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Carbon Nanofiber-Based Materials as Anode Materials for Lithium-Ion Batteries

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Abstract

Considerable efforts have been devoted to the research of high-performance and long-lifespan lithium-ion batteries (LIBs) for their applications in large-scale power units. As one of the most important components in LIBs, anode plays an important role in determining the overall performance of LIBs. Nowadays, graphite has been the most successfully commercialized anode material. However, its limited theoretical capacity (372 mA h g^{-1}) and limited power density seems insufficient for the next-generation LIBs. To overcome these problems, new materials with fundamentally higher capacity and higher power density are urgently needed. Recently, there is an ever-increasing interest in developing novel carbonaceous nanomaterials to replace graphite as the anode materials for LIBs. Such materials have included carbon spheres, carbon nanotubes, carbon nanofibers (CNFs), porous monoliths, and graphene. Among these alternative forms of carbon, CNFs and its morphological-controlled derivatives (such as porous or hollow CNFs) have attracted much attention due to their unique and interesting properties such as one-dimensional (1D) nanostructure, good electronic conductivity, and large surface areas. Moreover, these CNFs can be used to encapsulate various second phases to form some functional composite, meeting further requirements including higher energy density, higher power density or flexible requirements, for the advanced LIB operation.

Electrospinning is considered as a simple, versatile, and cost-effective industry-viable technology for preparing various CNFs and their composites in a continuous process, with controllable morphology. Therefore, in this chapter, we have summarized some recent progresses in electrospun nanofibrous carbon-based anode for LIBs, covering the structure evolution from solid CNFs into morphology-designed CNFs, and then their composites with various functional nanoparticles. We anticipate this paper can offer some useful information for some researchers in the area of energy storage and conversion and can inspire them.

Keywords: electrospinning, carbon-based nanofibers, anode, lithium-ion batteries, nanomaterials

1. Introduction

Energy conversion and storage become more and more important in the context of the increasing global energy demand because of the inadequacy of fossil fuels, climate change, and deteriorating environmental conditions. Currently, among the available energy conversion and storage technologies, lithium-ion battery (LIB) is the most versatile and successful technology that possess high-energy densities (2–3 times higher than conventional batteries), no memory effects, relatively slow self-discharge rates, and longer battery lifetimes, and therefore they have received intense attention from both the academic community and industry as the dominant power source in hybrid electric vehicles (HEVs), plug-in hybrid electric vehicles (PHEVs), and full electric vehicles (EVs) [1–4]. For further enhancing the performance of LIBs, many studies concentrated on changing either the chemical composition or macroscopic structure of the components [5, 6].

As one of the most important components in LIBs, anode plays an important role in determining the overall performance of LIBs. At present, most commonly used anode materials for commercial LIBs are graphite powders that have limited theoretical capacity (372 mA h g^{-1}) and long diffusion pathways for the lithium ions [7]. This may result in low energy and low power densities, which cannot meet the ever-expanding demands for next-generation LIBs. To resolve the problem, a variety of nanostructured carbonaceous materials have been investigated as anode materials for LIBs, such as carbon nanobeads [8], hollow carbon nanospheres [9, 10], carbon nanotubes [11–13], carbon nanofibers (CNFs) [14–16], graphenes [17–19], and their composites [20–22].

Among various carbon nanostructures, CNFs and its morphological-controlled derivatives (such as porous or hollow CNFs) have attracted much attention because they could provide an enhanced surface-to-volume ratio for the electrode–electrolyte interface, short transport lengths for ionic transport, and efficient one-dimensional (1D) electron transport along the longitudinal direction when compared to the powder materials [23]. Moreover, these CNFs can be used to encapsulate various second phases to form functional composite, meeting the ever-growing demand for advanced batteries. Electrospinning has been widely used as a simple, versatile, and cost-effective industry-viable technology to prepare various CNFs and their composites in a continuous process, with controllable morphology and compositions [24–42]. The principle of electrospinning has been well introduced in several excellent reviews on electrospun materials for energy-related applications [43–46]. In this chapter, we have summarized some recent advances in the area of 1D CNF-based materials for LIB anodes, covering the structure evolution from electrospun solid CNFs into morphology-constructed porous CNFs, and their composites with various functional nanoparticles.

2. Electrospun CNFs

2.1. Solid CNFs

Carbon materials including graphite, graphene, fullerenes, carbon nanotubes, and CNFs have attracted tremendous attention in both fundamental research and industrial applications, especially in the applications of energy storage and conversion devices such as LIBs [47, 48]. Among these various carbon materials, 1D electrospinning-derived CNFs are of high interest as potential anode materials due to their high-specific surface area, good conductivity, and structural stability, which are the key factors influencing the electrochemical properties of carbon electrodes [23, 49–52]. The 1D nature of the CNF anode not only facilitates the electron transport along the axial direction, but also reduces the lithium-ion diffusion distance through short radial direction, both of which are beneficial for the improved specific capacity and rate capability.

The CNFs can be derived from many synthetic or natural polymeric precursors such as polyacrylonitrile (PAN), polyvinyl pyrrolidone (PVP), polyvinyl alcohol (PVA), lignin, or cellulose. It should be noted that the physical and chemical properties of CNFs highly depend on the chemical structure of the carbon precursors. Currently, the commonly used precursor for CNFs is PAN, which has good spinnability, and can yield a high amount of carbon residue after simple stabilization and carbonization processes [44]. Moreover, owing to the robust integrated network structure and good electrical conductivity, PAN-derived CNF webs can be directly used as the anode materials without adding any adhesive and conductive additives, which can reduce the weight of anode, and thus improving the energy density of a full cell [53]. Endo's group [23] synthesized the PAN-derived CNF webs by the electrospinning technique combined with two-step heat-treatments and investigated their lithium-storage properties along the variation of carbonization temperature (from 700°C to 2800°C). The composition ratio of amorphous carbon and graphitic carbon in these CNFs was demonstrated to affect the reversible capacity, slope or plateau charge–discharge characteristic, and rate/cycling performance. The high-purity CNF web thermally treated at 1000°C shows the high-rate capability (350 mA h g⁻¹ at a charge current of 100 mA g⁻¹) owing to the interlinked nanofibers, a large accessible surface area, and relatively good electrical conductivity, which make it an ideal candidate for the anode material of high-power LIBs. Nevertheless, the large-scale applications of PAN-derived CNFs might be hampered by the following two reasons. First, PAN is a relatively expensive synthetic polymer, of which the price varies with that of the crude oil [54]. Second, PAN is hard to dissolve in many solvents, and its most commonly used solvent, dimethylformamide (DMF), is known to be harmful for human beings during the electrospinning process [55].

Water or ethanol/polymer system is a better choice to avoid the aforementioned problems and lower the production cost. PVP is the type of water-soluble polymer, and has been widely used in industry due to its merits of low cost, nontoxicity, and good compatibility with metallic precursors. The preparation process of well-controlled PVP-derived CNFs has also been comprehensively investigated; however, the lithium-storage of this fiber-based electrode is temporarily lower than that of PAN-derived CNFs [54]. Other common water-soluble CNF

precursors such as PVA [55, 56], lignin, and cellulose [57, 58] have been used to prepare fibrous electrode; nevertheless, all of them show low mechanical properties as compared with PAN-derived CNFs.

Coaxial electrospinning or coelectrospinning, a breakthrough in the electrospinning method, has been used to prepare core-shell soft-hard CNFs, in which a spinneret consisting of two coaxial capillaries is used, with PAN/DMF as the external solution and mineral oil as the inner solution (**Figure 1**) [59]. After the stabilization and carbonization processes, the soft-hard core-shell CNFs were obtained with shell PAN converted to hard carbon and core mineral oil decomposed to soft carbon. The coaxial CNFs combine the advantages of both hard carbon (possess a high capacity of $400\text{--}500\text{ mA h g}^{-1}$, but poor capacity retention performance) and soft carbon (has a lower, but reversible capacity of $200\text{--}300\text{ mA h g}^{-1}$, however, it shows a very serious voltage hysteresis during the delithiation process), and therefore exhibits enhanced reversible capacity as an anode in LIBs (390 mA h g^{-1} at a charge current of 100 mA g^{-1}) even though the kinetics of the charge process requires further improvement.

