Well-dispersed fluorine-doped tin oxide nanoparticles on the one dimensional network structure of carbon nanofibers for enabling ultrafast lithium storage

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Research Article

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Well-dispersed fluorine-doped tin oxide nanoparticles on the one dimensional network structure of carbon nanofibers for enabling ultrafast lithium storage

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Abstract

The growing environmental concerns have spurred a surge in the interest in eco-friendly energy storage devices. Because of their advantages, such as high energy density and long cycle life, Li-ion batteries (LIBs) are used in electronic devices and electric vehicles (EVs). However, the specific capacity and ultrafast cycling performance of the LIBs used in EVs require further improvement. In this study, well-dispersed fluorine-doped tin oxide (FTO) nanoparticles (NPs) were deposited on carbon nanofibers (CNFs) using horizontal ultrasonic spray pyrolysis deposition to obtain a CNF/FTO electrode. The F atoms in tin oxide increased its electrical conductivity. The one-dimensional CNF network structure enhanced the electrical conductivity of the electrode. The abundant active sites in nanosized FTO facilitated Li-ion diffusion. The well-dispersed FTO NPs on the CNF matrix prevented the agglomeration of the electrode material and substantial volume changes in the electrode during its cycling. At a current density of 100 mA/g, the CNF/FTO electrode exhibited a superior discharge capacity of 487.96 mAh/g with a capacity retention of 66.7% and even at an ultrafast current density of 2000 mA/g, it
demonstrated excellent performance with a discharge capacity of 289.3 mAh/g and a capacity retention of 93.6% after 500 cycles of operation.

**Running Title**: FTO NPs on CNFs for ultrafast LIBs

**Key words**: Li-ion batteries, Anode, Fluorine doped tin oxide, Carbon nanofibers, ultrafast Li storage ability

1. Introduction

With the environmental pollution resulting from the combustion of fossil fuels escalating, interest in eco-friendly energy storage devices has started to grow recently [1, 2]. In addition, the demand for high-performance energy storage devices used in various devices, ranging from small electronic devices (e.g., smartphones, tablets, and laptops) to electric vehicles (EVs), has increased. Among the various energy storage devices, Li-ion batteries (LIBs) have received considerable attention owing to their specific advantages, such as eco-friendliness, high energy density, and long cycle life [3, 4]. Owing to the explosive growth of the electric vehicle market, the demand for high-performance LIBs, the main power supply source of the EVs, is also significantly increasing. However, the limited mileage and long charging time of the EVs are the most significant emerging concerns, with most models of the EVs achieving approximately 300 miles per charge and requiring fast charging up to 80% in 1 h with a power consumption of 100 kW, compared to low mileage and charging speed [4, 5]. Because the fast charging of a battery rapidly decreases its life span, the current research on LIBs is focused on improving their ultrafast cycling performance.

Among the four main components of an LIB, namely the cathode, anode, electrolyte, and separator, the anode plays an important role in the ultrafast cycling of the LIB,
because of its high energy density and low charging speed [6]. Because graphite, the most commercialized anode material, has a low theoretical capacity (372 mAh/g) and poor Li storage kinetics, the development of alternative anode materials is important for facilitating ultrafast LIBs [6, 7]. As an anode material, a carbon nanofiber (CNF) offers several advantages, such as good electrical conductivity, high specific surface area, and high physical/chemical stability, surpassing other anode materials. Specifically, a CNF with a one-dimensional (1D) fiber structure overlaps with the other CNFs, forming a network structure, which enhances the electron transfer and Li-ion diffusion within the electrode in which it is used [8, 9]. However, CNFs also have the intrinsic limitations of carbon, such as low theoretical capacity. Therefore, strategies for developing the specific capacity of CNFs using the advantages of their structures would be necessary if they are to be used as ultrafast anode materials in LIBs.

