Preparation of bamboo carbon fiber and sandwich-like bamboo carbon fiber@SnO₂@carbon composites and their potential application in structural lithium-ion battery anodes

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Abstract: PAN-based carbon fibers have been studied in structural lithium-ion batteries (SLIBs), showing many better results and promises. However, the limitation in capacity is urgently solved. To remedy this shortage, one-dimensional (1D) bioinspired bamboo carbon fiber (BCF) and its composite (BCF@SnO₂@C) are successfully fabricated. In the BCF@SnO₂@C composite, the SnO₂ is sandwiched between the BCF template and the coated glucose-derived carbon, showing sandwich-like structure. Due to the combined superiority of bioinspired BCF with good conductivity and buffer effect and the SnO₂ with high theoretical specific capacity, the obtained BCF@SnO₂@C composites are expected to use as an anode material for traditional lithium-ion batteries and future structural lithium-ion batteries. A high reversible capacity of 627.1 mAh g⁻¹ is maintained over 100 cycles at a current density of 100 mA g⁻¹, showing a huge increase five times as high as the reported carbon fibers in SLIBs. Even at a high current density of 1000 mA g⁻¹, the substantial discharge capacity can still reach 409.1 mAh g⁻¹. These excellent performances in capacity could urgently solve the obsessional issue, the limitation of capacity in current SLIBs when use commercial carbon fibers as anode materials.

Keywords: structural lithium-ion batteries; anode; bamboo carbon fiber; sandwich-like structure

1. Introduction

Recently, due to their high conversion efficiency and good cycling performances, lithium-ion batteries (LIBs) have obtained huge success in electric vehicle and portable electronic devices [1, 2]. However, the current LIBs are only served as an electrical energy storage device. The ever-demanding standard is that the energy storage device can further include a mechanical structure [3]. This is to say, the energy storage device and the structural component should be combined into one unit, formation a combination in function and structure parts [4]. Thus, the storage of energy directly in the component of the device, such as the car door, roof etc. would meet ever-demanding standard, which is usually called as structural lithium-ion batteries (SLIBs) [3, 4].

This novel design could allow significant mass reductions. In one decade, the PAN-based carbon fibers have been studied in SLIBs, showing many better results and promises [3-7]. However, the most significant restriction in further practical application of SLIBs is relatively low theoretical capacity of the carbon fibers. Hence, this limitation in capacity is urgently solved. In recent years, the bamboo carbon fiber (BCF) has been explored, which shows many similar physical characteristics with the traditional PAN-based carbon fibers [8, 9]. Notably, the BCF also exhibited some advantages, such as being renewable, eco-friendly, and with good compatibility with other functional materials, *etc.* Therefore, the BCF reveals a wonderful application prospect in SLIBs to replace the traditional low-capacity carbon fibers.

In this work, the fabrication and application of the BCF in SLIBs is of great increasing interest. Experiment results also indicate that the BCF shows many improved results. To further enhance the capacity, we also prepare a bioinspired BCF@SnO₂@carbon (BCF@SnO₂@C) composite by using the BCF as a carbon resource and template, by combining the superiority of bioinspired carbon material and the high specific capacity anode material of SnO₂. After layer-by-layer fabrication, the composite with sandwich-like structure has many technological advantages to alleviate volume change during lithium insersion/exsersion process and thus leading to enhanced cycling performances when used as an anode material.

2. Experimental section

2.1 Preparation of the BCFs

The BCFs were prepared according to the previous literature with slight changes.[8] In a typical synthesis process, the bamboo chopsticks were initially processed into bamboo shavings and then cleaned by deionized water. After that, 1.0 g of bamboo shavings in 35 mL 6 M NaOH solution were put into a 50 mL Teflon-lined stainless steel autoclave, then maintained at 150 °C for 6 h and cooled naturally to room temperature. The as-prepared products were collected by vacuum filtration with common filter paper, washed with 150 mL distilled water only one time and dried in a vacuum oven at 60 °C overnight. Last, the BCFs were obtained by calcining the dried products at 700 °C for 2 h under a flowed Ar atmosphere. Subsequently, the BCFs were washed with distilled water several times to remove the residual NaOH and dried at 60 °C overnight. To further fabricate the composite with good combination between the BCFs and the active materials, the BCFs were pretreated by an acid treating process. In a typical process, 0.1 g of pristine BCFs was soaked in a 40 mL mixture of nitric acid and sulfuric acid (3:1 in volume) in a water bath for 12 h with magnetic stirring at room temperature. The resulting products were collected by filtration, washed with deionized water, and dried at 60 °C overnight.

