of SnO$_2$ microfibers, SnO$_2$ particles and commercial SnO$_2$, CR2032 coin-type half cells were assembled in Ar-filled glove box by using Na as the counter electrode. The electrochemical reactions of the three SnO$_2$ samples with Na were studied with CV in a voltage window of 2.5 V to 0.01 V with a scan rate of 0.1 mV s$^{-1}$ for five cycles, as shown in Figure 5.6. In the first cathodic scan, all curves for SnO$_2$ microfibers, SnO$_2$ particles and commercial SnO$_2$ show large differences from those obtained in the second cathodic scan, respectively, in the voltage window of 1 V to 0.01 V. This irreversibility between the first and second cathodic scans is mainly associated with the SEI
formation and the irreversible reactions between SnO$_2$ and Na$^+$ to form Na$_x$Sn. From the first anodic scan, major oxidation peaks are identified at 0.25 V and 1 V, which can be ascribed to reversible de-alloying of Na$_x$Sn. In the second cathodic scan, all three samples show a broad reduction peak from 1.0 V to 0.01 V, representing the reversible alloying process between Na$^+$ and Sn. The second and third cathodic scans and anodic scans show decent repeatability, respectively, suggesting good electrochemical reversibility of the SnO$_2$ microfibers, SnO$_2$ particles and commercial SnO$_2$. However, it is seen that for the SnO$_2$ microfibers, the oxidation peaks at 1.0 V exhibit increased intensities from the second to the fifth cycles, which is in coincidence with the specific discharge capacity changes observed in galvanostatic charge-discharge curves, as discussed below.
Figure 5.6 Cyclic voltammograms of SnO$_2$ microfibers (a), SnO$_2$ particles (b) and commercial SnO$_2$ (c) at a scan rate of 0.1 mV s$^{-1}$.

Galvanostatic charge-discharge tests were carried out within a voltage window of 2.5 V - 0.01 V to evaluate the electrochemical behaviors of the SnO$_2$ microfibers, SnO$_2$ particles and commercial SnO$_2$. Figure 5.7a-c represent the first five cycles of the charge-discharge profiles for SnO$_2$ microfibers, SnO$_2$ particles and commercial SnO$_2$ at a current density of 20 mA g$^{-1}$. The initial specific charge capacities for the microfibers, particles and commercial SnO$_2$ are 1352, 991 and 677 mAh g$^{-1}$, respectively. During the initial charge, a large irreversible charge plateau is noticed in all three curves, starting from about 1 V and continuing to 0.01 V. This observation agrees well with the initial irreversible cathodic peaks found in the cyclic
voltammograms (Figure 5.6). This large irreversible capacity loss is mainly contributed by the SEI film formation and the irreversible reaction between SnO$_2$ and Na$^+$ to form Na$_x$Sn. In the initial discharge curves, the SnO$_2$ microfibers, SnO$_2$ particles and commercial SnO$_2$ yield specific discharge capacities of 477, 238 and 244 mAh g$^{-1}$, respectively. The initial coulombic efficiencies for SnO$_2$ microfibers and SnO$_2$ particles are 35%, 24% and 36%, respectively. Similar to the CV results, the three samples show good reversibility from the second cycle, suggesting that the Na alloying and de-alloying reactions are highly reversible. The specific charge capacities from the second to the fifth cycles appear to be relatively constant, though, the specific discharge capacities for the SnO$_2$ microfibers shows an increase trend from 480 mAh g$^{-1}$ at the initial cycle to 550 mAh g$^{-1}$ at the fifth cycle. Figure 5.7d gives the cycling performance of the SnO$_2$ microfiber, SnO$_2$ particle and commercial SnO$_2$ electrodes for 30 cycles at 20 mA g$^{-1}$. The discharge capacity of the SnO$_2$ microfibers keeps increasing until the ninth cycle, achieving the highest capacity of 567 mAh g$^{-1}$. After repeated charge-discharge for 30 cycles, the specific discharge capacity of the SnO$_2$ microfiber electrode decays from 477 mAh g$^{-1}$ to 216 mAh g$^{-1}$, resulting in a capacity retention of 41%. On the contrary, the SnO$_2$ particle electrode and commercial SnO$_2$ electrode exhibit capacities of 158 and 229 mAh g$^{-1}$ after 30 cycles, corresponding to a capacity retention of 62% and 94%. Here, the capacity retentions are all based on the highest capacity value obtained for each sample. Although the particle and commercial SnO$_2$ electrodes possess higher capacity retentions, the fibrous electrode ends with a specific discharge capacity of 1.4 times of that for the particle electrode. It is seen from Figure 5.7d that the discharge capacity of the SnO$_2$ microfibers increases for about 10 cycles, then starts to decrease. The phenomenon of capacity increase in the initial
cycles has been reported by several researchers on SnO$_2$ based anodes.\textsuperscript{133,137,139,333–336} This capacity increase is believed to be an activation process and is considered to be due to the aggregation of SnO$_2$ nanoparticles.\textsuperscript{333,335,336} Because of the aggregation of SnO$_2$ nanoparticles, only the active material at the surface or outer layer of the aggregated particles can be accessed by the electrolyte and participate in the sodiation/desodiation reactions, resulting in low initial capacity.\textsuperscript{333,336} However, during the subsequent Na insertion/extraction cycles, the aggregated SnO$_2$ nanoparticles pulverize into smaller clusters due to the volume change, and as a result, more active material is exposed to the electrolyte and can be involved in the electrode reactions, which contribute to the increasing capacity.\textsuperscript{334,336} In the present study, the initial increase in the discharge capacity can be explained by the unique structure of the porous, fibrous electrode material, which is consisted of interconnected, fine SnO$_2$ nanoparticles. The interconnected SnO$_2$ nanoparticles in the SnO$_2$ microfibers firstly react with Na$^+$ to form Sn, then further alloy with Na$^+$ to form Na$_x$Sn, which leads to particle volume expansion; for the following Na de-alloy reaction, Na$^+$ deintercalates from the particles, forming metallic Sn nanoparticles and resulting in a volume shrinkage. During repeatedly Na alloying and de-alloying processes, fine nanoparticles fall off the SnO$_2$ microfiber electrode because of the volume change, which results in a capacity loss. On the other hand, more new surfaces that are originally unable to contact with the electrolyte, become exposed when particles fall off, activating more reaction sites. Although the exfoliation of the original surface active particles and the exposure of new surfaces are paradox to each other, the increase of discharge capacity in the initial cycles seems to suggest that the latter effect dominates in the first nine cycles.
After the tenth cycle, the discharge capacity begins to reduce when there is no more new surface to be exposed, and the exfoliation effect dominates the capacity change.

Figure 5.7 Galvanostatic charge-discharge curves of SnO$_2$ microfibers (a), SnO$_2$ particles (b) and commercial SnO$_2$ (c) at 20 mA g$^{-1}$; and cycling performance of the three samples at 20 mA g$^{-1}$ (d).
The electrochemical performance of the SnO$_2$ microfibers, SnO$_2$ particles and commercial SnO$_2$ was also evaluated at a much higher current density (640 mA g$^{-1}$) in the voltage window of 2.5 V – 0.01 V (Figure 5.7). The three electrodes all show similar charge-discharge profiles and plateaus as seen in the low current tests. All materials exhibit large irreversible charge capacities in the first cycle, and the SnO$_2$ microfibers also show discharge capacity increase in the first 25 cycles. The initial charge and discharge capacities for the fibrous electrode are 447 and 133 mAh g$^{-1}$, respectively, while the initial charge and discharge capacities for the particle electrode are only 66 and 34 mAh g$^{-1}$, respectively. As a comparison, the initial charge and discharge capacities of commercial SnO$_2$ sample are 59 and 33 mAh g$^{-1}$, respectively. After 50 charge-discharge cycles, the SnO$_2$ microfiber electrode maintains a discharge capacity of 158 mAh g$^{-1}$, corresponding to a capacity retention of 77%, while the discharge capacity and capacity retention for the SnO$_2$ particles at the 50$^{th}$ cycle are 36 mAh g$^{-1}$ and 92%, respectively. The commercial SnO$_2$ sample show a discharge capacity of 27 mAh g$^{-1}$, corresponding to a capacity retention of 82%. These results indicate that SnO$_2$ microfibers show significantly higher discharge capacity (4 times of that for the SnO$_2$ particles and commercial SnO$_2$) with good cycling stability at high current density.
Figure 5.8 Galvanostatic charge-discharge curves of SnO$_2$ microfibers (a), SnO$_2$ particles (b) and commercial SnO$_2$ (c) at 640 mA g$^{-1}$; and cycling performance of the three samples at 640 mA g$^{-1}$ (d).

