ABSTRACT

CHEN, CHEN. Application of Electrospun Carbon Nanofibers as Sodium-ion Battery Anode Materials. (Under the direction of Dr. Xiangwu Zhang).

The rapid development of demand for energy consuming has become a critical issue for human society and now the challenge of developing new energy storage devices is more prominent than ever. Lithium-ion batteries have been utilized in various applications due to its great advantages like long cycle life, high specific energy density, low self-discharge rate and no memory effect. However, the uneven distribution of lithium source and foreseeable price increase urge researchers to look for new candidates for energy storage. Sodium-ion batteries, as a low-cost alternative to lithium-ion batteries, have attracted tremendous attention due to its similar electrochemistry with lithium-ion batteries, unlimited source and low price. This stimulated the interest in exploring electrode materials for sodium-ion batteries, which have higher capacities and longer cycling life. Electrospinning is an efficient way to fabricate one-dimensional nanofibers with large surface area and controllable morphology. In this work, carbon nanofibers (CNFs) produced by electrospinning was first improved by nitrogen doping, which can improve the conductivity of carbon materials and create more active sites, thereby leading to enhanced sodium storage capability. Then, tin antimony nanoparticles were embedded into the CNFs which function as a carbon matrix to buffer the volume change of alloy nanoparticles, meanwhile provide good conductivity as a carbon network. At last, CNFs were employed as a conductive network base and molybdenum disulfide was deposited homogenously on the CNFs by a chemical vapor deposition (CVD) method. The morphology, electrochemical performance and reaction mechanism of N-doped CNFs, SnSb@CNFs and MoS$_2$@CNFs composites were carefully
studied by various techniques. Great reversibility and high capacity were achieved for CNF based materials for use as sodium-ion battery anodes. Therefore, this work demonstrated that electrospun CNFs have great potential to be utilized in synthesis of sodium-ion battery anode materials.
Application of Electrospun Carbon Nanofibers in Sodium-ion Battery Anode Materials

by
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A thesis submitted to the Graduate Faculty of North Carolina State University in partial fulfillment of the requirements for the degree of Doctor of Philosophy

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DEDICATION

To my beloved mother, father and all my family members.

It is you that make my dream come true.

It is you that make me a better man.
BIOGRAPHY

Chen Chen received his Bachelor degree in Textile Science and Engineering at Donghua University in 2012 and his master degree in Textile Engineering at North Carolina State University in 2013. He continued to enroll in the Fiber and Polymer Science Doctoral program in August 2013.
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CHAPTER 1. INTRODUCTION

Lithium-ion batteries were first developed as a high-energy density power source for electronic devices and were commercialized in 1991. They have been widely used in many applications like cellphones, laptops, and electronic vehicles (EVs) and so on. However, the rapid development of EVs and grid storage system influences the feasibility of lithium-ion batteries leading to a price fluctuation in the foreseeable future. Therefore, it is urgent for people to develop the diversity of energy storage devices and minimize the dependence on lithium-ion batteries.¹⁰

Sodium-ion batteries, due to its similar electrochemical reactions with lithium-ion batteries, were developed as one of the most promising batteries for large-scale energy storage systems due to their great advantages such as abundance and low cost. The most important two parts in the sodium-ion batteries are the cathode and anode, which are closely related to the energy density of the sodium-ion batteries. Since 2010, many research articles have been published on the feasibility of different cathode materials in sodium-ion batteries. Moreover, the difference and similarity in kinetics, thermodynamics, passivation layer formation, and reaction mechanism between sodium-ion batteries and lithium-ion batteries were extensively investigated.

Electrospinning, as one of the most facile ways to synthesize the one-dimensional nanomaterials, has attracted great attention and been applied in many fields such as medical, filtration, textiles, and energy storage. Many polymer nanofibers can be made into
electrospun nanofibers when appropriate polymer solutions are made. Polyacrylonitrile (PAN), as the main precursor to produce carbon nanofibers, has many advantages such as lower-cost, stronger mechanical properties and higher carbon yield.\textsuperscript{11–13} Due to the severe formation of the sodium dendrite when sodium metal is used as the anode material in sodium-ion batteries, new anode materials must be developed for sodium-ion batteries. The objectives of this research are to explore reaction mechanisms for sodiation/desodiation processes and to develop feasible anode materials for sodium-ion batteries using electrospinning method. As the base of this research, the carbon nanofibers developed by electrospinning were studied and further modification on the carbon nanofibers was also conducted by fabricating carbon nanofiber based composites. The electrochemical performance of these materials was carefully studied.
CHAPTER 2. LITERATURE REVIEW

2.1 Electrochemical energy storage systems

With the rapidly increasing demand for energy and consumption of limited fossil fuel resources on earth, renewable and environmentally friendly energy sources such as wind energy, solar energy and tidal energy have attracted great attention in recent years. Nevertheless, the direct energy output of these renewable energy sources is not stable or continuous, then large scale energy storage systems (ESSs) are highly necessary to collect and store the produced energy efficiently, at the same time, transport and provide smooth and safe energy output. Therefore, it is foreseeable that ESSs will play an important role in the renewable energy utilization in the future.

Batteries and supercapacitors are two most commonly used types of electrochemical ESSs. Supercapacitors, featured by their high power density, excellent reversibility and long cycle life, have been widely used in consumer electronics, memory back-up systems and industrial power and energy management. Based on different charge storage mechanism, supercapacitors can be classified into electrical double layer capacitors (EDLCs) and pseudo-capacitors. For EDLCs, the capacitance comes from the charged layers between electrode/electrolyte interfaces where the electrostatic charges accumulate. Therefore, the capacitance is strongly dependent on the surface area of the electrodes. On the other hand, the pseudo-capacitors work in a way that faradic processes take place as the charges are stored. However, compared with batteries, a relatively lower energy density of the
supercapacitors is determined by their electrochemical mechanism, because all the charges are only confined on the surface of the electrodes.\textsuperscript{17}

To date, various batteries have been studied and developed as useful energy storage devices such as lithium-ion batteries (LIBs), lithium-sulfur (Li-S) batteries, sodium-sulfur (Na-S) batteries and flow batteries.\textsuperscript{18–25}

For Li-S batteries, they are composed of three basic parts, a lithium metal anode, a sulfur contained composite cathode and an organic electrolyte. The reaction mechanism of a conventional Li-S battery can be described as that during the discharge process, the lithium metal is oxidized into lithium ions, at the same time, lose electrons, whereas sulfur will take lithium ions from the electrolyte and is reduced into lithium sulfide.\textsuperscript{26} The discharging reactions are shown as below:

\begin{align*}
\text{negative electrode: } & 2 \text{Li} \rightarrow 2 \text{Li}^+ + 2 e^- \quad (1) \\
\text{positive electrode: } & S + 2 \text{Li}^+ + 2e^- \rightarrow \text{Li}_2\text{S} \quad (2)
\end{align*}

When the sulfur cathode is fully reduced into lithium sulfide (Li\textsubscript{2}S), a theoretical capacity as high as 1672 mAh g\textsuperscript{-1} can be obtained. In addition, considering the abundance of sulfur sources on earth, Li-S batteries are promising high-energy density storage devices for the future. However, there are still some challenges hindering the utilization of Li-S batteries from theory to practice. First, the ultimate product Li\textsubscript{2}S in the Li-S batteries are produced progressively from various types of polysulfides as shown in Figure 1. Among the different polysulfides, the Li\textsubscript{2}S\textsubscript{n} (3 \leq n \leq 6) intermediates are soluble in the organic electrolyte which
gives rise to a shuttle mechanism and leads to the fast capacity fading.\textsuperscript{21,27–29} Secondly, the intrinsic insulation of sulfur and the reduction product such as Li$_2$S, Li$_2$S$_2$ during reaction, have adverse effect on the cycling performance and rate capability of Li-S batteries.\textsuperscript{30,31} Although great progress has been made in recent years, there is still a long way before finally obtaining stable and efficient Li-S batteries.

Figure 1. Voltage profiles of Li-S battery.\textsuperscript{29}
On the other hand, the traditional Na-S batteries, due to their high theoretical specific energy (~760 Wh kg\(^{-1}\)) and high energy efficiency, have shown great potential for stationary energy storage system.\(^{32,33}\) Currently, the Na-S technology has been commercially used in grid applications in many countries including USA, China, Korea, Switzerland, etc.\(^{33}\) The Na-S batteries use sodium β-alumina (NaAl\(_{11}\)O\(_{17}\)) as the electrolyte and are operated under a temperature as high as 300°C to keep the sodium metal and sulfur at the molten state.\(^{33,34}\) Because the sodium β-alumina (NaAl\(_{11}\)O\(_{17}\)) shows extremely high ionic conductivity only at high temperatures, which makes it possible to be employed as a Na-S battery electrolyte.\(^{35}\)

The chemical potential and the electrical energy originate from the reaction:

Anode: \(2Na - 2e^- \leftrightarrow 2Na^+\)  \hspace{1cm} (3)

Cathode: \(xS + 2Na^+ + 2e^- \leftrightarrow Na_2S_x\ (x = 3 \sim 5)\)  \hspace{1cm} (4)

Figure 2. Schematic illustration of a traditional Na-S battery.\(^{34}\)
However, the electrode materials (sodium and sulfur) are active and corrosive at molten state which are severe safety concerns.\textsuperscript{36,37} Moreover, additional energy is necessary to maintain the high temperature of the Na-S system and it, to some degree, counteracts considerable energy produced by the Na-S battery.\textsuperscript{36–38} Due to the reasons mentioned above, in order to extend the application of Na-S batteries, the critical way is to decrease the working temperature of Na-S batteries. Many efforts have been done to investigate the ambient temperature Na-S battery, but only limited progress has been made.\textsuperscript{25,36–40}

2.2 Introduction of lithium-ion batteries and sodium-ion batteries

2.2.1 Introduction of lithium-ion batteries

The rapid development of portable electronic devices since 1980s has witnessed the development of lithium-ion batteries since they endow the products with longer service life, small size and lightweight compared with conventional rechargeable batteries such as lead-acid and nickel-cadmium batteries.\textsuperscript{41} These advantages of lithium-ion batteries closely correlate with the light molecular weight of Li\textsuperscript{+}, small radius of Li\textsuperscript{+} and low redox potential [\(E\textsuperscript{o}(\text{Li}^+/\text{Li}) = -3.04\text{ V vs standard hydrogen electrode (SHE)})], because the fast diffusion rate of Li\textsuperscript{+} benefits from its small radius and low redox potential leading to a high-output voltage and therefore high-energy densities.\textsuperscript{34,42}

Generally, a lithium-ion battery consists of three parts including anode, cathode material and electrolyte between them which is either liquid or solid as shown in Figure 3. Basically, the
Li$^+$ transports between two electrodes under the help of electrolyte during charge-discharge process, meanwhile, the electronic components travel through an external circuit to provide energy. The reaction on the cathode is:

$$\text{LiCoO}_2 \leftrightarrow x \text{Li}^+ + x e^- + \text{Li}_{1-x}\text{CoO}_2$$  \hspace{1cm} (5)

The reaction on the anode is:

$$C_6 + x \text{Li}^+ + x e^- \leftrightarrow \text{Li}_xC_6$$  \hspace{1cm} (6)

Figure 3. Schematic illustration of a lithium ion battery.$^{43}$
During charge process, the Li\(^+\) in the LiCoO\(_2\) cathode is extracted from the layered LiCoO\(_2\) and after traveling to the graphite anode through the electrolyte, the Li\(^+\) is inserted into the graphite layers which are the most commonly used lithium-ion battery anode. The whole process is reversed in the discharge process.

If we look deep inside the lithium-ion battery as shown in Figure 4, \(\mu_A\) and \(\mu_C\) represent the electrochemical potentials of the anode which is the reductant and the cathode which is the oxidant, respectively. Provided that \(\mu_A\) is above the lowest unoccupied molecular orbital (LUMO), electron from anode will transfer to the electrolyte LUMO leading to the reduction of the electrolyte.\(^{44}\) Similarly, the electrolyte can be oxidized if the \(\mu_C\) of the cathode is lower than the highest occupied molecular orbital (HOMO) of the electrolyte.\(^{44}\)
Therefore, the thermodynamic stability of the battery is highly dependent on the electrode electrochemical potentials of anode ($\mu_A$) and cathode ($\mu_C$) materials and the electrochemical stability window of the electrolyte and it can be expressed as:\textsuperscript{44}

$$eV_{oc} = \mu_A - \mu_C \leq E_g$$

(7)
where \( eV_{oc} \) is the open-circuit voltage and \( e \) is the magnitude of the electron charge and \( E_g \) is the energy separation between LUMO and HOMO. However, if the electrolyte is reduced at the anode, a passivating solid electrolyte-interface (SEI) layer at the electrode/electrolyte boundary will be formed to stabilize the system by providing kinetic stability to a larger \( V_{oc} \).^44

As an energy storage device, energy density is an important criteria to evaluate the battery performance which can be calculated from the equation:

\[
Energy = \int_0^{\Delta t} IV(t)\ dt = \int_0^Q V(q)dq
\]

where \( Q \) is the total charge per unit weight (Ah kg\(^{-1}\)) or per volume (Ah L\(^{-1}\)), \( I \) is the charge or discharge current.\(^{43}\) The volumetric energy density (Wh L\(^{-1}\)) is more important in portable device batteries due to the limited size for these devices. Based on the Equation 8, the critical way to enhance the energy density of a battery is either by increasing the working voltage or using new electrode materials with higher capacity. Therefore, developing new electrolyte with higher voltage window is of great interest for increasing the working voltage. Moreover, finding high capacity anode and cathode, on which most research efforts are focusing, is another way to the problem.

### 2.2.2 Introduction of sodium-ion batteries

Sodium-ion batteries, as an analogue with lithium-ion batteries in electrochemistry, have been studied for decades since 1970s.\(^{45-47}\) However, after the success of commercial application of lithium-ion batteries, people pay less attention to sodium-ion batteries.\(^{48}\) With
the rapidly increasing demand for lithium, it is estimated that the mineable Li will probably exhaust under the average growth of 5% consumption per year.\textsuperscript{48,49} Therefore, in a foreseeable future, the concern of exhausting lithium resource and possible price fluctuation, in addition, considering the abundance of sodium, people restart to explore the application of sodium-ion batteries to partially replace lithium-ion batteries. Table 1 compares some basic characteristics of lithium and sodium.

<table>
<thead>
<tr>
<th>Lithium</th>
<th>Sodium</th>
<th>Category</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.76</td>
<td>1.06</td>
<td>Cation radius (Å)</td>
</tr>
<tr>
<td>6.9 g mol\textsuperscript{-1}</td>
<td>23 g mol\textsuperscript{-1}</td>
<td>Atomic weight</td>
</tr>
<tr>
<td>0</td>
<td>0.33V</td>
<td>E° (vs. Li/Li\textsuperscript{+})</td>
</tr>
<tr>
<td>$5000/ton</td>
<td>$150/ton</td>
<td>Cost, carbonates</td>
</tr>
<tr>
<td>3829</td>
<td>1165</td>
<td>Capacity (mAh g\textsuperscript{-1}), metal</td>
</tr>
<tr>
<td>Octahedral and tetrahedral</td>
<td>Octahedral and prismatic</td>
<td>Coordination preference</td>
</tr>
</tbody>
</table>

From Table 1, it is seen that sodium is less reducing than lithium (\textasciitilde2.71V vs. S.H.E., compared to \textasciitilde3.04 V) which means lower operating voltages for sodium-ion batteries.
compared with lithium-ion batteries. Additionally, the capacity of metallic electrodes between Na and Li shows another disadvantage of sodium-ion batteries. However, when considering the theoretical reversible capacity of LiCoO$_2$ and NaCoO$_2$ as layered oxides with the same crystal structure, only a 14% difference exists (274 and 235 mAh g$^{-1}$ for LiCoO$_2$ and NaCoO$_2$, respectively). Moreover, one of the merits from larger cation radius is the weaker solvation energy in polar solvents for Na$^+$ because the solvation energy is an important factor to determine the kinetics of alkali-ion insertion processes at the electrolyte interface. In addition, the high ion conductivity of Na$^+$-based electrolytes also makes a great contribution to the development of sodium-ion batteries which can enhance the performance and makes them as good as lithium-ion battery with respect to the conductivity.

### 2.2.3 Sodium ion battery cathode

Similar to lithium-ion battery cathode, sodium-ion battery cathode functions as a host material for Na which can accommodate Na$^+$ insertion/extraction at a reasonable voltage 2 V positive to that of Na metal. Increasing the cathode working voltage is a critical and efficient way to improve the energy density of sodium-ion battery. For sodium, it has a preference to form 6-coordination either in an octahedral or prismatic arrangement, which limit the available structure types for sodium-ion battery cathode materials. In contrast to the researches on anode and electrolytes, great progress has been made in sodium-ion battery cathode research. Various compounds with different structures have been studied as potential cathode materials including sulfides, fluorides, phosphates and sulfates, and oxides.
Among these cathode candidates for sodium-ion batteries, layered transition metal oxides show great advantages like simple structures, high capacities, and ease of synthesis. The general formula of layered transition metal oxides can be expressed as \( \text{Na}_x \text{T}_M \text{O}_2 \) (\( \text{T}_M = \text{Ti, V, Cr, Mn, Fe, Co, Ni, and a mixture of 2 or 3 elements with 2 oxidation states} \)) in which the \( \text{T}_M \text{O}_6 \) layers are the repeating sheets whereas sodium ions are sandwiched between the oxide layers. Based on different surrounding Na environments and possible packing of the layered sheets, Na layered oxides can be classified into three phases: O3-, P2-, and P3 as shown in Figure 5.

![Figure 5. Typical structure of (a) O3-, (b) P2-, and (c) P3-phase layered oxides.](image)

LiCoO\(_2\), as the most commonly used cathode material in lithium-ion battery since 1990, has a high energy density. However, its sodium analogue shows more complicated phase transitions during the desodiation process. The structure of the phase has a great effect on the electrochemical performance due to the different amount of Na in the pristine state and
kinetics affected by the surrounding environment of Na.\textsuperscript{56} For example, the low diffusion barrier and high ionic conductivity are beneficial to the P2- type cathode which shows better performance than the O3-phase from the 2\textsuperscript{nd} cycle.\textsuperscript{56,58–60}

Classified by the types of T\textsubscript{M} in the layered transition metal oxides, there are several different structures: single T\textsubscript{M} systems Na\textsubscript{x}T\textsubscript{M}O\textsubscript{2}, binary T\textsubscript{M} systems Na\textsubscript{x}T\textsubscript{M}T\textsubscript{M}’O\textsubscript{2} and ternary T\textsubscript{M} systems. For the single T\textsubscript{M} system, the study is fundamental and it is basis for binary and ternary systems because different types of transition metal with different crystallographic phases demonstrate various electrochemical properties including reversible capacity, voltage range, and cyclic profile.\textsuperscript{56} Generally, compared with single systems, higher reversible capacity, flat voltage profile and higher working voltage can be obtained by binary and ternary systems. For example, the O3-type NaFe\textsubscript{0.5}Co\textsubscript{0.5}O\textsubscript{2}, prepared by a solid-state method, shows larger reversible capacity and better rate capability than the NaFeO\textsubscript{2} and NaCoO\textsubscript{2} as shown in Figure 6.\textsuperscript{61}
Figure 6. Cycling performance of NaFeO$_2$, NaCoO$_2$ and NaFe$_{0.5}$Co$_{0.5}$O$_2$.$^{61}$

Phosphates are another kind of compounds that have been studied as sodium-ion battery cathode materials. Lithium phosphates have attracted lots of attention due to their structural and thermal stability and the higher redox potential in lithium-ion batteries.$^{48}$ Among various phosphates, NASICON (Na Super Ionic Conductor) type compounds seem to hold great promise as the cathode materials for sodium-ion batteries, which were first studied by Hong and Goodenough as Na$^+$ solid electrolytes.$^{48,62,63}$ Recently, a carbon coated Na$_3$V$_2$(PO$_4$)$_3$ was synthesized by a one-step solid state reaction and a reversible capacity of 93 mAh g$^{-1}$ could be obtained between 1.0-3.0 V associated with a V$^{4+}$/V$^{3+}$ and V$^{3+}$/V$^{2+}$ redox couple.$^{64}$ The electrochemical performance was then further enhanced by optimizing the electrolyte and decreasing the carbon content in the composite synthesized by Chen et al.$^{65}$ The coulombic
efficiency of the first cycle was as high as 98.7% and it maintained 99.8% in subsequent cycles in NaFSI/PC electrolyte with a reversible capacity of 107 mAh g\(^{-1}\).\(^{65}\) A full cell using Na\(_3\)V\(_2\)(PO\(_4\))\(_3\) carbon composite as cathode and hard carbon as anode was also assembled and evaluated. An average operating voltage of 2.7V corresponding to a theoretical energy density of 180 W h kg\(^{-1}\) could be obtained, but the coulombic efficiency was still low.

Phosphates with Fe (II) based on the Fe\(^{2+}\)/Fe\(^{3+}\) redox couple was also widely investigated due to the nontoxic and Earth-abundant property of Fe. As a sodium counterpart of LiFePO\(_4\), NaFePO\(_4\) has two different crystal structures, triphylite-type and maricite-type as shown in Figure7. Compared with triphylite-type NaFePO\(_4\), maricite-type structure shows more thermodynamically stability and is closely related to olivine-type structure.\(^{51}\) In contrast, the triphylite-type NaFePO\(_4\) is more electrochemically active and suitable for sodium-ion battery cathode application.\(^{66}-^{68}\) However, it is experimentally evident that the NaFePO\(_4\) has slower diffusion kinetics in sodium-ion batteries than that of LiFePO\(_4\) in lithium-ion batteries. Besides, the volume change between FePO\(_4\) and NaFePO\(_4\) is also larger than that between C-FePO\(_4\) and C-LiFePO\(_4\), which leads to a worse rate performance.\(^{69}\)
After many years’ study, the development of new cathode materials has led to increased energy density of sodium-ion batteries as shown in Figure 8. However, in contrast to the booming research progress of cathode materials, more attention should be put on the anode material of sodium-ion batteries which has become the bottleneck constrain.
2.2.4 Sodium-ion battery anode

Anode material is another critical issue to successfully develop sodium-ion batteries. Sodium metal has been excluded from the anode candidates due to the dendrite formation and low melting point of 97.7°C, which leads to severe safety issue. Due to the similar electrochemistry as lithium-ion battery, some anode material candidates for lithium-ion batteries can be utilized in sodium-ion batteries including carbonaceous materials, alloys, phosphorus/phosphide, metal oxides and sulfides. In the process of exploring anode materials for sodium-ion batteries, some important factors like electrolyte, binders and the solid...
electrolyte interphase (SEI) are inevitable, which can greatly influence the electrochemical performance of the anode materials.

SEI is a passivation layer on the electrode surface which can be formed at $\sim 0$ V vs Na/Na$^+$ when the polar aprotic electrolyte solvents are irreversibly reduced. The formation of the SEI on the electrode surface can prevent the direct contact between the electrode and electrolyte and realize a stable cycling performance. Many literatures reported the SEI in lithium-ion battery system, but SEI in sodium-ion battery system is different and more progress is still needed. It is pointed out that the SEI in sodium-ion batteries is not as stable as that in lithium-ion batteries due to the high soluble SEI composition of sodium-ion battery system such as sodium oxides, hydroxide, and carbonates.$^7$ Additionally, the organic compound that formed SEI in lithium-ion batteries are more soluble in electrolyte leading to less inorganic salt depositions on the anode material compared with that in sodium-ion batteries.$^7^2$ The high reversibility and good rate performance can benefit from the stable SEI on the anode material. In order to achieve a good electrochemical performance, the electrolyte itself and electrolyte additive also play an important role in suppressing the decomposition of the electrolyte which is related to the stable formation of the SEI.