2.2 Preparation of the BCF@SnO₂ and BCF@SnO₂@C composite

In a typical synthesis procedure, 12 mg of pretreated BCFs, 45.13 mg of SnCl₂·2H₂O and 200 mg of poly vinyl pyrrolidone (PVP) were dispersed in 30 mL deionized water under continuous ultrasonication for 0.5 h. Subsequently, the mixing was transferred to a 50 mL Teflon-lined autoclave, maintained at 180 °C for 4 h and cooled naturally to room temperature. The as-prepared BCF@SnO₂ products were collected by centrifugation, washed thoroughly by deionized water and absolute ethyl alcohol, and finally dried in a vacuum oven at 60 °C overnight. To fabricate the BCF@SnO₂@C composite, 12 mg of pretreated bamboo carbon fibers, different contents of glucose, 45.13 mg of SnCl₂·2H₂O and 200 mg of PVP were dispersed in 30 mL deionized water under continuous ultrasonication for 0.5 h. Herein, the contents of glucoses were set with two values of 200 mg and 500 mg, where the corresponding composites were denoted as BCF@SnO₂@C₁ and BCF@SnO₂@C₂, respectively. Then, the mixed solution was transferred to a 50 mL Teflon-lined autoclave, maintained at 180 °C for 4 h and cooled naturally to room temperature. The obtained products were collected,

washed, and finally dried. Last, the dried samples were heated to 400 °C with a ramp of 3 °C min⁻¹ and maintained for 2 h under a flowed Ar atmosphere. After that, tube furnace was allowed to cool to room temperature naturally, and the final BCF@SnO₂ and BCF@SnO₂@C composites were obtained.

2.3 Materials Characterization

The phase purity of the as-prepared products was determined by X-ray diffractometer (XRD, Bruker Corporation, Germany) with copper target at a scan rate of 4 °/min. The morphology was characterized by scanning electron microscope (SEM, HITACHI S-4800, Japan) at an acceleration voltage of 10 kV. Transmission electron microscopy (TEM) was performed on a FEI Tecnai G2 S-Twin instrument with a field emission gun operating at 200 kV. Thermogravimetric analysis (TGA) was performed in air from room temperature to 900 °C with a heating rate of 10 °C min⁻¹ by using an STA 449 Jupiter (NETZSCH) thermogravimetry analyzer.

2.4 Electrochemical Characterization

The N-methyl-2-pyrrolidone (NMP) slurries containing active material (BCF, BCF@SnO₂ and BCF@SnO₂@C composites), acetylene black and polyvinylidene fluoride (PVDF) with a weight ratio of 70:15:15 were coated onto a copper foil and then dried in a vacuum oven at 60 °C for 12 h. Then, the cells were assembled in a glove box filled with highly pure argon gas by using CR 2025 coin-type cell configuration with pure lithium as the counter electrode, a Celgard 2400 membrane as the separator, and 1 M LiPF₆ dissolved in ethylene carbonate and diethylene carbonate (1:1 in volume) as the electrolyte. The charge-discharge performance was tested between 0.01 V and 3.0 V using a programmable battery testing system (LAND CT2001A) at room temperature. The cyclic voltammogram (CV) measurements were performed on a BioLogic VMP3 Electrochemical Workstation.

3. Results and discussion

Fig. 1 shows the XRD patterns of the as-prepared samples. As presented in Fig. 1a, it can be clearly seen that the BCF after carbonization possess has one peak at around 26 °, corresponding to the (002) reflection of the graphitic stacking. Furthermore, the weak peak at 40~45 ° is the superposition of

the (100) and (101) reflections, which originates from the interlayer condensation and can efficiently enhance the conductivity of the sample [10, 11]. The XRD patterns of BCF@SnO₂, BCF@SnO₂@C₁ and BCF@SnO₂@C₂ composites are exhibited in Fig 1b-d, respectively. It can be seen that all diffraction peaks of these composites are in good agreement with the characteristic peaks of the SnO₂ phase (JCPDS 41-1445), indicating the pure phase of the active material in composites.