To further understand the electrochemical behaviors of the SnO$_2$ microfibers, SnO$_2$ particles and commercial SnO$_2$, rate capability study was performed from 2.5 V to 0.01 V with a stressful current range between 20 mA g$^{-1}$ to 640 mA g$^{-1}$. Figure 5.9 illustrates the rate performance of the three samples. It is seen that at a current density of 20, 40, 80, 160, 320 and 640 mA g$^{-1}$, the specific discharge capacities for the SnO$_2$ microfibers are 550, 471, 346, 254, 165 and 91 mAh g$^{-1}$, respectively. The specific discharge capacities of the SnO$_2$ particles achieved at 20, 40, 80, 160, 320 and 640 mA g$^{-1}$ are 267, 224, 184, 142, 88, 44 mAh g$^{-1}$,
respectively. At 20, 40, 8, 160, 320 and 640 mA g\(^{-1}\), the commercial SnO\(_2\) show discharge capacities of 238, 262, 231, 174, 108, and 65 mAh g\(^{-1}\), respectively. At all current densities, the SnO\(_2\) microfibers exhibit significantly higher discharge capacities compared to those for the SnO\(_2\) particles and commercial SnO\(_2\). When the current density goes back to 20 mA g\(^{-1}\), the discharge capacities retained for the SnO\(_2\) microfibers, SnO\(_2\) particles and commercial SnO\(_2\) are 355, 222 and 289 mAh g\(^{-1}\), respectively. For SnO\(_2\) microfibers, the capacity obtained at 640 mA g\(^{-1}\) in the rate performance test is smaller than that achieved in the charge-discharge test. This is probably due to the polarization and the volume change of the electrode material during repeated cycling. It is observed that SnO\(_2\) microfibers show more severe capacity decay at low current densities. The slow charge-discharge process at low current densities allows the active material to fully expand and contract, resulting in more active particles falling off the electrode. In contrary, at a high current density, the electrode is given less time for volume change, therefore, a relatively higher capacity with better cycling stability can be obtained. Therefore, when SnO\(_2\) microfibers were firstly cycled at several low current densities and then moved to the high current density, the electrode exhibited lower capacity, as compared to the capacity obtained by directly cycling at the high current density. However, this is one possible explanation, and further investigation is needed to completely understanding this phenomenon.
Figure 5.9 Rate capabilities of SnO$_2$ microfibers, SnO$_2$ particles and commercial SnO$_2$ at various current densities from 20 mA g$^{-1}$ to 640 mA g$^{-1}$.

The galvanostatic charge-discharge results demonstrate that the unique structure of the SnO$_2$ microfibers apparently contributes to the superior electrochemical behaviors in contrast to the particle rival. The structural uniqueness of the as-prepared SnO$_2$ microfibers includes interconnected, fine primary nanoparticles, large quantities of small pores between the nanoparticles, as well as 1D fibrous morphology that is helpful in keeping small overall material size and preventing particle self-aggregation. All the above-mentioned structural characteristics give rise to sufficient interfacial contact between the electrolyte and the electrode materials and therefore result in smaller electrochemical impedance and enhanced electrochemical performance including higher specific capacity, better cycling performance at high current density, and decent rate capability.
5.4 Conclusions

SnO$_2$ microfibers were prepared by centrifugal spinning of the SnCl$_2$/PAN precursor, followed by calcination process. Compared to the large plate-like SnO$_2$ particles synthesized from the same precursor solution, the 1D SnO$_2$ microfibers comprised of interconnected nanoparticles with open pores between the nanoparticles have a smaller overall size. The unique morphological characteristics of the SnO$_2$ microfibers lead to better electrolyte-electrode contact and reduced electrochemical impedance. Therefore, the SnO$_2$ microfibers exhibit improved electrochemical performance including higher discharge capacity, better cycling performance at high current density, and improved rate capability. The highest discharge capacity obtained for the SnO$_2$ microfibers is 567 mAh g$^{-1}$ at a current density of 20 mA g$^{-1}$. The microfibrous electrode sustains a high discharge capacity of 158 mAh g$^{-1}$ with a good capacity retention of 77% after 50 charge-discharge cycles at a high current density of 640 mA g$^{-1}$. In a stressful current range of 20 – 640 mA g$^{-1}$, the SnO$_2$ microfibers also show a good rate performance. The present study demonstrates that the centrifugally-spun SnO$_2$ microfibers composed of interconnected nanoparticles are a promising anode material for SIBs. Furthermore, centrifugal spinning can potentially become an important method for the industry to produce fibrous electrode materials in mass production. However, the electrochemical performance of SnO$_2$ microfibers can be further improved by two possible approaches. Firstly, the centrifugal spinning process can be optimized in order to achieve fibrous SnO$_2$ materials with smaller fiber diameters, which can further enhance the electrode-electrolyte contact and reduce electrochemical impedance, resulting in improved electrochemical performance. Secondly, instead of preparing pure SnO$_2$ microfibers, SnO$_2$/carbon composite fibers can be
fabricated using proper carbon precursor with thermal treatment in inert gas atmosphere. The introduced carbon can potentially wrap the SnO$_2$ nanoparticles, provide a conductive network and help buffer the volume change during repeated cycling, thereby, leading to enhance electrochemical performance.
CHAPTER 6. Lithium-Substituted Sodium Layered Transition Metal Oxide Fibers as Cathodes for Sodium-Ion Batteries

Abstract

Na layered transition metal oxide fibers with/without partial Li substitution were prepared by the combination of a novel centrifugal spinning method and thermal treatment. Compared to the Li-free fibers, the Li-substituted Na layered transition metal oxide fiber cathodes exhibit higher capacities, better cycling stability and enhanced rate capability. Among the studied Li-substituted Na layered transition metal oxide fibers, Na$_{0.8}$Li$_{0.4}$Ni$_{0.15}$Mn$_{0.55}$Co$_{0.1}$O$_2$ demonstrates the best overall electrochemical performance. The highest capacity of 138 mAh g$^{-1}$ is achieved at 15 mA g$^{-1}$. As the current density increased to 75 and 300 mA g$^{-1}$, Na$_{0.8}$Li$_{0.4}$Ni$_{0.15}$Mn$_{0.55}$Co$_{0.1}$O$_2$ fibers still deliver high capacities of 113 and 94 mAh g$^{-1}$, respectively. This specific fiber composition also yields stable cycling performance and superior rate performance at various current densities between 15 to 600 mA g$^{-1}$. The results suggest that partial Li substitution is an effective method to stabilize the structure of the Na layered transition metal oxide cathodes and hence enhance the electrochemical performance. It is also demonstrated that centrifugal spinning can be an attractive technology for mass production of micro-sized, fibrous electrodes.