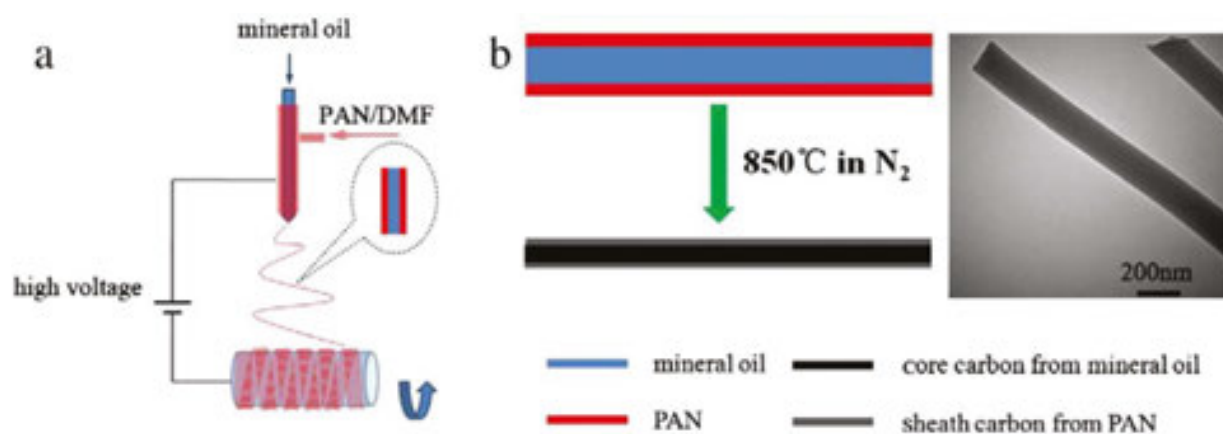


Figure 1. Schematic illustrations of (a) the coaxial electrospinning apparatus and (b) preparation of coaxial CNFs [59].

2.2. Porous CNFs

Recent research has showed that the introduction of various porous structures into CNFs could greatly enhance both the specific capacity/capacitance and the rate capability. This is because the incorporated pore can possibly create high-specific surface area that provides more charge transfer. Up to date, many strategies have been used to control the porous structure in CNFs for LIB application. Template-based processes are of great interest for the preparation of porous CNFs with high surface area. Kang's group [60] synthesized porous CNFs by etching off the silica template in CNFs from pyrolysis of the electrospun polyamic acid/tetraethoxysilane (TEOS) nanofibers. The porous CNF electrode showed a high reversible capacity of 445 mA h g^{-1} after 50 cycles, which is higher than that of commercial graphite (372 mA h g^{-1}). The nitrogen adsorption-desorption isotherms showed that the specific surface area can reach to $950\text{ m}^2\text{ g}^{-1}$, which is contributed to the large amounts of micropores. Here, the micropores can serve as the active "reservoir" for absorbing more lithium during cycling, thus improving the

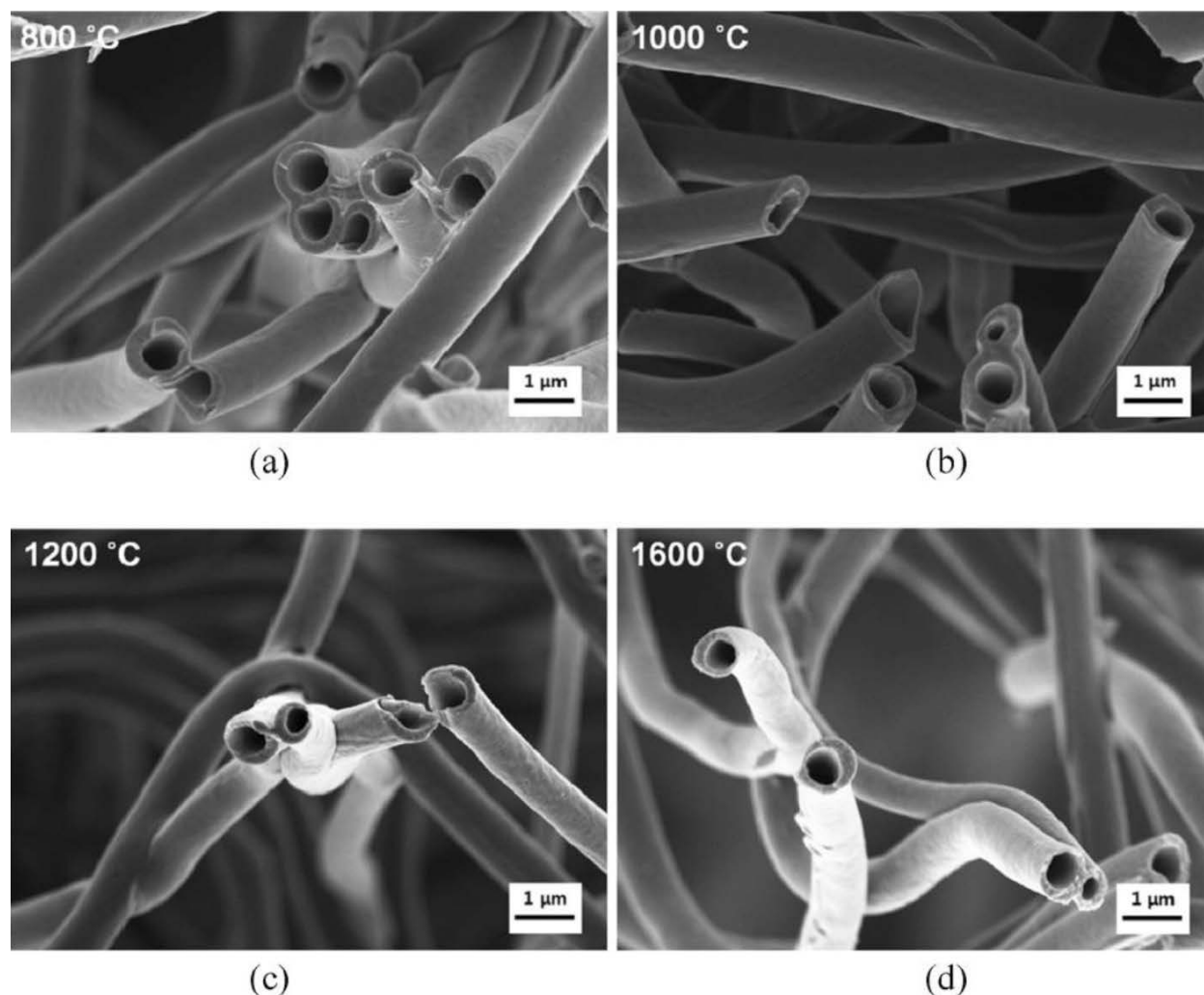


Figure 2. FE-SEM images of HCNFs carbonized at (a) 800°C, (b) 1000°C, (c) 1200°C, and (d) 1600°C [61].

lithium-storage capacity based on the bare CNFs. Lee et al. [61] have utilized coaxial electrospinning to fabricate hollow CNFs (HCNFs) as anode materials and studied the effect of carbonization temperature on the electrochemical performance. Styrene-co-acrylonitrile (SAN) and PAN in DMF solutions were served as the core and shell materials. The as-spun nanofibers were stabilized at 270–300°C for 1 h in air, and then carbonized at 800, 1000, 1200, and 1600°C for 1 h in nitrogen, respectively. During thermal treatment, the linear PAN molecules were transformed to the ladder structure and got carbonized in the following process; meanwhile, the core component burned out leading to the hollow structure (**Figure 2**). The large continuous hollow pore can facilitate the Li⁺-carrying electrolyte penetrate into the inner part of CNFs, thus highly reducing the Li⁺-diffusion distance, and making the full use of the active lithium-storage part at high charge–discharge rate. The capacities after 10 cycles at a current of 50 mA g⁻¹ were 390, 334, 273, and 243 mA h g⁻¹ in accordance to their carbonization temperature (800–1600°C), with a very high coulombic efficiency. The reversible

discharge capacities are slightly reduced even though four times higher current density is supplied (**Figure 3**).

