Formation of Carbon Nanofibers Grafted with TiO$_2$ Nanosheets as Advanced Anodes for Lithium Ion Batteries

Yan Guo, Na Fan and Changyan Li$^*$

College of Chemistry and Chemical Engineering, Inner Mongolia University, Hohhot 010021, P. R. China
Email: guoyan@imu.edu.cn

Abstract. Titanium dioxide (TiO$_2$)-based materials, including various polymorphic TiO$_2$ and several titanates, have been extensively studied for potential negative electrode materials for next-generation lithium ion batteries (LIBs). And it is indispensable to design a reasonable nanostructure. Novel nano-heterostructures composed of TiO$_2$ nanosheets on the surface of carbon nanofibers (CNF) have been synthesized by growing hydrogen titanate nanosheets on the CNF backbone, and then followed by thermal conversion to TiO$_2$ nanosheets. Owing to their structural advantages, the hybrid CNF@TiO$_2$ electrode delivers high capacities of 292 mAh g$^{-1}$ at a current density of 200 mA g$^{-1}$ with outstanding capacity retention over 200 cycles.

Keywords. Lithium ion battery, anode material, titanium dioxide.

1. Introduction

In the new era of science and technology, it is important to make breakthroughs in energy storage technology, the bottleneck facing the development of new energy. The development and application of energy storage technology will promote the utilization efficiency of clean energy and the development of new energy industry [1]. Lithium-ion batteries (LIBs) are widely used in small portable devices such as mobile phones and laptops, hybrid vehicles, electric vehicles, military communications, aerospace and other fields for its advantages of large capacity, high voltage, good safety performance, long cycle life [2]. In order to realize the high performance, low cost, high safety and environmental protection of lithium ion batteries, it puts forward higher requirements for electrode materials. At present, the most widely used anode materials in commercial applications are mainly graphite. However, since the oxidation-reduction potential is close to the potential of lithium metal, it is easy to cause metal lithium crystal clusters to precipitate and pierce the separator, causing short circuit of the battery and resulting in poor safety performance. At the same time, the formation of SEI film on the surface of graphite electrode will consume the limited amount of Li$^+$, which will also increase the interface resistance between the electrode and the electrolyte, and affect the high-rate capability of the battery [3].

The operating voltage of the titanium-based anodes for LIBs is above 0.8 V, which avoids decomposition of electrolyte and precipitation of lithium dendrites. Compared with graphite anodes, it is more safety and stable. Lithium-ion batteries with long life and high safety have received extensive attention. TiO$_2$ is the earliest studied metal oxide anode material with a theoretical capacity of more than 300 mAh g$^{-1}$, and the volume change during the lithium insertion process is less than 4%, which makes it have a long cycle life. TiO$_2$ has many different crystal forms, of which rutile TiO$_2$ has the most stable crystal structure, while anatase TiO$_2$ has the highest lithium intercalation activity [4-5]. Although TiO$_2$-based anode materials have many advantages as mentioned above, they also face a...
great challenge in practical applications, namely lower electron and ion conduction rates. Therefore, conventional bulk TiO$_2$-based materials tend to show lower electrochemical activity. By reducing the size of the particles, the storage performance of lithium can be increased, and the diffusion distance of charges can be shortened. By designing and constructing suitable nanostructures, the performance of the electrode material can be significantly improved. Therefore, many researchers have optimized the electrochemical properties by nanomaterializing electrode materials [6].

Since most titanium precursors (such as alkoxy titanates) have high reactivity and fast hydrolysis rates, the synthesis of TiO$_2$-based nanomaterials is generally realized by controlling the hydrolyzation of titanium precursor in the presence of a surfactant or other structure directing agent. The preparation of nanostructured TiO$_2$ by solvothermal methods using organic solvents to regulate the growth of TiO$_2$-based nanomaterials is very promising. The researchers have investigated the structural characteristics such as crystal growth behavior, crystal geometry, specific surface area, porosity and layered structure of TiO$_2$ in several common organic solvents and studied the electrochemical properties such as specific capacity, rate performance and cycle performance, hoping to optimize its electrochemical performance through structural regulation. However, the nanoscale TiO$_2$ particle structure is prone to aggregation, resulting in a significant decrease in the diffusion rate of lithium ions. By constructing nanocomposites by combining low-dimensional TiO$_2$ with carbon-containing carriers, the conductivity and structural stability of the electrode materials can be effectively improved and the TiO$_2$ particles can be effectively dispersed to avoid the aggregation of titanium dioxide particles, thereby overcoming the problem of slow diffusion rate of lithium ions. Common carbon materials such as carbon nanotubes, graphene, carbon cloth, etc. are used as carbon carriers to improve the electrochemical performance of TiO$_2$ [7].