Keywords: Sodium-ion battery, cathode, centrifugal spinning, sodium layered transition metal oxide, lithium substitution
6.1 Introduction

Currently, lithium-ion batteries (LIBs) are considered as one of the most widespread energy storage devices due to their desirable features including high energy density, high operating potential, long cycle life, low self-discharge, and wide temperature window. LIBs have been extensively used as the power source for portable electronics, hybrid electric vehicles, and plug-in hybrid electric vehicles (PHEVs).\(^2,^{337}\) However, the reducing size of Li reserves, rising cost for Li supplies and arguably geographical limitation of Li resources together hinder the vast adoption of LIBs.\(^89,^{95,96}\) Consequently, the identification of alternative energy storage systems is presently required as a valid step leading to the development of economically sustainable rechargeable batteries. Among various potential candidates, sodium-ion batteries (SIBs) appear to be a feasible alternative to LIBs due to the substantially lower cost and higher abundance of Na, which ranks the 6\(^{th}\) most abundant element in the Earth crust. Na’s similar chemistry to Li and its advantageous cost-effectiveness make SIBs a promising energy storage device of choice for large-scale, grid storage applications.\(^96\)

Recently, many types of materials have been investigated as potential cathodes for SIBs, including transition metal fluorides (NaMF, \(M = \text{Fe, Mn, Ni, Ti, Co, V}\))\(^{338,339}\), phosphate (NaFePO\(_4\))\(^{187,188}\), fluorophosphates (NaVPO\(_4\)F, Na\(_2\)FePO\(_4\)F)\(^{189,190}\), and NASICON-type compounds (Na\(_3\)V\(_2\)(PO\(_4\))\(_3\))\(^{191,192}\). In addition to the above-mentioned materials, Na layered transition metal oxides have become a group of attractive cathode candidate for SIBs mainly because Na (1.06 Å) has a larger ionic radius than Li (0.76 Å) and the octahedral or prismatic coordination in this group of materials is generally preferable for Na.\(^{161,167}\) Na layered
transition metal oxides can be categorized in two major groups: O3 and P2 type, in which Na ions are accommodated respectively at octahedral and prismatic sites, respectively. O3 type Na layered transition metal oxides, including NaCrO$_2$, NaVO$_2$, NaNi$_{0.5}$Mn$_{0.5}$O$_2$, NaTi$_{0.5}$Ni$_{0.5}$O$_2$, and NaNi$_{1/3}$Mn$_{1/3}$Co$_{1/3}$O$_2$, are all electrochemically active, but exhibit reversible capacities lower than 125 mAh g$^{-1}$. Generally, the P2-type Na layered transition layered transition metal oxides appear to achieve higher capacities as cathodes in SIBs than their O3-type rivals. Notably, Yabuuchi synthesized P2-type Na$_2$Fe$_{1/2}$Mn$_{1/2}$O$_2$ and achieved a reversible capacity of 190 mAh g$^{-1}$ at 12 mA g$^{-1}$ in a voltage range between 1.5 and 4.2 V. More recently, Hasa and co-worker prepared P2-type Na$_{0.5}$Ni$_{0.23}$Fe$_{0.13}$Mn$_{0.63}$O$_2$ and this cathode shows an initial discharge capacity of up to 200 mAh g$^{-1}$ at 15 mA g$^{-1}$ and over 150 mAh g$^{-1}$ at 100 mA g$^{-1}$ in a voltage window of 1.5-4.6 V.

Li-rich, Mn-excess material Li$_{1.2}$Ni$_{0.15}$Mn$_{0.55}$Co$_{0.1}$O$_2$ can deliver a high reversible capacity of over 250 mAh g$^{-1}$ when used as a LIB cathode, which is about 68% of its theoretical capacity and is higher than the capacities of many other cathode materials. As the SIB counterpart of Li$_{1.2}$Ni$_{0.15}$Mn$_{0.55}$Co$_{0.1}$O$_2$, Na$_{1.2}$Ni$_{0.15}$Mn$_{0.55}$Co$_{0.1}$O$_2$ also has the potential to deliver large capacity, but has not yet been reported in the literature. Therefore, we prepared this new cathode material that shares similar chemistry with Li$_{1.2}$Ni$_{0.15}$Mn$_{0.55}$Co$_{0.1}$O$_2$ and investigated its electrochemical performance. The theoretical capacity of Na$_{1.2}$Ni$_{0.15}$Mn$_{0.55}$Co$_{0.1}$O$_2$ is approximately 307 mAh g$^{-1}$ if Na is fully extracted from the material. Notably, the P2-type Na layered transition metal oxides are generally characterized by high capacity with limited cyclability, while the O3-type electrodes exhibit lower capacity but deliver better cycle life.
Hence, it becomes critically important to develop Na layered transition metal oxides that can simultaneously have high reversible capacity and extended cycle life. In both P2 and O3-type cathodes, partial substitution of Na with Li in the transition metal layer was reported as an effective approach to improve their structural stability and therefore greatly enhance the electrochemical performance such as cycling stability and rate capability. Herein, we prepared Li-substituted Na layered transition metal oxide fibers by a novel centrifugal spinning technology combined with thermal treatment in air. A series of Li-substituted Na layered transition metal oxide fibers, with various Na and Li contents were synthesized by changing the stoichiometric ratios between Na and Li salts in the precursor solutions. The resultant Li-substituted Na layered transition metal oxide fibers were found to exhibit the P2-layered structure. These Li-substituted Na layered transition metal oxide fibers demonstrated significantly improved electrochemical performance, as compared with the pristine cathode material without partial Li substitution (Na$_{1.2}$Ni$_{0.15}$Mn$_{0.55}$Co$_{0.1}$O$_2$). Among the studied Li-substituted Na layered transition metal oxide fibers, Na$_{0.8}$Li$_{0.4}$Ni$_{0.15}$Mn$_{0.55}$Co$_{0.1}$O$_2$ exhibited the most superior electrochemical performance. This cathode showed the highest reversible discharge capacity of 138 mAh g$^{-1}$ at a current density of 15 mA g$^{-1}$. At higher current densities of 75 and 300 mA g$^{-1}$, this cathode retained high capacities of 113 and 94 mAh g$^{-1}$, respectively. Stable cycling performance was achieved for the cathode after repeating charging and discharging for 50 cycles at 15 mA g$^{-1}$, 100 cycles at 75 mA g$^{-1}$ and 200 cycles at 300 mA g$^{-1}$. In a relatively stressful current range from 15 to 600 mA g$^{-1}$, the cathode also exhibited good rate capabilities. These results demonstrate that partial Li substitution is an effective method to stabilize the material structure and improve the electrochemical performance of Na layered
transitional metal oxide cathodes and Li-substituted Na layered transition metal oxide fibers fabricated via centrifugal spinning can be used as a promising cathode material candidate in SIBs.

6.2 Materials and Methods

6.2.1 Material preparation

Sodium nitrate (NaNO₃, 99.0%), lithium nitrate (LiNO₃, 99.99%), nickel(II) nitrate hexahydrate (Ni(NO₃)₂·6H₂O), manganese(II) nitrate tetrahydrate (Mn(NO₃)₂·4H₂O), cobalt(II) nitrate hexahydrate (Co(NO₃)₂·6H₂O), N,N-dimethylformide (DMF), 1-methyl-2-pyrrolidinone (NMP) were purchased from Sigma-Aldrich Chemical Company (USA). Polyacrylonitrile (PAN, 150,000 g mol⁻¹), BTY175 battery conductive additive, and polyvinylidene fluoride (Solef 5130) were purchased from Pfaltz & Bauer Inc., Blue Nano Inc., and Solvay, respectively. All chemicals were used as received.