Various electrolytes such as organic electrolyte solution, solid polymer electrolyte, gel polymer electrolyte, inorganic solid electrolyte have been widely studied in lithium-ion battery application. Among them, the organic electrolyte solution based on carbonate ester polar solvents is the most commonly used one due to its great advantages including wide
potential window, high ionic conductivity, good temperature performance, low toxicity, etc.\textsuperscript{51}

In order to explore the mechanism of SEI formation and stabilization in sodium-ion battery, hard carbon was used as the anode to study the performance of different electrolytes with NaClO\textsubscript{4} dissolved into different carbonate ester based solvents as shown in Figure 9.\textsuperscript{72}

**Figure 9.** Capacity retention for hard-carbon electrodes in the beaker-type cells with 1 mol dm\textsuperscript{-3} NaClO\textsubscript{4} dissolved in different solvent mixtures.\textsuperscript{51,72}

It is seen from Figure 9 that cells using propylene carbonate (PC) and the binary ethylene carbonate (EC)/ diethyl carbonate (DEC) mixed solution as electrolytes show better cycling stability over cells with other electrolyte solvents combination. Moreover, the relatively high
The melting point of EC (~37°C) seems to make PC a better choice as the electrolyte solvent for hard carbon anode in sodium-ion batteries. However, further investigation on the conductivity and viscosity of different electrolyte solvents has proven that EC/DEC based electrolytes have a higher conductivity compared with PC-based electrolytes as shown in Figure 10.

**Figure 10.** Conductivity (black bars and left hand side y axis) and viscosity (green bars and right hand side y axis) values of electrolytes based on 1 M NaClO$_4$ dissolved in various solvents and solvent mixtures.$^{73}$
From Figure 10, it is also noted that binary solvent-based electrolytes, especially the ones with EC involved, generally have higher conductivity than single solvent-based electrolytes. That is because among all the solvents, EC has the highest dielectric constant value which can ensure an improved dissociation of the salt.\textsuperscript{73} On the other hand, PC also has a high dielectric constant value but the ionic conductivity of the PC based electrolyte is not very high due to the high viscosity of PC. Therefore, for the binary-based electrolytes, even though the DME does not exhibit high dielectric constant value, the low viscosity property of DME makes EC: DME the electrolyte with highest ionic conductivity. It can be concluded that enhanced dissociation of the salt and low viscosity are two key parameters to obtain good ionic mobility in the sodium-ion battery electrolyte.\textsuperscript{73}

After applying these electrolytes into the assembled sodium-ion batteries with hard carbon as the anode, the binary-based PC:EC exhibits the best capacity retention as shown in Figure 11 (b). Based on the electrochemical impedance spectroscopy (EIS) analysis, the PC based electrolyte shows an increased charge transfer resistance upon cycling which is a sign of continuously growing SEI due to continuous electrolyte decomposition.\textsuperscript{73} In contrast, the stable charge transfer resistance is achieved for PC:EC based electrolyte which indicates that the SEI layer is stable, hence the best cycling stability is obtained.
Figure 11. (a) First cycle voltage versus capacity profiles for hard carbon electrodes cycled in 1M NaClO₄ in various solvent mixtures (recorded at C/20) and (b) discharge capacity versus cycle number for the corresponding cells.⁷³
In addition to the electrolyte itself, the electrolyte additive also plays an important role in improving the electrochemical performance. For lithium-ion batteries, many electrolyte additives like vinlylene carbonate (VC), fluoroethylene carbonate (FEC), and ethylene sulfite (ES) have been investigated and proven beneficial for stabilizing the SEI by suppressing electrolyte decomposition.\textsuperscript{74,75} In sodium-ion battery system, addition of FEC into the PC electrolyte can efficiently suppress the decomposition of PC and achieve good reversibility of the Na insertion because FEC can decompose at around 0.7 V at first cycle and form a stable SEI and passivation to prevent further electrolyte decomposion.\textsuperscript{76} Therefore, the sodium-ion battery performance can be noticeably optimized by using a suitable combination of electrolyte solvents and salts as well as the electrolyte additive.

Last but not least, the type of binders also influences the electrochemical performance of anode materials. Poly(vinylidene fluoride) (PVdF) has been widely used in commercial lithium-ion batteries for decades, whose main function is to turn powdery electrode materials into solid and keep attached on the metal current collector. As the development of new electrode materials such as Si and Sn, more requirements of binders are proposed including accommodating large volume change, providing sufficient binding properties with as low as binder content. Therefore, due to the poor ability to accommodate the volume expansion of PVdF and the toxic N-methyl pyrrolidone (NMP) that is used to dissolve PVdF, developing new types of binders becomes necessary.\textsuperscript{77} Recently, many water-soluble binders were developed including sodium carboxymethyl cellulose (CMC), polyacrylic acid (PAA) and alginate.\textsuperscript{78–83} In addition, these binders are nontoxic and most of them are derived from
natural resource which can help decrease the cost of the batteries. When tested with the Si anode in lithium-ion batteries, it can be seen from Figure 12 that compared with PVdF binder, great cycling stability can be achieved for other two cells, especially the one uses the alginate binder. Alginate not only ensures a weak binder-electrolyte interaction but also contributes to maintaining a stable SEI layer during charge/discharge process.\textsuperscript{78}

\textbf{Figure 12.} Reversible Li-extraction capacity of nano-Si electrodes with alginate, CMC, and PVDF binders versus cycle number collected for the current density of 4200 mA/g for cells cycled in the potential window of 0.01 to 1 V versus Li/Li\textsuperscript{+}.\textsuperscript{78}

CMC as a binder was also tested in sodium-ion batteries. PVdF and CMC were used as binders for hard carbon anodes and the electrochemical measurements were conducted using 1 mol dm\textsuperscript{-3} NaPF\textsubscript{6} PC solution without FEC and with 5\% FEC. In the case of the PVdF sample, as mentioned above, the FEC is beneficial to stabilize the SEI and achieve better
capacity retention. However, for the CMC binder sample, an adverse effect was surprisingly found on the one with FEC electrolyte additive. The electrode surface was studied using XPS and it was revealed that CMC functioned as a passivation layer that was covered on the hard carbon surface. If FEC additive was added, excessive surface film, which was the result of decomposed FEC, would be formed leading to increased resistance and therefore lower reversible capacity.\textsuperscript{51,84}

![Figure 13. Cycle performance of hard-carbon electrodes in NaPF\textsubscript{6} PC solutions with or without FEC addition: a) CMC and b) PVdF binders.\textsuperscript{84}](image)

\textbf{2.2.4.1 Carbonaceous materials}

In the process of exploring the storage mechanism of lithium in the carbonaceous materials, many models are proposed to explain the origin of the anomalous high capacity.\textsuperscript{51} As the first model describes, Li\textsuperscript{+} are accommodated ionic sites and Li\textsubscript{2} “covalent” sites between the carbon layers as shown in Figure 14.\textsuperscript{51,85} For the second model, Li or Na inserts into micropores by intercalation into the interstitial space sandwiched with hexagonally bonding
The Li or Na first inserts between the carbon layers at the slope region (above 0.2V) in the potentiogram, then transfers into the micropores of hard carbon in plateau regions.\textsuperscript{51}

**Figure 14.** Schematic illustration for the coexistence of two types of Li site in PPP-based carbon. Reduced aromatic rings are represented by hexagonals. The Li ions and atoms are denoted by empty and solid circles for sites A and B, respectively. Covalent bonds between two Li atoms in site B are shown by heavy lines.\textsuperscript{85}

For lithium-ion batteries, graphite is the most widely used anode material due to its high gravimetric and volumetric capacities. During the reaction, the Li\textsuperscript{+} can be intercalated between the graphene layers by stages and the graphite is reduced stepwise to LiC\textsubscript{6}, delivering a capacity of 360 mAh g\textsuperscript{-1} which is very close to its theoretical capacity (372 mAh g\textsuperscript{-1}).\textsuperscript{88} However, it is extremely difficult for Na\textsuperscript{+} to insert into graphite and only < 35mAh g\textsuperscript{-1}
capacity can be obtained corresponding to a product of \( \sim \text{NaC}_{186} \), which delivers much smaller capacity.\(^{89}\) That’s because the interlayer distance of graphite (\( \sim 0.34 \) nm) is too small compared with the required minimum interlayer distance of 0.37nm for Na insertion and there is also no strong driving force for \( \text{Na}^+ \) insertion.\(^{89,90}\) Hu \textit{et al} \(^{90}\) had further insight into the mechanism of the Na-insertion into carbon material and calculated the energy cost for sodium and lithium insertion into carbon as a function of carbon interlayer distance based on the balance of attractive van der Waals interactions between carbon layers and repulsive interactions between Na or Li ions and carbon. The \( \text{NaC}_6 \) shows a larger equilibrium interplanar distance (0.45nm) than \( \text{LiC}_6 \) (0.37nm) due to the larger radius of \( \text{Na}^+ \).\(^{90}\) Therefore, for graphite which has an interlayer space of 0.335 nm, the energy cost for Li-insertion (0.03eV) is much smaller than that of Na-insertion (0.12eV) and it is the reason that sodium ions cannot intercalate into graphite to deliver high capacity.\(^{90}\) However, as the Figure 15 shows, when the interlayer space is increased to 0.37nm, the energy cost for Na-insertion is significantly dropped to 0.053eV which is easier to overcome. The study indicates that the minimum interlayer space of carbon material for Na-insertion is 0.37nm. Due to the reasons mentioned above, it urges people to look for other materials to be used as sodium-ion battery anode.

At first, in order to decrease the energy cost for Na-insertion into graphite, an expanded graphite was produced by a two-step oxidation-reduction process which increased the interlayer distance of graphite to 0.43 nm as shown in Figure 16.\(^{91}\)
Figure 15. Theoretical energy cost for Na (red curve) and Li (blue curve) ions insertion into carbon as a function of carbon interlayer distance. The inset illustrates the mechanism of Na and Li ions insertion into carbon.
Figure 16. (a) Na\(^+\) cannot be electrochemically intercalated into graphite because of the small interlayer spacing. (b) Electrochemical intercalation of Na\(^+\) into GO is enabled by the enlarged interlayer distance because of oxidation. However, the intercalation is limited by steric hindering from large amounts of oxygen-containing groups. (c) A significant amount of Na\(^+\) can be electrochemically intercalated into EG owing to suitable interlayer distance and reduced oxygen-containing groups in the interlayers.\(^9\)

The expanded graphite, as shown in Figure 17 (c), can deliver a capacity of 284 mAh g\(^{-1}\) at 20 mA g\(^{-1}\) with good capacity retention (73.92% after 2,000 cycles) as shown in Figure 17 (c). During the sodiation/desodiation process, there were mainly two stages involved: the sloping voltage profile between 2.0 and 0.3 V corresponding to insertion/extraction of Na\(^+\) between graphene layers in expanded graphite and the low-voltage plateau might represent the Na\(^+\) insertion/extraction in the pores/defects of graphene layers.\(^{91-93}\) Further exploration indicates that the capacity is mainly limited by the ion diffusion process due to a linear relationship between the capacity and the reciprocal square root of scan rate and majority of the capacity comes from the highly reversible intercalation reaction instead of the capacitive contribution.\(^9\) As shown in Figure 17 (d), the rate performance is conducted from a current density of 20 mA g\(^{-1}\) to 200 mA g\(^{-1}\), and when the current density is increased to 200 mA g\(^{-1}\),...
the reversible capacity is decreased to 100 mAh g\(^{-1}\) which is not satisfactory for sodium-ion battery anode application.

Figure 17. (c) Long-term cycling stability of EG-1 h. Note that 20mAg\(^{-1}\) was used for the initial 10 cycles. At the 11th cycle, the current was changed to 100mAg\(^{-1}\) and held constant during the rest of the test. (d) Rate capability test for EG-1 h. Note that the cell was pre-cycled at 20mAg\(^{-1}\) for 20 cycles before the rate performance test.\(^{91}\)

In addition to the modified graphite, disordered carbon such as soft and hard carbon shows great potential as anode material for sodium-ion batteries, especially the hard carbon due to its high capacity, natural abundance etc.\(^{94,95}\) Figures 18 and 19 show the difference between the soft and hard carbons. The hard carbon is generally formed from precursors with little hydrogen or much oxygen and it displays two domains: graphite-like layers and micropores.\(^{96}\) However, it is difficult to remove the turbostratic disorder in the hard carbon and there is no trace of true graphite structure even under 3000\(^{\circ}\)C.\(^{96}\)
Figure 18. Schematic representation of the structure of a graphitizing (but non-graphitic) carbon (soft carbon).  

Figure 19. Schematic representation of the structure of non-graphitizing carbon (hard carbon).
Hard carbon spherules prepared from sucrose at different temperatures were investigated by Huang et al.\textsuperscript{97} It is found that the plateau capacity increases with increased carbonization temperatures for the hard carbon which results from the increased quantity of the nanopores as shown in Figure 20.\textsuperscript{97} Because the plateau at the low potential region can be ascribed to the adsorption–desorption in the nanopores of carbon materials.\textsuperscript{86,87,98}

**Figure 20.** Discharge and charge curves for the 1st, 2nd and 10th cycles of (a) HCS1000, (b) HCS1300 and (c) HCS1600; (d) relation curves of the plateau and slope capacity and carbonization temperature.\textsuperscript{97}
In order to improve the electrochemical performance of sucrose-based hard carbon materials, NaHCO₃ was used to produce submicron- and nano-sized pores during the two-stage sintering process. From the XRD pattern, it was found that with an increased amount of NaHCO₃ in the sucrose precursor, the interlayer spacing of achieved nanoporous sucrose-based hard carbon (NSHC) increased. Because the decomposition of NaHCO₃ in NSHC-20 produced significant internal pressure and disrupted the interlayer interaction as in thermal expansion of graphite, it facilitated the Na⁺ insertion into graphene layers leading to an improved Na⁺ storage capability. Additionally, as shown in Figure 21, the increased NaHCO₃ also helps to create a porous structure leading to higher surface area which is beneficial to increase the capacity of hard carbon.

**Figure 21.** (left) Low and (right) high magnification FESEM images of (A) SHC, (B) NSHC-2.5, (C) NSHC-5, (D) NSHC-10, and (E) NSHC-20.
It is noted that the cycling performance is enhanced when NaHCO$_3$ is added. However, for different NaHCO$_3$ contents, the highest capacity is achieved by the one with 5% NaHCO$_3$ as shown in Figure 22, which is mainly attributed to the contribution of the optimized nanometric pore structures.\textsuperscript{99}

![Figure 22. Capacity retention (A) SHC, (B) NSHC-2.5, (C) NSHC-5, (D) NSHC-10, and (E) NSHC-20 during 100 cycles at 20 mA g$^{-1}$.\textsuperscript{99}]

Except for the hard carbon spherules, some other hard carbon materials with different morphologies were also studied. Graphene, as one of the most intriguing and promising materials, has been utilized in many applications due to its high electrical conductivity, high surface area and so on. Dou \textit{et al} studied the electrochemical properties of sodium ion storage
in reduced graphene oxide (RGO).\textsuperscript{100} The graphene oxide was prepared from natural graphite using a modified Hummers’ method and followed by annealing at 750°C for 5h in nitrogen atomosphere.\textsuperscript{100,101} During the first charge-discharge process, there was a large irreversible capacity loss which was attributed to the SEI formation. Noticeably, after the first cycle, there was a pronounced cathodic peak near 0.01 V but no anodic peak was observed in the reverse cycle which indicated that in the low-voltage area, the Na\textsuperscript{+} adsorption occurred on the graphene sheets and/or active sites.\textsuperscript{100} After cycling for 250 cycles, a reversible capacity of 174.3 mAh g\textsuperscript{-1} could still be maintained under a current density of 0.2C (40mA g\textsuperscript{-1}) demonstrating good repeatability. Compared with the sucrose-derived hard carbon spherules, the RGO demonstrated better rate capability. When the current density was increased to 0.5C, 1C, 2C, 5C, reversible capacities of 217.2, 176.4, 150.9, 118.7, and 95.6 mAh g\textsuperscript{-1} could be achieved respectively. The good electrochemical performance can be ascribed to several factors. Firstly, the graphene sheets are interconnected into network in the RGO host which can minimize the diffusion lengths of Na-ions within the electrode.\textsuperscript{100} Secondly, the introduction of surface defects, heteroatoms, and hydrocarbons from the oxidation process is beneficial to the sodium incorporation.\textsuperscript{100} Moreover, a thin wrinkled structure is formed by the overlap of single graphene layers and it is favorable to insertion of the relatively large Na ions.\textsuperscript{100}

Additionally, one-dimensional carbon materials such as carbon nanotubes, nanowires and nanofibers have attracted tremendous attention due to their flexibility, uniform structure, and good conductivity.\textsuperscript{90,102} Recently, Chen et al.\textsuperscript{103} used a simple electrospinning method to
produce PAN nanofibers and achieved the carbon nanofibers by further thermal treatment. Based on the charge/discharge profile as shown in Figure 23 (b), no obvious voltage plateau is observed which indicates that sodium adsorption/insertion on/between graphene layers in the carbon nanofibers is the predominant mechanism during charge/discharge process as shown in Figure 23 (c).

Figure 23. (b) Charge/discharge curves of the carbon nanofiber electrode; (c) schematic illustration of the sodium storage mechanism in carbon nanofibers.\textsuperscript{103}
Due to the high reversible adsorption/insertion sodium storage mechanism, carbon nanofibers show good cycling performance. A reversible capacity of 217 mAh g$^{-1}$ still could be maintained after 50 cycles under a current density of 50 mA g$^{-1}$, corresponding to a capacity retention as high as 93.5%. Even when the current density was increased to 2 A g$^{-1}$, the carbon nanofiber electrode could still deliver an initial capacity of 173 mA h g$^{-1}$ and maintained a capacity of 169 mA h g$^{-1}$ after 200 cycles.

On the other hand, nitrogen-doping has been demonstrated to be useful to efficiently enhance the electrochemical performance of carbon-based anode materials in lithium-ion batteries, because the N-doping can create extrinsic defects leading to improved electronic conductivity and reactivity.$^{104}$ This strategy can be applied in modifying the sodium-ion battery anode material as well.

Huang et al.$^{104}$ used polypyrrole (PPy) as the carbon nanofiber precursor, which has a high nitrogen content, to produce the functionalized interconnected N-doped carbon nanofibers (FN-CNFs). The FN-CNFs were obtained after carbonization at 600°C for 2h with a fiber diameter around 100 nm as shown in Figure 24. As the elemental analysis showed, the weight contents of C, O, N and H in the FN-CNFs were 73.82%, 9.25%, 13.93% and 1.96%, respectively. Due to the high nitrogen content in PPy precursor, the obtained FN-CNFs can be seen as in situ nitrogen-doped, and it is a facile way to increase the nitrogen in the CNFs compared with surface chemical modification method.
In this study, X-ray photoelectron spectroscopy (XPS) was utilized to study the surface chemistry of FN-CNFs. The deconvolution of the N 1s spectrum showed that there are three different kinds of nitrogen in the FN-CNFs, pyridinic (N-6), pyrrolic/pyridone (N-5) and quaternary (N-Q) nitrogen, whose peaks are located at 398.3, 400.3 and 401.9 eV, respectively, as shown in Figure 25.\textsuperscript{104–106} It is generally accepted that nitrogen doping is favorable for lithium kinetics because nitrogen has a higher electronegativity and smaller diameter leading to stronger interaction between the formed carbon structure.\textsuperscript{107,108} In addition, nitrogen doping can induce a large amount of defects on the graphene layers which can function as Li\textsuperscript{+} insertion sites and improve the lithium storage capacity.\textsuperscript{107,109–113} However, the nitrogen doping also has adverse effect on the electrochemical performance of carbon materials. It is reported that the increased nitrogen content, especially the pyridinic nitrogen, always leads to a lower coulombic efficiency in the first cycle.\textsuperscript{114} Pyridinic nitrogen, which has a lone pair of electrons, is located at edges of the graphene layers. During the first

**Figure 24.** SEM images for (a) PPy precursor and (b) FN-CNF.\textsuperscript{104}
reduction process, the nitrogen atoms can function as active sites for electrolyte decomposition, meanwhile, trap the solvated lithium cations on them, therefore leading to the irreversible capacity.\(^{105}\) Besides, large surface area is also beneficial to the decomposition of electrolyte in the nitrogen-rich carbon materials because the electrolyte is more likely to contact with the decomposition active sites.

**Figure 25.** XPS spectra of the FN-CN: (a) C 1s, (b) O 1s and (c) N 1s. (d) Schematic model of N- and O-containing surface functional groups on FN-CN.\(^{104}\)
As the CV shows in Figure 26 (a), the reduction peak at 1.0V is attributed to the SEI formation. After the first cycle, there is an increase in the reduction current between 1.10-1.88V in the subsequent cycles as well as a broad redox range from 0.6-2.0V, which result from the reaction between sodium and the functional groups on the carbon surface. This is a general phenomenon that can be observed in the case of lithium-ion battery when the nitrogen-rich carbon is used as the anode material.\textsuperscript{115–117}

\begin{figure}
\centering
\includegraphics[width=\textwidth]{figure26.png}
\caption{Electrochemical performance of the FN-CN as an anode material for Na-ion battery: (a) CV curves of the FN-CN electrode between 0.01 and 2 V at a scan rate of 0.1 mV s\textsuperscript{-1}, (b) galvanostatic charge/discharge profiles at a current density of 50 mA g\textsuperscript{-1}, (c) cycle performance of the FN-CN electrode, and (d) capacity retention dependent on cycle and rate.\textsuperscript{104}}
\end{figure}
Moreover, the oxidation current between 0 and 0.48 V has an obvious increase after first cycle which is a sign of adsorption with charge transfer on both sides of single graphene layers, and reaction of Na\(^+\) between nitro groups or carbonyl groups. The FN-CNFs show excellent cycling performance and rate capability. Under a current density of 200 mA g\(^{-1}\), a capacity of 134.2 mAh g\(^{-1}\) is stabilized after 200 cycles. In the rate performance test, when a current as high as 20 A g\(^{-1}\) is applied, the FN-CNFs still can deliver a capacity of 73 mAh g\(^{-1}\).

![Figure 27. Schematic illustration of sodium storage mechanism in FN-CNФ.](image)

The excellent electrochemical performance can be attributed to several reasons. At first, the 3-D networks formed by carbon nanofibers can facilitate ion transport, meanwhile, provide access of the electrolyte to the surface active sites as shown in Figure 27. Secondly, the O-containing and N-containing functional groups are beneficial to the acceleration of surface
redox reactions. At last, the in situ nitrogen doping has created a large amount of defects on the surface of graphene layers which can further enhance the sodium storage capability.

2.2.4.2 Alloy materials

Extensive studies of alloy anodes in lithium-ion batteries have been carried out due to their high theoretical capacity, low redox potential and safety characteristics. In the periodic table of elements, most of the elements in group 14 and 15 can interact with a larger number of Na to form binary compounds, delivering much higher capacity than carbon materials as shown in Figure 28.