Fig. 2 shows the representative SEM images of the obtained products. The bamboos after alkali treatment in 6 M NaOH solution give the bamboo fibers, and carbonization of bamboo fibers gives the BCFs. As shown in Fig. 2a and Fig. S1 (Supporting Information), the diameters of the BCFs are varied from 4 μm to 12 μm , and with the mean diameter of approximately 7 μm , which is similar with the PAN-based carbon fibers in SLIBs [12]. Fig.2b shows the high-resolution SEM image of the BCFs, which presents the wrinkle-like surface morphology of BCFs. The SEM images of the BCF@SnO₂ composite are exhibited in Fig. 2c-d. The low-resolution one (Fig. 2c) shows that the BCF@SnO₂ composites are inherited the 1D structure from the BCFs (Fig. 2a). And the high-resolution one (Fig. 2d) displays that the SnO₂ coated on BCFs has the particle size ranging from decades nanometers to hundreds nanometers. Fig.2e and 2f present the high-resolution SEM images of BCF@SnO₂@C₁ and BCF@SnO₂@C₂ composites, respectively, which show different contents of amorphous carbon derived from glucose coated onto the SnO₂ layer to form the sandwich-like structure.

To determine the actual contents of BCFs and amorphous carbon in the composite, thermogravimetry analysis is conducted. As shown in Fig. 3a, the contents of BCF and SnO₂ in the BCF@SnO₂ composite are 33.84 wt. % and 66.16 wt. %, severally. The total carbon contents of the BCF@SnO₂@C₁ and BCF@SnO₂@C₂ composites are 43.23 wt. % and 56.34 wt. %, respectively. Therefore, the contents of amorphous carbon in the BCF@SnO₂@C₁ and BCF@SnO₂@C₂ composites are approximately 9.39 wt. % and 22.50 wt. %, respectively. To further confirm the structure of the composites, TEM analysis has been carried out. As shown in Fig. 3b, the thickness of SnO₂ layer in the BCF@SnO₂ composite is about 0.64 μm . Furthermore, the thicknesses of amorphous carbon layer in the BCF@SnO₂@C₁ and BCF@SnO₂@C₂ composites are approximately 65 nm and 140 nm, respectively.

On the basis of the advantages of its unique 1D morphology and the BCF-based structure, the obtained BCF and its composites are expected to meet potential application as anode materials for SLIBs. To easily evaluate their lithium storage performances, the CR 2025 coin-type half cell is

assembled with BCF and its composites as working electrode and pure lithium foil as both counter and reference electrode.

Fig. 4 shows the CV curves of the BCF and BCF@SnO₂ composite in the initial three cycles. In the first cycle of the BCF (Fig. 4a), a weak cathodic peak around 1.45 V is ascribed to the irreversible reactions between the electrode and electrolyte [13]. Another peak at about 0.35 V is associated with the electrolyte decomposition and the formation of the solid electrolyte interface (SEI) layer on the surface of the active materials [14]. Both the peaks do not appear in the second cycle, and would result in the large irreversible capacity loss in the first discharge. In the following cycles, all peaks are stable and reversible, which indicates the reactions of lithium insertion/extraction become highly reversible. The lithium intercalation reactions take place below 0.5 V and the lithium deintercalation process at broad anodic peak launches at 0.28 V, in agreement with many reported carbon species [8, 15]. Fig. 4b shows the CV curve of the BCF@SnO₂ composite in the initial three cycles. Similarly, a weak cathodic peak around 1.48 V in the first scan is ascribed to the irreversible reactions between the electrode and electrolyte. In the first cathodic sweep, the huge cathodic peak around 0.82 V is ascribed to the reductive transformation of SnO₂ to Sn and Li₂O and the subsequent decomposition of the electrolyte to form the SEI film. This peak disappears in the second cycle, reflecting the stable property of SEI film in the first cycle. Furthermore, it is replaced by a peak around 0.95 V in the following cycles, ascribed to the transformation of SnO₂ to Sn and Li₂O. The peak located at 0.1 V is corresponding to the alloying reaction of metallic Sn to Li_xSn ($x \leq 4.4$). During the anodic process, the peaks located at about 0.55 V and 1.3 V correspond to the dealloying reaction from Li_xSn to Sn and the delithiation reactions of Sn and Li₂O to SnO₂, respectively [16-17]. Except for the first cycle, all peaks are stable and reversible in the following cycles, reflecting the good electrochemical reversibility in the BCF@SnO₂ composite anode.