To prepare the precursor fibers, PAN powder was firstly dissolved into DMF solvent with a weight percentage of 12 wt. %. After the PAN/DMF solution was stirred for over 24 hours, sodium, nickel, manganese and cobalt nitrates were mixed into the solutions stoichiometrically and stirred for another 24 hours to obtain homogeneous precursor solutions. Four precursor solutions were made, in which the molar ratio between Na and Li were 1.2:0, 1.0:0.2, 0.8:0.4 and 0.6:0.6, while the ratio of Ni, Mn and Co in the precursor solutions was kept constant at 0.15:0.55:0.1. In the precursor solutions, the total weight percentage of the metal nitrates with respect to PAN was 40 wt. %. The precursor fibers were then prepared by a novel centrifugal
spinning approach. During centrifugal spinning, the precursor solutions were firstly loaded into the spinneret. The spinneret has 3 cm diameter and multiple 0.4 cm-diameter nozzles. After the solutions were injected into the spinneret, a rotational speed of 4,000 rpm was applied to produce precursor fibers. The fibers were deposited on aluminum collectors which are located radially to the spinneret with a 10 cm distance.

Li-substituted Na layered transition metal oxide fibers were prepared by calcinating the precursor fibers in a two-step method. Firstly, the precursor fibers were treated in air at 500 °C for 5 hours with 2 °C min\(^{-1}\) heating rate to decompose the nitrates. Then, the intermediate precursor fibers were further heated to 900 °C with 2 °C min\(^{-1}\) heating rate and held for 10 hours to form the Li-substituted Na layered transition metal oxide fibers, while in the meanwhile, the PAN component was completely decomposed. The molar ratio between Ni, Mn, Co and O was kept constant in all four calcinated samples (0.15:0.55:0.1:2), while the molar ratio between Na and Li varied. For simplicity, we denoted Na\(_{1.2}\)Ni\(_{0.15}\)Mn\(_{0.55}\)Co\(_{0.1}\)O\(_2\), Na\(_{1.0}\)Li\(_{0.2}\)Ni\(_{0.15}\)Mn\(_{0.55}\)Co\(_{0.1}\)O\(_2\), Na\(_{0.8}\)Li\(_{0.4}\)Ni\(_{0.15}\)Mn\(_{0.55}\)Co\(_{0.1}\)O\(_2\), and Na\(_{0.6}\)Li\(_{0.6}\)Ni\(_{0.15}\)Mn\(_{0.55}\)Co\(_{0.1}\)O\(_2\) as Na\(_{1.2}\)NMCO, Li\(_{0.2}\)-Na\(_{1.0}\)NMCO, Li\(_{0.4}\)-Na\(_{0.8}\)NMCO, and Li\(_{0.6}\)-Na\(_{0.6}\)NMCO, respectively. Similarly, the reference sample Li\(_{1.2}\)Ni\(_{0.15}\)Mn\(_{0.55}\)Co\(_{0.1}\)O\(_2\) was denoted as Li\(_{1.2}\)-NMCO. As a comparison between the fibrous electrode and particle electrode, Na\(_{0.8}\)Li\(_{0.4}\)Ni\(_{0.15}\)Mn\(_{0.55}\)Co\(_{0.1}\)O\(_2\) particles were prepared using the same precursor for Na\(_{0.8}\)Li\(_{0.4}\)Ni\(_{0.15}\)Mn\(_{0.55}\)Co\(_{0.1}\)O\(_2\) fibers and calcinated using the same thermal treatment protocol.
6.2.2 Structural analysis

The morphology of Li-substituted Na layered transition metal oxide fibers and the reference particles were investigated using field emission scanning electron microscope (FESEM-JEOL 6400F SEM at 5 kV). X-ray diffraction (XRD, Rigaku Smartlab, Cu Kα, λ = 1.544 Å) was conducted to characterize the crystal structures of Li-substituted Na layered transition metal oxide fibers and particles. The XRD patterns were obtained within a 2θ range of 5-90° and a step size of 0.02°.

6.2.3 Electrochemical evaluation

The electrochemical behavior of Li-substituted Na layered transition metal oxide fibers and particles was evaluated using coin cells (CR2032-type). The working electrodes were synthesized by mixing Li-substituted Na layered transition metal oxide fibers/particles (70 wt. %) with conductive additive (BTY 175, 20 wt. %) and polyvinylidene fluoride (PVDF, Solef 5130, 10 wt. %) in N-methyl-2-pyrrolidone (NMP) solvent. Then, the prepared slurries were casted onto carbon-coated aluminum foil (the current collector) and vacuum-dried overnight. The dried electrodes were cut from the carbon-coated foil using a puncher with a diameter of 1/2”. Na foil was cut directly from pure Na dry stick for use as the counter electrode. The working electrodes and Na counter electrode were partitioned by glass fiber separator (Whatman GF/D glass microfiber filters) impregnated with electrolyte consisting of 1 M NaClO₄ in solvent composing of ethylene carbonate (EC) and dimethyl carbonate (DMC) by a volume ratio of 1:1. Prior to the electrochemical tests, the cells were kept rested over 24 hours.
Galvanostatic charge/discharge performance were investigated by Arbin BT2000 battery tester in a voltage range of 4.2-1.5 V vs Na+/Na at current densities of 15, 75 and 300 mA g\(^{-1}\). The rate capabilities of Li-substituted Na layered transition metal oxide fibers and particles were investigated at various current densities from 15 to 600 mA g\(^{-1}\).

6.3 Results and Discussion

PAN/nitrate precursor fibers were prepared via a novel centrifugal spinning technology that enables rapid fiber production. Figure 6.1a sketches the lab-scale centrifugal spinning instrument used in the present study. The centrifugal spinning instrument mainly includes a Teflon spinneret with multiple fine nozzles, high speed motor equipped with DC motor controller, and aluminum collectors. To prepare the precursor fibers, the precursor solutions containing PAN and different amounts of Na, Li, Ni, Mn, and Co nitrates were fed into the spinneret through the top opening, and then high-speed rotation was applied. When the rotational speed accelerated to a value at which the centrifugal force can overcome the surface tension of the precursor solutions, liquid jets were initiated from the nozzles on the spinneret. During the movement in a circular trajectory course, the liquid jets were stretched and the solvent (DMF) gradually evaporated. Finally, dried precursor fibers deposited onto the rod-shaped collectors. Two leather pieces can be found in Figure 6.1a, and they were installed to generate lifting air so that the fibers were collected on the upper area of the spinning platform, forming freestanding nonwoven mats that were easy to remove. Figure 6.1b illustrates the precursor fibers prepared via centrifugal spinning. The precursor fibers contain PAN as the polymer carrier, and homogeneously distributed metal salts within the fibers. The precursor
fibers were thermally treated in air in a two-step treatment: the first step at 500 °C facilitated the decomposition of the metal nitrates, while the second step at 900 °C allowed the formation of Li-free or Li-substituted Na layered transition metal oxide fibers. The schematic illustration of the as-synthesized Na or Li-substituted Na layered transition metal oxide fibers is shown in Figure 6.1c. The centrifugal spinning route used in the present study is novel and promising in the preparation of fibrous Na layered transition metal oxide electrode materials, mainly because this spinning technology uses well-mixed precursor solutions that accommodates uniform metal ion distribution in the final product. So far, most reported fibrous electrode materials were prepared by electrospinning, which is slow, unsafe, and high cost. To the best of our knowledge, centrifugal spinning has not been used in sodium-ion battery electrode preparation. Compared with electrospinning, centrifugal spinning can generate fine fibers from more concentrated polymer solutions so that less solvent is needed. This method also avoids the use of high voltage, which is a safety concern in electrospinning. More importantly, centrifugal spinning can produce tens of grams of fine fibers per nozzle per hour, and such high production rate is at least two orders of magnitude higher than that of electrospinning. Overall, the above-mentioned advantages make centrifugal spinning an attractive approach for both academia and industry due to its large production rate, high safety, and low cost. Therefore, we used this rapid and scalable method for preparing fibrous electrode materials, and the results obtained in this study can potentially provide a solution to industrial, mass production of fibrous electrodes.
Figure 6.1 Schematic illustration of (a) centrifugal spinning instrument, (b) a centrifugally-spun PAN/nitrate precursor fiber, and (c) a Li-substituted Na layered transition metal oxide fiber.