Among these elements, Si has attracted tremendous attention in lithium-ion battery anode application because $\text{Li}_{1.5}\text{Si}_4$ can be formed during the electrochemical reaction, which is the most Li-rich phase, meanwhile, exhibiting an extremely high theoretical capacity 4200 mAh g$^{-1}$. However, in sodium-ion battery, a high temperature is necessary for Na insertion into silicon, which is a barriers for Si application in sodium-ion battery.
In spite of the high theoretical capacity, the alloy anode materials inevitably suffer from the high initial irreversible capacity and rapid capacity loss during charge/discharge process. Because, during the charge/discharge process, the sodiation and desodiation of the alloy material cause a volume expansion/extraction, leading to cracking and pulverization of active particles and this results in the disconnection between the active alloy particles and...
conducting agent even the current collector. Considering the large radius of the sodium ion, the volume change in sodium-ion battery is expected to be severer than that in lithium-ion battery. In Figure 29, it demonstrates the volume change as the sodiation process continues in many alloy materials.

**Figure 29.** (Color online) The volume change (Å³/M) compared to elemental M for known crystalline Na-M alloys (M ¼ Si, Ge, Sn, Pb) increases linearly as a function of Na content. A linear fit shows each Na atom occupies 30.3 Å³ on average, independent of M, or Na content. In addition, Na is calculated to occupy a constant volume (30.3 Å³) as the Na content increases in the Na-alloy compound, which is approximately twice the volume of the lithium
This directly causes a smaller volumetric energy density and larger volume change of Na-ion battery anode compared with lithium-ion battery. In order to overcome these challenges of the alloy anode materials, many strategies have been developed.

### 2.2.4.2.1 Tin and antimony alloy electrode materials

Both tin and antimony can form binary compounds with Na and deliver capacity. For tin, a fully sodiated Na$_{15}$Sn$_4$ can deliver a high capacity of 847 mAh g$^{-1}$, and during the discharge process, five plateaus can be observed corresponding to different phases: Sn, Na$_{0.6}$Sn, Na$_{1.2}$Sn (amorphous), Na$_5$Sn$_2$, and Na$_{15}$Sn$_4$ as shown in Figure 30.

**Figure 30.** Electrochemical potential profiles obtained during the first (black) and second (gray) cycles for Sn film electrodes cycled between 0.005 and 2 V.
At first, different binders were used for the Sn anodes and their electrochemical performance were investigated. Recently, Dai et al.\textsuperscript{133} found that a conductive binder poly(9,9-dioctylfluorene-co-fluorenone-co-methylbenzoic ester) (PFM) was able to improve the performance of tin anode. Compared with CMC and PVdF binder, the tin anode using PFM showed higher specific capacity and higher cycling stability without any carbon black.\textsuperscript{133}

Due to the good conductivity and high binding ability of PFM binder, all the Sn particles including the isolated particles will be electrically connected and fully sodiated during the charge/discharge process, leading to a high capacity as shown in Figure 31.\textsuperscript{133}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure31.png}
\caption{The first charge and discharge voltage profiles of (a) Sn/PFM, (b) Sn/CMC and (c) Sn/PVDF electrodes. The charge and discharge rate is C/50 (16 mA g\textsuperscript{-1}, 0.012 mA cm\textsuperscript{2}).\textsuperscript{133}}
\end{figure}
Besides, PAA as another binder that can efficiently alleviate material volume change was also studied and it delivered high discharge and charge capacities of 880 and 760 mAh g\(^{-1}\), respectively. When the PAA binder is adopted for the Sn electrode, a higher specific capacity and coulombic efficiency are obtained compared with the one using a PVdF binder as shown in Figure 32. Nevertheless, the cycling stability of Sn/PAA electrode is still unsatisfactory due to the large volume change during charge/discharge process. These results demonstrate that the volume change buffering effect from different binders is limited in terms of improving electrochemical performance of Sn anode. Some other strategies have to be combined to further enhance the Sn anode performance.

**Figure 32.** Reversible capacity variation of (a) hard-carbon with PVdF binder, (b) Sn-PAA and (e) Sn-PVdF.\(^{134}\)
Furthermore, by changing the upper voltage limit from 1.5 V to 0.8 V, which could prevent the full sodiation of Sn and therefore decrease the volume change, the cycling stability of Sn anode in the first 10 cycles was improved without sacrificing much capacity.\textsuperscript{134} Then, after adding a small amount of FEC into the electrolyte, the capacity retention of the Sn/PAA electrode was further enhanced due to the stabilized SEI formation. The charge capacity was increased to 274 mAh g\textsuperscript{-1} from 21 mAh g\textsuperscript{-1} and a reversible capacity over 500 mAh g\textsuperscript{-1} was still maintained after 20 cycles.

Carbon coating is one of the most common and efficient ways to alleviate the volume change and form stable SEI for alloy anode materials. Wang \textit{et al.}\textsuperscript{135} used resorcinol–formaldehyde (RF) resin as the carbon source and embedded the Sn nanoparticles into the porous carbon to investigate the reaction process of Sn/C electrode in sodium-ion and lithium-ion batteries. Based on the CV curves and the charge/discharge profiles, Sn formed stepwise alloys in both sodium-ion and lithium-ion batteries but the capacity delivered was higher in lithium-ion batteries. On the other hand, the cycling stability in sodium-ion and lithium-ion batteries is comparable as shown in Figure 33. However, due to the slow diffusion of Na ions, high SEI film resistance and large charge-transfer resistance, the Sn/C electrode showed poor capacity retention and rate capability in sodium-ion battery.\textsuperscript{135}
Figure 33. Capacity performance of mesoporous C/Sn anodes during charge/discharge cycles at 20 mA g$^{-1}$ in Na-ion and Li-ion batteries.\textsuperscript{135}

Chen \textit{et al.}\textsuperscript{136} used the same resorcinol–formaldehyde (RF) resin as the carbon source and much smaller Sn nanoparticles (~8 nm) were homogeneously encapsulated into the spherical carbon matrix using a spray method. Based on the electrochemical test results, better
electrochemical performance was obtained. In the initial cycle, it delivered a reversible capacity of 493.6 mA h g\(^{-1}\) under a current density of 200 mA g\(^{-1}\) and as the current density gradually increased to 500, 1000, 2000, and 4000 mA g\(^{-1}\) in the next few cycles, it still kept a reversible capacities of 447, 420, 388, and 349 mA h g\(^{-1}\), respectively (Figure 34 a).\(^{136}\) After the current density was switched back to 200 mA g\(^{-1}\), the capacity could be recovered to 492 mA h g\(^{-1}\) within few cycles immediately. In order to test the long-term stability of the Sn/C electrode, the cell wa galvanostatically discharged and charged at 1A g\(^{-1}\) and capacities of 425 mA h g\(^{-1}\), 411 mA h g\(^{-1}\), 418 mA h g\(^{-1}\), 410 mA h g\(^{-1}\), 419 mA h g\(^{-1}\), and 415 mA h g\(^{-1}\) were delivered at 20, 100, 200, 300, 400, and 500 cycles, respectively.

Figure 34. 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\(^{-1}\).\(^{136}\)

When examining the morphology of the Sn/C electrode after long-term cycling, it was found that the Sn/C electrode with a larger Sn particles was collapsed to some extent. On the contrary, the Sn/C electrode with smaller Sn particle size still kept a structural integrity. In general, three factors have contributed to the superior electrochemical performance of the
Sn/C electrode. Firstly, the ultrasmall Sn nanoparticle could efficiently reduce the absolute strain and improve the utilization of the active materials. Secondly, the carbon matrix could efficiently alleviate the large volume change to prevent Sn particle aggregation during charge/discharge process. Finally, the uniform distribution of the Sn nanoparticles in the carbon frame was important to enable a balanced strain all over the whole composite.

Recently, Hu et al. used intrinsically soft and porous wood fibers as Sn supporter to alleviate the electrode pulverization and enhance the sodium ion diffusion kinetics, leading to an improved capacity retention and rate performance. Besides, the pores in the wood fiber allowed for intercellular fluid transportation, which made them an excellent electrolyte reservoir. In order to study the alleviation function of the wood fiber, a stiff oxide layer between the wood fiber and SWCNT layer were introduced to compare the cycling performance between them and the results are shown in Figure 35. Base on the cycling performance, in spite of the capacity decay in the first few cycles due to the rearrangement of the fibers during sodiation and loss of electrical contact between individual fibers and at the fiber–coin cell case interface, the Sn on the wood fiber substrates still showed a lifetime more than 400 cycles. As a comparison, the Sn deposited on the rigid fiber substrate and Cu current collector can only survive no more than 50 cycles. Further insight on the mechanism of the buffering effect of wood fiber revealed that the soft wood fiber could accommodate the sodiation/desodiation-induced stresses through a wrinkling deformation which was conducive to the relief of the Sn particle pulverization. However, the buffering effect
would be weakened as the mass loading of Sn increases which could induce a mechanical degradation and hinder the electrochemical cycling performance.\textsuperscript{137}

Figure 35. Electrochemical performance of the Sn anodes. (a) Galvanostatic charge/discharge voltage profiles of Sn@WF at the 1st, 2nd, 100th, and 400th cycle at a rate of C/10. (b) Cycling performance of Sn@WF, Al\textsubscript{2}O\textsubscript{3} coated fiber, and Cu current collector at a rate of C/10. The inset illustrates the structure of the wood fiber and Al\textsubscript{2}O\textsubscript{3} coated fiber.\textsuperscript{137}
A tin coated nanoforest with Ni-coated tobacco mosaic virus (TMV) as the substrates was also examined by Wang et al. The TMV has been proved a useful and versatile template to create 3D nanoforest electrodes. The whole synthesizing process is shown in Figure 36.

Figure 36. Schematic illustration of nanohierarchical 3D anode arrays consisting of TMV1cys/Ni/Sn/C self-aligned on stainless steel.
The cycling performance of the 3D C/Sn/Ni/TMV was evaluated between 0.05 and 1.5 V under a current density of 50 mA g\(^{-1}\). As a comparison, a layer of Sn with the same thickness was also coated on the stainless steel, together with a 3D Sn/Ni/TMV1cys without carbon coating as control samples. In the first cycle, all the three samples show an initial capacity around 730 mAh g\(^{-1}\) which is close to the theoretical capacity of Sn as shown in Figure 37. As for the 2D Sn film, the capacity fading is severe and only 9% percent of initial capacity is kept after 5 cycles. On the other hand, the Sn/Ni/TMV1cys nanoforest anode also suffers from a capacity fading, which can maintain 30% of its initial capacity after 20 cycles, but the capacity retention is improved significantly compared with the 2D Sn thin film. Moreover, it demonstrates that the thin layer (5 nm) carbon coating plays an important role in improving the cycling stability of the 3D C/Sn/Ni/TMV1cys electrode.\(^{138}\)

![Figure 37. Cycling performance of 2D Sn thin film, 3D Sn/Ni/TMV1cys, and 3D C/Sn/Ni/TMV1cys anodes.\(^{138}\)](image-url)
In addition to Sn, antimony is another promising alloy anode material candidate for sodium-ion battery due to its high theoretical capacity of 660 mAh g$^{-1}$ upon full sodiation to Na$_3$Sb and good kinetic performance.$^{141}$ However, the capacity fading from the severe volume change is still the main concern for the application of Sb anode materials.

Recently, Zhou et al.$^{142}$ prepared a Sb nanoparticle decorated nitrogen-doped carbon sheets through a sol–gel method. It is found that the composite showed an initial capacity of 796.3 mA h g$^{-1}$, with a coulombic efficiency of 42.8% under the current density of 50 mA g$^{-1}$. After 60 cycles, a capacity of 305 mAh g$^{-1}$ was still maintained corresponding to a capacity retention of 89.5%. Additionally, the composite also shows good rate capability. When the current density was gradually increased to 10 A g$^{-1}$, the corresponding capacity was 142 mAh g$^{-1}$ and the capacity could recover to 298 mA h g$^{-1}$ immediately after the current density was switched back to 50 mA g$^{-1}$. The good electrochemical performance could be ascribed to several factors. Firstly, the porous carbon nanosheets with numerous open channels not only could facilitate the diffusion of both the electrolyte and Na$^+$ ions, but also buffer the volume change of the Sb particles (~390% volume expansion from Sb to Na$_3$Sb).$^{142}$ Secondly, a large amounts of topological defects were introduced to the graphene layer of carbon nanosheets which was beneficial to the sodium adsorption and surface capacitive effects.$^{142,143}$ Finally, due to the nitrogen doping effect, the Sb nanoparticles were uniformly dispersed into the carbon nanosheets to avoid particle aggregation of the Sb nanoparticles.

In order to carefully study the reaction progress of Sb with Na, another Sb/C composite prepared by a simple mechanical milling method of commercial Sb powder with super P
carbon was also investigated by Yang et al.\textsuperscript{144} It was revealed that there are two pairs of well-defined symmetric redox bands at 0.65/0.93 V and 0.40/0.78 V as shown in Figure 38. It indicated that the Na alloying/dealloying with Sb was a two-step reaction with two different phases: NaSb and Na\textsubscript{3}Sb.\textsuperscript{144} This result was also confirmed by Monconduit et al.\textsuperscript{145}

\begin{figure}[h]
\centering
\includegraphics[width=0.8\textwidth]{fig38.png}
\caption{The CV curve of the Sb/C nanocomposite at a scan rate of 0.1 mV s\textsuperscript{-1} (vs. Na\textsuperscript{+}/Na).\textsuperscript{144}}
\end{figure}

Yang et al found that the Sb/C composite showed a very high initial charge/discharge capacities of 717/610 mA h g\textsuperscript{-1} and the capacity was stabilized around 580 mA h g\textsuperscript{-1} since the second cycle.\textsuperscript{144} In the long-term cycling test, the Na–Sb/C half cells were cycled with and without FEC to explore the effect of electrolyte additive on the cycling stability. As shown in Figure 39, without the FEC additive, the Sb/C electrode began to suffer rapid capacity fading
from 50th cycle and failed at around 80th cycle. On the contrary, The FEC-containing Sb/C electrode could maintain a capacity of 575 mAh g⁻¹ over 100 cycles without obvious capacity loss, which demonstrated that the electrolyte additive had an advantageous effect on the structural stability of the SEI film of Sb/C anode.¹⁴⁴

![Figure 39. Changes of the cycling capacities and SEI film resistances of the Sb/C anodes in the 1.0 mol L⁻¹ NaPF₆ + EC-DEC electrolyte with (red) and without (blue) the addition of 5% FEC additive. ¹⁴⁴](image)

Due to the great advantages of Sn and Sb and the buffering effect of a binary alloy composite, some Sn/Sb alloy anodes materials have also been studied. Monconduit et al.¹⁴⁶ focused on the mechanism of the reaction between Sn/Sb alloy and Na. It was evidenced that after
sodiation, the Sn/Sb alloy formed an amorphous phase instead of crystalline phase in metals of Sn and Sb.\textsuperscript{146}

Liu and coworkers synthesized a SnSb/C composite using a simple ball milling method.\textsuperscript{147} Based on the analysis of the CV curve, it is found that the alloying and dealloying reactions in sodium-ion battery might occur in a sequential manner based on the Sn-rich and Sb-rich phases.\textsuperscript{147} Good cycling performance was shown by the cycling plots of the SnSb/C nanocomposite electrodes. After 50 cycles, the SnSb/C electrode maintained a capacity of 435 mAh g\textsuperscript{-1}, corresponding to a capacity retention of 80\%. The good cycling stability could be assigned to the confinement of the binary metal system, in which the two metals functioned as the conductive buffer matrix for each other to maintain structural integration.\textsuperscript{147}

\textbf{2.2.4.3 Metal sulfide materials}

Two dimensional layered metal sulfides MS\textsubscript{x} including MoS\textsubscript{2}, WS\textsubscript{2}, SnS\textsubscript{2} and SnS have been widely studied as potential anode materials for lithium-ion batteries.\textsuperscript{148–156} For the MS\textsubscript{x} materials, the Van der Waals force across gaps between S–M–S sheets can provide space for the ions insertion reversibly.\textsuperscript{157} Therefore, during the Li\textsuperscript{+} or Na\textsuperscript{+} intercalation, besides the reduction of M\textsuperscript{4+} to M\textsuperscript{3+}, Li or Na ions can also diffuse into the Van der Waals gaps, delivering high capacity.\textsuperscript{157–159} However, the application of these materials is hindered by a few problems. First, the significant volume change during charge/discharge process still need to be relieved to achieve good cycling stability. Secondly, the intrinsic low conductivity of these materials affect their Na storage ability adversely. Finally, these 2D materials tend to
restack to minimize the surface energy, due to their thermal instability property which results from the high surface energy and interlayer van der Waals attractions.\textsuperscript{160,161}

Among these metal sulfides materials, MoS\textsubscript{2} attracts tremendous attention due to its unique layered structure which is favorable for initial ion intercalation/de-intercalation.\textsuperscript{162} Recently, David \textit{et al.}\textsuperscript{163} fabricated a MoS\textsubscript{2}/reduced graphene oxide (RGO) paper composite and used it as a self-standing anode material for sodium-ion batteries. The composite was prepared by vacuum filtration of RGO and MoS\textsubscript{2} sheets at the same time and different MoS\textsubscript{2} contained composites were obtained (20MoS\textsubscript{2} means the weight percent of MoS\textsubscript{2} in the composite is 20\%). The cycling performance was tested under a current density of 25 mA g\textsuperscript{-1}. As Figure 40 shows, after the capacity loss in the initial cycle, a capacity of 123, 172, and 218 mA h g\textsuperscript{-1} could be obtained for 20MoS\textsubscript{2}, 40MoS\textsubscript{2}, and 60MoS\textsubscript{2}, respectively. Among these composites, 60MoS\textsubscript{2} showed the highest capacity with a 83\% capacity retention and approximately 98\% average efficiency after 20 cycles.\textsuperscript{163}
In addition to the electrochemical tests, the paper composite also showed good mechanical properties in the tensile tests. However, the capacity delivered by the composite was not high enough and in the rate performance test, the largest current density applied is quite low (100 mA g\(^{-1}\)).

In addition, similar to the expanded graphite, the distance between two layers of MoS\(_2\) is an important factor for the Na insertion process. Therefore, an ultrathin MoS\(_2\) nanosheets with an expanded interlayer distance were prepared by Su \textit{et al.}\(^{164}\) In the process of synthesizing the MoS\(_2\) nanosheets, formamide was used as an efficient delaminating agent to intercalate into the interlayer spaces of the MoS\(_2\) which could weaken the interlayer attraction of MoS\(_2\).\(^{164,165}\) Then, after the ultrasonication treatment, MoS\(_2\) nanosheets with a larger interlayer space could be collected. From the XRD pattern, it could be seen that the

**Figure 40.** Sodium charge capacity of various electrodes at a constant current density of 25 mA g\(^{-1}\).\(^{163}\)
exfoliated MoS$_2$ nanosheets had a lower degree of (002) reflection, which indicated a larger interlayer space compared with the bulk MoS$_2$.\textsuperscript{164} Moreover, the stronger (002) and (100) diffraction peaks of the exfoliated MoS$_2$ demonstrated that it had a better crystallinity after the treatment.

**Figure 41.** a) Rietveld refinement of XRD pattern for exfoliated MoS$_2$ nanosheets. The observed and calculated intensities are represented by red crosses and the blue solid line, respectively. The bottom wine-coloured line shows the fitting residual difference. The Bragg positions are represented by light-green ticks. The inset presents magnified XRD patterns of exfoliated and bulk MoS$_2$. b) The refined structural model of the exfoliated MoS$_2$ viewed along the [110] and [001] directions. The Mo and S atoms are coloured in purple and yellow, respectively.\textsuperscript{164}
Different current densities were used to test the cycling stability of the MoS$_2$ nanosheets as shown in Figure 42 (a). In the first cycle, all the samples under different current density show high discharge capacity (above 800 mA g$^{-1}$). After 100 cycles of charge/discharge, the MoS$_2$ nanosheets electrode still could maintain reversible capacity of 330, 305 and 251 mA h g$^{-1}$ under the current density of 80, 160 and 320 mA g$^{-1}$, respectively.

Figure 42. a) Cycling performance of exfoliated MoS$_2$ nanosheets at current densities of 80, 160, and 320 mA g$^{-1}$. b) Rate performance of exfoliated MoS$_2$ nanosheets at varied current densities.\textsuperscript{164}
The good rate performance was also confirmed by cycling the Na half-cell under current density of 40, 80, 160, and 320 mA \( \text{g}^{-1} \) as shown in Figure 42 (b). In this research, a facile way to increase the interlayer distance of MoS\(_2\) was carried out which could promote the intercalation and accommodation of Na ions efficiently.\(^{164}\) In addition, the nanosheets guaranteed a large surface area which was beneficial to the contact between electrolyte and active material. These two factors made a great contribution to the superior electrochemical performances for sodium storage of MoS\(_2\) nanosheets.

In order to take deep insight on the reaction mechanism between Na and MoS\(_2\), a MoS\(_2\)/C nanosphere composite was fabricated by Wang et al.\(^{166}\) As an efficient way to study the electrochemical reaction process, CV curves of MoS\(_2\) (nanosheets) electrode and MoS\(_2\)/C (nanospheres) electrode are shown in Figures 43 (a) and (b), respectively. For the MoS\(_2\) nanosheets, three reduction peaks at 1.2, 0.7 and 0.005 V and three corresponding oxidation peaks at 0.6, 1.7 and 2.2 V could be observed in the first cycle. Since the second cycle, the reduction peak at 1.2V shifted to 1.4V, which could be attributed to the intercalation of sodium ions into MoS\(_2\) interlayer.

\[
\text{MoS}_2 + x \text{Na}^+ + x \text{e}^- \rightarrow \text{Na}_x\text{MoS}_2
\]

As for the peak at 0.7V, it is the result of the conversion reaction:

\[
\text{Na}_x\text{MoS}_2 + (4-x) \text{Na}^+ + (4-x) \text{e}^- \rightarrow 2\text{Na}_2\text{S} + \text{Mo}^{163,166}
\]

The sharp peak at 0.005 V represented the Na\(^+\) storage process in the interface between Na\(_2\)S and Mo.\(^{166,167}\) The SEI was formed at 0.7V and it was stabilized since the second cycle due to the decreased intensity of the peak. On the other hand, the MoS\(_2\)/C composite showed similar
reduction and oxidation peaks in the CV curves but not as prominent as MoS$_2$ nanosheets due to the interference of Na-ion insertion/extraction to carbon coating layer.\textsuperscript{166}

\textbf{Figure 43.} (a) Cyclic voltammograms of MoS$_2$ electrode and (b) MoS$_2$/C electrode between 0.005 V–2.5 V with a scan rate of 0.1 mV/s; (c) Charge and discharge profiles of MoS$_2$ electrode and (d) MoS$_2$/C electrode vs. Na$^+$/Na with a cut-off window 0.005–2.5 V.\textsuperscript{166}

Under the help of carbon coating, the MoS$_2$/C composite showed a good cycling performance. In the first cycle, it delivered a high capacity of 671 mAh g$^{-1}$ and maintained at 520 mAh g$^{-1}$ for 50 cycles. Even at a high current density of 2C, it still kept a capacity of 390 mAh g$^{-1}$. 