Tin oxide (SnO$_2$) is a prospective anode material for use in LIBs owing to its high theoretical capacity (1493 mAh/g), nontoxicity, and low cost [10]. However, the high theoretical capacity accompanies the large volume expansion about 300% and agglomeration, therefore the SnO$_2$ has the low cycling stability by the crack and low Coulombic efficiency [11, 12]. Furthermore, because of the low electrical conductivity of SnO$_2$ ($\sim 1 \times 10^4$ S/cm), the challenges mentioned significantly aggravate at ultrafast current densities [10]. To overcome these challenges and enhance the ultrafast Li storage capability of SnO$_2$, studies have been frequently conducted to control hollow and porous SnO$_2$ structures and those with different morphologies, such as nanoparticles (NPs), nanotubes, and nanorods [13–17]. These structures can slightly enhance the transportation capability of Li ions in a LIB and alleviate the mechanical stress within it caused by volume expansion, resulting in an increase in the rate performance of the battery.
Nevertheless, the agglomeration that occurs in the nanostructure of an electrode disturbs its electrochemical performance. Therefore, the use of the composites of SnO$_2$ and carbon materials, such as graphene, reduced graphene oxide, carbon nanotubes, and CNFs, is a powerful strategy that will enhance the cycling stability of the battery by effectively preventing SnO$_2$ agglomeration. However, the baled SnO$_2$ NPs in the composite have the negative effect on the capacity and cycling stability, to materialize the well-dispersed structure is the key point as the anode materials of LIBs. However, doping SnO$_2$ with heteroatoms, such as Sb$^{5+}$, Zn$^{2+}$, and F$^-$, is an effective tactic that can be employed to enhance the electrical conductivity of an SnO$_2$ electrode and Li-ion diffusion within it [18, 19].

Therefore, we deposited well-dispersed and highly conductive fluorine-doped tin oxide (FTO) NPs on a 1D CNF network structure using horizontal ultrasonic spray pyrolysis deposition (HUSPD). Because of the 1D network structure of the CNFs, the electron transfer and Li-ion diffusion within the electrode increased, and the FTO NPs on the CNFs network structure enhanced the specific capacity and ultrafast cycling performance of the electrode. Moreover, unlike other vacuum-based deposition processes, HUSPD is a solution-based deposition process that is simple and cost-effective. During HUSPD, the FTO NPs were deposited on the CNFs with good dispersion, enhancing the cycling stability of the electrode by preventing the agglomeration of its electrode material and further increasing its Li storage capability by increasing the number of active sites in the FTO NPs. The electrode with well-dispersed NPs and a 1D network structure displayed an enhanced rate performance with cycling stability at an ultrafast current density.
2. Experimental Details

CNF/FTO electrodes were fabricated via electrospinning and HUSPD. To fabricate the Bare CNF electrode, 10 wt% polyacrylonitrile was first dissolved in N, N-dimethylformamide by stirring for 3 h, and the resulting solution transferred to a syringe. Electrospinning was conducted while maintaining a 13 kV voltage, a 0.03 mL/h feeding rate, a distance of 15 cm between the needle (23 gauge) and collector, and a humidity below 15%. Polyacrylonitrile (PAN)-based nanofibers were stabilized at 280 °C in air, and carbonized at 800 °C in a nitrogen atmosphere, and Bare CNF electrodes were successfully fabricated. The Bare CNF electrodes were first etched with hydrofluoric and nitric acids (1:1) for 6 h. Secondly, 0.68 M SnCl\(_2\) and 1.19 M NH\(_4\)F were dissolved in deionized water with 5 vol% ethyl alcohol to obtain an FTO precursor solution for use in HUSPD. An ultrasonic atomizer (1.6 MHz) was used at a chamber temperature of 420 °C to perform HUSPD on the CNFs. Argon was the carrier gas, flowing at a rate of 10 L/min. To optimize the amount of FTO deposited on the electrodes, three different spray times were used, namely 6, 16, and 26 min, and the corresponding electrodes obtained are referred to as CNF/FTO6, CNF/FTO16, and CNF/FTO26, respectively.

The structures and morphologies of the electrodes were investigated using field-emission scanning electron microscopy (FESEM, Hitachi S-4800) and high-resolution transmission electron microscopy (HRTEM, JEOL JEM-2100F). Energy-dispersive spectroscopy (EDS) mapping was employed to observe the distribution of the elements in the electrodes. The crystal structures of the electrodes were analyzed using X-ray diffraction (XRD, Rigaku D/Max-2500) in the range of 10°–90° with a step size of 0.02°. The component ratios of the electrodes were investigated using thermogravimetric analysis (TGA, Nicolet iS50), while their chemical bonding states were analyzed using
X-ray photoelectron spectroscopy (XPS, ESCALAB 250).