The morphologies of as-spun PAN/nitrate precursor fibers and the resultant Li-substituted Na layered transition metal oxide fibers with various Na and Li contents were examined by SEM. The SEM images of representative Li-substituted Na layered transition metal oxide fibers with a specific composition of Li$_{0.4}$Na$_{0.8}$-NMCO and the corresponding precursor fibers are shown in Figure 6.2. It is seen from Figures 6.2a and b that the typical precursor fibers show smooth surface without bead formation. The precursor fibers are continuous and overlay with each other to form a 3D network structure with interconnected pores between the fibers. The average diameter of the precursor fibers is about 3µm. The as-spun precursor fibers were thermally treated in air with a two-step treatment at 500 °C and 900 °C, respectively, to form Li-substituted Na layered transition metal oxide fibers. Figures 2c and d demonstrate the
morbidity of the as-prepared Li$_{0.4}$-Na$_{0.8}$-NMCO fibers. It is seen that after the two-step thermal treatment, the obtained Li$_{0.4}$-Na$_{0.8}$-NMCO fibers lose the smooth surface structure and are no longer continuous. The average fiber diameter shrinks from 3µm to 1µm due to the removal of the polymer component and the decomposition of the nitrates. The resultant fibers still maintain a short fibrous structure and 1D architecture. In recent LIB and SIB material studies, employing 1D nano-/micro-structure becomes an attractive method to improve the electrochemical performance of electrode materials. In bulk electrode materials, active particles tend to aggregate due to their high surface energy, resulting in the formation of large secondary particles. The inner part of the aggregated particles is difficult to be utilized and barely contributes to the electrode capacity because of the insufficient electrode-electrolyte contact. In contrast, the 1D structured electrode materials show unique fibrous architecture and interconnecting nature, and can hinder the self-aggregation of active particles. Compared to traditional electrode materials, the 1D structure electrode materials possess large effective electrode-electrolyte contact area and better electrolyte wettability during cycling, which contribute to enhanced electrochemical performance. Moreover, the unique 1D structure provides well-guided and shortened transport pathways for both ions and electrons, facilitating rapid and efficient ionic/electronic transport and resulting in improved electrochemical performance.$^{125,343–345}$ In the present study, Li$_{0.4}$-Na$_{0.8}$-NMCO fibers can potentially facilitate sufficient electrode-electrolyte contact and rapid ionic/electronic transportation throughout the material, which in turn lead to reduced electrochemical impedance and enhance electrochemical performance.
Figure 6.2 SEM images of PAN/nitrate precursor fibers for Li$_{0.4}$-Na$_{0.8}$-NMCO (a, b), and corresponding Li$_{0.4}$-Na$_{0.8}$-NMCO fibers (c, d).

The crystal structures of Li-free and Li-substituted Na layered transition metal oxide fibers were investigated using XRD and results are given in Figure 6.3. For comparison, the XRD pattern of Na-free Li$_{1.2}$-NMCO particles is also provided. In the XRD pattern of Na$_{1.2}$-NMCO fibers (curve 3a), major peaks are identified at 2-theta angles of 16.0°, 32.3°, 36.3°, 39.9°, 44.0°, 49.3°, 62.3°, 65.1° and 67.5° and these peaks are characteristic peaks for typical P2-type Na layered transition metal oxides.\textsuperscript{167,172,173} For the XRD pattern of the reference
sample (Li\textsubscript{1.2}-NMCO particles, curve 3e), strong diffraction peaks are observed at 2-theta angles of 18.8°, 37.1°, 44.9°, 49.0°, 59.0°, 64.7°, 65.5°, and 68.8°. These diffraction peaks are typical for Li-rich Mn-based oxide cathodes in Li-ion batteries and can be attributed to the α-NaFeO\textsubscript{2} structure.\textsuperscript{346,347} It is seen from curves 3b, c and d that as the relative content ratio of Na/Li decreases from 1.0/0.2, 0.8/0.4 to 0.6/0.6, the diffraction peaks representing Na-free Li\textsubscript{1.2}-NMCO increases, indicating that these Li-substituted Na layered transition metal oxide fibers are solid solutions of Li\textsubscript{1.2}-NMCO in Na\textsubscript{1.2}-NMCO with various stoichiometric ratios.

Figure 6.3 XRD patterns of Na\textsubscript{1.2}-NMCO fibers (a), Li\textsubscript{0.2}-Na\textsubscript{1.0}-NMCO fibers (b), Li\textsubscript{0.4}-Na\textsubscript{0.8}-NMCO fibers (c), Li\textsubscript{0.6}-Na\textsubscript{0.6}-NMCO fibers (d), and Li\textsubscript{1.2}-NMCO particles (e).
The electrochemical performance of both Li-free and Li-substituted Na layered transition metal oxide fibers is evaluated using galvanostatic charge-discharge tests within a voltage range of 4.2-1.5 V at a current density of 15 mA g\(^{-1}\) and the results are demonstrated in Figure 6.4. It is seen that the initial charging of all four cathode materials proceeds predominantly in two stages. In the first stage, the voltage increases to above 2 V rapidly, and then shows a potential plateau between 2 and 3.8 V. When the electrode is further charged from 3.8 to 4.2 V, a second voltage plateau appear from 4 to 4.2 V, however, this charge plateau becomes less apparent in the following charge curves. For Na-free Li-rich, Mn-excess oxide cathodes such as Li\(_{1.2}\)-NMCO, the initial charge curve generally displays a charge plateau at 4.4 to 4.6 V, which is attributed to the irreversible extraction of Li from Li\(_2\)MnO\(_3\) of the solid solution cathode materials.\(^{346}\) This charge plateau is usually absent from the second charge curve and the irreversible reaction results in the irreversible capacity loss of the first cycle. Similarly, the charge plateau at 4 to 4.2 V in the Li-substituted Na layered transition metal oxide fibers can be ascribed to possible Na/Li extraction from the as-prepared solid solution cathodes. The initial charge capacities of Na\(_{1.2}\)-NMCO, Li\(_{0.2}\)-Na\(_{1.0}\)-NMCO, Li\(_{0.4}\)-Na\(_{0.8}\)-NMCO, and Li\(_{0.6}\)-Na\(_{0.6}\)-NMCO fibers are 144, 204, 280 and 237 mAh g\(^{-1}\), respectively, while the corresponding initial discharge capacities are 94, 135, 124 and 125 mAh g\(^{-1}\), respectively. All the Li-substituted Na layered transition metal oxide fibers exhibit higher initial discharge capacities than that of the pristine Na\(_{1.2}\)-NMCO fibers. The electrochemical performance of Na\(_{1.2}\)-NMCO, Li\(_{0.2}\)-Na\(_{1.0}\)-NMCO, Li\(_{0.4}\)-Na\(_{0.8}\)-NMCO, and Li\(_{0.6}\)-Na\(_{0.6}\)-NMCO fibers was further investigated at a medium current density of 75 mA g\(^{-1}\) and a high current density of 300 mA g\(^{-1}\) in a potential window of 4.2 to 1.5 V. The charge-discharge curves obtained at 75 and 300 mA g\(^{-1}\) can be
seen in Figures 6.5 and 6.6, respectively. Comparing Figures 6.5 and 6.6 with Figure 6.4, it is seen that the charge-discharge curves at the medium and high current densities show similar charge/discharge plateaus to those found in the low current density tests, suggesting the good rate capability of these cathode materials.

Figure 6.4 Charge-discharge curves of Na$_{1.2}$-NMCO fibers (a), Li$_{0.2}$-Na$_{1.0}$-NMCO fibers (b), Li$_{0.4}$-Na$_{0.8}$-NMCO fibers (c), and Li$_{0.6}$-Na$_{0.6}$-NMCO fibers (d). The current density was 15 mA g$^{-1}$. 