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The results addressed the importance of the carbon coating in obtaining good electrochemical performance for MoS$_2$. 
CHAPTER 3. Research Objectives

Electrospinning is a facile way to fabricate nanofibers from different polymer precursors and different fiber morphologies can be obtained by adjusting the electrospinning parameters. Due to the unique properties of electrospinning, it has become one of the most commonly used methods to synthesize carbon nanofibers which can be achieved by further thermal treatment on the as-spun polymer nanofibers. By selecting different polymer precursors or adding different amount of pore formation agent, carbon nanofibers with different properties such as conductivity and surface area, can be fabricated.

1-D materials such as carbon nanofibers, nanowires and nanotubes have been widely used in energy storage applications. They can be directly used as electrode active materials or active material carriers. When utilized as sodium-ion battery anode material, the different properties of the carbon nanofibers will have different effects on the resultant electrochemical performance.

The first objective of this work is to modify the chemical composition of PAN-derived carbon nanofibers by adding nitrogen doping agent to improve its sodium storage capability. Urea is a cheap chemical product with high nitrogen content. It was added into the PAN precursor solution and electrospun into nanofibers. After thermal treatment, the obtained carbon nanofibers show higher nitrogen content as expected which was demonstrated to be beneficial to the electrochemical performance of carbon material as sodium-ion battery anode. The results of this work are discussed in Chapter 4.
The second objective of this work is to fabricate an alloy/carbon nanofiber composite and use it as a high-performance sodium-ion battery anode. Utilization of alloy material as sodium-ion battery anode faces many challenges such as large volume change during charge/discharge process, unstable SEI formation on the electrode and aggregation of alloy particles. Encapsulating alloy nanoparticles into the carbon nanofiber matrix is expected to alleviate the volume change, prevent the aggregation of alloy particles and form a conductive network for stable electrochemical reactions. Different amounts of active material precursor were added into the PAN solution to get alloy/carbon nanofiber composites. The electrochemical performance of these composites with different active material loadings was evaluated. The results of this work are discussed in Chapter 5.
CHAPTER 4. A facile way to synthesize nitrogen-doped electrospun carbon nanofibers as anode material for high-performance sodium-ion batteries

Abstract

Nitrogen (N)-doped carbon nanofibers (CNFs) were synthesized using a facile electrospinning technique with the addition of urea as a nitrogen-doping agent. The amount of urea was selectively adjusted to control the degree and effect of N-doping. The morphology of N-doped CNFs was investigated by scanning electron microscopy, transmission electron microscopy, and X-ray diffraction, while their electrochemical performance was studied using cyclic voltammetry and galvanostatic charge-discharge. It was found that the nitrogen content of N-doped CNFs increased significantly from 11.31% to 19.06% when the amount of urea increased from CNFs to 30U-CNFS. N-doping played an important role in improving the electrochemical performance of the CNFs by introducing more defects in the carbon structure. Results showed N-doped CNFs with the highest nitrogen content (19.06%) exhibited a reversible capacity of 354 mAh g\(^{-1}\) under a current density of 50 mA g\(^{-1}\) and when the current density was increased to 1 A g\(^{-1}\), a capacity of 193 mAh g\(^{-1}\) was still maintained. Therefore, the N-doped CNFs show great potential as suitable sodium-ion battery anode material.
4.1 Introduction

With the constantly increasing energy demand, various energy storage techniques are attracting considerable attention since the past few decades. In our daily life, lithium-ion batteries are the predominant energy storage device for laptops, cellphones, electrical vehicles, and so on. However, limited reserve, unevenly distribution, and foreseeable increasing cost of lithium recourses become obstacles for the use of lithium-ion batteries in large scale applications, such as stationary storage and smart power grid, and these disadvantages begin to make people pursue other low-cost energy storage devices.\textsuperscript{72,168–171}

As a feasible alternative, sodium-ion batteries show the merits of natural abundance on earth, low cost, and suitable redox potential (0.3 V above that of lithium).\textsuperscript{172,173} However, due to the larger radius of Na\textsuperscript{+} than Li\textsuperscript{+}, it is a great challenge to find suitable cathode and anode materials to obtain adequate specific capacity, high coulombic efficiency as well as long cycle life.\textsuperscript{174} Considering the analogous reaction mechanism with Li-ion batteries, various sodium compounds have been investigated as the candidates for sodium-ion battery cathode materials such as NaVPO\textsubscript{4}F,\textsuperscript{175} P2-Na\textsubscript{x}[^{Fe_{1/2}Mn_{1/2}}]O\textsubscript{2},\textsuperscript{172} Na\textsubscript{4}Fe(CN)\textsubscript{6},\textsuperscript{176} and Na(Ni\textsubscript{0.5}Mn\textsubscript{0.5})O\textsubscript{2}.\textsuperscript{177}

As for the anodic materials, it is known that Na\textsuperscript{+} hardly intercalates into the carbon sheets of graphite to form Na-C compounds (specific capacity < 35 mAh g\textsuperscript{-1}) due to the larger size of the Na\textsuperscript{+}. Therefore, graphite, the standard anode material in commercial lithium-ion batteries,
cannot be directly used in sodium-ion batteries. Recently, many research efforts were focused on the utilization of metals, such as tin and antimony, as the anode materials in sodium-ion batteries due to their high theoretical capacities, resulted from an alloying/dealloying mechanism similar to that in lithium-ion batteries. For example, Chen et al. produced a Sn/C nanocomposite, which delivered a reversible capacity of 415 mAh g\(^{-1}\) after 500 cycles at a high current density of 1 A g\(^{-1}\). Zhang et al. encapsulated SnSb alloy into a carbon nanofiber matrix and achieved a reversible capacity of 357 mAh g\(^{-1}\) after 200 cycles with a capacity retention as high as 93.7% after 200 cycles. However, the main challenge of using alloy-type anode material for sodium-ion batteries lies in minimizing the structure instability resulting from Na\(^+\) alloying/dealloying during charging-discharging process, which leads to severe volumetric expansion/contraction (420% for Sn after full sodiation).

Although graphite cannot be used in sodium-ion batteries, many other carbonaceous materials can be inserted by Na\(^+\). Among all types of carbonaceous materials, hard carbon is a very promising candidate to be utilized in sodium-ion batteries. Na\(^+\) was first found to be able to intercalate with hard carbon by Stevens and Dahn and lots of work have been conducted to improve its electrochemical performance thereafter. Bommier et al. prepared hard carbon spherules from sucrose and achieved a capacity of 250 mAh g\(^{-1}\) at 40 mA g\(^{-1}\). However, as the applied current density increased to 1 A g\(^{-1}\), the reversible capacity decreased to 100 mAh g\(^{-1}\), indicating poor rate capability. Carbon nanofibers were also
developed directly by carbonizing the polypyrrole nanofiber precursor and a specific capacity of 150 mAh g\(^{-1}\) could be maintained after 200 cycles under a current density of 50 mA g\(^{-1}\) which was still limited and not satisfactory.\(^{104}\)

Nitrogen (N) doping is a good strategy to improve the electrochemical performance of carbonaceous materials.\(^{120,184}\) Introducing abundant nitrogen into the carbonaceous materials can generate extrinsic defects which can function as reactive sites with Na\(^+\); in the meantime, enhance the electric conductivity, leading to a higher Na\(^+\) storage capacities.\(^{120,184,185}\) In addition, the existence of quaternary nitrogen and pyridinic nitrogen can facilitate the interaction between the functional groups and protons leading to the increased pseudocapacitance.\(^{186}\)

Electrospinning has been proved a useful and convenient strategy to produce nanofibers which can form a three dimensional network and is desirable to be applied in the energy storage materials.\(^{125,187–189}\) Many nanofiber-based materials have been produced using electrospinning, whose electrochemical properties were carefully studied and used in energy storage applications.\(^{125,171,181,189–192}\)

In this article, we introduce a facile way to synthesize N-doped carbon nanofibers (CNFs) using electrospinning and subsequent thermal treatment of precursor solutions composed of
polyacrylonitrile (PAN) and urea. To investigate the contribution of different N-doping levels, the amount of urea in the precursor solutions was varied. The resultant N-doped CNFs delivered a high reversible capacity of 354.0 mA g\(^{-1}\) at a current density of 50 mA g\(^{-1}\) when the nitrogen content was 19.06%. These N-doped CNFs also exhibited stable cycling performance and good rate capability. It is therefore demonstrated that N-doping is an effective method to improve the electrochemical performance of carbon materials, and N-doped CNFs can be used as potential anodes in practical sodium-ion batteries.

4.2 Experiment

4.2.1 Electrospinning of urea-contained PAN nanofibers

Urea, PAN (M\(_w\) = 150,000) and N,N-dimethylformamide were purchased from Sigma-Aldrich and were used to prepare urea-contained PAN nanofibers without further purification. In a typical process, 0.8g PAN was added into 9.2g N,N-dimethylformamide to form an 8% solution under magnetic stirring overnight. Urea/PAN solutions with various urea contents (10, 30, and 50 wt.% in PAN) were prepared by adding 0.08g, 0.24g and 0.4g urea, respectively, into the transparent PAN solution. Pure PAN solution without the addition of urea was also used as a control. After stirring for another 2h, the clear solutions were electrospun into urea/PAN nanofibers. During the electrospinning, the voltage applied and the needle-to-collector distance were 15kV and 15cm, respectively, and the flow rate used was 0.75 mL/h. It was found the electrospinnability of 50% urea/PAN solution was poor and
did not produce uniform fibers. Hence, only nanofibers containing 0, 10 and 30 wt.% urea were further treated and tested.

4.2.2 Formation of N-doped carbon nanofibers

The as-prepared urea/PAN nanofibers were put into a muffle furnace and stabilized at 250°C for 2h with a heating rate of 5°C/min under air atmosphere. Subsequently, the stabilized nanofibers were further carbonized at 700°C for 3h with a heating rate of 2°C/min under the protection of nitrogen atmosphere to obtain N-doped CNFs. The carbonized nanofibers made from 0, 10, and 30 wt.% urea/PAN nanofibers were denoted as CNFs, 10U-CNFs, and 30U-CNFs, respectively.

4.2.3 Structure characterization

The morphology of CNFs, 10U-CNFs, and 30U-CNFs was investigated using a FEI Verios 460L field emission scanning electron microscope (FESEM) and the field emission STEM – (JEOL 2010F). Their crystal structure was characterized by XRD (Rigaku SmartLab X-ray diffractometer with Cu Kα radiation) from 10 to 60°. The Raman spectra were recorded using a Renishaw-1000 Raman spectroscopy with an excitation wavelength of 514.5 nm between 700 cm\(^{-1}\) to 2000cm\(^{-1}\). Fourier transform infrared spectrometer (FTIR, Thermo Nicolet Nexus 470) was used to investigate the chemical structure of the nanofibers. The chemical state of the carbon, nitrogen and oxygen in the nanofibers was characterized by X-ray photoelectron spectroscopy (XPS) using a SPECS system with PHOIBOS 150 analyzer. A CHN elemental analysis was performed to study the elemental component of CNFs, 10U-CNFs, and 30U-CNFs.
4.2.4 Electrochemical evaluation

Electrochemical tests were conducted with CR2032 coin cells. The working electrodes were prepared by mixing the active material, carbon conductive agent and sodium carboxymethyl cellulose (CMC) binder in deionized water to make slurries with weight ratio of 70:15:15. The well-mixed slurries were cast on thin copper foil and dried in vacuum at 80°C. Metallic sodium (Sigma-Aldrich) was used as the counter electrode. NaClO₄ (Sigma-Aldrich, ≥98.0%) was dissolved in propylene carbonate (PC, Sigma-Aldrich, 99.7%) to form a 1M solution to be used as the electrolyte. Glassfiber (Whatman, grade GF/D) was used as the separator. The cells was assembled in an argon-filled glove box. The charge-discharge tests were performed on a Land CT2001 battery tester with a voltage range of 0.01-2.5V. Cyclic voltammetry (CV) measurements were performed by a Gamry Reference 600 between 2.5 and 0.01 V with a scan rate of 0.05 mV s⁻¹.
4.3 Results and discussion

4.3.1 Structure characterization

![SEM images of (A) CNFs, (B) 10U-CNFs, and (C) 30U-CNFs.](image)

**Figure 44.** SEM images of (A) CNFs, (B) 10U-CNFs, and (C) 30U-CNFs.

Figure 44 show SEM images of the carbonized CNFs, 10U-CNFs and 30U-CNFs. It is seen that all nanofibers have smooth surfaces without the presence of beads or clots. The fibers are interconnected with each other randomly, forming 3-D non-woven networks, which could potentially create effective conducting pathways and facilitate the Na\(^+\) transfer. Figure 45 presents TEM images of the CNFs, 10U-CNFs and 30U-CNFs. Under lower resolution, all
three fibers show relative smooth surfaces which agree with the observation from SEM images. When they were examined with a higher resolution, no obvious stacking of graphene layers can be found, indicating that CNFs, 10U-CNFS and 30U-CNFS are mainly composed of amorphous carbon. Additionally, the disperse rings of selected area electron diffraction (SAED) patterns of CNFs, 10U-CNFS and 30U-CNFS also confirm their amorphous carbon structure.
Figure 45. TEM images of CNFs (A,B), 10U-CNFs (C,D), and 30U-CNFs (E,F). Insets in (B,D,F) are SAED patterns.

The structure of CNFs, 10U-CNFs and 30U-CNFs was further examined using XRD. From Figure 46, it can be seen that two broad peaks appear at around 25° and 43.1° for CNFs, 10U-CNFs and 30U-CNFs, which can be assigned to the (002) and (100) planes of graphite,
respectively. In addition, these two board peaks shown in the XRD results indicate the lack of crystallinity in CNFs, 10U-CNFs and 30U-CNFs, which is beneficial for the intercalation and de/intercalation of Na\(^+\).\(^{193}\) The interplanar spacing (\(d_{002}\)) of graphite is around 0.336 nm, which is too small for the effective intercalation of Na\(^+\).\(^{116,194}\) However, according to the Bragg’s law, the interplanar spacing (\(d_{002}\)) of CNFs, 10U-CNFs and 30U-CNFs was calculated to be 0.350 nm, 0.354 nm and 0.356 nm, respectively, which are sufficient for reversible Na\(^+\) intercalation/deintercalation.\(^{116}\)

![Figure 46. XRD patterns of CNFs, 10U-CNFs, and 30U-CNFs.](image)
Raman spectroscopy is a useful technique to study the subtle structural variation in carbon materials. Typically, two peaks are shown in the CNFs Raman curve, G-band (at 1580 cm\(^{-1}\)) which results from the vibration of sp\(^2\)-bonded carbon atoms, and D-band (at 1350 cm\(^{-1}\)) which is mainly ascribed to the defects or disordered carbon. Basically, the integral intensity ratio of D-band and G-band (\(I_D/I_G\)) is always used to evaluate the disorder degree of the carbon material.\(^{195}\) From Figure 47, it can be calculated that the \(I_D/I_G\) ratios for CNFs, 10U-CNFs and 30U-CNFs are 1.081, 1.208, and 1.282, respectively. It is seen that the \(I_D/I_G\) ratio increases as the nitrogen content increases in the materials, corresponding to the increased urea content in the PAN precursor from 0% to 30%. The result indicates that the presence of more introduced nitrogen in the CNFs creates more defects and structural disorder in the materials. As reported in the literature, higher contents of disordered carbon with various other defects (e.g., sp\(^3\) bonded carbon, dangling bonds, vacancies and topological defects), can facilitate the Na\(^{+}\) insertion, therefore, leading to enhanced reversible capacities.\(^{187,193,196,197}\) The Raman spectra results demonstrate that the addition of urea in the PAN precursor enhances the disorder degree of the carbon materials, and the possible reason is that the nitrogen atoms from urea can damage the integrity of the graphene layers of the CNFs during the carbonization process. As a consequence, more defects are created as the addition of urea increases in the PAN precursor.
Figure 47. Raman spectra of CNFs, 10U-CNFS, and 30U-CNFS.

The chemical structure of CNFs, 10U-CNFS and 30U-CNFS was studied by FTIR spectroscopy. From Figure 48, it is seen that the shapes of the absorption bands for all three fibers are similar. Two peaks at 1581 cm$^{-1}$ and 1192 cm$^{-1}$ in the absorption bands are clearly shown for CNFs, 10U-CNFS and 30U-CNFS, and they can be assigned to the combination of C=C and C=N vibrations and the C-O vibration, respectively. Between the peaks at 1581 cm$^{-1}$ and 1192 cm$^{-1}$, two additional peaks corresponding to the C=N and C-N vibrations also exist at 1374 cm$^{-1}$ and 1284 cm$^{-1}$, respectively. In general, it is believed that the C=N and
C-N in PAN-derived CNFs come from the conversion of C≡N.\textsuperscript{198,199} However, considering the higher nitrogen content in the 10U-CNFs and 30U-CNFs, it is obvious that urea which is the nitrogen doping agent also contributes to the formation of C=N and C-N in these two fibers.

\textbf{Figure 48.} FTIR spectra of CNFs, 10U-CNFs, and 30U-CNFs.

The chemical composition and nature of chemical bonding of CNFs, 10U-CNFs and 30U-CNFs were further investigated by XPS analysis, and the results are shown in Figure 49. All fibers exhibit three distinct peaks which can be assigned to C 1s, N 1s and O 1s, respectively.
The N 1s spectrum in nitrogen-doped carbon is complicated and generally can be deconvoluted into 4 individual peaks which represent the pyridinic nitrogen (N-6) at 398.7 ± 0.3eV, pyridonic nitrogen (N-5) at 400.3 ± 0.2eV, quaternary nitrogen (N-Q) at 401.4 ± 0.5eV, and oxidized nitrogen at 402-405 eV.\textsuperscript{113}

Figure 49. XPS spectra of CNFs, 10U-CNFs, and 30U-CNFs.
Figure 50. N 1s fine spectra of CNFs (A), 10U-CNFs (B), and 30U-CNFs (C).

As shown in Figure 50, the N 1s spectra of CNFs, 10U-CNFs and 30U-CNFs are deconvoluted into three peaks at 398.7eV, 400.3eV, and 401.7eV, corresponding to the N-6, N-5, and N-Q, respectively. Both N-6 and N-5 are nitrogen atoms located at the edge or defect sites of the graphene layers. Nevertheless, N-6 bonds with two sp$^2$ carbon atoms to form a 6-member ring, while N-5 also bonds with two carbon atoms as N-6, except for forming a 5-member ring in which the nitrogen contributes two electrons to the π system.$^{113}$
N-Q is also called graphitic-N which is bonded with three $sp^2$ carbon atoms and located inside the graphene layer. It can be seen as a carbon atom in the graphene layer replaced by a nitrogen atom. These three types of nitrogen configurations are shown schematically in Figure 51.

**Figure 51.** Schematic illustration of different forms of nitrogen in nitrogen-doped carbon materials.

Efforts have been taken to investigate the electrochemical function of these three different forms of nitrogen in the carbonaceous materials.\textsuperscript{112,200} It is believed that the $sp^2$ hybridized N-6 and N-Q nitrogens can enhance the electronic conductivity and therefore contribute to
the improved electrochemical performance of the carbon materials.\textsuperscript{200,201} Moreover, the introduction of nitrogen, especially N-6 which is more chemically active, into the carbon host induces defects which can function as active sites for Na\textsuperscript{+} insertion, therefore leading to the enhancement of Na storage capacity.\textsuperscript{113}

Table 2. Relative integrated intensities (\%) of different elements in CNFs, 10U-CNFS, and 30U-CNFS from XPS spectra.

<table>
<thead>
<tr>
<th>Sample</th>
<th>% C 1s</th>
<th>% N 1s</th>
<th>% O 1s</th>
<th>Pyridinic-N (N-6)</th>
<th>Pyridonic – N (N-5)</th>
<th>Quaternary-N (N-Q)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CNFs</td>
<td>84.096</td>
<td>12.875</td>
<td>3.028</td>
<td>47.40</td>
<td>40.64</td>
<td>11.96</td>
</tr>
<tr>
<td>10U-CNFS</td>
<td>81.055</td>
<td>13.955</td>
<td>4.990</td>
<td>53.41</td>
<td>33.30</td>
<td>13.29</td>
</tr>
<tr>
<td>30U-CNFS</td>
<td>75.528</td>
<td>22.256</td>
<td>2.216</td>
<td>53.45</td>
<td>30.47</td>
<td>16.08</td>
</tr>
</tbody>
</table>

Table 2 shows the integrated intensities of different elements in CNFs, 10U-CNFS, and 30U-CNFS from XPS spectra. It is seen that as the urea content increases in the PAN precursor, the nitrogen content in the resultant CNFs increases as well. In addition, with the addition of urea, the proportions of N-6 and N-Q in 10U-CNFS and 30U-CNFS are remarkably increased, whereas the proportion of N-5 decreases, which are desirable for the improvement of electrochemical performance. CNH elemental analysis results of CNFs, 10U-CNFS and 30U-CNFS are shown in Table 3. The nitrogen contents of CNFs, 10U-CNFS and 30U-CNFS were
measured to be 11.31%, 15.32% and 19.06%, respectively, which agree with the data obtained from XPS spectra. XPS spectrum data and element analysis results demonstrate that the introduction of urea into the precursor is a facile way to increase the N-doping degree of carbon materials.

Table 3. C,N,H elemental analysis of CNFs, 10U-CNFs, and 30U-CNFs.

<table>
<thead>
<tr>
<th>Sample</th>
<th>% C</th>
<th>% N</th>
<th>% H</th>
</tr>
</thead>
<tbody>
<tr>
<td>CNFs</td>
<td>75.42</td>
<td>11.31</td>
<td>1.63</td>
</tr>
<tr>
<td>10U-CNFs</td>
<td>72.95</td>
<td>15.12</td>
<td>1.32</td>
</tr>
<tr>
<td>30U-CNFs</td>
<td>71.22</td>
<td>19.06</td>
<td>1.61</td>
</tr>
</tbody>
</table>

4.3.2 Electrochemical evaluation

Figure 52 shows the charge and discharge curves of CNFs, 10U-CNFs and 30U-CNFs under a current density of 50 mA g⁻¹. It is seen that during the first discharge process, a distinct plateau can be found at around 0.5V for both CNFs and 10U-CNFs. However, the plateau shifts to 0.15V for 30U-CNFs. Discharge capacities of 441.8, 570.8 and 591.1 mAh g⁻¹ can be obtained for CNFs, 10U-CNFs and 30U-CNFs in the first cycle, corresponding to the coulombic efficiencies of 52.8%, 55.7% and 64.8%, respectively. These coulombic efficiency values are higher than those reported in many other works.⁹⁰,¹⁰³
During the first cycle, the irreversible capacities can mainly be attributed to the formation of solid electrolyte interphase (SEI) on the surface of CNFs due to the decomposition of electrolyte and the irreversible insertion of sodium ions into special positions in the vicinity of residual H atoms.\textsuperscript{116,120,201,202} It is also commonly believed that the irreversible capacity loss of nitrogen-rich carbon is proportional to the N-6 content in the material.\textsuperscript{113,193} This is because N-6 is located at the edge or defect site of the graphene layer with a lone pair of
electrons and often acts as an active site for electrolyte decomposition in the first charge-discharge process and trap the solvated lithium cations. However, in our study, CNFs with the highest N-6 proportion (30U-CNFs), exhibit the highest coulombic efficiency. On the other hand, CNFs have the lowest N-6 proportion among CNFs, 10U-CNFs and 30U-CNFs, but their coulombic efficiency is also the lowest (i.e., high irreversibility capacity). Similar phenomenon has also been observed by some groups in the nitrogen-rich carbon materials. The higher coulombic efficiency for 30U-CNFs can be attributed to two reasons. First, it is evident that a large contact area between the electrolyte and active material could give rise to more server SEI formation, leading to higher irreversible capacity loss in the first cycle. In our case, the surface area of the sample is small. For example, based on the N₂ adsorption-desorption isotherms of 30U-CNFs in Figure 53, the BET surface area of the sample is calculated as 8.1571 m²/g. Based on previous study, a smaller surface area is beneficial for mitigating the SEI formation and therefore improving the first-cycle coulombic efficiency.
Secondly, compared with defects at the interface between the nanosheets which can facilitate the SEI formation, the internal defects such as the ones in basal-plane can still provide reversible capacity due to its isolation from electrolyte. In our case, it is possible that the nitrogen doping process in 10U-CNFS and 30U-CNFS has generated more internal defects instead of the defects at the interface and both the high capacity and coulombic efficiency benefit from the increased amount of internal defects. Additionally, for all the three samples, the charge-discharge curves predominantly show sloping features instead of obvious plateau.