The electrochemical performance of each of the electrodes was investigated using coin-type half cells (CR2032, Hohsen Corporation). A prepared electrode served as the anode, a Li foil (Honjo Chemical, 99.99%) was used as the anode, a porous polypropylene membrane acted as the separator, and 1.6 M LiPF$_6$ solution dissolved in a mixture of ethylene carbonate and dimethyl carbonate (1:1 vol%) served as the electrolyte. The anode slurry was prepared by homogenizing a mixture comprising, 70 wt% of one of the fabricated electrodes as the active material, 20 wt% of polyvinylidene fluoride) as the binder, and 10 wt% of Ketjen black as the conductive material. The solvent used in the slurry preparation was N-methyl-2-pyrrolidinone (NMP, Aldrich). The slurry was thereafter coated on a Cu foil substrate (Nippon Foil, 18 μm) as the current collector and dried in a vacuum-oven at 130 °C for 10 h. All of the coin-type half-cells were assembled in a glove box filled with high-purity argon gas having H$_2$O and O$_2$ contents of less than 5 ppm. To analyze the electrochemical kinetics of the electrodes, electrochemical impedance spectroscopy (EIS) measurements of them were performed in the range of $10^3$–$10^{-2}$ Hz. The galvanostatic charge/discharge (GCD) performance of each electrode was examined using a battery cycler system (WMPG 3000, WonATech Corp.,) in the potential range of 0.05–3.0 V (vs. Li/Li$^+$). The cycling stabilities of all the electrodes were investigated at a current density of 100 mA/g for up to 100 cycles, and the rate capabilities of all the electrodes were analyzed at the current densities 100, 300, 700, 1000, 1500, and 2000 mA/g. The ultrafast cycling performance of each electrode was measured at 2000 mA/g after 500 cycles. Furthermore, the cyclic voltammetry measurements (CVs) of the Bare CNF and CNF/FTO16 electrodes were performed within the potential range of 0.05–3.0 V (vs. Li/Li$^+$) at scan rates of 0.1, 0.3, 0.5, 0.7, and 0.9 mV/s using a
potentiostat/galvanostat (PGST302N).

3. Results and Discussion

Figs. 1(a), (b), and (c) show the schematic illustrations of the HUSPD system structure used in the study, deposition mechanism of the HUSPD system, and the CNF/FTO electrode structure. The precursor solution droplets were developed for use with FTO employing an ultrasonic atomizer and had to be horizontally transferred to the chamber because of the presence of carrier gas (Fig. 1(a)). The nucleation of FTO occurred via the following steps (Fig. 1(b)): absorption of the precursor droplets by the CNF surfaces in the chamber, evaporation of the precursor solution, condensation of the precursor solute, and thermal decomposition of the precursor droplets. This thermal decomposition of the precursor droplets occurs via the following chemical reactions (Equation 1–4) [20, 21].

\[
\text{SnCl}_4 + 2\text{H}_2\text{O} \rightarrow \text{Sn(OH)}_4 + 4\text{HCl} \quad (1)
\]

\[
\text{Sn(OH)}_4 + \text{NH}_4\text{F} \rightarrow \text{SnO}_2\text{F} \quad (2)
\]

\[
\text{HCl} + \text{NH}_4\text{F} \rightarrow \text{NH}_4\text{Cl} + \text{HF} \quad (3)
\]

\[
\text{SnCl}_4 + 2\text{H}_2\text{O} + \text{NH}_4\text{F} \rightarrow \text{SnO}_2\text{F} + 3\text{HCl} + \text{NH}_4\text{Cl} + \text{HF} \quad (4)
\]

As the deposition time increased, the FTO crystallized and grew in the presence of a continuous supply of precursor droplets. Finally, the FTO NPs deposited uniformly on the surfaces of the CNFs (Fig. 1(c)). These FTO NPs have an increased number of active sites and facilitates the diffusion of the Li ions while enhancing the specific capacity of the electrode.