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Figure 6.5 Charge-discharge curves of Na_{1.2}-NMCO fibers (a), Li_{0.2}-Na_{1.0}-NMCO fibers (b), Li_{0.4}-Na_{0.8}-NMCO fibers (c), and Li_{0.6}-Na_{0.6}-NMCO fibers (d). The current density was 75 mA g$^{-1}$. 
Figure 6.6 Charge-discharge curves of Na$_{1.2}$-NMCO fibers (a), Li$_{0.2}$-Na$_{1.0}$-NMCO fibers (b), Li$_{0.4}$-Na$_{0.8}$-NMCO fibers (c), and Li$_{0.6}$-Na$_{0.6}$-NMCO fibers (d). The current density was 300 mA g$^{-1}$.

Figure 6.7 compares the cycling performance of Li-free and Li-substituted Na layered transition metal oxide fibers at current densities of 15, 75 and 300 mA g$^{-1}$ within a potential window of 4.2 to 1.5 V. It is seen from Figure 6.7a that at a current density of 15 mA g$^{-1}$, reversible capacities of 94, 135, 124 and 125 mAh g$^{-1}$ are delivered in the first cycle for Na$_{1.2}$-NMCO, Li$_{0.2}$-Na$_{1.0}$-NMCO, Li$_{0.4}$-Na$_{0.8}$-NMCO, and Li$_{0.6}$-Na$_{0.6}$-NMCO fibers, respectively. After repeatedly charge and discharge for fifty cycles, specific capacities of 71, 93, 79 and 86
mAh g\(^{-1}\) are sustained for Na\(_{1.2}\)-NMCO, Li\(_{0.2}\)-Na\(_{1.0}\)-NMCO, Li\(_{0.4}\)-Na\(_{0.8}\)-NMCO, and Li\(_{0.6}\)-Na\(_{0.6}\)-NMCO fibers, respectively. All the Li-substituted Na layered transition metal oxide fibers show higher specific discharge capacities in all 50 cycles. Although the Li\(_{0.2}\)-Na\(_{1.0}\)-NMCO fibers maintain the highest discharge capacity of 93 mAh g\(^{-1}\) after fifty cycles, the highest specific capacity of 138 mAh g\(^{-1}\) is achieved at the third cycle of Li\(_{0.4}\)-Na\(_{0.8}\)-NMCO fibers. The Li-substituted Na layered transition metal oxides exhibit a slightly increasing trend in the discharge capacities for the first several cycles, indicating this type of cathode materials might need a long activation process before the highest utilization is reached. The cycling performance of Na\(_{1.2}\)-NMCO, Li\(_{0.2}\)-Na\(_{1.0}\)-NMCO, Li\(_{0.4}\)-Na\(_{0.8}\)-NMCO, and Li\(_{0.6}\)-Na\(_{0.6}\)-NMCO fibers at 75 mA g\(^{-1}\) is compared in Figure 6.7b. After a hundred charge-discharge cycles, the specific discharge capacities of Na\(_{1.2}\)-NMCO, Li\(_{0.2}\)-Na\(_{1.0}\)-NMCO, Li\(_{0.4}\)-Na\(_{0.8}\)-NMCO, and Li\(_{0.6}\)-Na\(_{0.6}\)-NMCO fibers are 69, 96, 91 and 93 mAh g\(^{-1}\), respectively, corresponding to capacity retentions of 80%, 83%, 81% and 89%. Figure 6.7c displays the cycling performance of the cathode materials at 300 mA g\(^{-1}\) for two hundred cycles. All cathode materials show insignificant capacity loss during the prolonged cycling tests: after two hundred cycles, the specific capacities retained for Na\(_{1.2}\)-NMCO, Li\(_{0.2}\)-Na\(_{1.0}\)-NMCO, Li\(_{0.4}\)-Na\(_{0.8}\)-NMCO, and Li\(_{0.6}\)-Na\(_{0.6}\)-NMCO fibers are 53, 70, 75 and 63 mAh g\(^{-1}\), corresponding to capacity retentions of 79%, 82%, 81% and 82%, respectively. These results show that Li-substituted Na layered transition metal oxide fibers yield higher discharge capacities and better cycling stability, indicating that the partial Li substitution is an effective approach to sustain the structural stability of the Na layered transition metal oxide cathodes and therefore leads to enhanced electrochemical performance.
Figure 6.7 Cycling performance of Na$_{1.2}$-NMCO, Li$_{0.2}$-Na$_{1.0}$-NMCO, Li$_{0.4}$-Na$_{0.8}$-NMCO, and Li$_{0.6}$-Na$_{0.6}$-NMCO fibers at current densities of 15 (a), 75 (b) and 300 (c) mA g$^{-1}$.

The rate performance of Li-free and Li-substituted Na$_{1.2}$-NMCO fibers was examined in a voltage window of 4.2 to 1.5 V with various current densities of 15, 30, 75, 150, 300 and 600 mA g$^{-1}$ and the results are shown in Figure 6.8a. Figures 6.8b, c, d and e provide the
corresponding voltage profiles at each current density. It is seen that when the current density
increases, lower capacities are obtained for all four cathode materials, however, the charge-
discharge curves maintain the same trend. For Na$_{1.2}$-NMCO fibers, specific discharge
capacities of 100, 76, 65, 58, 50 and 42 mAh g$^{-1}$, respectively, are obtained at current densities
of 15, 30, 75, 150, 300 and 600 mA g$^{-1}$. At the highest current density of 600 mA g$^{-1}$, Na$_{1.2}$-
NMCO fibers retain 42% of the original capacity at 15 mA g$^{-1}$. As the current density returns
to 15 mA g$^{-1}$, the discharge capacity goes back to 85 mAh g$^{-1}$, corresponding to 85% of the
initial discharge capacity. On the contrary, the three Li-substituted Na layered transition metal
oxide fibers demonstrate higher discharge capacities at all current densities, compared to Na$_{1.2}$-
NMCO fibers. Among all the studied cathode materials, Li$_{0.4}$-Na$_{0.8}$-NMCO fibers exhibit the
best rate performance and deliver reversible capacities of 140, 119, 105, 94, 82 and 68 mAh g$^{-1}$,
respectively, at 15, 30, 75, 150, 300 and 600 mA g$^{-1}$. At 600 mA g$^{-1}$, Li$_{0.4}$-Na$_{0.8}$-NMCO fibers
maintain 49% of the original capacity at 15 mA g$^{-1}$. As the current density retrieves at 15 mA
g$^{-1}$, Li$_{0.4}$-Na$_{0.8}$-NMCO fibers show a discharge capacity of 127 mAh g$^{-1}$, corresponding to 91%
of the initial capacity value.
Figure 6.8 Rate capabilities of Na\textsubscript{1.2}-NMCO, Li\textsubscript{0.2}-Na\textsubscript{1.0}-NMCO, Li\textsubscript{0.4}-Na\textsubscript{0.8}-NMCO, and Li\textsubscript{0.6}-Na\textsubscript{0.6}-NMCO fibers in a current range of 15 to 600 mA g\textsuperscript{-1} (a); corresponding voltage profiles of Na\textsubscript{1.2}-NMCO fibers (b), Li\textsubscript{0.2}-Na\textsubscript{1.0}-NMCO fibers (c), Li\textsubscript{0.4}-Na\textsubscript{0.8}-NMCO fibers (d), and Li\textsubscript{0.6}-Na\textsubscript{0.6}-NMCO fibers (e).
The significantly enhanced electrochemical performance of the Li-substituted Na layered transition metal oxide fibers is largely contributed by the Li stabilizing effect in the transition metal layers of the materials. Several studies reported partially substitution of Na with Li and the results suggest that such method is effective in improving the electrochemical performance for SIB cathode materials.\textsuperscript{180–186} Li substitution strategy has been applied in both P2 and O3 type materials. It is commonly believed that the substituted Li ions share the adjacent transition metal sites with Mn and Ni ions, which results in minimal anti site disorder. In this way, the added Li in the cathode materials is expected to stabilize the transition metal layer and counter the movement of Ni into the Na layer during repeated Na intercalation and deintercalation.\textsuperscript{181,184,186} Therefore, the substituted Li in the structure can help prevent phase transformation and mitigate structural degradation during cycling, resulting in improved electrochemical performance. In the present study, various stoichiometric proportions between Li and Na were investigated to determine the optimum composition. The electrochemical performance of Na\textsubscript{1.2}-NMCO, Li\textsubscript{0.2}-Na\textsubscript{1.0}-NMCO and Li\textsubscript{0.4}-Na\textsubscript{0.8}-NMCO gradually improves due to the effect of partial Li substitution. However, for Li\textsubscript{0.6}-Na\textsubscript{0.6}-NMCO, the Li concentration is too high and the excess Li leads to the formation of more Li\textsubscript{2}MnO\textsubscript{3} impurities, which in turn reduces the electrode capacity.\textsuperscript{180} Therefore, it is determined that the composition Li\textsubscript{0.4}-Na\textsubscript{0.8}-NMCO has the optimum stoichiometric proportion among all the Li-substituted Na layered transition metal oxide fiber cathodes studied in this work.