Figure 53. N₂ adsorption-desorption isotherms of 30U-CNFS.
at low potentials, which indicates a sodium storage mechanism of adsorption/insertion on/between graphene layers.\textsuperscript{205,206}

\textbf{Figure 54.} Cyclic voltammograms of CNFs (A), 10U-CNFS (B), and 30U-CNFS (C).

CV tests were conducted to investigate the electrochemical process for the first three cycles of CNFs, 10U-CNFS and 30U-CNFS. Before N-doping, CNFs exhibit a cathodic peak at 0.54V versus Na\textsuperscript{+}/Na, which represents the formation of SEI.\textsuperscript{113,116,188} After N-doping, the cathodic peak of 10U-CNFS at 0.54V is not as distinct as that of CNFs, indicating the
reduced SEI formation in 10U-CNFs compared with CNFs. For 30U-CNFs, the cathodic peak for SEI formation appears in the first cycle at 0.13 and 0.54V. After the first cycle, the apparent cathodic peak disappears for all three fibers which indicates a stabilized SEI formation. Compared with CNFs, from the CV curve, it is seen that the oxidation current of 30U-CNFs between 0.01-0.2V in the subsequent cycles is significantly larger than the oxidation current in the first cycle. The same phenomena can be observed for the sample of 10U-CNFs as well. On the contrary, for the CNFs sample, there is no distinct oxidation current increase in the second and third CV cycles compared with the first cycle. As indicated by previous studies, the increased oxidation current in the subsequent cycles can be assigned to the reaction between Na\(^+\) and nitro groups or carbonyl groups on the graphene layers.\(^{104,120,207}\) Compared with CNFs, for 10U-CNFs and 30U-CNFs, the increased current in the subsequent CV cycles indicates the presence of more N-contained functional groups in 30U-CNFs and 10U-CNFs than CNFs and these functional groups can play a role as active sites to react with Na\(^+\). Meanwhile, this also accords with the results of XPS and elemental analysis about the progressively increased nitrogen content in 10U-CNFs and 30U-CNFs. In addition, after the first cycle, all three fibers show a board redox peak in the potential range of 0.5-1.5V, which can be attributed to the reaction of Na\(^+\) with functional groups on the carbon surface. Meanwhile, the weak redox peaks of the CV profile also show some characteristic of capacitive sodium storage behavior for all three samples. After the first cycle, the shape of all three CV curves almost overlap with each other suggesting a stable and reversible electrochemical reaction.
Figure 55. Cycling performance of CNFs, 10U-CNFs, and 30U-CNFs under the current density of 50 mA g\(^{-1}\).

Figure 55 shows the cycling performance of CNFs, 10U-CNFs and 30U-CNFs under a current density of 50 mA g\(^{-1}\) within the potential range of 0.01-2.5V. CNFs, 10U-CNFs and 30U-CNFs exhibit initial capacities of 383.3, 320.8 and 233.2 mAh g\(^{-1}\), which decrease slightly to 354.0, 283.3 and 211.7 mAh g\(^{-1}\), respectively, after 100 cycles, corresponding to capacity retentions of 92.36%, 88.31% and 90.78%. The capacity losses mainly occur in the first few cycles and the coulombic efficiencies increase rapidly to above 99% after the initial cycles for all three fibers, indicating their good reversibility. 30U-CNFs were also cycled
under a high current density of $1 \text{ A g}^{-1}$, as shown in Figure 56. A reversible capacity of 216.0 mAh g$^{-1}$ can be obtained in the initial cycle, and after 1000 cycles, a capacity of 201.5 mAh g$^{-1}$ is still maintained, which shows an extremely high capacity retention of 93.29%. To the best of our knowledge, the reversible capacity obtained in this work is higher than those reported in most previous works which use carbonaceous anode materials for sodium-ion batteries.

**Figure 56.** Cycling performance of 30U-CNFs under the current density of $1 \text{ A g}^{-1}$. 
The rate performance of CNFs, 10U-CNFS and 30U-CNFS was also investigated by increasing the charge-discharge current density gradually from 50 mA g$^{-1}$ to 1.6 A g$^{-1}$ (Figure 57). It is seen that with increase in current density, the reversible capacities of CNFs, 10U-CNFS and 30U-CNFS gradually decrease and after the current density goes back to 50 mA g$^{-1}$, the capacities also return to their initial values, which indicate the excellent stability of nanofiber structures. In addition, under all current densities, 30U-CNFS show the highest...
reversible capacities. The good rate performance of the N-doped CNFs can be attributed to the intrinsic merit of nitrogen atom, which has a higher electronegativity and smaller diameter than carbon, and it will generate a stronger interaction between carbon structure which is beneficial for the sodium kinetics.\textsuperscript{107,108}

![Image](A)![Image](B)

**Figure 58.** 30U-CNPs after cycling for 1000 cycles under the current density of 1 A g\(^{-1}\).

Further insight of the electrode structure stability was obtained by observing the morphology of 30U-CNPs under TEM after 1000 cycles under the current density of 1A g\(^{-1}\). The electrode was taken out from the cycled cell and washed with propylene carbonate for three times to remove the electrolyte residual. From Figure 58, it is seen that the integrity of the fiber morphology is preserved and structure damage can hardly be detected after 1000 cycles. This result reveals that even under a high current density of 1A g\(^{-1}\), the morphology of the
nitrogen-doped CNFs is still stable, which is another evidence of the excellent performance of the nitrogen-doped CNFs.

In summary, nitrogen-doped CNFs exhibit excellent electrochemical performance, which can be attributed into several reasons. Firstly, the interconnected fiber structure forms a conductive network which promotes the effective transfer of Na$^{+}$ and electrons. Secondly, the nanosized CNFs can increase the contact surface between the electrolyte and active material to further shorten the diffusion path of Na$^{+}$. Thirdly, the high nitrogen content of nitrogen-doped CNFs not only provides a large amounts of active sites for Na$^{+}$ insertion but also enhances the conductivity of the fibers (function of quaternary nitrogen). Finally, it is also believed that the nitrogen doping is beneficial to the rate performance of the material by improving the capacitive function.\textsuperscript{186}

4.4 Conclusions

Nitrogen-doped CNFs were fabricated by a facile electrospinning method and used as a sodium-ion battery anode. The morphology, chemical structure and electrochemical performance of the nitrogen-doped CNFs were carefully studied. The nitrogen-doped CNFs show high reversible capacity and excellent rate performance, which are benefited from the nitrogen doping and the unique fiber morphology of the material. When the current density is 50 mA g$^{-1}$, a high capacity of 340 mAh g$^{-1}$ was obtained. Remarkably, even under a high current density of 1 A g$^{-1}$, a reversible capacity of 193.1 mAh g$^{-1}$ was still maintained with a
capacity retention of 98.47% which is among the highest reversible capacity ever got. It is, therefore, demonstrated that nitrogen-doped CNFs are a promising anode material candidate for sodium-ion batteries.
CHAPTER 5. Tin Antimony Alloy-Filled Porous Carbon Nanofiber Composite for Use as Anode in Sodium-Ion Batteries

Abstract

Lithium-ion battery is currently the dominate energy storage technology for electronic devices and electric vehicles. However, the predictable rising cost of lithium raw materials results in increasing interests in less expensive rivals, such as sodium-ion battery. In this work, tin antimony (SnSb) alloy-filled porous carbon nanofiber composite was prepared as a sodium-ion battery anode material by a simple electrospinning method with subsequent thermal treatment. The spinning solution contained antimony tin oxide nanoparticles as the SnSb alloy precursor, polyacrylonitrile as the carbon precursor, and polymethyl methacrylate (PMMA) as the pore generator. The resultant SnSb/C nanofiber composite formed a continuous conductive network, which was favorable for enhancing the electrochemical performance. The presence of SnSb alloy significantly increased the energy storage capacity of the composite due to its high theoretical capacity. The porous structure created by the decomposition of PMMA polymer provided free space to buffer the volume change of the SnSb alloy during the sodiation-desodiation process. The resultant SnSb@C nanofiber composite exhibited high capacity and stable rate capability, and was demonstrated to be a promising anode candidate for sodium-ion batteries.
5.1 Introduction

Since Sony produced the first commercial lithium-ion battery in the early 1990’s, the characteristics of high energy density, no memory effect, and long lifespan make lithium-ion batteries the most used energy storage system in various applications such as portable electronics including laptops, cellphones, electric vehicles and hybrid electric vehicles.\textsuperscript{70,208}

However, considering the limited lithium source on earth and the continuously increasing energy demand, other feasible energy storage technologies must be developed to resolve the foreseeable cost issue of lithium-ion batteries.\textsuperscript{209} As an alternative material, sodium possesses similar chemical properties to lithium, but has lower cost and higher abundance. Hence, using the same mechanism and similar material structures, low-cost sodium-ion batteries can be developed for large-scale applications.\textsuperscript{210}

So far, sodium-ion battery research mainly focused on cathode materials including NaVPO\textsubscript{4}F,\textsuperscript{175} Na\textsubscript{0.44}MnO\textsubscript{2},\textsuperscript{211} Na\textsubscript{0.85}Li\textsubscript{0.17}Ni\textsubscript{0.21}Mn\textsubscript{0.64}O\textsubscript{2},\textsuperscript{212} etc.. Compared with the development of cathode materials, fewer studies were performed on the development anode materials. Graphite, a commercial anode material in lithium-ion batteries, was first studied for use as sodium-ion battery anode, but it was difficult for sodium ions to intercalate into the basal planes of graphite.\textsuperscript{213,214} Other carbonaceous materials have also been studied as sodium-ion battery anodes. For example, the nitrogen-doped porous carbon fibers prepared by Yan et al.\textsuperscript{215} showed a reversible capacity of around 230 mAh g\textsuperscript{-1} with good rate performance, and a template carbon produced by Philipp et al.\textsuperscript{216} exhibited a reversible
capacity of around 140 mAh g$^{-1}$ in 40 cycles. One major disadvantage of these carbonaceous anode materials are their relatively low capacities. Tin (Sn) and antimony (Sb) based materials have been widely investigated as lithium-ion battery anodes due to their high theoretical capacities (993 mAh g$^{-1}$ for Sn and 660 mAh g$^{-1}$ for Sb).\textsuperscript{217-220} Analogously, sodium ions are also found to be able to intercalate with Sn and Sb to form sodium alloys in a similar way with lithium alloys, producing theoretical capacities of 847 mAh g$^{-1}$ ($\text{Na}_{15}\text{Sn}_4$) and 660 mAh g$^{-1}$ ($\text{Na}_3\text{Sb}$) for Sn and Sb, respectively.\textsuperscript{221} For example, Takayuki Yamamoto \textit{et al.}\textsuperscript{222} prepared Sn electrodes and achieved a high initial capacity of 790 mAh g$^{-1}$. But the capacity reduced quickly to only 150 mAh g$^{-1}$ after 30 cycles. In lithium-ion batteries, the rapid capacity decay of Sn and Sb based anodes is typically ascribed to the large volume changes of Sn and Sb particles during the lithiation-delithiation process. Such volume change leads to the pulverization of electrodes, which in turn causes the breakdown of electric conductive network and insulation of the active material.\textsuperscript{223} As sodium ions have larger radius than lithium ions, even larger volume changes can be predicted in the sodiation-desodiation process when Sn and Sb are used as the anode materials in sodium-ion batteries. Therefore, the technological impact of developing alloy-based sodium-ion anode materials with stable structure and excellent cycling behavior would be significant and needs further exploration.

In this article, we report a Sn/Sb alloy nanoparticle-filled porous carbon (SnSb@C) nanofiber composite produced by an inexpensive electrospinning approach with subsequent thermal
treatment. Figure 59 illustrates schematically the preparation procedure of the SnSb@C nanofiber composite. Electrospun composite nanofibers were first prepared using a mixed solution, containing antimony tin oxide (ATO) nanoparticles as the SnSb alloy precursor, polyacrylonitrile (PAN) as the carbon precursor, and polymethyl methacrylate (PMMA) as the pore generator. These electrospun precursor nanofibers were then thermally-treated to form the SnSb@C nanofiber composite structure, during which ATO was reduced to SnSb alloy, PAN was converted to carbon matrix, and PMMA was completely decomposed to form a porous architecture inside the nanofibers. The electrochemical performance, including specific capacity, cycling stability, and rate capability, of the SnSb@C nanofiber composite was evaluated by galvanostatic charge-discharge tests. The results demonstrated that the carbon nanofiber matrix and the porous architecture work synthetically to buffer the volume change of the SnSb alloy during the sodiation-desodiation process, leading to high capacity, good cycling performance, and high rate capability of the SnSb@C nanofiber composite anode.
Figure 59. Schematic for preparation of SnSb@C nanofiber composite.

5.2 Experimental

PAN solution (8%) in DMF was prepared by vigorous mechanical stirring for 5h at 60 °C. ATO nanoparticles (ATO:PAN = 1:1, 0.5:1, and 0:1 by weight) and PMMA polymer (PMMA:PAN = 1:10 by weight) were then added into the PAN solution and vigorously stirred for 24 h at room temperature to obtain homogeneous dispersions for electrospinning.

Precursor nanofibers were prepared by electrospinning with an applied voltage of 15 kV, a solution flow rate of 0.75 mL/h, and a needle tip-to-collector distance of 15 cm. To form SnSb@C nanofiber composites, electrospun precursor nanofibers were first stabilized in air at 280 °C for 5.5 h with a heating rate of 5 °C/min and then carbonized at 700 °C in argon for 3 h with a heating rate of 2 °C/min. During this process, PAN was converted to form the carbon nanofiber matrix and ATO was reduced to SnSb alloy nanoparticles while PMMA
was decomposed completely, resulting in the formation of a porous structure within the carbon matrix.

The XRD analysis was conducted using a Rigaku SmartLab X-ray diffractometer with Cu Kα radiation between 2θ angles from 20° to 70°. Field-emission scanning electron microscopy (FESEM, JEOL 6400) and field-emission transmission electron microscopy (FETEM, Hitachi HF2000) were employed to characterize the morphology of precursor nanofibers and SnSb@C nanofiber composites. CHN elemental analysis was conducted to examine the compositions of SnSb@C nanofiber composites.

SnSb@C nanofibers (80 wt. %) were ground into the powder form and mixed with carbon black (10 wt. %) and alginic acid sodium salt (10 wt. %) to form a homogeneous slurry with deionized water as the solvent. The slurry was then pasted on a copper foil, followed by drying in a vacuum oven for 24 hours. CR2032-type coin cells were assembled in an argon-filled glove box using sodium metal as the counter electrode and a microporous glass fiber membrane (Whatman) as the separator. The electrolyte used in this study was 1M NaClO₄ in a solvent of ethylene carbonate and diethyl carbonate (EC/DEC, 1:1 by volume).

Cyclic Voltammetry (CV) measurements were performed by Gamry Reference 600 Potentiostat/Galvanostat/ZRA system in a voltage range of 2.5 to 0.01 V with a scan rate of 0.05 mV s⁻¹. Galvanostatic charge–discharge tests were conducted using LAND CT2001A battery testing system in a voltage range of 0.01 to 2.5 V.
5.3 Results and Discussion

Figure 60 (A) shows the SEM images of electrospun precursor nanofibers with an ATO:PAN weight ratio of 0.5:1. It is seen that the as-spun precursor nanofibers are continuous and have relatively uniform diameters. A few knob-like structures are detected from the surface of the nanofibers, which can be attributed to the agglomeration of ATO nanoparticles.
Figure 60. SEM images of ATO@PAN/PMMA nanofibers with ATO:PAN ratio of 0.5:1.

Figure 60 (B) shows SEM images of SnSb@C nanofibers carbonized from precursor with ATO:PAN ratio of 0.5:1. Similar to the precursor nanofibers, SnSb@C nanofibers also form
a three-dimensional network structure. A few knots, representing the aggregation of the nanoparticles, can still be detected. TEM images of these SnSb@C nanofibers are shown in Figure 61. SnSb nanoparticles formed in-situ during carbonization are nano-sized and can facilitate a shorter lithium ion diffusion path length. These SnSb nanoparticles are encapsulated inside the carbon nanofibers. Encapsulating high-capacity active materials into a carbon matrix is a common practice for accommodating their large volume changes for the purpose of improving the cycling performance.\textsuperscript{125} From Figure 61, it is also seen that a porous structure has been formed around SnSb nanoparticles inside the carbon nanofiber matrix, which is mainly resulted from the decomposition of PMMA. The porous structure can help buffer the large volume changes of SnSb nanoparticles during sodiation-desodiation process and prevent the fracture of the carbon nanofiber matrix.
Figure 61. TEM images of SnSb@C nanofibers magnifications prepared from precursor with ATO:PAN ratio of 0.5:1.
XRD patterns of ATO precursor nanoparticles and SnSb@C nanofibers are shown in Figure 62. In Figure 62 (A), characteristic peaks are observed at 26.4°, 33.8°, 38.0°, 39.0°, 51.7°, 61.9°, 64.8°, and 66.0° for ATO nanoparticles. In Figure 62 (B), the peaks at 30.7°, 32.0°, 44.1° and 45.1° can be attributed to metallic Sn phase while the peaks at 29.1°, 41.5°, 41.7°, 51.2°, and 60.2° can be ascribed to the SnSb phase, indicating the reduction of the ATO nanoparticles and the formation of Sn and SnSb phases. Hence, during the thermal treatment, the ATO nanoparticles were transformed to SnSb nanoparticles, consisting of Sn and SnSb phases, by using pyrolytic carbon as a reduction agent under the inert argon atmosphere. Based on the elemental analysis, there are 52.8% SnSb, 41.1% carbon, 1.0% hydrogen, and 5.1% nitrogen in the SnS@C nanofiber composite prepared from precursor with ATO:PAN ratio of 0.5:1.
Figure 62. XRD patterns of (A) ATO nanoparticles, and (B) SnSb@C nanofibers prepared from precursor with ATO:PAN ratio of 0.5:1.
Figure 63 compares the Raman spectra of carbon nanofibers and SnSb@C nanofibers (ATO:PAN = 0.5:1). For both nanofibers, there are two distinct peaks at 1600 (G band) and 1350 cm\(^{-1}\) (D band), which are associated with the vibration of sp\(^2\) bonded carbon in planar sheets and the presence of defects and disordered carbon, respectively. The intensity ratios of the D band and G band, i.e., \(I_D/I_G\) ratio, is often used to assess the disorder feature of carbon materials. From Figure 49, it is seen that the \(I_D/I_G\) ratios of carbon nanofibers and SnSb@C nanofibers are 1.18 and 1.19, respectively. The relatively high \(I_D/I_G\) ratios suggest the disordered nature of the carbon structure in both carbon nanofibers and SnSb@C nanofibers.

![Raman spectra of carbon nanofibers and SnSb@C nanofibers](image)

**Figure 63.** Raman spectra of (A) carbon nanofibers, and (B) SnSb@C nanofibers prepared from precursor with ATO:PAN ratio of 0.5:1.
Figure 64 shows the cyclic voltammetry (CV) test results of SnSb@C nanofibers with different ATO:PAN ratios. In Figure 64 (A), the electrochemical behavior of pure carbon nanofibers (i.e., ATO:PAN = 0:1) was studied. In the first reduction scan, the peak shown at 0.5V is due to the formation of solid electrolyte interface (SEI) on the surface of carbon nanofibers. The sodiation process in the carbon nanofibers mainly occurs at 0.02V which corresponds to the peak in the Figure 64 (A). For SnSb@C nanofibers prepared from precursor with ATO:PAN ratio of 0.5:1, the peak at 0.35V in the first cycle can be mainly ascribed to the irreversible reaction that produces the SEI film. After the first cycle, the reductive peak at 0.02 can be assigned to the Na-ion insertion into the carbon matrix while that at 0.5V is for Na-ion insertion to the SnSb nanoparticles to form Na$_{15}$Sn$_4$ and Na$_3$Sb. Correspondingly, the oxidative peaks at 0.1V, 0.5V and 0.6V indicated the Na-ion extraction from carbon matrix, Na$_{15}$Sn$_4$ phase, and Na$_3$Sb phase. With the ATO:PAN ratio increased to 1:1, the electrochemical behavior of the electrode does not change and the oxidative peaks at 0.1V, 0.5V and 0.6V and reductive peaks at 0.02 and 0.5V still can be seen in the CV curve.
Figure 64. Cyclic voltammetry curves of SnSb@C nanofibers prepared from precursor with different ATO:PAN ratios: (A) 0:1, (B) 0.5:1, (C) 1:1.

Figure 65 shows the charge-discharge curves of SnSb@C nanofibers prepared from precursors with different ATO:PAN ratios. The current density used was 500 mA g\(^{-1}\). For the pure carbon nanofibers (ATO:PAN = 0:1), an initial capacity of 380 mAh g\(^{-1}\) and reversible capacity of 161 mAh g\(^{-1}\) can be obtained and during the first cycle, a discharge plateau at 0.5V can be observed which relates to the SEI formation and corresponds to the peak
observed in the CV curve (Figure 64). For SnSb@C nanofibers prepared from precursor with ATO:PAN ratio of 0.5:1, the specific discharge capacity at the first cycle is 470 mAh g\(^{-1}\), with a Coulombic efficiency of 82.6%. The irreversible capacity loss in the first cycle is mainly attributed to the reduction of the electrolyte for SEI formation on the surface of the electrode during the first discharge step.\(^{224}\) For the SnSb@C nanofibers prepared from precursor with ATO:PAN ratio of 1:1, the specific discharge capacity is 859 mAh g\(^{-1}\) at the first cycle and the Coulombic efficiency is 76.0%. The initial capacity loss of SnSb@C nanofibers prepared with a lower ATO:PAN ratio of 0.5:1 is much smaller than that of SnSb/C nanofibers prepared with a higher ATO:PAN ratio of 1:1. From the subsequent discharge curves, the plateau at 0.5V indicates the Na-ion insertion into SnSb nanoparticles, which corresponds to the peak at 0.5V in the CV curve. After the 2\(^{nd}\) cycle, the specific capacity tends to stabilize and the Coulombic efficiency increases to above 95.0%.
Figure 65. Charge-discharge curves of SnSb@C nanofibers prepared from precursors with different ATO:PAN ratios: (A) 0:1, (B) 0.5:1, (C) 1:1.