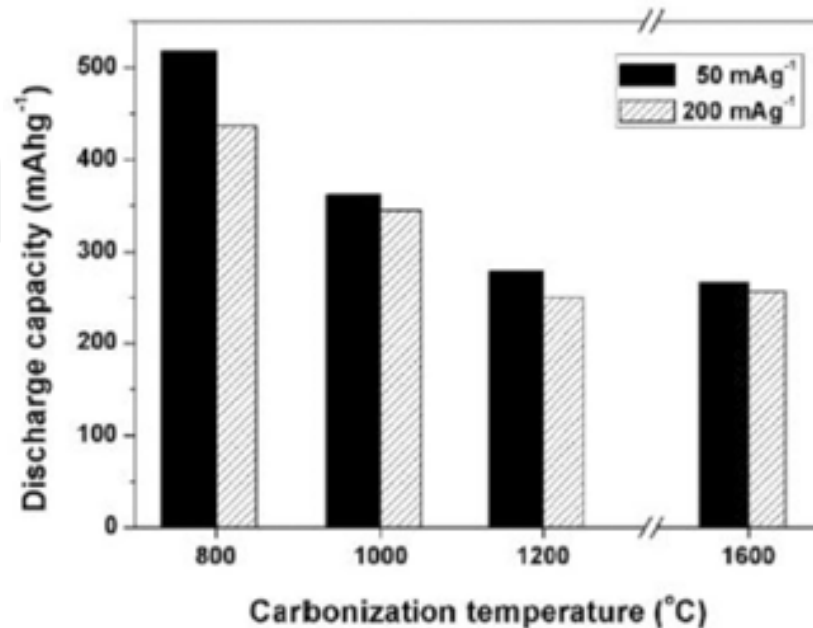


Figure 3. Discharge capacity vs. discharge rate for the HCNFs carbonized at various temperatures [61].

Recently, nitrogen-doped carbon materials are a researchers owing to the high capacity and rate capability [10, 62–65]. In a recent research, Liu et al. fabricated a new type of nitrogen-doped carbon tube by pyrolyzing polydopamine (PDA) using silica nanofibers as templates (**Figure 4**) [65]. The SiO₂ NFs were first fabricated by an electrospinning technique and subsequent calcination in air, and then immersed in a dopamine aqueous solution (pH: ~8.5). Subsequently, the dopamine monomers were covalently joined via aryl–aryl linkages owing to the oxidization and cyclization reactions, forming a PDA coating layer on the surface of the SiO₂ NFs. Then, the core–shell SiO₂ NFs/PDA nanofibers were carbonized at 750°C for 3 h in a N₂ atmosphere. Finally, N-CTs were obtained by etching off the silicate template with sodium hydroxide solution. The N-CTs show a fibrous morphology (diameter, 200–400 nm; length, several micrometers), a typical hollow feature (wall thickness, ~16 nm), and discontinuous and randomly constructed graphene-like layers (the d₀₀₂ interlayer spacing, 0.354 nm) (**Figure 5**). The PDA-derived carbon tubes (N-CTs) as anode materials for LIBs show a remarkable self-improved capacity along cycling. This is contributed to the continuous interlamellar spacing expansion between the graphene-like carbon layers during cycling. (**Figure 6**) Moreover, owing to the unique hollow structure, ultrafine carbon-tube wall, and nitrogen doping, the N-CT electrode shows very high specific capacity, outstanding rate capability, and robust durability, giving a superior reversible capacity of 1635 mA h g⁻¹ at 100 mA g⁻¹ after 300 cycles and 1103 mA h g⁻¹ at 500 mA g⁻¹ after 500 cycles. The excellent electrochemical performance makes the N-CTs a potential anode material for the next-generation LIBs.

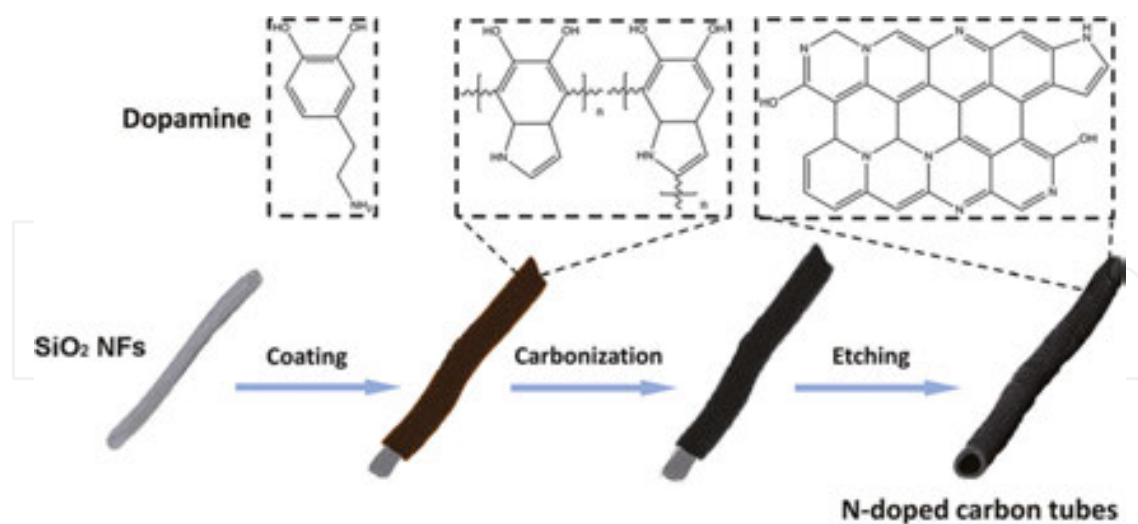


Figure 4. Schematic illustration of the synthesis of N-doped carbon tubes [65].

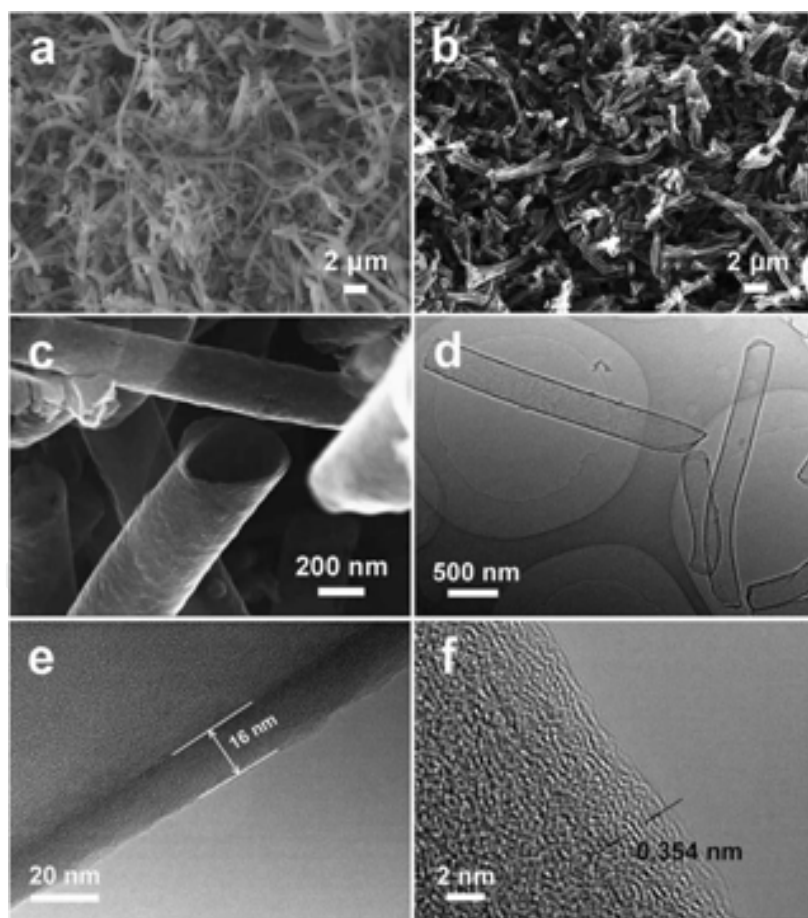


Figure 5. (a) SEM image of SiO₂ NFs, (b and c) SEM images of N-CTs, and (d–f) HR-TEM images of N-CTs [65].