Fig. 2. shows low-resolution (Figs 2(a)–(d)) and high-resolution (Figs. 2(e)–(h)) FESEM images of the Bare CNF, CNF/FTO6, CNF/FTO16, and CNF/FTO26 samples. As the low-resolution FESEM images of the Bare CNF sample indicates, the sample has...
a 1D structure with a smooth surface and a diameter in the range of 371.16–434.98 nm. By contrast, the CNF/FTO samples have a 1D structure with a bumpy surface because of the FTO NPs deposited on the CNF surfaces. As the FTO NP deposition time increased, the diameters of samples gradually increased (CNF/FTO6: 451.33–458.26 nm, CNF/FTO16: 420.50–464.54 nm, and CNF/FTO26: 884.44–917.08 nm). The CNF/FTO6 sample exhibits isolated FTO NPs (142.56–156.88 nm) owing to the insufficient deposition time; the CNF/FTO16 sample shows well-deposited FTO NPs along the 1D CNF structure. The sizes of these deposited FTO NPs have sizes similar to those of FTO NPs (165.68–186.55 nm) and diameters comparable to those of the CNF/FTO6 sample. However, due to the long deposition time, the CNF/FTO26 sample showed large FTO NPs (374.96–395.48 nm), which reduced the number of active sites in FTO and hindered Li-ion diffusion and electron transfer during cycling. Therefore, owing to the optimum deposition time of the CNF/FTO16 sample, well-dispersed FTO NPs could prevent substantial volume changes in the electrode and its agglomeration during its cycling, enhancing its cycling stability [10, 22].

To analyze the morphology and nanostructure of the CNF/FTO16 sample, we performed a TEM analysis of the sample. In the low-resolution TEM image of the CNF/FTO16 sample (Fig. 3(a)), dark spots representing FTO NPs (169.23–184.41 nm) are arranged along the 1D CNF structure, and the diameter range from 421.51 to 459.54 nm is in good agreement with the SEM results. Furthermore, in the high-resolution TEM image of the CNF/FTO16 sample (Fig. 3(b)), a 0.243 nm interlayer spacing corresponding to the (110) plane of FTO, which has a larger interlayer spacing than SnO$_2$ (0.24 nm) owing to the higher ionic radius of its substitutionally doped F$^-$ ions (0.133 nm) compared with that of substituted O$^{2-}$ ions (0.132 nm), was observed [23]. TEM-EDS was conducted
to confirm the elemental distribution in the CNF/FTO16 electrode. As shown in Fig. 3(c), C elements are predominantly distributed within the inner parts of the 1D structure, while O, F, and Sn elements are predominantly distributed within its outer parts. This distribution pattern indicates the successful formation of FTO at the CNF surfaces. Because FTO NPs have an abundant number of active sites and facilitate Li-ion diffusion, the CNF/FTO16 sample exhibited an increased specific capacity at an ultrafast current density.

An XRD analysis of the samples was performed to determine their crystal structures, as shown in Fig. 4(a). The Bare CNF sample shows only a broad diffraction peak at ~24.40°, corresponding to the (002) plane of amorphous carbon [24]. By contrast, the CNF/FTO6, CNF/FTO16, and CNF/FTO26 samples exhibit sharp diffraction peaks at ~26.45°, ~33.73°, ~37.98°, and ~51.72° along with a broad diffraction peak that could be attributed to amorphous carbon. These diffraction patterns indicate the formation of FTO with the (110), (101), (200), and (211) planes on the CNF structure. Moreover, the peak positions of FTO was slightly shifted toward the lower angles compared to those of SnO$_2$ (~26.61°, ~33.90°, ~37.98°, and ~51.82°, which correspond to the (110), (101), (200), and (211) planes, respectively), which can be attributed to the F$^-$ ions having a large ionic radius of 0.133 nm when substituted with O$^{2-}$ sites that had an ionic radius of 0.132 nm. These results imply that FTO NPs were successfully formed on the CNFs, and that the F$^-$ ions have been successfully doped into the FTO NPs [25]. TGA measurements were performed to confirm the number of FTO NPs deposited (Fig. 4(b)). Although the Bare CNF electrode showed a complete weight loss, the CNF/FTO sample showed a gradually decreasing weight loss (CNF/FTO6: 7.71%, CNF/FTO16: 13.88%, and CNF/FTO26: 20.69%) with increasing deposition time. To characterize the chemical bonding states of
the electrodes, XPS analysis of the Bare CNF and CNF/FTO16 samples was performed, and the XPS spectra were calibrated using ~284.5 eV, binding energy of C 1s. The Sn 3d XPS spectrum of the CNF/FTO16 sample (Fig. 4(c)) exhibits two characteristic peaks at ~486.7 eV and ~487.7 eV corresponding to Sn 3d$_{5/2}$ and two other characteristic peaks at ~495.2 eV and ~496.3 eV corresponding to Sn 3d$_{3/2}$, whereas the corresponding spectrum of the Bare CNF sample does not exhibit such characteristic peaks [26]. In addition, the four peaks relate to the chemical bonding structure of Sn-Sn (~486.7 eV and ~495.2 eV) and Sn-F (~487.7 eV and ~496.3 eV), implying that F has been doped into the SnO$_2$ lattice, which can boost the ultrafast cycling performance of the electrode by providing extra electrons. The F atoms doped into SnO$_2$, increase the electrical conductivity of the electrode by providing extra electrons that are free, thereby enhancing its ultrafast cycling performance [23, 27]. In contrast to the Bare CNF sample, the CNF/FTO16 sample displays in its O 1s XPS spectrum, three characteristic peaks at ~530.3 eV, ~530.8 eV, and ~532.2 eV, corresponding to C-O, Sn-O, and C=O bonds, respectively, (Fig. 4(c)). Thus, the results confirm that the highly conductive FTO was successfully deposited on the 1D network structure of the CNFs, causing an increase in their electrical conductivity.