As a negative electrode of LIBs, TiO$_2$ has the advantages of good safety, long life and good cycle stability, which meets the higher safety requirements of next-generation LIBs and becomes an ideal alternative to traditional carbon anodes. However, the intrinsic conductivity of TiO$_2$ is low, and the capacity attenuation is severe when charging and discharging under large currents, which is a major factor limiting its large-scale commercial application. In recent years, the researchers have carried out a lot of modification work on TiO$_2$ materials in order to improve the rate performance, but most of the results cannot be applied to actual production due to high cost and complicated process. Therefore, the search for a low-cost, simple way to obtain high-performance TiO$_2$ materials is still a hot spot in the research of anode materials in the future. This paper takes tetrabutyl titanate as raw material, carbon nanofibers (CNF) as substrate and creates a nanocomposite of TiO$_2$ and CNF named as CNF@TiO$_2$ by planting the TiO$_2$ nanosheets on the surface of CNF through solvothermal method.

2. Experimental Section

2.1. Activation of CNF
10 ml of deionized water and 500 mg of carbon nanofibers (CNF) were added to the three-necked flask, and then 30 ml of concentrated sulfuric acid were slowly added under the action of magnetic stirring, then 10 ml of concentrated nitric acid were added dropwise. After that, the three-necked flask was put into the oil pan for condensation and reflux for 8 h at 100 °C. When the reaction was completed, the supernatant was removed by centrifugation, and the obtained product was repeatedly washed and centrifuged with deionized water. When the product could not be centrifuged, it was transferred to a suction bottle and repeatedly rinsed with deionized water until the filtered deionized water was neutral, and then the product was placed in an oven and dried at 80 °C to obtain activated CNF.

2.2. Preparation of CNF@TiO$_2$ Composite Material
The activated CNF was put into a 50 ml beaker, and 10 ml of DMF was added. Then the beaker was placed in a magnetic stirrer. 30 ml of isopropanol was slowly added and mixed evenly. Then 1 ml of butyl titanate was added and dispersed by ultrasonication for 1 h to obtain a mixed solution. The
mixed solution was transferred to a 50 ml hydrothermal reaction vessel and placed in an oven at 200 °C for 20 h. Then, the obtained product was centrifuged and the precipitate was collected. Later, the obtained product was thoroughly washed with ethanol and dried in an oven at 80 °C for 12 h to obtain hydrogen titanium oxide hydrate, which was named CNF@HT. Subsequently, CNF@HT was placed in a tube furnace and heated to 450 °C at a heating rate of 1 °C min⁻¹ in nitrogen for 2 h to obtain a composite material of TiO₂ and CNF, named as CNF@TiO₂.

2.3. Preparation of CNF@TiO₂ Anode Material

The CNF@TiO₂ composite material prepared above was mixed with carbon black and PVDF binder in a ratio of 8:1:1, and the slurry was evenly spread onto the copper foil. After drying, the copper foil was punched into a circular pole piece with a diameter of 1.25 cm using a sheet-punching machine and adopted as lithium ion negative electrode material. The lithium sheet was used as counter electrode and reference electrode, and 1 M LiPF₆ was used as electrolyte. Then a button battery was fabricated in an argon-filled glove box for experiment.