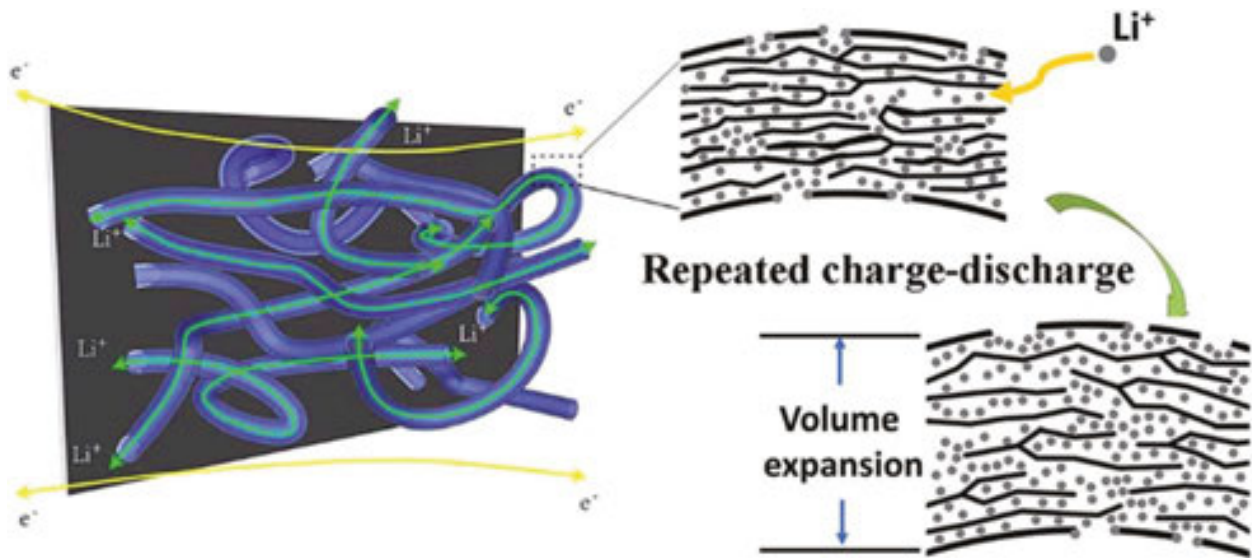


Figure 6. Illustration of lithium-ion storage/transport in N-CTs during the repeated lithiation and delithiation processes [65].

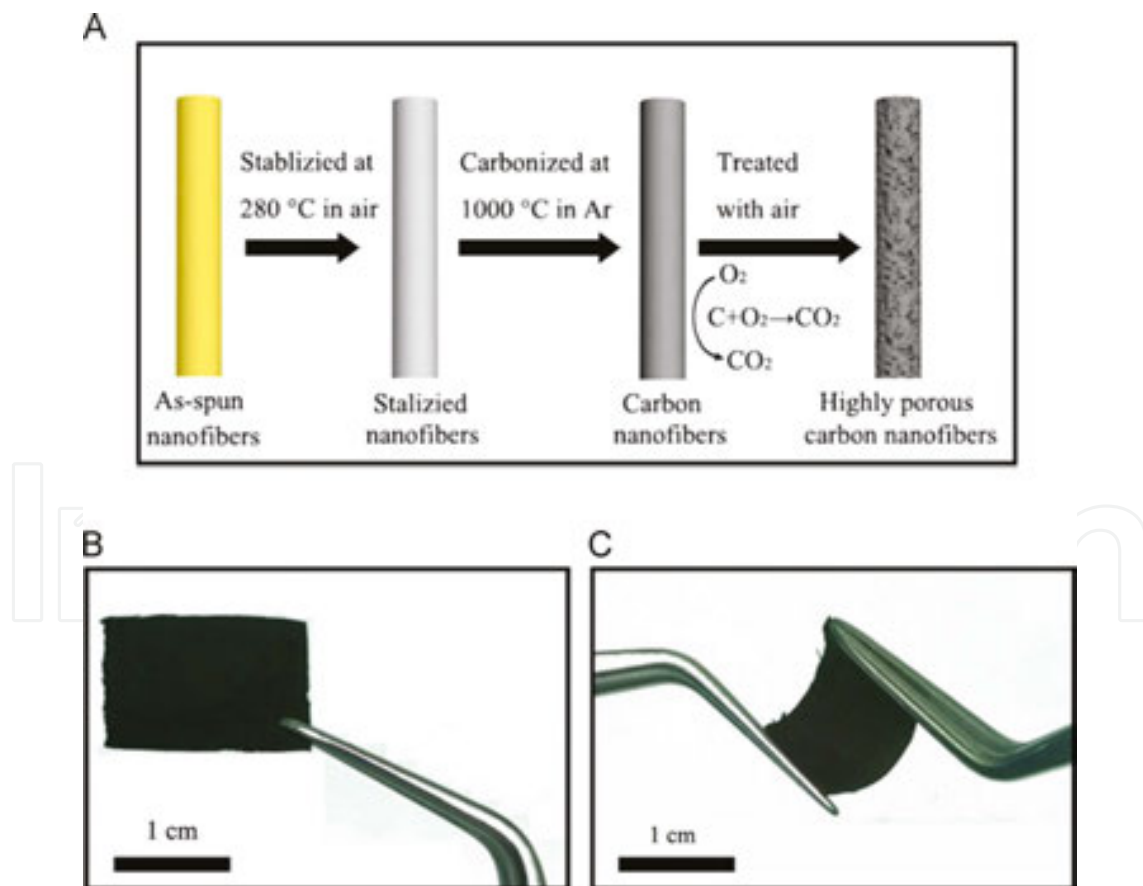


Figure 7. (a) Schematic illustration of the preparation of the HPCNF electrode. (b and c) Photographs of supported and flexible HPCNF film [68].

Besides, some other additives such as ZnCl_2 and H_3PO_4 usually act as the activating agents to produce porous structures in CNFs [66, 67]. These activating agents lead to large amounts of micropores in the surface of CNFs, thus providing more surface active sites for absorbing the Li^+ . Lately, a novel and simple method (air activation method) have attracted much attention as the method needs no template and activating agents. Yu's group [68] prepared highly porous CNFs (HPCNFs) by two-step carbonization of electrospun PAN nanofibers. During carbonization process at 1000°C in Ar, a certain volume of air were mixed into the Ar flow, where the CNFs were partially burnt off and numerous micro/mesopores were formed simultaneously (**Figure 7**). The as-synthesized HPCNFs exhibit a paper-like external morphology and highly porous internal nanostructure. When used as a binder-free anode in LIBs, the HPCNFs deliver a very high capacity of 1780 mA h g^{-1} at 50 mA g^{-1} after 40 cycles, greatly improved rate capacity and ultralong cycle life (1550 mA h g^{-1} at 500 mA g^{-1} after 600 cycles) in comparison with CNFs. The outstanding electrochemical performance is contributed to the electrospinning-derived 3D porous interconnected networks and the air-activated mesoporous structure in the CNFs that can facilitate the electrolyte into the electrode, thus reducing the Li^+ diffusion distance. Consideration of the low-cost and efficient preparation, this method is hoped to design highly porous materials in large-scale production used for advanced energy-storage devices.