The cycling performance of SnSb@C nanofibers prepared from precursors with different ATO:PAN ratios were also evaluated at a current density of 500 mA g$^{-1}$ and the results are shown in Figure 51. Pure PAN-derived carbon nanofibers (ATO:PAN = 0:1) show a capacity of 130 mAh g$^{-1}$ in most cycles and this capacity value is significantly lower than those of SnSb@C nanofibers prepared with ATO:PAN ratios of 0.5:1 and 1:1. This indicates that the
majority of the capacity of SnSb@C nanoparticles is provided by SnSb nanoparticles. From Figure 66, it is seen that when the ATO:PAN is 0.5:1, a reversible capacity of 380 mAh g\(^{-1}\) is achieved after the first cycle, and the capacity decreases gradually to 356 mAh g\(^{-1}\) at the 200th charge-discharge cycle, indicating a capacity retention of as high as 93.7%. When the ATO:PAN ratio is 1:1, a high initial capacity is expected due to the presence of higher amount of SnSb nanoparticles. A high reversible capacity of 649 mAh g\(^{-1}\) is achieved after the first cycle, however, the capacity reduces to 410 mAh g\(^{-1}\) at the 200th cycle, indicating a capacity retention of 63.2%. Therefore, the capacity retention of SnSb@C nanofibers prepared with ATO:PAN ratio of 1:1 is lower than that of SnSb@C nanofibers with ATO:PAN ratio of 0.5:1. This is because in SnSb@C nanofibers prepared with ATO:PAN ratio of 1:1, some SnSb nanoparticles may not be completely encapsulated inside the carbon nanofiber matrix and the volume change of unprotected SnSb nanoparticles is not effectively buffered during the sodiation-desodiation process, resulting in larger capacity loss. The excellent cycling behavior for SnSb@C nanofibers prepared with ATO:PAN ratio of 0.5:1 can be attributed to both the buffering effect of carbon nanofiber matrix and the void space surrounding the SnSb nanoparticles.
Figure 66. Cycling performance of SnSb@C nanofibers prepared from precursors with different ATO/PAN ratios under current density of 500 mA g⁻¹.

The rate capability of SnSb@C nanofibers prepared from precursor with ATO:PAN ratio of 0.5:1 was studied by increasing the current density sequentially from 50 mA g⁻¹ to 100 mA g⁻¹, 200 mA g⁻¹, 500 mA g⁻¹, and 1 A g⁻¹, respectively (Figure 67). It is seen that at 50 mA g⁻¹, the SnSb@C nanofibers deliver a capacity of 590 mA g⁻¹. As the current density increases, the capacity decreases gradually, however, a relatively high capacity of 370 mAh g⁻¹ is still maintained at 1 A g⁻¹, corresponding to a capacity retention of 62.7% with respect to the
capacity at 50 mA g$^{-1}$. When the current density returns back to 50 mA g$^{-1}$ after 50 cycles, a capacity as high as 560 mAh g$^{-1}$ is restored, which confirms the stable structure of SnSb@C nanofibers. First, this excellent rate capability may be attributed to the binary alloy of SnSb, because the introduction of another metal phase can effectively relieve the volume change during sodiation/desodiation process. Secondly, the porous carbon nanofiber structure, which can accommodate the volume change of SnSb nanoparticles while providing conductive pathways for both electrons and Na ions. Moreover, the porous structure around the nanoparticles can also facilitate the diffusion of the electrolyte and Na ions, which promotes the kinetics of electrode reactions.

![Graph](image)

**Figure 67.** Rate capability of SnSb@C nanofibers prepared from precursor with ATO:PAN ratio of 0.5:1 from 50 to 1000 mA g$^{-1}$. 
To investigate the morphology change of SnSb@C nanofibers, the cell was disassembled and examined by TEM after 200 charge–discharge cycles (Fig. 68). It can be seen that the spherulitic structure of SnSb nanoparticles was maintained and that most particles were still encapsulated in the carbon nanofiber matrix, suggesting that pulverization and aggregation of SnSb nanoparticles inside the carbon nanofiber matrix were effectively alleviated.

Figure 68. TEM image of SnSb@C nanofibers after 200 charge-discharge cycles under the current density of 500mA g⁻¹.
5.4 Conclusion

In this work, ATO nanoparticles, PAN and PMMA were utilized to produce a SnSb nanoparticle-filled porous carbon fiber composite for use as the anode material in sodium-ion batteries. The morphology, active material content and electrochemistry performance were evaluated by XRD, SEM, TEM, and elemental analysis. The uniform and stable porous structure, confirmed by the SEM and TEM images, can provide space and confinement for SnSb nanoparticles and buffer the volume expansion-contraction during repeated charge-discharge cycling. The high capacity and excellent cycling performance under high current density demonstrated the good electronic contact from carbon nanofibers during cycling and the excellent stability of the active material.
CHAPTER 6. SnSbS\textsubscript{x} encapsulated carbon nanofiber composite as high performance sodium-ion battery anode material

Abstract

A SnSbS\textsubscript{x}/porous carbon nanofiber (SnSbS\textsubscript{x}/PCNF) composite is successfully prepared by electrospinning followed by a sulfuration treatment. The as-prepared SnSbS\textsubscript{x}/PCNF composite exhibits a unique two-dimensional nano-sheet morphology. As a result, the SnSbS\textsubscript{x}/PCNFs can deliver a high reversible capacity of 646.9 mAh g\textsuperscript{-1} and achieve good cycling stability and rate capability when used as anode materials for sodium-ion batteries (SIBs). The improved electrochemical performance of SnSbS\textsubscript{x}/PCNFs can be ascribed to the synergistic effects of SnSbS\textsubscript{x} nano-sheets and sulfurated PCNFs (SPCNFs), which can not only provide electronic conductivity but also buffer the volume change of the SnSbS\textsubscript{x} nano-sheets during sodiation/desodiation process. Additionally, the sulfuration process generates a sulfur doping effect on the PCNFs, further enhancing their sodium storage ability. Therefore, SnSbS\textsubscript{x}/PCNFs show great potential as anodes for high-performance SIBs.
6.1 Introduction

Due to their long cycle life, high energy density and good safety property, lithium-ion batteries (LIBs) have revolutionized our daily life and been widely used as the predominant power source for portable devices, electric vehicles (EVs) and so on.\textsuperscript{210,225,226} However, the rapidly increased consumption of lithium resources leads to the concern of foreseeable price increase of LIBs.\textsuperscript{227} Recently, SIBs, as a promising alternative to LIBs for grid-scale energy storage, have attracted tremendous attention. However, the development of high-performance electrode materials is still the critical issue to realize practical SIBs. Inspired by the similarity in electrochemistry with LIBs, many materials have been investigated as cathode materials for SIBs including P2- or O3-layered oxides (NaFeO\textsubscript{2}, Na\textsubscript{x}[Fe\textsubscript{y}Mn\textsubscript{1−y}]O\textsubscript{2}),\textsuperscript{228–231} polyanionic compounds (NaFePO\textsubscript{4}, Na\textsubscript{2}FeP\textsubscript{2}O\textsubscript{7}, Na\textsubscript{2}MnP\textsubscript{2}O\textsubscript{7}),\textsuperscript{66,232,233} and some miscellaneous Na insertion materials (FeF\textsubscript{3}, Fe\textsubscript{2}(CN)\textsubscript{6}).\textsuperscript{234,235} Up to date, much progress has been made on the SIB cathode research and utilization of suitable cathode materials with hard carbon anode can achieve a high energy density of 300 mWh g\textsuperscript{−1} for SIBs, which is competitive to the graphite/LiMn\textsubscript{2}O\textsubscript{4} system.\textsuperscript{226}

However, in order to commercialize SIBs, another major obstacle that should be addressed is to develop qualified anode material with high capacity and good stability. So far, various materials, such as titanium oxides/compounds (TiO\textsubscript{2}, lithium titanate),\textsuperscript{236,237} carbon materials (hard carbon, carbon nanosheets and carbon nanofibers),\textsuperscript{72,238,239} metal alloy (Sn, Sb)\textsuperscript{20,182,209} and binary compounds (metal oxides, metal sulfides),\textsuperscript{225,227,240} have been investigated as anode materials for SIBs. However, for titanium oxides/compounds and carbonaceous materials, the main disadvantage is their relatively low capacity (<350 mAh g\textsuperscript{−1}). On the other
hand, some metals can form alloy with Na delivering high gravimetric and volumetric specific capacities (847 mAh g\(^{-1}\) for Sn, 660 mAh g\(^{-1}\) for Sb).\(^{20}\) Nonetheless, compared with Li\(^+\), due to the larger ionic radius of Na\(^+\), the volume change of these materials during charge/discharge process is more severe than that in LIBs, which can result in pulverization of materials and gradual loss of electrical contact with the current collector, causing fast capacity degradation. Therefore, it is difficult to obtain stable alloy-based anode materials for SIBs.

Recently, the two-dimensional transition metal dichalcogenides (TMDs) such as MoS\(_2\), WS\(_2\), SnS and SnS\(_2\), have attracted great research interest as anode materials for SIBs, due to their unique layered structure, which allows the reversible Na\(^+\) insertion/extraction and delivers superior theoretical capacities (946 mAh g\(^{-1}\) for Sb\(_2\)S\(_3\),\(^{241}\) 670 mAh g\(^{-1}\) for MoS\(_2\),\(^{166}\) 1022 mAh g\(^{-1}\) for SnS\(^{242}\)). Among these metal sulfides, SnS\(_2\) has a CdI\(_2\)-type lamellar structure, in which the tin atoms are located in the center and sandwiched between two layers of sulfur atoms.\(^{243}\) The tin and sulfur atoms are stacked on each other via Van der Waals interactions with an interlayer spacing of 0.5899 nm, which is sufficient for Na\(^+\) insertion/extraction.\(^{243}\) During charge/discharge process, the SnS\(_2\) undergoes a combined conversion and alloying reaction:

\[
4\text{Na}^+ + \text{SnS}_2 + 4e^- \rightarrow 2\text{Na}_2\text{S} + \text{Sn} \quad (1)
\]

\[
\text{Sn} + 3.75\text{Na}^+ + 3.75e^- \rightarrow \text{Na}_{3.75}\text{Sn} \quad (2)
\]

delivering a high capacity of 1136 mAh g\(^{-1}\).\(^{244}\) Moreover, due to the relative weak covalent bond between Sn and S, reaction 1 is highly reversible, which ensures to maintain a high
reversible capacity of SnS₂, making SnS₂ an promising anode material candidate for SIBs.²⁴⁵ However, it is noted that the bare SnS₂ still shows poor cycling stability and rate performance due to its low conductivity and large volume change during sodiation/desodiation process. To facilitate the high reversible capacity and stable cycling performance of SnS₂, incorporating SnS₂ with carbonaceous materials is an efficient way that can improve the electrochemical performance of SnS₂ by increasing the conductivity and accommodating the volume change. Xiu et al. used a hydrothermal method to synthesize the SnS₂/graphene composite.²⁴⁶ The as-prepared SnS₂/graphene nano-composites show a two-dimensional structure and it can deliver a reversible capacity of 670 mAh g⁻¹ after 60 cycles under the current density of 20 mA g⁻¹.²⁴⁶ The improved electrochemical performance can be ascribed to the good electronic conductivity and buffering effect from the graphene. A exfoliated-SnS₂ was restacked on the graphene layers by the hydrolysis of lithiated SnS₂ to synthesize the exfoliated SnS₂/graphene composite structure.²⁴⁷ Composites with different amounts of graphene were prepared and evaluated. The best performance was achieved by the one with 20 mg graphene added, which delivered a capacity of ~600 mAh g⁻¹ after 300 cycles under a current density of 200 mA g⁻¹.²⁴⁷

During the synthesis process of these metal sulfides such as SnS₂,²⁴⁶ SnS–MoS₂,²⁴⁸ Ni₃Co₆S₈,²⁴⁹ different sulfur-containing chemicals such as L-cysteine, thiourea, hydrogen sulfide were used to sulfurate the metal precursors under high temperature and/or pressure. Despite the fact that good electrochemical performance has been made for these composites by combining the metal sulfides with carbon, few efforts addressed the effect of sulfuration process on the carbon materials. In this work, a SnSbSₓ/porous carbon nanofiber nano-
composite was synthesized by sulfurating the SnSb/PCNFs composite using a hydrogen sulfide gas to react with the alloy under a relatively high temperature. The sodium storage capability and rate capability were investigated for SnSbSx/PCNFs and SnSb/PCNFs. Moreover, the sulfuration process was also conducted on the pure PCNFs to achieve sulfurated porous carbon nanofibers whose morphology, structure and electrochemical performance were also studied and compared with the PCNFs to evaluate the influence of the sulfuration process comprehensively.

6.2 Experimental

6.2.1 Chemicals
Polyacrylonitrile (PAN, average Mw ~ 150 000, Aldrich), polymethylmethacrylate (PMMA, average Mw ~ 120 000, Aldrich), antimony tin oxide (SnO2/Sb2O5, ATO, particle diameter < 50 nm, Aldrich), N,N-dimethylformamide (DMF, 99.8%, Aldrich), propylene carbonate (PC, 99.7%, Sigma-Aldrich), ethylene carbonate (EC, 98%, Aldrich), sodium (Na, Aldrich), sodium perchlorate (NaClO4, 98%, Aldrich) were purchased and used without further purification.

6.2.2 Nanofiber preparation
At first, 0.8g PAN, 0.4g PMMA and 0.4g ATO precursor were added into 9.2g DMF and kept stirring for 12h to form a homogenous solution for electrospinning. Electrospinning was then conducted with an applied voltage of 15 kV, a solution flow rate of 0.75 mL h⁻¹, and a needle tip-to-collector distance of 15 cm. Afterwards, the as-spun nanofibers were first
stabilized in air at 250 °C for 3 h with a heating rate of 5 °C min\(^{-1}\), and then carbonized at 700 °C in nitrogen for 5 h with a heating rate of 2°C min\(^{-1}\) to obtain the SnSb/PCNF composite. The pure PCNFs without SnSb particles were also prepared at the same condition.

### 6.2.3 Sulfidization process

After obtaining the SnSb/PCNFs, the composite was loaded into a ceramic boat and another ceramic boat containing thiourea was put at the upflow of the furnace. The SnSb/PCNFs were sulfurred at 350 °C for 6 h under the protection of nitrogen gas flow. During the thermal treatment, the thiourea decomposed and hydrogen sulfide gas was released. The SnSb/PCNFs reacted with the hydrogen sulfide and transformed into SnSbS\(_x\)/PCNFs. Pure PCNFs were also treated under the same sulfidization condition as above to achieve SPCNFs.

### 6.2.4 Structural characterization

The crystal structure of the SnSb/PCNFs, SnSbS\(_x\)/PCNFs, PCNFs and SPCNFs was investigated by X-ray diffractometry (XRD, Rigaku SmartLab) with Cu K\(\alpha\) radiation between 20 angles from 10° to 60°. Morphological features were studied using field-emission scanning electron microscopy (FE-SEM, FEI Verios 460L) and high-resolution transmission electron microscopy (HR-TEM, JEM-2100F). The Raman spectra were recorded using a Renishaw-1000 Raman spectroscopy with an excitation wavelength of 514.5 nm. The elemental chemical surface states were characterized by X-ray photoelectron spectroscopy (XPS) using a SPECS system with PHOIBOS 150 analyzer.
6.2.5 Electrochemical measurements

SnSb/PCNFs, SnSbSx/PCNFs, PCNFs and SPCNFs were grounded and mixed with carbon black and alginic acid sodium salt binder to form a homogeneous slurry with deionized water as the solvent, respectively. The weight ratios of active materials, carbon black and alginic acid sodium salt binder are 7:2:1. The slurry was casted on the copper foil, followed by drying in a vacuum oven at 80°C for 12 hours to form the working electrode. The coin cells (CR2032) were used in this study, and the half cells were assembled in an Ar-filled glove box with a sodium metal foil (Sigma-Aldrich) as the counter electrode. A glass fiber GF/D (Whatman) filter was used as the separator. The electrolyte used was a solution of 1 M NaClO₄ dissolved in a 1 : 1 volume mixture of ethylene carbonate–propylene carbonate (EC–PC). Cyclic voltammetry (CV) measurements were carried out by Gamry Reference 600 Potentiostat/Galvanostat/ZRA system within the potential window of 2.5–0.01 V. Electrochemical impedance spectroscopy (EIS) was measured within a frequency range of 0.01 Hz–100 kHz using the Gamry Reference 600 Potentiostat/Galvanostat/ZRA system. Galvanostatic charge–discharge tests were performed using a LAND CT2001A battery testing system in a voltage range of 0.01– 2.5 V and the capacity values were calculated based on the total composite weight.
6.3 Results and Discussion

Figure 69. SEM images of (A) ATO nanoparticles, (B) SnSb/PCNFs, (C, D) SnSbSₓ/PCNFs, (E) PCNFs, and (F) SPCNFs.
Figure 69 A shows that the ATO precursor has particle morphology with a uniform particle size around 50 nm. The relatively small particle size of the precursor not only favors a good dispersion in the PAN/PMMA/DMF solution, but also helps the uniform distribution of ATO in the electrospun nanofibers. Figure 69 B shows the fibrous morphology of as-prepared SnSb/PCNFs. The nanofibers are continuous with a uniform diameter of around 200 nm. The nanofiber surface is slightly rough, resulting from the decomposition of PMMA and the produced CO$_2$ gas during the reduction of ATO to SnSb. From the SEM image of SnSb/PCNFs, some alloy particles with large sizes are detectable on the surface of the PCNFs, which can be ascribed to the high carbonization temperature and the low melting point of Sn.$^{250}$ These exposed alloy particles will directly contact with the electrolyte and this may cause the pulverization of alloy particles and the loss of capacity during charge/discharge process. From Figure 69 C and D, it is seen that after sulfuration, there are many nano-sized fish scale-like sheets uniformly anchored on the surface of the PCNFs. Under higher resolution, the SEM image shows that the nano-sized sheets are around 100 nm and most of them are actually still constrained by the PCNF layer, which could provide the conductive pathway for the SnSbS$_x$ during charge/discharge process.

Furthermore, Figures 69 E and F display the SEM images of PCNFs and SPCNFs, respectively. Both PCNFs and SPCNFs show smooth surface and uniform diameters around 200 nm without impurities detected. The continuous fiber morphology is believed to be beneficial to enhancing the Na$^+$ mobility during sodiation/desodiation process, ensuring good electrochemical performance.$^{251,252}$
Figure 70. TEM images of SnSb/PCNFs under different magnifications.

The TEM and high resolution TEM (HR-TEM) were subsequently utilized to explore insight into the morphologies and structures of the SnSb/PCNFs, SnSbS_x/PCNFs, PCNFs and SPCNFs. From Figure 70 A, it can be seen that many SnSb alloy particles with particle size around 50 nm are embedded into the PCNF matrix and porous structures are also formed.
around the alloy particles, which could result from the reaction between ATO and pyrolysis carbon during carbonization process.\textsuperscript{253} However, some agglomerated alloy particles with larger sizes are also observed inside and outside the PCNFs. This is closely related to the high carbonization temperature because the low melting temperature (232 °C) of tin makes itself easy to grow into larger grains under high temperature.\textsuperscript{250} Moreover, the alloy particles that formed outside the PCNFs might contribute to the capacity loss during charge/discharge process due to the absence of protection from the PCNFs.

**Figure 71.** (A-E) TEM images of SnSbS\textsubscript{x}/PCNFs and selected area electron diffraction (SAED) images of SnSbS\textsubscript{x} and (F) measurement of interlayer distance of SnS\textsubscript{2} in the SnSbS\textsubscript{x}/PCNFs.
For SnSbS\textsubscript{x}/PCNFs, as shown in Figures 71 A and B, the nano-sized SnSbS\textsubscript{x} exhibits a nano-sheet architecture and exhibit uniformly dispersion throughout the whole PCNF framework, which are consistent with the observation from the SEM images. In particular, after sulfuration, some SnSb particles with large size turn into SnSbS\textsubscript{x} showing a crumpled cluster morphology and remain inside the PCNF matrix with a size around 100 nm (Figure 71 C). As shown in Figure 71 D and E, when observed under a higher resolution, it can be seen that the nano-sized sheets demonstrate layered structure and each sheet unit is piled up by 8-12 layers of SnSbS\textsubscript{x} with an interlayer spacing around 0.59 nm, which is also confirmed by the measurement in Figure 71 F. A possible growth mechanism for the unique SnS\textsubscript{2} sheet structure was proposed, which may be related to a heterogenous nucleation process. During the sulfuration process, the initially formed SnS\textsubscript{2} nuclei will facilitate further growth of SnS\textsubscript{2} on its top surface by acting as the crystal seeds\textsuperscript{254}. According to the crystal growth habits of SnS\textsubscript{2}, it tends to grow along its c-axis but the existence of carbon materials can effectively prevent the persistent nuclei growth and lead to the few-layer morphology\textsuperscript{255}. In addition, a thin layer of carbon shell with a thickness around 3-5 nm is found to cover the SnSbS\textsubscript{x} nano-sheets, the intimately-contacted carbon shell not only can inhibit the continuous growth of SnSbS\textsubscript{x} nano-sheets along the c-axis to maintain a small size, but also protect SnSbS\textsubscript{x} from the direct contact with the electrolyte during charge/discharge process. Based on previous study, it has also been demonstrated that the stereo structure of SnSbS\textsubscript{x} can enhance the Na\textsuperscript{+} diffusion and cushion the volume change of SnSbS\textsubscript{x}\textsuperscript{256}. Indeed, the addition of PMMA in the solution created the porous structure in the CNF framework, which not only suppresses the
agglomeration of tin during calcination but also offers space for the nucleation and growth of SnSbS_x.

**Figure 72.** TEM images of (A, B) PCNFs and (C, D) SPCNFs.

Based on Figure 72, it is seen that both PCNFs and SPCNFs exhibit smooth surface with an average diameter around 200 nm, which is consistent with the SEM observation and no obvious lattice fringes can be observed in PCNFs and SPCNFs under higher resolution,
indicating an amorphous carbon feature. However, it is still difficult to observe any morphology or structure difference between PCNFs and SPCNFs from the TEM images.

**Figure 73.** XRD patterns of (A) ATO nanoparticles, (B) SnSb/PCNFs, (C) SnSbS\textsubscript{x}/PCNFs and (D) PCNFs and SPCNFs.