3. Results and Discussions

In the experiments, commercially produced carbon nanofibers with a diameter of 100 to 200 nm and a length of about several tens of micrometers were used as carriers. Figure 1 shows the FESEM and TEM pictures of CNF@HT. It can be seen from figure 1a that after the solvothermal reaction, the hydrogen titanium oxide hydrate nanosheets are uniformly distributed along the axial direction on the surface of the carbon nanofibers and formed a dense coating layer, which constitutes the core-shell structure with carbon nanofibers as the core and the hydrogen titanium oxide hydrate nanosheet as the shell, and the core-shell composite has a diameter of about 400-500 nm. The microscopic morphology of CNF@HT was further studied by high-power FESEM and TEM, as shown in figure 1. From the FESEM photograph, it can be clearly seen that the CNF@HT shell is composed of unoriented ultra-thin nanosheets, and the nanosheets are interconnected to form a complete hierarchical network structure closely arranged on the carbon nanofiber substrate. The TEM photographs (figures 1d-1f) further confirm the above conclusion that the ultra-thin nanosheets are radially distributed on the surface of the carbon nanofibers.

When CNF@HT was calcined at a high temperature in nitrogen, it was converted into CNF@TiO₂. The FESEM and TEM photographs of CNF@TiO₂ samples are shown in figure 2. It can be seen from the FESEM photograph that the sample after high temperature calcination still maintains the overall morphology of the precursor. The TiO₂ nanosheets are more firmly and tightly grown on the surface of the carbon fiber, which reduces the structural defects of the titanium dioxide and improves the crystal structure and electronic structure, benefiting the transmission of lithium ions and electrons. The TEM photographs show that the surface of CNF@TiO₂ consists of ultra-thin nanosheets with a thickness of about a few nanometers. These nanosheets are interlaced to form a complex hierarchical network structure. The TEM analysis results are completely consistent with that of FESEM.

The XRD spectra of CNF@HT and CNF@TiO₂ samples are shown in figure 3. It can be seen from the XRD spectrum of CNF@HT (figure 3a) that the sample showed a distinct absorption peak at 8.9°, which matched with the hydrogen titanium oxide hydrate (JCPDS No. 44-0130). The XRD spectrum of the CNF@TiO₂ sample is shown in figure 3b. It can be seen from the figure that the diffraction peak coincides with the peak of TiO₂ (JCPDS No. 21-1272), which further confirms the complete conversion of CNF@HT after calcination. No characteristic peak of carbon is found on the XRD spectrum mainly due to the small amount of CNF and the outer layer being completely covered by the nanosheet of TiO₂.

The N₂ adsorption and desorption isotherm and pore distribution curves for the CNF@TiO₂ sample are shown in figure 4. It can be seen from the adsorption-desorption isotherm diagram that the sample has a significant hysteresis loop, indicating that it is mainly mesoporous; when p/p₀ is greater than 0.9, the adsorption amount is significantly increased, indicating that it has a large pore structure at the same time. It can be seen from the pore distribution curve that the pore size distribution of the sample
is wide, but it mainly consists of small mesopores of 2 to 10 nm, as well as some large mesopores of 10 to 50 nm and a small number of macropores. The macropores may be a result of the gap between the nanosheets. The BET specific surface area of the sample was 114.2 m² g⁻¹.

![Figure 1](image1.png)

**Figure 1.** (a-c) FESEM and (d-f) TEM characterizations of the CNF@HT.

![Figure 2](image2.png)

**Figure 2.** (a-c) FESEM and (d-f) TEM characterizations of the CNF@TiO₂.

![Figure 3](image3.png)

**Figure 3.** XRD patterns of (a) CNF@HT and (b) CNF@TiO₂.
The thermal weight loss test of CNF@TiO$_2$ was carried out in air atmosphere to study its thermal weight loss behavior. The heating rate was set to 10 °C min$^{-1}$, and the thermogravimetric curve obtained is shown in figure 5. It can be seen from the figure that when the temperature is lower than 200 °C, the thermal weight loss mainly manifests as the removal of the physically adsorbed water and the chemically bound water on the surface of the material; when the temperature is higher than 500 °C, the carbon nanofibers begin to burn and decompose; when the temperature is more than 700 °C, the carbon nanofibers gradually burned out, and the thermogravimetric curve showed a small weight loss with increasing temperature. The mass of CNF in the sample is about 16% of the total weight.