To investigate the electrochemical kinetics of the Bare CNF, CNF/FTO6, CNF/FTO16, and CNF/FTO26 electrodes, an EIS analysis was performed using fresh cells. The Nyquist plots displayed a single semicircle in the high frequency region, indicating that the charge transfer resistance ($R_{ct}$) is related to the interfacial resistance between the anode and electrolyte, and an oblique line in the low frequency region, representing the Warburg impedance [28–29]. In the Nyquist plots of the cells (Fig. 5(a)), the CNF/FTO16 electrode exhibits the smallest $R_{ct}$ owing to its increased electrochemical conductivity caused by F doping and the well-dispersed FTO NPs on the CNFs. The Li-ion diffusion coefficients
of the electrodes were calculated based on the oblique lines in the low-frequency regions of the Nyquist plots and using the following equations (Equation 5 and 6), [30].

\[
Z_R = \sigma_w \omega^{-1/2} + R_e + R_{ct}
\]

\[
D = \frac{(RT)^2}{2A^2n^4F^4C^2}\sigma_w
\]

where \(R_e\) is the bulk resistance in the cell; \(\sigma_w\) is the Warburg impedance coefficient related to the Li-ion diffusion resistance; and \(D, R, T, A, n, F,\) and \(C\) indicate the Li-ion diffusion coefficient, gas constant, temperature, electrode area, number of electrons per molecule, Faraday constant, and Li-ion concentration, respectively. According to Fig. 5(b), the \(\sigma_w\) values of the Bare CNF, CNF/FTO6, CNF/FTO16, and CNF/FTO26 electrodes are 45.5, 35.06, 13.82, and 40.91 \(\Omega \text{ cm}^2/s^{1/2}\), respectively. The Li-ion diffusion coefficients of the Bare CNF, CNF/FTO6, CNF/FTO16, and CNF/FTO26 electrodes obtained by calculation using their \(\sigma_w\) values were \(1.6 \times 10^{-13}\), \(2.8 \times 10^{-13}\), \(17.8 \times 10^{-13}\), and \(2.0 \times 10^{-13} \text{ cm}^2/s\), respectively. Compared with the Bare CNF electrode, the CNF/FTO electrodes showed higher Li-ion diffusion coefficients. However, the CNF/FTO26 electrode displayed a lower Li-ion diffusion coefficient than the CNF/FTO16 electrode, owing to the interruption of Li-ion diffusion within it by the overly deposited FTO NPs. Therefore, the CNF/FTO16 electrode, which has an optimum number of deposited FTO NPs, shows enhanced ultrafast cycling performance owing to its highly conductive and well-dispersed FTO NPs.