The XRD pattern of Sn\textsubscript{0.92}Sb\textsubscript{0.08}O\textsubscript{2.04} precursor is shown in Figure 73 A. All the reflection peaks at 26.5, 33.8, 38.0, 39.0, 42.6, 51.8, 54.8, and 57.8° can be well indexed to the
antimony tin oxide. After the ATO nanoparticles were encapsulated into the electrospun PAN/PMMA nanofibers and carbonized at 700°C under the protection of nitrogen, a reaction was conducted as follows:

\[
\text{Sn}_{0.92}\text{Sb}_{0.08}\text{O}_{2.04} + C \rightarrow \text{SnSb} + \text{Sn} + \text{CO}_2 \uparrow
\]

During this thermal treatment, the ATO nanoparticles are reduced into SnSb alloy and metallic Sn in the existence of pyrolytic carbon. From Figure 73 (B), it is seen that the strong peaks at 29.1, 41.5, and 51.6° can be assigned to the rhombohedral \(\beta\)-SnSb phase (JCPDS no. 33-0118) and the peaks at 30.5, 32.0, 44.1 and 45.1° can be ascribed to the \(\alpha\)-Sn phase (JCPDS no. 04-0673). No peaks from ATO can be found in the XRD pattern of SnSb/PCNFs, revealing a complete transformation of ATO to SnSb alloy and metallic Sn. After the carbonization process, a sulfuration process was conducted at 350°C and the SnSb/PCNFs reacted with the hydrogen sulfide (H\(_2\)S) gas which came from the thermal decomposition of thiourea, leading to the transformation of SnSb/PCNF composite into SnSbS\(_x\)/PCNFs. From Figure 73 C, there are several sharp diffraction peaks at 15.0, 28.3, 32.2, 41.9, 50.0, and 52.5°, which can be indexed to the hexagonal phase of SnS\(_2\) (JCPDS no. 23-677). However, we can barely detect the peaks from Sb\(_2\)S\(_3\) or Sb\(_2\)S\(_5\) in the Figure 73 C. It is probably due to the small crystal size or the amorphous structure of the formed SbS\(_x\).\(^{257}\)

Moreover, the XRD patterns of PCNFs and SPCNFs are shown in Figure 73 D. Two broad peaks around 25.1° and 43.7° are presented in the XRD patterns of both PCNFs and SPCNFs and these two peaks can be attributed to the (002) and (100) diffraction modes, respectively, indicating an amorphous structure of carbon materials. Notably, the located position of (002)
diffraction peak for SPCNFs is $\theta = 25.2^\circ$, lower than that of PCNFs ($25.4^\circ$) and based on Bragg’s law, it can be calculated that the SPCNFs have an enlarged interlayer distance than PCNFs.
Figure 74. Raman spectra of (A) SnSb/CPNFs, SnSbS₆/PCNFs and detailed spectra from 100-400 cm⁻¹ in SnSbS₆/PCNFs, (B) PCNFs and SPCNFs.
Raman spectroscopy is sensitive to the changes in the structure of carbon materials, which makes it a powerful tool in the characterization of carbon materials. Figure 74 A shows the Raman spectra of the SnSb/PCNFs and SnSbSₓ/PCNFs. Two prominent peaks at around 1590 cm⁻¹ and 1350 cm⁻¹ are displayed, which can be assigned to the G band and D band, respectively. The G band is associated with the disorder degree of graphene in the carbon materials, while the D band is closely related to the first-order scattering of the phonon vibrations mode E₉ observed for sp² carbon domains.²³⁹ Therefore, the disorder degree of carbon materials can be evaluated by calculating the intensity ratio of D band and G band (I_D/I_G). As shown in Figure 74 A, the I_D/I_G ratio for SnSb/PCNFs is obviously lower than that of SnSbSₓ/PCNFs. The higher I_D/I_G for SnSbSₓ/PCNFs indicates that more defects are introduced into the carbon matrix of the SnSbSₓ/PCNFs, which possibly results from the sulfuration process. In order to test the hypothesis, the effect of sulfuration process on the structure of PCNF, the Raman spectra of PCNFs and SPCNFs are also shown in Figure 74 B. It is calculated that the I_D/I_G ratio for PCNFs and SPCNFs are 1.01 and 1.11, respectively, which indicates that both PCNFs and SPCNFs show low degree of graphitization. The higher I_D/I_G ratio of SPCNFs is an evidence of higher disordered structure or existence of more defects. The increased amorphous structure of SPCNFs is probably produced in the sulfuration process, during which the hydrogen sulfide gas was produced and sulfur doping was conducted on the PCNFs. In addition, from the inset in Figure 74 A, a peak located at 303 cm⁻¹ can be detected in the SnSbSₓ/PCNFs Raman spectra, which can be assigned to the A₁g modes of SnS₂.²⁴⁶,²⁵₈ It also confirms the successful synthesis of SnS₂ in the SnSbSₓ/PCNFs.
Figure 75. XPS spectra of (A) Sn 3d, (B) S 2p in SnSbS\textsubscript{x}/PCNFs, (C) S 2p in PCNFs and SPCNFs, and (D) deconvolution of S 2p spectra in SPCNFs.

X-ray photoelectron spectroscopy was also performed to investigate the surface electronic states and composition of the as-prepared samples. At first, the oxidation state of Sn in the SnSbS\textsubscript{x}/PCNFs was studied. The high-resolution XPS spectra of Sn shows that two peaks at 486.6 and 495.1 eV are shown in Figure 75 A, corresponding to the Sn 3d\textsubscript{5/2} and Sn 3d\textsubscript{3/2} of Sn\textsuperscript{4+}, respectively.\textsuperscript{259} From Figure 75 B, it is seen that the XPS spectrum of S 2p binding
energies of SnSbS$_x$/PCNFs shows two peaks at 161.8 and 163.2 after deconvolution, which can be ascribed to the S$^{2-}$ in the metal sulfide.\textsuperscript{260} The XPS results above are evidence of pure SnS$_2$ composition in the SnSbS$_x$/PCNFs. In order to investigate the effect of sulfuration process on the carbon matrix, XPS was also conducted on the PCNFs and SPCNFs. The S 2p binding energies of PCNFs and SPCNFs are shown in Figure 75 C. Compared with PCNFs, a small amount of sulfur is integrated into the SPCNFs due to the presence of the board peak at 164 eV. After deconvolution, two peaks located at 164.2 and 165.4 are displayed, as shown in Figure 75 D, and the appearance of these two peaks is in accord with sulfur doping in the carbon materials.\textsuperscript{261} Besides, the peak at 164.2 also suggests that the sulfur exists in the state of –C-S-C-\textsuperscript{262} From the XPS results, it is found that the sulfuration process can induce sulfur heteroatoms into the carbon nanofibre structure to produce a sulfur-doping effect.
Figure 76. CV curves for the first three cycles of (A) SnSb/PCNFs, (B) SnSbSx/PCNFs, (C) PCNFs, and (D) SPCNFs at a scanning rate of 0.1 mV s\(^{-1}\).

Cyclic voltammetry (CV) was performed to explore the sodium storage mechanism. For SnSb/PCNFs, it is seen from Figure 76 A that there is a broad reduction peak from 1.0 – 0.6V during the first cathodic scan, which disappears in the subsequent cycles and can be attributed to the decomposition of electrolyte and solid electrolyte interphase (SEI) formation on the electrode surface. Another reduction peak at 0.35V is related to the Na-Sn and Na-Sb alloying process forming Na\(_{15}\)Sn\(_4\) and Na\(_3\)Sb. After the first cycle, the alloying process occurs from 0.2-0.7V, corresponding to the board reduction peak in the CV curve. In addition,
a sharp peak at 0.01V can be observed in the first and subsequent scans, which can be assigned to the Na\(^+\) insertion into nanopores of PCNFs.\(^{103}\) In the reversed anodic scan, three oxidation peaks at 0.02, 0.25 and 0.65V are detected. The peak at 0.02V represents the desodiation process of Na\(^+\) from CNFs, which, accompanied with the reduction peak at 0.01V, can also be observed in the CV curves of PCNFs (Figure 76 C). Moreover, the peaks at 0.25 and 0.65V are ascribed to the dealloying reactions of Na\(_{15}\)Sn\(_4\) and Na\(_3\)Sb into metallic Sn and Sb. For SnSbS\(_x\)@PCNFs, it is seen from Figure 76 B that three peaks located at around 1.72, 1.15 and 0.59V can be identified during the first cathodic scan. Among these three peaks, the two cathodic peaks at higher voltage (1.72 and 1.15 V) are associated with the intercalation process of Na\(^+\) into SnS\(_2\) leading to the formation of Na\(_x\)SnS\(_2\), while the peak at 0.59V represents the conversion reaction:

\[
\text{Na}_x\text{SnS}_2 + (4-x) \text{Na}^+ + (4-x) \text{e}^- \rightarrow \text{Sn} + 2\text{Na}_2\text{S}
\]

This reaction results in the formation of metallic Sn and Na\(_2\)S.\(^{124}\) Then the Na-Sn alloying reaction occurs between Na\(^+\) and the produced Sn in the potential range from 0.59V to 0.01V, which correlates to the board cathodic peak in the CV curve. The sharp reduction peak, contributed by the Na\(^+\) insertion into PCNFs at 0.01V, is also observed in the CV curve of SnSbS\(_x\)/PCNFs. In the anodic scans, compared with the CV curve of SnSb/PCNFs, the oxidation peaks at 0.02, 0.25 and 0.65V are still discernible which stand for the desodiation of Na\(^+\) from CNFs (0.02V) and the dealloying reactions of Na\(_{15}\)Sn\(_4\) and Na\(_3\)Sb (0.25 and 0.65V), respectively. However, it is noted that another oxidation peak localized at 1.15V is also detected in the CV curve of SnSbS\(_x\)/PCNFs, which can be assigned to the reversible re-
sulfuration of Sn into SnS$_2$ phase. Additionally, the CV curves of PCNFs and SPCNFs are also shown in Figure 76 (C), (D). For PCNFs, a reduction peak at 0.7V during the first cycle can be ascribed to the SEI formation. As mentioned above, the sharp reduction peak at 0.01V and the oxidation peak at 0.02 V are related to the Na$^+$ insertion and extraction process in the carbonaceous materials, respectively.$^{90,116,263}$ After the first cycle, the reduction peak at 0.01V and the oxidation peak at 0.02 V are still prominent and the broad reduction range from 1-0.01V is ascribed to the sodium adsorption/insertion on/into graphene layers in the PCNFs.$^{118,183,251}$ For SPCNFs, except for the reduction peak at 0.5V in the first cycle that represents the SEI formation, compared with the CV curves of PCNFs, SPCNFs display similar sodium storage behavior. The reduction peak at 0.01V, the oxidation peak at 0.02 V as well as the broad reduction range from 1-0.01V are all discernable. However, another oxidation bump around 1.7V appears in the CV curve of SPCNFs. Based on previous studies,$^{264–266}$ the oxidation peak at high potential can be assigned to the Na binding with heteroatoms on the surface of the anode materials which may testify the assumption from the XPS analysis that sulfur doping was induced on the PCNFs during sulfuration process.
The electrochemical performance was further investigated by cycling tests and the results are demonstrated in Figure 77. For the first cycle, the discharge and charge capacity are 782.0 and 500.8 mAh g\(^{-1}\) for SnSb/PCNFs and 1015.6 and 646.9 mAh g\(^{-1}\) for SnSbS\(_x\)/PCNFs, respectively, corresponding to a coulombic efficiency of 64.04% and 63.69%. After 50 cycles, the reversible capacity for SnSb/PCNFs and SnSbS\(_x\)/PCNFs are 365.2 and 396.9 mAh g\(^{-1}\), respectively. The higher capacities of SnSbS\(_x\)/PCNFs result from the higher theoretical capacity and unique morphology. Notably, the nano-sized sheet structure in SnSbS\(_x\)/PCNFs is beneficial to the Na\(^+\) mobility by reducing the diffusion pathway and the carbon matrix also ensures an effective buffering effect during sodiation/desodiation process. In addition, in order to evaluate the effect of sulfuration on the electrochemical performance of PCNFs, the
cycling performance of PCNFs and SPCNFs is also shown in Figure 77. After cycling for 50 cycles, a reversible capacity of 242.2 and 270.0 mAh g\(^{-1}\) are obtained for PCNFs and SPCNFs, respectively, demonstrating that the induced sulfur doping during the sulfuration can effectively improve the electrochemical performance of the PCNFs.

![Graph](image.png)

**Figure 78.** Rate performance of SnSbS\(_x\)/PCNFs.

Figure 78 presents the rate performance of SnSbS\(_x\)/PCNFs. The half-cell was first evaluated at 50mA g\(^{-1}\) and the current density gradually increased to a high value of 3.2 A g\(^{-1}\). The SnSbS\(_x\)/PCNFs can maintain a reversible capacity of 597.3, 543.6, 466.4, 402.6, 342.3, 278.5 mAh g\(^{-1}\) under the current density of 100, 200, 400, 800, 1600 and 3.2 A g\(^{-1}\), respectively. When the current density reaches 3.2 A g\(^{-1}\), the SnSbS\(_x\)/CNFs still keeps 43.7% of its original
capacity and this confirms the excellent structure stability and electrochemical reversibility of SnSbS_x/PCNFs.

**Figure 79.** EIS spectra of PCNFs and SPCNFs.

The EIS measurement of PCNFs and SPCNFs was also conducted to study their kinetic difference as illustrated in Figure 79. Both Nyquist plots of PCNFs and SPCNFs display a single depressed semicircle in the high-medium frequency region and an inclined line at low frequency. Notably, for SPCNFs, the semicircle diameter is smaller than that of PCNFs.
manifesting improved charge transfer kinetics after the sulfuration treatment. Because the sulfur-doping can increase the Fermi level of carbon materials and this can lead to higher electronic conductivity.\textsuperscript{267}

6.4 Conclusion

In conclusion, the SnSbS\textsubscript{x}/PCNFs were synthesized \textit{via} a facile electrospinning approach and evaluated as sodium-ion battery anode. The SnSbS\textsubscript{x}/PCNFs delivered high reversible capacity with excellent cycling stability. Firstly, the good electrochemical performance can be attributed to the unique nano-sized morphology of SnSbS\textsubscript{x}, which can effectively reduce the Na\textsuperscript{+} diffusion pathway and the volume change during sodiation/desodiation process. Secondly, the SnSbS\textsubscript{x} nano-sheets are uniformly distributed into the PCNF matrix and the good distribution can further balance and alleviate the expansion/contraction stress. Thirdly, the one-dimensional PCNFs can promote the electrons and Na\textsuperscript{+} diffusions. In addition, the influence of sulfuration process on the PCNFs was also explored. After the sulfuration process, it is found that sulfur doping is obtained on the PCNFs and the induced heteroatoms and defects are proved to be beneficial to the Na\textsuperscript{+} mobility by EIS results, leading to the enhancement in electrochemical performance. These results demonstrate that sulfuration can positively affect the electrochemical performance of SnSb alloy and carbon matrix simultaneously and achieve better performance. This work provides a facile way to modify the alloy/carbon composite to synthesize high performance anode materials for SIBs.
CHAPTER 7. Chemical vapor deposited MoS$_2$/electrospun carbon nanofiber composite as anode material for high-performance sodium-ion batteries

Abstract

Due to its high theoretical capacity and unique layered structure, MoS$_2$ has attracted tremendous attention as a sodium-ion battery anode material. However, the electrochemical performance of MoS$_2$ based anodes is hindered by its low intrinsic conductivity and large volume change during cycling. In this report, nano-sized MoS$_2$ sheets were synthesized using a facile and scalable chemical vapor deposition method on the surface of electrospun carbon nanofibers (CNFs). The morphology of the resultant MoS$_2$@CNFs was investigated by scanning electron microscopy, transmission electron microscopy and X-ray diffraction, while their electrochemical performance was studied using cyclic voltammetry and galvanostatic charge-discharge. The results demonstrated that a strong interconnection between MoS$_2$ nanosheets and CNFs was formed and the conductive network of CNFs was beneficial for the sodium ion kinetics. When investigated as an anode for sodium-ion batteries, a high reversible capacity of 380 mA h g$^{-1}$ was obtained after 50 cycles with good cycling stability. In particular, MoS$_2$@CNFs delivered a capacity of 198 mA h g$^{-1}$ under a high current density of 1 A g$^{-1}$ after 1000 cycles, indicating their great potential as anode material for long-life sodium-ion batteries.
7.1 Introduction

Over the past decades, tremendous work has been done to improve the performance of lithium-ion batteries (LIBs), which are the predominant energy provider for today’s laptops, cellphones, and electric vehicles (EVs).\textsuperscript{268–271} In spite of the advantages of LIBs, such as high energy density and long life cycle, the rareness, uneven distribution and rising price of lithium resources encourage people to explore alternative energy storage systems. Recently, sodium-ion batteries (SIBs) have gained much attention as a promising candidate to replace LIBs in large-scale electric storage applications because sodium has similar electrochemical behavior as lithium, but is much more abundant and has significant low cost advantage.\textsuperscript{104,272,273} Stemming from the similar LIB chemistry, a large amount of SIB cathode materials have been studied.\textsuperscript{65,175,176,274} However, more efforts are needed to improve the performance of SIB anodes. \(\text{Na}^+\) has larger radius and smaller diffusion rate than \(\text{Li}^+\), and hence it is difficult for \(\text{Na}^+\) to insert into graphite, the traditional LIB anode material, which has high degree of crystallinity and small interlayer distance of 0.34 nm. Carbonaceous materials with lower or no crystallinity, such as hard carbon, have larger interlayer distances and allow the insertion of \(\text{Na}^+\) in SIBs.\textsuperscript{99,104,116,171,194,275} However, most current carbonaceous materials, like petroleum coke, pyrolytic carbon, and carbon black, can only provide reversible capacities between 100-300 mAh g\(^{-1}\), even at low current densities.\textsuperscript{93,103,276} In addition to carbonaceous materials, transition metals, such as Sn, Sb, and Ge, were investigated as SIB anodes because they can form alloys with large amount of sodium and deliver high capacities.\textsuperscript{137,142,180,277,278} Unfortunately, transition metals experience large volume changes during sodiation/desodiation, which cause extremely severe structural
pulverization, leading to exfoliation of active materials from current collector and this will severely impede the performance of the materials.

Recently, there is a growing interest in exploring transition metal dichalcogenides with layered structure, such as MoS$_2$, SnS$_2$ and WS$_2$, as anode materials for SIBs. For example, Prikhodchenko et al. reported the use of SnS$_2$@graphene composite as a SIB anode material and found it delivered a reversible capacity of 600 mAh g$^{-1}$ at a current density of 50 mA g$^{-1}$ after 50 cycles. A three-dimensional WS$_2$-decorated reduced graphene oxide composite was fabricated by Kang et al, and the layered WS$_2$ can facilitate the Na$^+$ insertion, leading to a relatively high capacity of 334 mAh g$^{-1}$ after 200 cycles under 200 mA g$^{-1}$. Molybdenum disulfide (MoS$_2$), a typical transition metal dichalcogenide also has a layered graphene-like structure. Due to its unique physical and chemical properties, MoS$_2$ has been extensively investigated in various applications including supercapacitors, hydrogen evolution catalysis, and hydrogen storage. Recently, MoS$_2$ was found to possess a high theoretical capacity of 670 mAh g$^{-1}$ when used as an anode material in SIBs. However, MoS$_2$ suffers from low intrinsic conductivity and rapid capacity fading caused by its large volume change during sodiation/desodiation process. So far, two general strategies have been studied to address these drawbacks of MoS$_2$ materials. The first strategy is to synthesize few or single-layered MoS$_2$ which can accommodate the large strain and lower the barrier for sodium intercalation. The other strategy is to apply a carbon coating on the surface of MoS$_2$ particles which can constrain the volume change and improve the material conductivity.
In this work, we used a chemical vapor deposition (CVD) method to deposit MoS$_2$ nanosheets with controllable layer structure directly onto the surface of electrospun carbon nanofibers (CNFs) to form a MoS$_2$@CNF hybrid anode structure. Nanostructured MoS$_2$ was formed directly on CNFs during the CVD process, which led to intimate interfacial contact between MoS$_2$ and CNFs, ensuring good conductivity and volume change buffering. As a result, the produced MoS$_2$@CNF hybrid structure showed high electrical conductivity, improved cycling stability and good rate performance. As far as we know, this is the first report on using the CVD method to produce well-controlled hybrid structure of MoS$_2$ and CNFs, which can be used as a promising anode candidate for SIBs with high capacity and stable cycling performance.

7.2 Experimental

7.2.1 Experimental Chemicals

Polyacrylonitrile (PAN, average Mw $\approx 150,000$, Aldrich), N,N-dimethylformamide (DMF, 99.8%, Aldrich), molybdenum chloride (MoCl$_5$) (99.99%, Sigma-Aldrich), sulfur powder (Sigma-Aldrich), propylene carbonate (PC, anhydrous, 99.7%, Sigma-Aldrich), sodium metal (Sigma-Aldrich), and sodium perchlorate (NaClO$_4$, 98%, Aldrich) were used as received without further purification.

7.2.2 Carbon Nanofiber Preparation

PAN/DMF solution (8 wt%) was first prepared by adding weighed PAN directly into DMF, followed by vigorous mechanical stirring for 3 h at 60 °C. The PAN/DMF solution was used
to prepare PAN precursor nanofibers by electrospinning. During electrospinning, the applied voltage used was 15 kV, with a flow rate of 0.75 mL/h, and the distance between needle tip and grounded collector was 15 cm. The electrospun PAN nanofibers were stabilized in air at 280 °C for 3 h with a heating rate of 5 °C min\(^{-1}\), and then carbonized at 900 °C in nitrogen for 3 h with a heating rate of 2 °C min\(^{-1}\). CNFs were obtained after the thermal treatment.

7.2.3 CVD of MoS\(_2\) on Carbon Nanofibers

![Schematic of formation process of MoS\(_2\)@CNF composite.](image)

**Figure 80.** Schematic of formation process of MoS\(_2\)@CNF composite.

MoS\(_2\) materials were deposited onto CNFs by CVD in a tube furnace under ambient-pressure (Figure 80). In the furnace, molybdenum chloride powder and excessive sulfur powder (molybdenum chloride: sulfur is 1:5 by weight) were placed at the upstream and CNFs were placed in the downstream.\(^ {294} \) Argon was used as the carrier gas with a flow rate set at 30 sccm. The growth temperature was 550 °C. During the synthesis, two reactions occurred simultaneously: the first reaction was between vapor phase precursors to produce gaseous
MoS₂, and the second reaction was for the gaseous MoS₂ species to precipitate onto the CNF substrate to form MoS₂@CNFs.

7.2.4 Structural Characterization
The morphology and composition of the synthesized MoS₂@CNFs were characterized by scanning electron microscopy (SEM, Verios), transmission electron microscopy (TEM, JEOL 2010F), and Aberration Corrected STEM (FEI Titan 80-300). X-ray diffraction (XRD) was conducted using a Rigaku Smartlab X-ray diffractometer with Cu Kα X-ray resource and X-ray photoelectron spectroscopy (XPS) was carried out to study the chemical composition of materials using a SPECS System with PHOIBOS 150 analyzer with an Mg Kα X-ray source. The carbon contents in the MoS₂@CNFs were determined using thermogravimetric analysis (TG, PerkinElmer) under air atmosphere at a heating rate of 10°C min⁻¹ from 20°C to 900°C.

7.2.5 Electrochemical Evaluation
For electrochemical evaluation, the working electrode was prepared by grounding and mixing MoS₂@CNFs with carbon black, alginic acid sodium salt and deionized water with a weight ratio of 7:1.5:1.5, followed by drying in vacuum at 80°C for 12h. A control sample was also prepared by using commercial MoS₂ particles, carbon black, alginic acid sodium salt and deionized water with the same weight ratio. CR2032 coin-type half cells were assembled to perform the electrochemical experiments. During the assembling, a sodium
metal disk was used as the counter electrode with a glass fiber mat as a separator and 1.0M NaClO₄ in polycarbonate (PC) as the electrolyte. Cyclic voltammetry (CV) measurements were recorded using Gamry Reference 600 Potentiostat/Galvanostat/ZRA system between 0.01 and 2.5 V with a scan rate of 0.05 mV s⁻¹. The discharge and charge measurements of the cells was conducted using a LAND CT2001A battery testing system in a voltage range of 0.01–2.5 V.