To demonstrate the advantages of using 1D fibrous cathodes instead of traditional particle cathodes in sodium-ion batteries, Na\textsubscript{0.8}Li\textsubscript{0.4}Ni\textsubscript{0.15}Mn\textsubscript{0.55}Co\textsubscript{0.1}O\textsubscript{2} particles were prepared using
the same precursor and thermal treatment condition for Na$_{0.8}$Li$_{0.4}$Ni$_{0.15}$Mn$_{0.55}$Co$_{0.1}$O$_2$ fibers. Figure 6.9 shows the SEM images of the Na$_{0.8}$Li$_{0.4}$Ni$_{0.15}$Mn$_{0.55}$Co$_{0.1}$O$_2$ particles. It is seen that due to the high temperature thermal treatment and the self-aggregation nature of particles, the as-prepared particles are formed by aggregation of small primary particles (Figure 6.9b), and the as-prepared particles also tend to further aggregate (Figure 6.9a). The particle aggregation results in poor electrolyte/electrode contact and insufficient utilization of the active materials, and hence lead to inferior electrochemical performance compared to 1D fibrous electrode. Since the particles and the fibers were synthesized using the same precursor and same thermal treatment condition, the XRD patterns (Figure 6.10) exhibit same peaks at the same 2-Theta angles and no impurity can be observed. Figure 6.11 compares the charge-discharge curves for the fiber and particle electrodes and their cycling performance at a current density of 75 mA g$^{-1}$. The initial discharge capacities for the particles and fibers are 90 and 113 mAh g$^{-1}$, respectively, and the discharge capacities after 50 cycles for the particles and fibers are 98 and 107 mAh g$^{-1}$, respectively. Both samples exhibit capacity retention over 95%, however, the fiber sample shows higher discharge capacity. This is closely linked to the self-aggregation of particles and the advantages of the 1D fibrous structured electrode compared to the particle electrode, which have been discussed earlier.
Figure 6.9 SEM images of Li_{0.4}Na_{0.8}-NMCO particles at different magnifications.

Figure 6.10 XRD patterns of Li_{0.4}Na_{0.8}-NMCO particles and fibers.
Figure 6.11 Charge-discharge curves of Li$_{0.4}$-Na$_{0.8}$-NMCO fibers (a) and Li$_{0.4}$-Na$_{0.8}$-NMCO particles (b); Cycling performance of Li$_{0.4}$-Na$_{0.8}$-NMCO fibers and particles (c). The current density was 75 mA g$^{-1}$.

So far, most Na layered transition metal oxide cathodes for SIBs were prepared in the form of small particles and their specific capacities ranged from 100 to 200 mAh g$^{-1}$ at low current densities.$^{14-29}$ The highest specific capacity achieved for the fibrous cathodes prepared in the present study is 140 mAh g$^{-1}$, which is medium among the reported capacity values. However, in most reported studies, the cycling performance of the cathode materials was evaluated at low to medium current densities ($<$100 mA g$^{-1}$) with limited cycling numbers ($<$50
cycles).\textsuperscript{14-29} Since long-term cyclability and rate capability are important for the practical application of SIBs, the cycling performance of Na$_{1.2}$-NMCO, Li$_{0.2}$-Na$_{1.0}$-NMCO, Li$_{0.4}$-Na$_{0.8}$-NMCO and Li$_{0.6}$-Na$_{0.6}$-NMCO fibrous cathodes was evaluated at medium (75 mA g$^{-1}$) and high (300 mA g$^{-1}$) current densities for 100 and 200 cycles, respectively, in the present study. The obtained capacity retentions range from 80\% to 90\%, which is satisfactory for SIB cathodes. Moreover, comparing the capacity retention values of the fibrous cathodes in this study with other Na layered transition metal oxide cathodes for the same cycle number (\textit{i.e.}, 50 cycles), the achieved capacity retentions fall in the range between 90\% to 96\%, which is higher than most reported results, giving the condition that the current densities used in this study are higher than those used in literature.\textsuperscript{14-29} Therefore, the fibrous structure employed in this study is effective in improving the electrochemical performance of Na layered transition metal oxide cathodes.

6.4 Conclusions

Na layered transition metal oxide fibers with/without partial Li substitutions were synthesized via centrifugal spinning with subsequent heat treatment. Various fibrous cathodes with different Na/Li stoichiometric ratios were obtained by changing the contents of Na and Li salts in the precursor solutions. Compared to the Na$_{1.2}$Ni$_{0.15}$Mn$_{0.55}$Co$_{0.1}$O$_2$ fibers, the Li-substituted Na layered transition metal oxide fibers show higher capacities, better cycling stabilities and improved rate performance. Among the studied cathode materials, Li$_{0.4}$-Na$_{0.8}$-NMCO fibers exhibits the most superior electrochemical performance: they deliver the highest capacities of 138 mAh g$^{-1}$ at 15 mA g$^{-1}$, 113 mAh g$^{-1}$ 75 mA g$^{-1}$, and 94 mAh g$^{-1}$ at 300 mA g$^{-1}$.
In a stressful current range between 15 to 600 mA g$^{-1}$, Li$_{0.4}$Na$_{0.8}$-NMCO fibers maintain 49% of the original capacity at the highest current density of 600 mA g$^{-1}$, and retrieves 91% of its initial capacity as the current density returns to 15 mA g$^{-1}$. It is therefore demonstrated that partial Li substitution in the Na layered transition metal oxide fibers can be considered as an effective route to improve the structural stability and enhance the electrochemical performance of the Na layered transition metal oxides. Moreover, centrifugal spinning can be a promising approach in the fabrication of micro-sized fibrous electrode materials due to its high cost effectiveness and scale-up capability.
CHAPTER 7. Conclusions and Recommendation Work

7.1 Conclusions

Compared with traditional electrospinning method, centrifugal spinning offers advantages including high safety, high production rate and low cost. This novel technology can significantly benefit the industry for mass production of fibrous materials including polymer fibers, carbon fibers and ceramic fibers. Carbon fibers and ceramic fibers prepared via centrifugal spinning can be potentially used in high-performance energy storage devices such as electric double-layer capacitors (EDLCs) and sodium-ion batteries (SIBs).

The major findings of each chapter can be summarized as follows.