3. Composite anodes with CNFs

The capacities of pure CNFs are insufficient for high-performance batteries. Therefore, various components such as silicon, tin and tin oxides, titanium oxides, and other metal oxide nanoparticles have been loaded into CNFs via an electrospinning process to enhance the performance.

3.1. Si-loaded CNF composite anodes

Silicon nanoparticles (with a theoretical specific capacity of 4200 mA h g^{-1}) could be incorporated into the CNF matrix by electrospinning PAN-Si nanoparticles and the subsequent carbonization to improve the poor cycling performance resulted from large volume changes ($\sim 400\%$) and nanoparticle aggregation upon the alloying and dealloying reaction with Li^+ [69, 70]. By optimizing the Si content, Si particles were dispersed homogeneously along the fibers, thus inhibiting the agglomeration of Si nanoparticles and suppressing mechanical failure during Li^+ insertion and extraction [71]. Additionally, introduction of various porous structures into CNFs could greatly enhance the specific capacity and rate performance of Si/CNF composite electrodes. For example, porous Si/CNF composites used without binding and conductive additives showed high discharge capacity of 1100 mA h g^{-1} at a high current density of 200 mA g^{-1} [72].

Another example, Si-CNF core-shell fibers with void space in the core section were fabricated by coaxial electrospinning, in which Si-PMMA was chosen as the core and PAN as the shell [73]. After carbonization process, PAN can still remain stable in the shell, while PMMA could be removed to form the void space in the core of the fibers, which can accommodate the volume

expansion of Si (**Figure 8**). This unique Si–CNF core–shell structure shows a high capacity of 1384 mA h g^{-1} at a rate of $C/10$ and an outstanding cycle life of 300 cycles with 99% capacity retention. Another promising strategy to improve the performance of Si/CNFs is adding conductive component such as graphitized carbon [74] or TiO_2 [75] into the electrospun Si–CNF composite. The electrical conduction of the surrounding material significantly improved the reversible capacity and cycling stability.

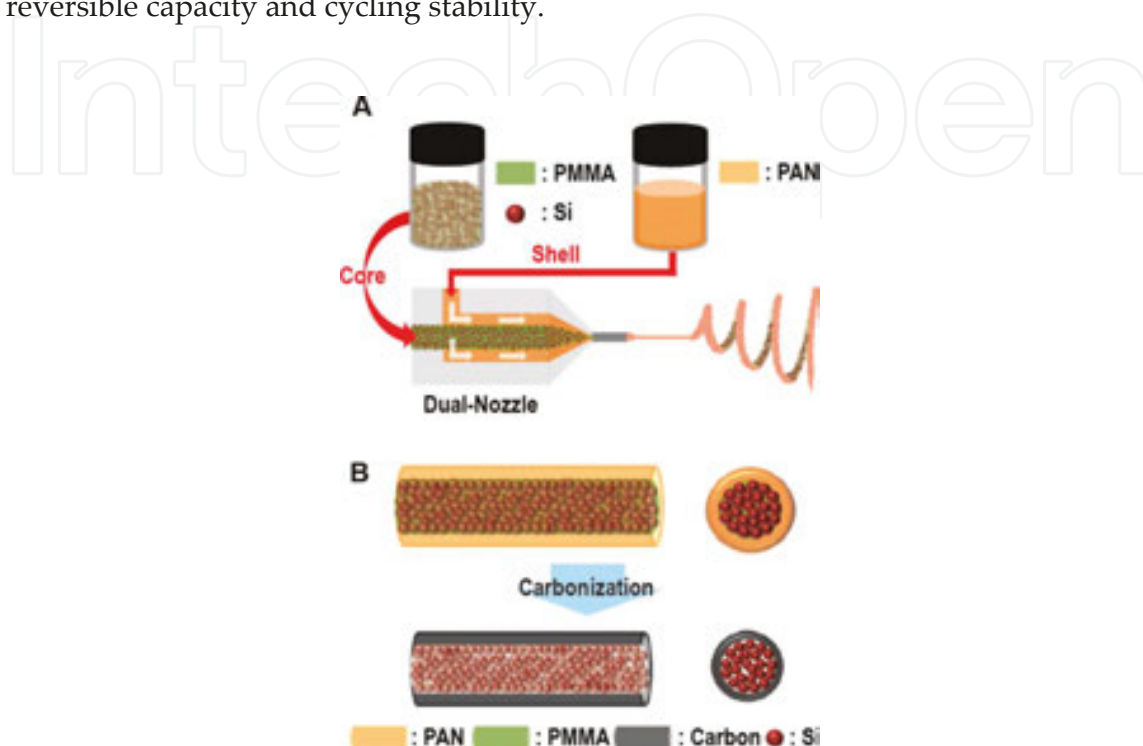


Figure 8. Schematic illustration of Si–CNF core–shell fibers [73].

3.2. Tin-based composite anodes with CNFs

Tin and its oxides have much higher theoretical capacities (Sn : 992 mA h g^{-1} , SnO_2 : 780 mA h g^{-1}) than the commercial graphite (372 mA h g^{-1}), but they also suffer from large volume changes and nanoparticle aggregation during cycling, resulting in capacity and stability losses. Dispersing these metallic nanoparticles into CNFs via electrospinning is an efficient approach to overcome these drawbacks because CNFs can hinder particle aggregation, provide continuous long-distance electron transport pathway, support numerous active sites for charge-transfer reactions, and eliminate the need for binding or conducting additive [23]. Yu et al. [53] fabricated a reticular Sn/CNF webs used as anodes for rechargeable LIBs via electrospinning technique and carbonization treatment, and studied the carbonization temperature effect on electrochemical performance of the Sn/CNF webs. It is demonstrated that carbonization temperature will influence Sn grain size, surface area or fiber diameter, and the electrical conductivity of CNFs, which dominate the electrochemical performance of the electrode. The Sn/CNF webs carbonized at 850°C exhibited a reversible capacity of 450 mA h g^{-1} after 30 cycles at a current of 25 mA g^{-1} . Herein, the overall capacity looks low because the direct electro-

spinning technique limits the loading amount of active materials (with ~22 wt% Sn particles), which could be improved by constructing novel nanostructures.

Porous or hollow structure is introduced into Sn/CNF systems to enhance the cycling stabilities and rate capabilities. Sn nanoparticles have been encapsulated into porous multichannel carbon microtubes (SPMCTs) [76] and bamboo-like hollow CNFs (SBCNFs) [77] using a single-nozzle and a coaxial electrospinning technique, respectively. Such porous or hollow carbon shells could provide appropriate void volume to buffer the large volume change, prevent pulverization of the Sn nanoparticles, serve as an electron supplier, and allow more Li^+ access. As a result, both of them showed good cycling stabilities and excellent rate capabilities. Specifically, the SBCNFs display a better cycling stability and a more excellent rate capability with a reversible discharge capacity as high as 480 mA h g^{-1} at 5 C after 100 cycles.