Figs. 6(a) and (b) show the GCD voltage profiles of the Bare CNF and CNF/FTO16 electrodes measured at a current density of 100 mA/g. In the first cycle, compared with the discharge capacity of the Bare CNF electrode (820.2 mAh/g), the discharge capacity of the CNF/FTO16 electrode is higher (1515.1 mAh/g). Furthermore, in the first cycle of the CNF/FTO16 electrode, a voltage plateau (~ 0.8 V) was observed, which coincided
with the lithiation of SnO$_2$ (SnO$_2$ + 4Li$^+$ + 4e$^-$ → 2Li$_2$O + Sn) and the concurrent formation of a solid electrolyte interface layer, causing irreversible loss of electrode capacity [31]. Additionally, the voltage plateaus of the discharging/charging process at 0.3/0.7 V and 0.85/1.25 V can be clearly observed in Fig. 5(b). These voltage plateaus relate to the alloying/dealloying reactions of Li-Sn (Sn + xLi$^+$ + xe$^-$ ↔ Li$_x$Sn), and the lithiation/delithiation of CNF (C + xLi$^+$ + xe$^-$ ↔ Li$_x$C), respectively [31, 32]. Moreover, to quantify the surface-induced capacitance and ion diffusion resulting from electrochemical reactions, we conducted CV tests on the Bare CNF and CNF/FTO16 electrodes at scan rates of 0.1, 0.3, 0.5, 0.7, and 0.9 mV/s. The capacitive contributions, including the surface-induced capacitance (pseudocapacitive, $k_1v$) and ion diffusion ($k_2v^{1/2}$), of the Bare CNF and CNF/FTO16 electrodes during the charge/discharge reaction were calculated (Equations 7) [33].

$$i (V) = k_1v + k_2v^{1/2}$$  \hspace{1cm} (7)

These results (Fig. 6(d)) show that the pseudocapacitive contributions of the electrodes gradually increase with increasing scan rate, indicating that pseudocapacitive reactions are more important than ion diffusion. At any scan rate, the CNF/FTO16 electrode has a higher pseudocapacitive contribution than the Bare CNF electrode, which can be attributed to the effective electrochemical double reaction resulting from the highly conductive structures of the FTO NPs that are well deposited on the CNFs with efficient charge transfer. Therefore, this read to the superb ultrafast cycling performance of CNF/FTO16 electrode.

Fig. 7(a) shows the cycling stability testing of the Bare CNF, CNF/FTO6, CNF/FTO16, and CNF/FTO26 electrodes conducted over 100 cycles at a current density of 100 mA/g. All electrodes exhibited a Coulombic efficiency exceeding 95% after four cycles of
operation, indicating that a reversible electrochemical reaction had occurred. Among the electrodes tested, the CNF/FTO16 electrode exhibited the highest specific capacity of 488.0 mAh/g with a capacity retention of 74.3%, after 100 cycles; the CNF/FTO6 and CNF/FTO26 electrodes exhibited specific capacities of 310.4 and 382.7 mAh/g, respectively, with capacity retentions of 71.7% and 67.7%, respectively. These results indicate that the specific structure of the CNF/FTO16 electrode effectively improves its discharge capacity and cycling stability owing to the increased number of active sites and availability of sufficient space to accommodate the volume changes of the FTO NPs during cycling. Additionally, as shown in Fig. 7(b), we conducted GCD tests at current densities between 100 and 2000 mA/g to confirm the rate performance of the electrodes. As the current density increased, the CNF/FTO16 electrode exhibited the highest specific capacity of 66.3% among the electrodes; the specific capacities of the Bare CNF, CNF/FTO6, and CNF/FTO26 electrodes were 262.8, 418.2, and 490.3 mAh/g, respectively. The excellent rate performance of the CNF/FTO16 electrode can be attributed to its high conductivity, caused by F doping of SnO$_2$ and the well-dispersed FTO NPs on the CNFs. To confirm the effect of the CNF/FTO electrode structures on their ultrafast cycling performance, we conducted an ultrafast cycling stability test after 500 cycles at a current density of 2000 mA/g, as shown in Fig. 7(c). After 500 cycles, the CNF/FTO6 and CNF/FTO26 electrodes had specific capacities of 106.4 and 219.6 mAh/g, respectively, with capacity retentions of 66.2% and 91.0%, respectively, whereas the CNF/FTO16 electrode exhibited a superior specific capacity of 289.2 mAh/g with a capacity retention of 93.6%. This excellent ultrafast electrochemical performance of the CNF/FTO16 electrode can be explained as follows: (1) the increased specific capacity can be attributed to the increased number of active sites resulting from nanosized FTO;
(2) the enhanced ultrafast capacity of the electrode would have resulted from the increased electrical conductivity of the highly conductive FTO within a 1D CNF network structure; and (3) the superb ultrafast cycling stability of the electrode arose from the prevention of significant volume changes and agglomeration in the electrode by the well-dispersed FTO NPs on the CNF matrix.