(I) Parameter Study and Characterization of Centrifugally-Spun Polyacrylonitrile Nanofibers

A facile lab-scale centrifugal spinning device was established. The device was effective in generating continuous polymer fibers by applying high-speed rotational movement on the spinneret. This novel spinning method has several surpassing advantages: (a) the device is simple to establish; (b) no electric field is used; (c) fiber formation is independent of solution conductivity; (d) the technology allows the use of highly concentrated solutions; (e) the technology is low cost and can be scaled up. In order to harness this technology, the effects of solution intrinsic properties such as rheological behavior and surface tension, and operational parameters such as rotational speed, nozzle diameter, and nozzle-collector distance, were investigated. Using polyacrylonitrile (PAN) as an example, correlations between the fiber morphology and the above-mentioned solution intrinsic properties and operational parameters
were successfully established. The results demonstrate that by selectively adjust solution intrinsic properties and operational parameters, the morphology of the resultant PAN nanofibers can be easily manipulated. Consequently, centrifugal spinning, a low-cost and scalable approach, can be a promising alternative to electrospinning in mass production of nanofibers.

(II) Centrifugally-Spun Porous Carbon Fibers as Binder-Free Electrodes for Electric Double-Layer Capacitors

Porous carbon nanofibers (PCNFs) were produced by centrifugal spinning of blend precursor solutions composing of PAN and PMMA with various weight ratios combined with subsequent two-step thermal treatment in argon atmosphere at different temperatures. The centrifugally-spun PAN/PMMA blend fibers showed smooth and bead-free fibers with an island-in-sea structure, where PMMA was the island while PAN was the sea. The thermal treatment eliminated the PMMA component and converted PAN into CNFs, resulting in the formation of PCNFs. The as-prepared PCNFs were directly used as binder-free electrodes for EDLCs. Electric conductivity and specific surface area are two key factors that dominate the capacitive performance of EDLC electrodes; therefore, their influence on the electrochemical performance was assessed by adjusting the relative weight ratios between PAN and PMMA and the thermal treatment temperatures. The cyclic voltammograms and galvanostatic charge/discharge curves show near-rectangular and near-linear shapes, respectively, suggesting good EDLC behavior. Among all PCNFs studied, those produced from precursor fibers with PAN/PMMA weight ratio of 7/3 at 900 °C exhibited the highest specific capacitance of 144 F g⁻¹ at 0.1 A g⁻¹. These PCNFs also demonstrated a good rate capability of
74% from current density of 0.1 A g\(^{-1}\) to 2 A g\(^{-1}\). PCNFs also showed stable cyclability. The highest cycling stability of 90% over 1,000 cycles was achieved by PCNFs prepared from precursor fibers with PAN/PMMA weight ratio of 7/3 at 800 °C. The results therefore demonstrate that the PCNFs prepared by centrifugal spinning can be promising EDLC electrodes and centrifugal spinning is a simple and efficient strategy for PCNF production.

(III) Centrifugally-Spun \(\text{SnO}_2\) Microfibers Composed of Interconnected Nanoparticles as Anode for Sodium-Ion Batteries

\(\text{SnO}_2\) microfibers were prepared by combining centrifugal spinning of the \(\text{SnCl}_2/\text{PAN}\) precursor fibers with subsequent calcination process in air. Compared to the commercial \(\text{SnO}_2\) and \(\text{SnO}_2\) particles calcinated from the same precursor solution using the same heating protocol, the one-dimensional (1D) \(\text{SnO}_2\) microfibers comprised of numerous interconnected nanoparticles with inter-particle pores. \(\text{SnO}_2\) microfibers showed a smaller overall size in contrast to \(\text{SnO}_2\) particles. The unique morphological characteristics of \(\text{SnO}_2\) microfibers resulted in enhanced electrolyte-electrode contact and reduced electrochemical impedance. Hence, \(\text{SnO}_2\) microfibers demonstrated improved electrochemical performance in sodium-ion batteries (SIBs) including higher discharge capacity, better cycling performance at high current density, and improved rate capability. In this work, the highest obtained discharge capacity for \(\text{SnO}_2\) microfibers was 567 mAh g\(^{-1}\) at 20 mA g\(^{-1}\). The microfibrous electrode sustained a high discharge capacity of 158 mAh g\(^{-1}\) with a good capacity retention of 77% after 50 cycles at a high current density of 640 mA g\(^{-1}\). \(\text{SnO}_2\) microfibers also showed a good rate performance in a stressful current range of 20 – 640 mA g\(^{-1}\). The present study suggests that the centrifugally-
spun SnO$_2$ microfibers composed of interconnected nanoparticles are a promising anode material for SIBs. Moreover, centrifugal spinning can potentially become an important method for the industry to produce fibrous electrode materials for SIBs in mass production.

(IV) Lithium-Substituted Sodium Layered Transition Metal Oxide Fibers as Cathodes for Sodium-Ion Batteries

Na layered transition metal oxide fibers with/without partial Li substitutions were prepared via centrifugal spinning with following high temperature thermal treatment. A series of fibrous cathodes with various Na/Li stoichiometric ratios were obtained by varying the contents of Na and Li salts in the precursor solutions. In comparison to the Na$_{1.2}$Ni$_{0.15}$Mn$_{0.55}$Co$_{0.1}$O$_2$ fibers, the Li-substituted Na layered transition metal oxide fibers possess higher capacities, stable cycling performance and better rate performance. Among the investigated compositions, Li$_{0.4}$-Na$_{0.8}$-NMCO fibers exhibits the most superior electrochemical performance: they deliver the high capacities of 138, 113, and 94 mAh g$^{-1}$ at 15, 75, and 300 mA g$^{-1}$, respectively. In a stressful current range between 15 to 600 mA g$^{-1}$, Li$_{0.4}$-Na$_{0.8}$-NMCO fibers maintain 49% of the original capacity at the highest current density, and retrieves 91% of its initial capacity as the current density returns to 15 mA g$^{-1}$. This work demonstrates that partial Li substitution can be considered as an effective route to improve the structural stability and enhance the electrochemical performance of the Na layered transition metal oxide cathodes. Moreover, centrifugal spinning is a promising method in the fabrication of micro-sized fibrous electrode materials due to its low cost and scale-up capability.
7.2 Recommendation Work

The recommendation work includes but is not limited to:

(I) Improving the Electrochemical Performance of Centrifugally-Spun Anodes and Cathodes for Sodium-Ion Batteries Using Carbon Composites

In this work, SnO$_2$ microfibers and lithium-substituted sodium layered transition metal oxide fibers were prepared and evaluated as anode and cathode in sodium-ion batteries, and these materials show good electrochemical performance. However, their performance can be further improved by making composites of the active materials with carbon based materials. A part of the recommendation work can be fabricating carbon fiber composites with the alloy reaction based anodes Sn and SnO$_2$. These materials show severe volume change upon continuous sodiation and de-sodiation. If the active materials can be dispersed within the carbon fiber matrix, their volume change issue can be largely addressed. Some electrode materials also suffer from low electric conductivity, which results in low capacity, poor cycling stability and low rate capability. In this case, if the active materials are encapsulated within carbon fibers, or if the active materials are surface coated with carbon via deposition or pyrolysis approaches, their electric conductivity and overall electrochemical performance can be improved.

(II) Using Centrifugally-Spun Fibers in Other Energy Storage Applications

In addition to using centrifugal spinning for making electrode materials in lithium-ion batteries, sodium-ion batteries and electric double-layer capacitors, the centrifugally-spun fibers can also be applied in other energy storage purposes. For example, this method can be employed to prepare porous membranes for battery separators. The porous carbon fibers
prepared via centrifugal spinning can be used as an interlayer in lithium-sulfur batteries. Moreover, this method can be used to fabricate both fibrous electrodes for supercapacitors and rechargeable batteries, and the as-prepared electrodes can be adopted in hybrid energy storage devices such as lithium-ion capacitors, which utilize the battery electrode as anode and the electric double-layer electrode as cathode. Hence, the potential future work can include the effort to investigate the applications of centrifugally-spun fibers in various energy storage applications.
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