SnO_x/CNF composites have been synthesized by electrospinning and subsequent thermal treatment [78, 79]. For example, ultrauniform $\text{SnO}_x/\text{carbon}$ nanohybrid (denoted as U- SnO_x/C) has been fabricated by solvent replacement and subsequent electrospinning homogeneous dispersion of SnO_2 nanoparticles in PAN/DMF solution [79]. The strong interaction between SnO_x and nitrogen-containing CNFs (Sn–N bonding) could effectively confine the uniformly embedded SnO_x . This unique nanostructure can not only suppress the agglomeration of SnO_x and tolerate the substantial volume change during cycling, but also enhance the transport of both electrons and ions due to shortened conducting and diffusion pathways. As a consequence, the U- SnO_x/C nanohybrids exhibit a high reversible capacity of 608 mA h g^{-1} after 200 cycles, with excellent rate capability. However, the effect of homogeneous distribution is also limited. Sn- or SnO_2/CNF composites have also been doped with various transition metals, such as Co, Cu and Ni, to improve the cycling stability and rate performance. Co–Sn alloy particles embedded in CNFs improved the cycling stability by increasing the conductivity of the CNF and also enhanced the specific anodic capacity because of different Co–Sn alloys in the structure, as controlled by the carbonization temperature [80]. Incorporation of amorphous Cu into Sn/CNF achieved the highest cycling stability of 490 mA h g^{-1} after 600 cycles at a current density of 156 mA g^{-1} [81]. Addition of Ni into SnO_2 CNF suppressed the reduction of SnO_2 to Sn during carbonization and the agglomeration of SnO_2 , thus enhancing the cycling stability [82].

In recent literature, Yu et al. [83–86] have achieved the in-site addition of transition metallic (Ti and Cu) and nonmetallic elements (P and B) into SnO_x/CNF composites for the enhancement of cycling stability and rate performance via the electrospinning technique and subsequent thermal treatments. It was demonstrated that the doped SnO_x nanoparticles were all ultrafine and uniformly dispersed in the conductive CNF matrix, and the doping content should be kept to an optimal value. The incorporation of heteroatoms into SnO_x/CNFs endowed them with the enhancement of cyclic capacity retention and rate performance compared with the pristine SnO_x/CNFs (Table 1) due to the more complete reversible conversion reaction and the higher Li^+ -diffusion coefficient. Especially, the addition of Cu into SnO_x/CNFs exists in the form of Cu_2O , which can be transformed into Cu nanoparticles dispersed in a lithia matrix (Li_2O), inhibiting the aggregation of Sn particles in the following alloying–dealloying cycling (**Figure 9**). Meanwhile, the existence of Cu nanoparticles not only improves

the Li⁺-transport capability and the electronic conductivity of the overall electrode, but also enhances the chemical reacting activity of Sn back to SnO_x during the Li⁺-extraction process; therefore, the addition of Cu⁺ can endow the SnO_x/CNF electrode with greatly enhanced reversible capacity and rate capability [86].

Materials	Performance	Rates	References
SnO _x /CNFs	640 mA h g ⁻¹ after 60 cycles	200 mA g ⁻¹	85
	230 mA h g ⁻¹ after 100 cycles	2 A g ⁻¹	
Ti-doped SnO _x /CNFs	670.7 mA h g ⁻¹ after 60 cycles	200 mA g ⁻¹	84
	302.1 mA h g ⁻¹ after 80 cycles	2 A g ⁻¹	
P-doped SnO _x /CNFs	676 mA h g ⁻¹ after 100 cycles	200 mA g ⁻¹	85
	288 mA h g ⁻¹ after 120 cycles	2 A g ⁻¹	
B-doped SnO _x /CNFs	670.2 mA h g ⁻¹ after 100 cycles	200 mA g ⁻¹	86
	300 mA h g ⁻¹ after 80 cycles	2 A g ⁻¹	
Cu-doped SnO _x /CNFs	743 mA h g ⁻¹ after 100 cycles	200 mA g ⁻¹	87
	347 mA h g ⁻¹ after 1000 cycles	5 A g ⁻¹	
SnO ₂ @PC/CTs	1045 mA h g ⁻¹ after 300 cycles	500 mA g ⁻¹	88
	499 mA h g ⁻¹ after 1000 cycles	2 A g ⁻¹	
U-SnO _x /CNFs	608 mA h g ⁻¹ after 200 cycles	500 mA g ⁻¹	80
	175 mA h g ⁻¹ after 40 cycles	5 A g ⁻¹	

Table 1. Electrochemical performance of Sn-based composites with CNFs.

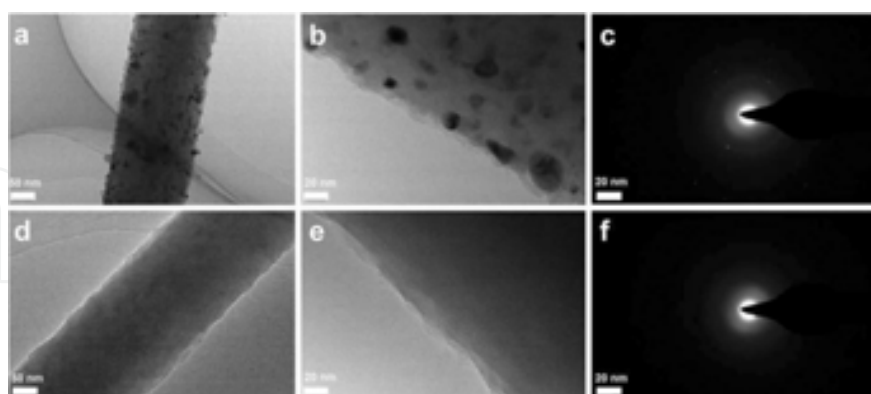


Figure 9. (a and b) HRTEM images of SnO_x/CNFs and (c) corresponding selected area electron diffraction (SAED) pattern; (d and e) HRTEM images of SnO_x-20%Cu/CNFs and (f) corresponding SAED pattern after 1000-cycle performance test at a current density of 2 A g⁻¹ [86].

Highly enhanced performance of SnO₂ could be achieved by designing a novel 1D nanostructure. Liu et al [87] have designed and synthesized a novel fiber-in-tube hierarchical nanostructure of SnO₂@porous carbon in carbon tubes (denoted as SnO₂@PC/CTs), with 1D

SnO₂@PC as the fibrous core and PDA-derived carbon tubes as the tubular shell, through N-doped carbon coating on electrospun hybrid nanofiber template and a post-etching technique (Figure 10). The internal PC skeleton could link and support SnO₂ nanoparticles for inhibiting the nanoparticle aggregation during cycling, while the external carbon protective shell could confine the volume expansion of SnO₂ for preserving the integrity of the overall electrode and facilitate electron and ion transport to the internal active materials. As a result, compared with SnO₂/CTs (without internal porous carbon skeleton), the SnO₂@PC/CT nano hybrids exhibit a higher reversible capacity of 1045 mA h g⁻¹ at 0.5 A g⁻¹ after 300 cycles and a high-rate cycling stability after 1000 cycles (Table 1) compared with those of SnO₂/CTs (without internal porous carbon skeleton). This unique 1D hierarchical nanostructure could be extended for improving other high-capacity metal oxides materials such as MnO/MnO₂, Fe₂O₃, and Co₃O₄.

3.3. Ti-based composite anodes with CNFs

TiO₂ has been regarded as a promising high-rate anode material due to its low cost, high working voltage, and structural stability during lithium insertion and extraction processes [88–93]. Bulk TiO₂ particle has poor ion and electron conductivity, which has limited its practical capacity and high-rate capability. So much attention has been paid to produce nanostructured