4. Conclusion

In this study, we synthesized well-dispersed FTO NPs on CNFs using electrospinning and HUSPD. At the optimum deposition time of 16 min, the FTO NPs were uniformly deposited on the surface of the CNFs, which caused an increase in the charge-transfer kinetics of the number of active sites. The CNF/FTO16 electrode exhibited a superior discharge capacity of 487.96 mAh/g and a capacity retention of 66.7% at a current density of 100 mA/g. Moreover, during the ultrafast cycle test conducted at a current density of 2000 mA/g, the CNF/FTO16 electrode demonstrated an excellent discharge capacity of 289.2 mAh/g and a capacity retention of 93.6% after 500 cycles. The remarkable ultrafast specific capacity of the electrode can be attributed to several factors: firstly, the increased number of active sites and the facilitated Li-ion diffusion are the results of the presence of FTO NPs. Moreover, the high electrical conductivity provided by conductive FTO enhances the performance of the electrode owing to the integration of FTO with the 1D network structure of the CNFs. Moreover, the excellent cycling stability of the electrode was achieved by effectively mitigating the severe volume exchange and agglomeration in the electrode by well-dispersed FTO NPs within the CNF matrix. Thus, we believe that well-dispersed, highly conductive FTO on the 1D network structures of CNFs offers a promising approach for advancing the ultrafast Li-storage ability of LIBs.
Conflict of interest

The authors declare no conflicts of interest.

Acknowledgements

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Figure captions

Figure 1 Schematic images of (a) constitution of HUSPD system, (b) deposition mechanism of FTO NPs on CNFs, and (c) structure of FTO NPs coated on CNF with 1D network structure.

Figure 2 (a-d) Low- and (e-f) high-resolution FESEM images of Bare CNFs, CNF/FTO6, CNF/FTO16, and CNF/FTO26.

Figure 3 (a) Low- and (b) high-resolution TEM images, and (c) TEM-EDS mapping results of CNF/FTO16.

Figure 4 (a) XRD and (b) TGA results of Bare CNF, CNF/FTO6, and CNF/FTO16, and CNF/FTO26, and XPS spectra of (c) Sn 3d and (d) O 1s of Bare CNF and CNF/FTO16.

Figure 5 (a) The Nyquist plots, (b) relationship between $Z_{\text{real}}$ and $\omega^{-0.5}/s^{-0.5}$, and (c) Li-ion diffusion coefficient of Bare CNF, CNF/FTO6, CNF/FTO16, and CNF/FTO26.

Figure 6 (a) Cycling stability with Coulombic Efficiency at 100 mA/g for 100 cycles, (b) rate performance, and (c) ultrafast cycling stability at 2000 mA/g for 500 cycles of Bare CNF, CNF/FTO6, CNF/FTO16, and CNF/FTO26 electrode.

Figure 7 Galvanostatic charge-discharge voltage profiles of (a) Bare CNF electrode and (b) CNF/FTO16 electrode, (c) CV curves with separation of the capacitive current for the filled regions and the diffusion current for vacant regions at 0.1 mV/s of CNF/FTO16 electrode, and (d) are comparison ratio of the capacitive (C) contributions and the diffusion (D) contribution of Bare CNF and CNF/FTO16 electrode.
*If possible, we want all of our figures to be published with color.

Figures

Figure 1. Yoon et al.
Figure 2. Yoon et al.
Figure 3. Yoon et al.
Figure 4. Yoon et al.
Figure 5. Yoon et al.
Figure 6. Yoon et al.
Figure 7. Yoon et al.
Graphical Abstract

The well-dispersed fluorine-doped tin oxide nanoparticles on the one dimensional network structure of carbon nanofibers (CNF/FTO) were fabricated by horizontal ultrasonic spray pyrolysis deposition. The CNF/FTO16 electrode showed the highest ultrafast discharge capacity of 289.2 mAh/g and a capacity retention of 93.6% after 500 cycles at current density of 2000 mA/g, which were mainly attributed to the increased active site and prevented agglomeration by well-dispersed FTO NPs on network structure of CNFs.