In this part, the application of CNF@TiO$_2$ as a negative electrode material in LIBs was further studied. By using CNF@TiO$_2$ as the active electrode material and lithium foil as the counter electrode and reference electrode, the electrochemical performance was studied in the half-cell system. Constant current charge and discharge tests were performed on LIBs composed of CNF@TiO$_2$ at a current density of 200 mA g$^{-1}$. The constant current charge and discharge curves of the first, second and fifth test are shown in figure 6a. It can be seen from the figure that there is a certain irreversible capacity during the first discharge/charge process, which may be caused by the SEI film formed in the decomposition of the electrolyte or incomplete decomposition of Li$_2$O. The specific capacity of the second discharge and charge was 319 mAh g$^{-1}$ and 301 mAh g$^{-1}$, respectively, and the coulombic efficiency was 94%. The charge and discharge curves of the fifth and the second test almost coincide, indicating that the electrode material has good structural stability. As shown in figure 6b that the specific capacity of CNF@TiO$_2$ electrode can still be maintained at 292 mAh g$^{-1}$ after 200 cycles at 200 mA g$^{-1}$, and the capacity retention rate can reach 91% compared with the second discharge specific capacity, indicating that the CNF@TiO$_2$ electrode material has stable cycle performance.

The rate performance curve of CNF@TiO$_2$ electrode material in 10 constant current charging and discharging cycle with different current densities of 200-4000 mA g$^{-1}$ is shown in figure 6c. When the current densities are 200, 400, 800, 1000, and 4000 mA g$^{-1}$, the average specific capacities are 310,
253, 211, 197, and 124 mAh g$^{-1}$, respectively. After 50 cycles, when the current density is reduced to 200 mA g$^{-1}$, the average specific capacity can be restored to 289 mAh g$^{-1}$, the attenuation rate is only 7% compared with the specific capacity at the initial, showing excellent rate capability. It is mainly attributed to its unique structural characteristics. The ultra-thin nano-sheet structure effectively increases the active site of the electrode/electrolyte interface, which is beneficial to the improvement of specific capacity. Meanwhile, it shortens the transmission distance of electrons and ions, improving the rate performance. Besides, the carbon fiber substrate facilitates the rapid transmission of electrons and increases the stability of the electrode material.

In summary, the CNF@TiO$_2$ electrode material exhibits high specific capacity and good cycle performance mainly due to the following three factors: First, the 2D nanosheet structure is beneficial to increase the contact area between the electrode material and the electrolyte, promoting the electrochemical reactions. Second, the gap between the nanosheets is beneficial to the storage of electrolyte and increases the ion transport rate. Third, the CNF skeleton facilitates electron conduction and ensures structural stability, thereby improving the cycle performance of the CNF@TiO$_2$ electrode material.

Figure 6. Electrochemical evaluations of the CNF@TiO$_2$ electrode: (a) charge-discharge voltage profiles at a current density of 200 mA g$^{-1}$; (b) cycling performance at a current density of 200 mA g$^{-1}$; and (c) the rate capability at different current densities.

4. Conclusions
In conclusion, we have fabricated the CNF@TiO$_2$ integrated electrodes by a simple solvothermal method followed by thermal treatment. Benefitting from the good contact between TiO$_2$ nanosheets and CNF backbone, the integrated electrodes own good electronic conductivity and structural stability. What's more, the 2D structure of TiO$_2$ nanosheets contributes to the diffusion of Li$^+$ ions. These structural features enable their application as promising integrated electrodes for lithium ion batteries. The CNF@TiO$_2$ integrated electrodes manifest outstanding cyclability and rate capability.

Acknowledgments
The authors acknowledge the financial support from the National Natural Science Foundation of China (Grant No. 21701090), the Natural Science Foundation of Inner Mongolia Autonomous Region of China (Grant No. 2017BS0203), and the Program of Higher-level Talents of Inner Mongolia University (Grant No. 21300-5165154).

References
[1] Goodenough J B, Kim Y. 2014 Chem. Mater. 22 587
[2] Tarascon J. M., Armand M. 2001 Nature 414 359
[3] Reddy M V, Subba Rao G V, Chowdari B V R. 2013 Chem. Rev. 113 5364
[4] S. Ding, Z. Wang, S. Madhavi, X. W. Lou 2011 J. Mater. Chem. A 21 13860
[5] Su X, Wu Q L, Zhan X, et al. 2012 J. Mater. Sci. 47 2519
[6] Chen Z, Belharouak I, Sun Y K, et al. 2013 Adv. Funct. Mater. 23 959
[7] H. B. Wu, X. W. (David) Lou, and H. H. Hng 2012 Chem. Eur. J. 18 3132