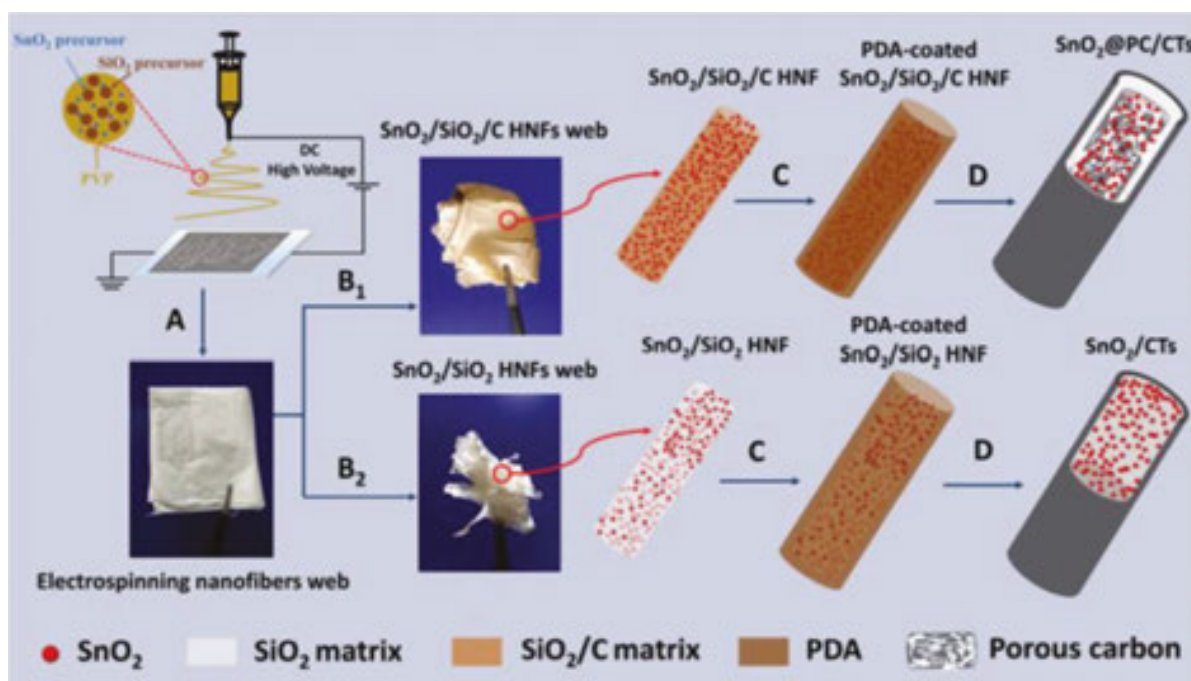


Figure 10. Schematic illustration on the preparation of SnO₂@PC/CT and SnO₂/CT nano hybrids: (A) preparing nanofiber web using electrospinning technique; (B) calcining electrospun nanofiber web (B₁) at 500°C for 1 h in air to obtain SnO₂/SiO₂/C HNF web and (B₂) at 600°C for 6 h in air to obtain SnO₂/SiO₂ HNF web (C) coating PDA on the surface of SnO₂/SiO₂/C HNFs or SnO₂/SiO₂ HNFs at room temperature; (D) carbonizing two types of PDA-coated HNFs at 600°C, and then etching SiO₂ to obtain SnO₂@PC/CTs with a fiber-in-tube hierarchical nanostructure or SnO₂/CTs with a particle-in-tube nanostructure [87].

and open-channeled TiO_2 materials, which can provide increased reaction active sites and short diffusion lengths for electron and lithium-ion transport [94–100].

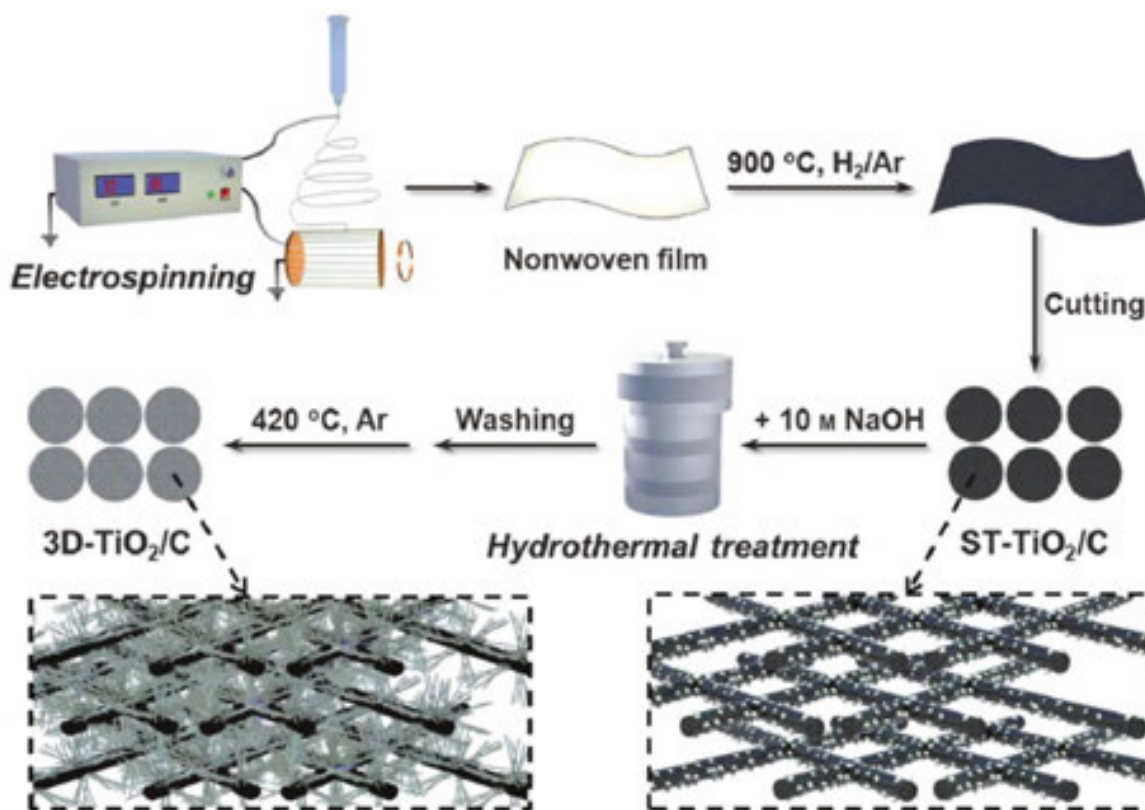


Figure 11. Schematic representation of the preparation for the 3D porous TiO_2 nanotube/carbon nanofiber architecture (ST- TiO_2/C : electrospun TiO_2/C nanofibers after calcination as a starting raw material; 3D- TiO_2/C : 3D porous TiO_2 nanotube/carbon nanofiber architecture prepared by a hydrothermal method) [106].

Moreover, tailoring these TiO_2 fibers by coating or incorporation of carbon materials can greatly influence the capacity values and hence the battery performance [101, 102]. CNFs have also been used to load TiO_2 particles or fibers for improving electrochemical performance [103–106]. The TiO_2 -CNF composite nanofibers were prepared by electrospinning technique and thermal treatment. Owing to the unique features of encapsulating TiO_2 nanocrystals into porous conductive carbon matrix, the composite nanofibers demonstrated an excellent electrochemical performance [103, 104]. A coaxial electrospinning technique combined with subsequent calcination treatment was also used to develop porous TiO_2 -CNFs for LIB anodes [105]. In addition, a 3D porous architecture composed of TiO_2 nanotubes connected with a CNF matrix was successfully prepared by a hydrothermal method using electrospun rutile TiO_2/C nonwoven as the starting raw material (**Figure 11**) [106]. With its unique structure and connected conductive CNF network, the 3D architecture of the electrode resulted in superior rate performance: the reversible capacities were 214, 180, 138, and 112 mA h g^{-1} at the rate of 5, 10, 20, and 30 C, respectively. Additionally, the 3D structured electrode shows a very stable cycling performance, especially at a high rate of 30 C, without undergoing decay after 1000 cycles.

Spinel $\text{Li}_4\text{Ti}_5\text{O}_{12}$ has attracted particular attention for LIB application due to its nearly zero-strain characteristics [107]. However, the practical application of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ in LIBs is hampered by its poor natural electronic conductivity. In order to improve the conductivity of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ materials, various approaches such as surface coating with conductive materials, e.g., Ag nanoparticles [108, 109], dispersion of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ nanoparticles into a carbon matrix [110–112], and preparation of submicron or nanosized $\text{Li}_4\text{Ti}_5\text{O}_{12}$ [113, 114] aiming to significantly shorten the Li^+ -diffusion length, etc., have been developed.