7.3. Results and Discussion

![XRD patterns](image)

**Figure 81.** XRD patterns of bulk MoS₂ particles (A) and MoS₂@CNFs (B).

XRD was performed to compare the crystal structure of MoS₂@CNFs with that of commercial MoS₂ particles (Figure 81). MoS₂ particles exhibited characteristic peaks at 14.4°, 33.3°, 39.5°, 58.3° and 60.1°, which could be assigned to the (002), (100), (103), (110), and (008) planes of MoS₂, respectively (JCPDS Card No. 37–1492), indicating good
crystallinity and high phase purity. The characteristic peaks of MoS$_2$ at 14.3°, 33.3°, 39.5°, 58.3° and 60.1° were still discernable and clear in MoS$_2$@CNFs although the peak intensities were weaker than those of the MoS$_2$ particles due to the existence of CNFs. The interlayer spacing values ($d_{002}$) of MoS$_2$ particles and MoS$_2$@CNFs could be calculated based on Bragg’s law, which were 0.619 nm and 0.633 nm, respectively. As compared with MoS$_2$ particles, MoS$_2$@CNFs had larger interlayer spacing of (002) plane, which might be due to the relatively low deposition temperature of 550°C during the CVD process$^{295,296}$. From Figure 81, it was also seen that MoS$_2$@CNFs exhibited a broad peak at 24.7°, which could be assigned to the (002) plane of the CNF substrate.

![Figure 82. TGA curve of MoS$_2$@CNFs.](image)
In order to investigate the composition of MoS$_2$@CNFs, thermogravimetric analysis (TGA) measurement was conducted and the result was shown in Figure 82. It was seen that MoS$_2$@CNFs exhibited a weight loss of 4% before 100°C, which could be ascribed to the removal of absorbed moisture. The combustion of CNFs occurred between 450-725°C, corresponding to a weight loss around 63%, while MoS$_2$ was oxidized to form MoO$_3$ during this process. After 725°C, there was another obvious weight loss which resulted from the evaporation of MoO$_3$ in air atmosphere.$^{227}$ Based on the TGA result, the content of MoS$_2$ in the MoS$_2$@CNF was calculated to be 41.14%.
**Figure 83.** SEM images of MoS$_2$@CNFs (A, B, C), CNFs (D), and bulk MoS$_2$ (E, F).

Figures 83A-C showed the SEM images of MoS$_2$@CNFs. The nanofibers with an average diameter of around 300 nm intersected with each other, forming a conductive pathway. Considering the high electrical resistance of MoS$_2$, the one-dimensional fibrous structure of conductive CNFs was expected to be beneficial to the electrochemical performance of MoS$_2$@CNFs. From the high-resolution SEM image in Figure 83C, it was clearly seen that
MoS$_2$ forms nanosheets closely attached on the surface of CNFs without apparent MoS$_2$ agglomeration observed, which might stem from the stabilization function of the graphene layers in the CNFs.$^{161}$ From Figure 83 D, it was also seen that before the deposition of MoS$_2$, the CNFs showed a smooth surface with an average diameter of around 300 nm. The nano-sized CNFs could provide large surface area which is critical to the homogeneous distribution of MoS$_2$ nanosheets. The structure of the commercial MoS$_2$ particles was also investigated by SEM (Figures 83 E and F). It was seen that MoS$_2$ particles also had a layered structure with a wide particle size distribution ranging from few micrometers to over 10 micrometers.
Figure 84. TEM images (A, B, C) and HRTEM images (D, E, F) of MoS$_2$@CNFs. Measurement of interlayer distance of MoS$_2$ in MoS$_2$@CNF (G).
TEM images of MoS$_2$@CNFs were shown in Figures 84A-F. The low-magnification TEM images in Figures 84A-C confirmed that the nanofibers had a diameter of about 300 nm and the ultrathin MoS$_2$ nanosheets were uniformly anchored on the surface of the CNFs, which were consistent with the SEM results. Furthermore, the high-resolution TEM images in Figures 5D-F showed that each MoS$_2$ nanosheet was composed of several stacked MoS$_2$ layers which was in agreement with the hexagonal lattice of the MoS$_2$ phase, and for each MoS$_2$ nanosheet unit, the thickness was around 10 nm. Furthermore, from Figure 84G, it was measured that the interlayer spacing for MoS$_2$ sheets were 0.634 nm, which was in accordance with the XRD results. Focusing on the interface between MoS$_2$ and CNFs, an intimate contact between the MoS$_2$ nanosheets and CNFs was observed, which could not only facilitate the effective ion transfer but also prevent the volume expansion of the MoS$_2$ sheets during charge/discharge process. In addition, the stack of MoS$_2$ layers in the c-axis was partially inhibited with the existence of amorphous carbon, leading to the formation of MoS$_2$ sheet structure with few layers on the CNF surface.$^{288,297}$
Figure 85. Element maps of MoS$_2$@CNFs (A), carbon (B), molybdenum (C), and sulfur (D).

The elemental distribution of MoS$_2$@CNFs was further examined by EDX. From Figure 85, it was evident that Mo and S elements were uniformly distributed over the entire surface of the CNFs.
Figure 86. TEM images of MoS$_2$@CNFs after ultrasonification for 30 minutes.
A strong connection between MoS$_2$ nanosheets and CNFs was believed to be favorable for the mobility and transport of ions and electrons in this one-dimensional fibrous MoS$_2$@CNF hybrid structure during the charge/discharge process, thereby providing good conductivity for the anchored MoS$_2$ sheets and improving their electrochemical performance. In order to verify the good interaction between the MoS$_2$ nanosheets and CNFs, MoS$_2$@CNFs were dispersed into ethanol and ultrasonicated for 30 min, which were then examined by TEM (Figure 86). It was seen that the MoS$_2$@CNF hybrid structure still kept its structural integrity and no isolated MoS$_2$ nanosheets can be observed. This demonstrated that the strong interconnection between MoS$_2$ nanosheets and CNFs was maintained after ultrasonification, which was beneficial to the structural integrity and electrochemical performance of MoS$_2$@CNFs.

![Figure 87. XPS spectra of MoS$_2$@CNFs: Mo 3d spectrum (A), and S 2p spectrum (B).](image)

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The composition of MoS$_2$@CNFs was further analyzed by X-ray photoelectron spectroscopy (XPS). As shown in Figure 87, the Mo 3d spectrum showed a doublet with binding energies at 229.50 eV (3d$^{5}$/2) and 232.65 eV (3d$^{3}$/2), indicating that Mo took a 4$^+$ oxidation state as Mo$^{4+}$ in MoS$_2$ nanosheets. In Figure 87, the peaks at 226.6, 162.0 and 163 eV could be indexed to S2s, S2p$^{3}$/2 and S2p$^{1}$/2, respectively. Based on the XPS analysis, the molar ratio S/Mo ratio was around 2.04, which confirmed the formation of MoS$_2$ on CNFs.
Figure 88. CV curves for MoS$_2$ bulk particles (A) and MoS$_2$@CNFs (B) at a scan rate of 0.1 mV s$^{-1}$.

In order to investigate the reaction mechanism in sodium-ion batteries, CV tests for both MoS$_2$ particles and MoS$_2$@CNFs were conducted in the potential range of 0.01-2.5 V with a
scan rate of 0.05 mV s\(^{-1}\), and the results were compared in Figure 88. As shown in Figure 88A, in the first cycle, MoS\(_2\) particles exhibited three reduction peaks at 0.01 V, 0.71 V and 0.92 V, respectively. The peaks at 0.71 V and 0.92 V could be assigned to a two-step insertion of sodium ions into MoS\(_2\), forming Na\(_{0.5}\)MoS\(_2\)/NaMoS\(_2\) and MoS\(_2\)/Na\(_{0.5}\)MoS\(_2\), respectively, by the reaction of MoS\(_2\) + xNa\(^+\) + xe\(^-\) → Na\(_x\)MoS\(_2\).\(^{272,295-297}\) The broad reduction peak between 0.01-0.35 V was associated to the formation of solid electrolyte interphase (SEI), which was responsible for the capacity loss in the first charge/discharge cycle, and the reversible conversion reaction: Na\(_x\)MoS\(_2\) + (4-x)Na + (4-x)e\(^-\) → 2Na\(_2\)S + Mo.\(^{163,166}\) Moreover, as for the sharp peak at 0.01 V, there was also literature report showing that it was related to the Na\(^+\) storage in the Na\(_2\)S and Mo interface.\(^{284}\) Correspondingly, in the first cycle, three oxidation peaks located at 1.35 V, 1.79 V, and 2.28 V could be observed. Among these three oxidation peaks, the peaks at 1.35 V and 1.79 V represented a continuous oxidation reaction process of Mo to MoS\(_2\).\(^{163,281}\) The small peak at 2.28V might be attributed to the desodiation process of Na\(^+\) from the MoS\(_2\) interlayer. During the 2\(^{nd}\) and 3\(^{rd}\) cycles, the reduction peak at 0.92 V shifted to 1.2 V while the peak at 0.71 V nearly disappeared. The oxidation peaks at 1.35 V and 2.28 V still existed, but the peak at 1.79 V diminished and turned into a broad oxidation process between 1.5 and 1.8V. The CV curves of MoS\(_2\)@CNFs in Figure 88B showed similar electrochemical reaction processes as bulk MoS\(_2\), however, the reduction peaks at 0.71 V and 0.92 V and oxidation peaks located at 1.35 V, 1.79 V, and 2.28 V were not as distinct as those for MoS\(_2\) particles, probably due to the introduction of carbon in MoS\(_2\)@CNFs. From Figure 88B, it was also seen that the CV curves of MoS\(_2\)@CNFs
were nearly overlapped after the first cycle, indicating the good reversibility of the sodiation/desodiation process.

Figure 89. Galvanostatic discharge/charge profiles of MoS$_2$ bulk particles (A) and MoS$_2$@CNFs (B).
The galvanostatic charge/discharge behaviors of MoS$_2$ particles and MoS$_2$@CNFs were evaluated under a current density of 50 mA g$^{-1}$ within the potential range of 0.01-2.5 V. Figure 89A showed the charge/discharge curves of MoS$_2$ particles. During the first sodiation process of MoS$_2$ particles, three distinct plateaus could be observed at 0.92 V, 0.71 V and 0.01 V which were in good agreement with the CV curves. The plateaus located at 0.92 V and 0.71 V could be ascribed to the process of Na$^+$ intercalation into the MoS$_2$ interlayers, forming MoS$_2$/Na$_{0.5}$MoS$_2$ and Na$_{0.5}$MoS$_2$/NaMoS$_2$, respectively. During the discharge process from 0.92 V, the conversion reaction between Na ions and MoS$_2$ finally produced Mo and Na$_2$S. The third plateau at 0.01 V represented the Na$^+$ insertion into the interface between Mo and Na$_2$S. However, after the first cycle, the plateau at 0.01 V was not as distinct as in the first cycle, indicating that Na$^+$ might not be able to be fully extracted from the interface between Mo and Na$_2$S, which also partially contributed to the capacity loss in the first cycle. Moreover, after the first cycle, the charge/discharge curves showed a sloping feature, indicating the reversible conversion reaction, because the sloping curve could be ascribed to the decomposition of 1T-Na$_x$ MoS$_2$ which was formed during the sodiation process by the conversion reaction between Na$^+$ and MoS$_2$. During the desodiation process in the initial cycle, three plateaus could be found at around 1.35 V, 1.79 V, and 2.28 V. The plateaus at 1.35 V and 1.79 V represented the oxidation of Mo to MoS$_2$ and the plateau at 2.28 V probably indicated the extraction of Na$^+$ from the MoS$_2$ interlayer. As mentioned above, it was seen that these plateaus were in good agreement with the observations in CV curves. The plateau at 1.79 V was also predominant in subsequent cycles, indicating good reversibility of the oxidation process from Mo to MoS$_2$. The
charge/discharge curves of MoS$_2$@CNFs were shown in Figure 89B. Unlike MoS$_2$ particles, from the first cycle, the charge/discharge curve of MoS$_2$@CNFs showed a sloping feature without prominent plateau at 0.71 V or 0.92 V in the first sodiation process. During the charge process, the plateau around 1.79 V could still be observed which was consistent with CV curve, but it was not as conspicuous as the one in the case of MoS$_2$ particles, which to some degree, could be ascribed to the addition of carbon and the small size of MoS$_2$ nanosheets in the hybrid structure. The addition of carbon led to the formation of nano-sized MoS$_2$ sheets, resulting in an increased solid-solution region during the electrochemical reaction which would decrease the miscibility gap and redox potential.\textsuperscript{272,299,300} This partially caused the sloping curve in the charge/discharge curves for MoS$_2$@CNFs. From Figures 10A and B, it was seen that the initial charge and discharge capacities were 631.8 mAh g$^{-1}$ and 709.5 mAh g$^{-1}$ for MoS$_2$ particles, and 485.8 mAh g$^{-1}$ and 754.7 mAh g$^{-1}$ for MoS$_2$@CNFs, corresponding to a coulombic efficiency of 89.05% and 64.37%, respectively. Noticeably, MoS$_2$@CNFs showed lower coulombic efficiency than MoS$_2$ particles in the first cycle, which was probably due to the relatively low coulombic efficiency (52.78%) of CNF materials due to the formation of SEI and irreversible sodium absorption onto some functional groups in the carbon structure.\textsuperscript{103,104,171,183,239}
Figure 90. Cycling performance of (A) pure CNFs, bulk MoS$_2$ particles and MoS$_2$@CNFs at current density of 50 mA g$^{-1}$, and (B) MoS$_2$@CNF at current density of 1 A g$^{-1}$.

Figure 90A showed the cycling behaviors of MoS$_2$ particles and MoS$_2$@CNFs under 50 mA g$^{-1}$ in a potential range of 0.01-2.5 V. For comparison, the cycling behavior of CNFs was also
shown. It was seen that MoS$_2$ particles delivered a charge capacity of 631 mAh g$^{-1}$ in the first cycle, which was close to the theoretical capacity of pristine MoS$_2$ (670 mAh g$^{-1}$). However, MoS$_2$ particles experienced rapid capacity fading during the charge/discharge process. The specific capacity decreased from 631 mAh g$^{-1}$ to 80 mAh g$^{-1}$ after 50 cycles, and only 12.68% of its initial capacity was retained. CNFs exhibited excellent cycling stability, but they only delivered a relatively low specific capacity of 214 mAh g$^{-1}$ even at the first cycle. In comparison, MoS$_2$@CNFs not only delivered a relatively high specific capacity of 754.7 mAh g$^{-1}$ at the first cycle, but also exhibited stable cycling, maintaining a reversible capacity of 380 mAh g$^{-1}$ after 50 cycles. This corresponded to an improved capacity retention of 78%. In order to evaluate the long-term cycling stability, MoS$_2$@CNFs were also cycled under a significantly higher current density of 1 A g$^{-1}$ for 1000 cycles (Figure 90B). After the initial activation process, MoS$_2$@CNFs showed relatively slow capacity decay in 1000 cycles. A reversible capacity of 198 mAh g$^{-1}$ was maintained after 1000 cycles, corresponding to a capacity retention of 77.95%.
Figure 91. Rate capacity of MoS$_2$@CNFs and MoS$_2$ particles at different current densities in the potential range of 0.01–2.5 V.

The rate performance of MoS$_2$@CNFs and MoS$_2$ particles was evaluated under the current density of 50 mA g$^{-1}$ first, which was progressively increased to 100 mA g$^{-1}$, 200 mA g$^{-1}$, 400 mA g$^{-1}$, 800 mA g$^{-1}$, 1.6 A g$^{-1}$, until reaching a highest current density of 3.2 A g$^{-1}$ (Figure 91). The MoS$_2$ particles suffered severe capacity fading as the current density increased, exhibiting poor rate capability. In comparison, for MoS$_2$@CNFs, reversible capacities of 347.5, 315.0, 277.5, 237.5, 195.0, and 147.5 mAh g$^{-1}$ were obtained for current densities of 100 mA g$^{-1}$, 200 mA g$^{-1}$, 400 mA g$^{-1}$, 800 mA g$^{-1}$, 1.6 A g$^{-1}$, and 3.2 A g$^{-1}$, respectively. The
rate retentions of the MoS$_2$@CNFs and MoS$_2$ particles were 44.7% and 9.5% respectively, when the current density increased from 50 mA g$^{-1}$ to 3.2 A g$^{-1}$, indicating reasonable rate capability of MoS$_2$@CNFs. For MoS$_2$@CNFs, the capacity returned to 367.5 mAh g$^{-1}$ when the current density decreased back to 50 mA g$^{-1}$, demonstrating excellent structural stability.

![Figure 92](image.png)

**Figure 92.** Electrochemical impedance spectra of MoS$_2$ particles and MoS$_2$@CNFs.

To achieve more insight in the mechanism of electrochemical performance improvement, the electrochemical impedance spectroscopy (EIS) measurements were carried out to
characterize MoS$_2$ particles and MoS$_2$@CNFs, as shown in Figure 92. The impedance spectra were composed of a semicircle at medium frequency and a sloping straight line at low frequency. The semicircle could be used to explain the charge-transfer impedance ($R_{ct}$) of the electrode reaction coupled with the electrode/electrolyte interface.\textsuperscript{28} The low-frequency sloping straight line could be attributed to the Warburg impedance ($Z_w$), corresponding to solid-state diffusion of sodium ions into the bulk electrode ($R_e$).\textsuperscript{301–304} It was obvious that the $R_{ct}$ value of MoS$_2$@CNFs was significantly lower than that of MoS$_2$ particles, which suggested that CNFs could provide good conductivity to the connected MoS$_2$, leading to an enhanced electron transport and electrochemical reaction kinetics of the electrode.
Figure 93. TEM images of MoS$_2$@CNFs after 500 discharge/charge cycles under current density of 1A g$^{-1}$ (A, B) and measurement of interlayer distance of MoS$_2$ in MoS$_2$@CNFs (C).

After cycling performance test, the cell was disassembled to examine the structural integrity of MoS$_2$@CNFs by TEM. As revealed from Figures 93A and B, MoS$_2$ nanosheets were still closely attached on the CNF surface. Moreover, the layered structure of MoS$_2$ was
well preserved as an integrity with CNF matrix and based on the measurement in Figure 93C, the interlayer distance of MoS\textsubscript{2} nanosheets increased slightly from 0.633 nm to 0.635 nm after cycling, which could be attributed to the volume expansion of MoS\textsubscript{2} during the Na\textsuperscript{+} insertion/extraction process. It was, therefore, demonstrated that CNFs were effective in alleviating the pulverization and aggregation of the MoS\textsubscript{2} nanosheets, ensuring a long cycle life.

Figure 94. Schematic illustration of sodium storage mechanism in MoS\textsubscript{2}@CNFs.
As discussed above, MoS\textsubscript{2}@CNFs exhibited better electrochemical performance than MoS\textsubscript{2} particles in terms of cycling performance and rate capability. The improved electrochemical performance of MoS\textsubscript{2}@CNFs could be ascribed to several factors: (a) the one-dimensional fibrous CNF substrate could provide good conductivity to the tightly connected MoS\textsubscript{2} nanosheets which was favorable for the Na\textsuperscript{+} and electrons transfer kinetics (Figure 94); (b) the thickness of MoS\textsubscript{2} nanosheets was less than 15 nm which significantly deceased the pathway for the Na\textsuperscript{+} diffusion; (c) the large surface area of MoS\textsubscript{2} nanosheets enabled the effective contact between the electrolyte and the electrode active material; (d) the MoS\textsubscript{2} nanosheets had strong interconnection with the CNF substrate which could efficiently buffer the volume change during the sodiation/desodiation process; and (e) the CVD process ensured the uniform dispersion of MoS\textsubscript{2} nanosheets on the CNF surface. All of these factors contributed to determine the good sodium storage performance of the MoS\textsubscript{2}@CNFs.

7.4. Conclusion

This work introduces a facile way to synthesize MoS\textsubscript{2} deposited CNF hybrid structure with superior structural integrity and good electrochemical performance. The SEM, TEM and XRD results suggest that the ultrathin MoS\textsubscript{2} nanosheets have triangle shape and exhibit good crystallinity. The uniform dispersion of MoS\textsubscript{2} nanosheets on the conductive CNF substrate contributes to the good cycling stability of MoS\textsubscript{2}@CNFs. As a result, a reversible capacity of 380 mAh g\textsuperscript{-1} can be maintained after 50 cycles under a current density of 50 mA g\textsuperscript{-1}. Moreover, the hybrid structure can deliver a stable capacity of 198 mAh g\textsuperscript{-1} at a high current
density of 1 A g\(^{-1}\). Compared with commercial MoS\(_2\) particles, the enhanced electrochemical performance of MoS\(_2@\)CNFs can be attributed to the formation of fibrous CNF structure, which prevents the agglomeration of MoS\(_2\), enables faster ion transfer and good contact with electrolyte, and buffers the volume change of MoS\(_2\). These results demonstrate that MoS\(_2@\)CNFs have promising potential to be used as a sodium-ion battery anode material.
FUTURE WORK

Electrospun-derived carbon nanofibers have been used as a basic material to improve the electrochemical performance of sodium-ion battery anode materials. To further enhance the performance and address the challenges in the experiments, some future work still need to be done:

For the nitrogen-doped CNFs project, urea which is a common material with high nitrogen content, has been utilized as an efficient nitrogen–doping material and high nitrogen content CNFs have been fabricated. It is found that introduction of more nitrogen in the CNFs can significantly improve the electrochemical performance of CNFs. In the future work, different doping materials such as melamine and sulfur can be introduced to explore the mechanism and effect of doping process. Melamine can be used due to its low cost and higher nitrogen content which is expected to be a more efficient nitrogen-doping agent. Introduction of sulfur into the carbon material is another approach to modify the electrochemical properties of carbon material and its effect on electrochemical performance in sodium-ion battery anode application needs to be investigated carefully.

For the Sn/Sb nanoparticle-confined CNFs project, CNFs have been proved a suitable carbon matrix to provide buffering effect on the alloy nanoparticles to alleviate the volume change during charge/discharge process. In the future work, different alloy precursors and surfactant can be used to control the alloy particle size in the CNFs, which is a critical factor for the alloy anode material performance of SIBs. In addition, in order to increase the active material content, various alloy oxide nanofibers with different morphologies can also be fabricated by
adjusting the electrospinning and thermal treatment conditions. After obtaining alloy oxide nanofibers, a carbon coating process can be conducted to further enhance the cycling stability. Additionally, CNFs can also be used as a conductive network to enhance the conductivity of some active materials including metal oxide and alloy sulfide, e.g., TiO$_2$, SnS, SnS$_2$, MoS$_2$ and WS$_2$ which suffer from the intrinsically poor conductivity. Recommendation work can include fabricating metal oxide/CNF or metal sulfide/CNF composites by encapsulating the active materials into CNFs or depositing active particles onto the surface of CNFs. Benefiting from the conductive network of carbon nanofibers, the electrochemical performance of these composites will be investigated and a better understanding of reaction mechanism of the active materials can be obtained.

At last, graphene or reduced graphene oxide has been widely studied as an “assistant” to improve the electrochemical performance of many anode material candidates for lithium-ion batteries, due to its good conductivity and flexibility. The research on graphene-participated anode composite for sodium-ion battery anode is necessary. In the future, sodium-ion batteries with high performance anode material can be evaluated to examine its potential in grid energy storage field.
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