$\text{Li}_4\text{Ti}_5\text{O}_{12}$ /carbon hybrid nanowebs consisting of interconnected nanofibers were prepared by a combination of electrospinning and subsequent thermal treatments [115, 116]. The as-prepared $\text{Li}_4\text{Ti}_5\text{O}_{12}$ /carbon nanowebs exhibited high reversible charge stability and good cycling performance (166 mA h g^{-1} at 0.1 C). Highly porous $\text{Li}_4\text{Ti}_5\text{O}_{12}$ /C nanofibers are successfully designed and prepared through electrospinning combined with a post-two-step annealing process [117]. The $\text{Li}_4\text{Ti}_5\text{O}_{12}$ /C hybrid with a well-defined porous nanoarchitecture exhibits ultrahigh cycling rates and superior cycling stability. Mesoporous structures were also obtained by adding an amphiphilic triblock copolymer surfactant into a PVP solution, driving the self-assembly of a hydroxyl Li–Ti–O precursor to form mesopores after calcination [118]. Even better performances were obtained from combining dual-phase $\text{Li}_4\text{Ti}_5\text{O}_{12}$ – TiO_2 with CNFs, prepared by immersing TiO_2 /CNF in a LiOH solution at high temperatures. This imparted a pseudocapacitive effect, with a 204 mA h g^{-1} discharge capacity after 200 cycles at 100 mA g^{-1} from an initial capacity of $\sim 220 \text{ mA h g}^{-1}$ [119].

3.4. Other metal oxide/CNF composites

Many other metal oxide nanoparticles have also been incorporated into the CNF matrix for the usage of LIB anode materials. For example, the MnO_x particles, existed as MnO or Mn_3O_4 , were incorporated into porous CNFs via electrospinning technique and subsequent heat treatment [120]. The porous MnO_x /C nanofibers experienced limited volume change with Li^+ insertion/extraction because the ductile and strong C matrices suppressed the disintegration and aggregation of MnO_x . Compared with pure CNF anodes, the MnO_x /C exhibited larger charge and discharge capacities (542 mA h g^{-1} for MnO_x /C and 396 mA h g^{-1} for pure CNF at the 50th cycle) [121]. MnO_x was also incorporated into fibrous structures by the electrochemical deposition of MnO_x nanoparticles on PAN-based electrospun CNFs [122]. Similarly, Zhang et al. [123] prepared porous Co_3O_4 –CNFs, which show an improved electrochemical performance compared to pure Co_3O_4 nanoparticles. C/ Fe_3O_4 nanofibers with amorphous C structure and crystalline Fe_3O_4 particles were carbonized at a relatively low temperature (600°C), and showed high reversible capacity of 1007 mA h g^{-1} at the 80th cycle and excellent rate capability [124]. Recently, maghemite ($\gamma\text{-Fe}_2\text{O}_3$) nanoparticles were uniformly coated on CNFs by a hybrid synthesis procedure combining an electrospinning technique and hydrothermal method. Electrospun PAN nanofibers serve as a robust support for iron oxide precursors during the hydrothermal process and successfully limit the aggregation of nanoparticles at the following carbonization step (**Figure 12**) [125]. Such design not only increases the loading of Fe_2O_3 up to more than 60%, but also limits the aggregation of nanoparticles in the following

carbonization step, which leads to a high reversible capacity of above 830 mA h g⁻¹ after 40 cycles.

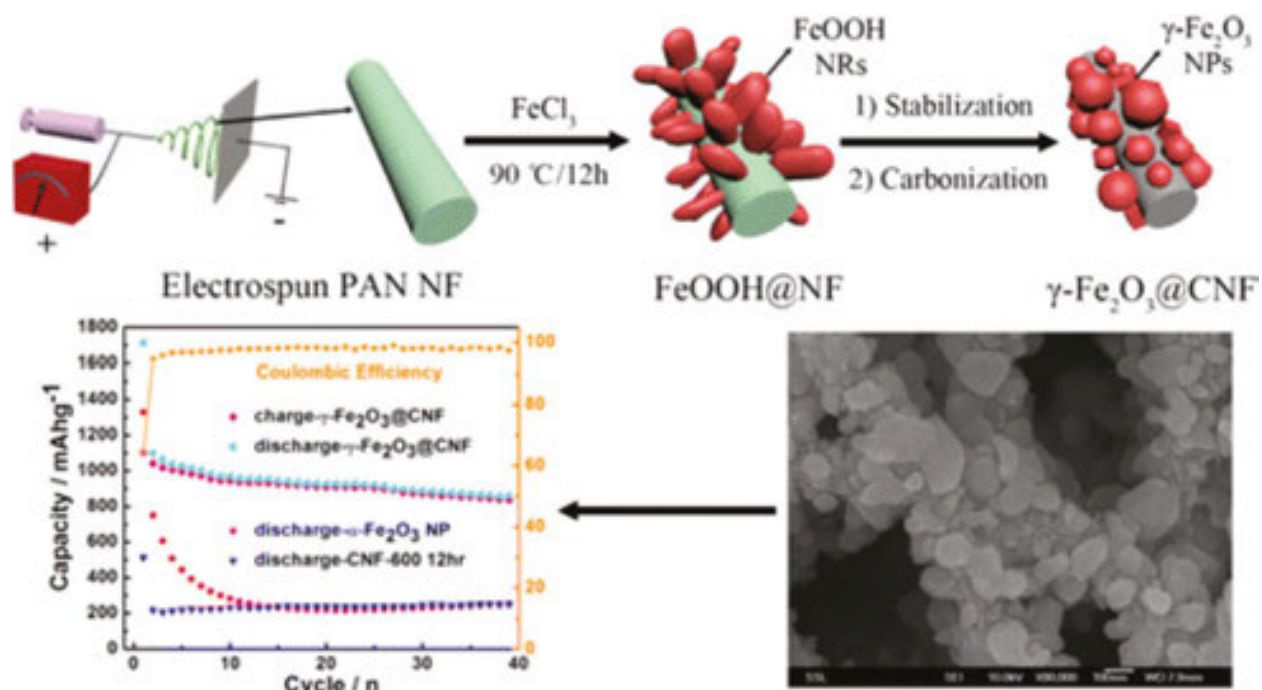


Figure 12. Schematic of the preparation of γ -Fe₂O₃@CNFs and its microstructure and performance [125].

4. Summary and perspective

In this chapter, the progress in electrospun CNFs and the composites with CNFs, which are used as LIB anode materials, has been summarized. Silicon, tin-based materials, and transition metal oxides are the candidates for the next generation anodes due to their expected high theoretical capacity, but suffer from some issues such as the vast volume change and low electronic conductivity, which could result in lower cycling stability and rate performance. Fortunately, these issues might be solved via composing with electrospun CNF matrix due to their superior mechanical properties and electrical conductivity as well as unique 1D nanostructure. More importantly, these CNF-based composite anodes with an interfibrous web structure could be directly used as anodes without any conductive agent and binder or current collectors, which can greatly reduce the inactive weight and cost of the cells, and significantly improve the electrochemical performance of LIBs [126, 127]. Further enhancement of electrochemical performance could be achieved by constructing controllable 1D nanostructures and doping various materials with CNF-based hybrid nanofibers.

In addition, sodium-ion batteries (SIBs) are new-emerged promising candidates for new battery systems especially for large-scale and long-term electric energy storage applications

due to their cost advantages [5, 6, 128–133]. Currently, many researchers have paid more attention to electrospun materials for SIBs [134–142]. So far, research has mainly focused on the electrode materials based on electrospun 1D composite with CNFs. By constructing controllable 1D nanostructure to take full advantage of the electrospun materials including shorter diffusion pathways, high surface areas and porosities, good mechanical strengths, etc., one can find the wide use of the electrospun materials in commercial LIBs or SIBs, and even in flexible battery devices in the years ahead.

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