Fig. 5 shows the initial two charge and discharge curves of the BCFs, BCF@SnO₂, BCF@SnO₂@C₁ and BCF@SnO₂@C₂ composites measured between 0.01 and 3.0 V at a current density of 100 mA g⁻¹, respectively. The first discharge curve of BCFs (Fig. 5a) presents a big voltage platform at around 0.8 V, corresponding to the decomposition of the electrolyte and the formation of SEI film on the electrode surface. Another discernible voltage plateau below 0.5 V suggests the lithium intercalation reactions with BCFs. The initial specific discharge and charge capacities of the BCFs anode are 808.7 and 269.4 mAh g⁻¹ with an initial coulombic efficiency of 33.3%. The tremendous

irreversible capacity losses may be attributed to the formation of SEI film on the electrode surface in the first discharge. However, in Fig. 5b-d, the BCF@SnO₂ and BCF@SnO₂@C composites exhibit two voltage plateaus in the discharge process, reflecting the two-step lithium insertion process including conversion and alloying reaction. The voltage plateau around 0.95 V corresponds to the transformation of SnO₂ to Sn and Li₂O, and the voltage plateau below 0.6 V suggests the alloying reaction of Sn to alloyed Li_{4.4}Sn. The two-step reactions are all reversible in the cycles. In the charge curve, the voltage plateau around 0.5 V and 1.4 V are ascribed to the dealloying reaction from Li_xSn to Sn and the delithiation reactions from Sn and Li₂O to SnO₂, respectively. For the BCF@SnO₂ composite, the initial specific discharge and charge capacities of 1789.7 and 1035.1 mAh g⁻¹ are delivered with an initial coulombic efficiency of 57.8%. Compared with the BCFs, the discharge and charge capacities increase manyfold, indicating that the specific capacity of BCF@SnO₂ composite delivered mainly by the SnO₂ instead of the BCFs. For the BCF@SnO₂@C composites (Fig.5c-d), after coated with glucose-derived carbon on the surface of SnO₂ layer, the capacitive contribution from the carbon component leads to a wide potential window, particularly in the charge curve. Moreover, because of more carbon component in the BCF@SnO₂@C composites, the specific capacity is sacrificed.

Fig. 6 depicts the charge-discharge capacities *versus* cycle number profiles of as-prepared products at a current density of 100 mA g⁻¹. It can be seen that the BCFs anode exhibit long cycling stability, although with low specific capacity of 178.3 mAh g⁻¹ after 100 cycles. It is notable that this value of 178.3 mAh g⁻¹ is high than that of reported value (60-170 mAh g⁻¹) of the PAN-based carbon fibers in SLIBs, showing great prospect in SLIBs. Because of the high theoretical specific capacity of SnO₂, the BCF@SnO₂ composite delivers an enhanced discharge capacity of 1079.0 mAh g⁻¹ after first cycle. However, the specific capacity of bare BCF@SnO₂ composite displays a continuous decline. After 100 cycles, the specific discharge capacity has faded to 275.3 mAh g⁻¹. Therefore, we further improve the capacity retention of bare BCF@SnO₂ composite by introducing the glucose-derived carbon coated onto the surface of the SnO₂ layer to fabricate a sandwich-like composite. As shown in Fig. 6c, after a small number of carbon coated, the BCF@SnO₂@C₁ composite presents many enhancement in capacity retention. After 100 cycles, a high specific discharge capacity of 500.4 mAh g⁻¹ still maintains. Furthermore, after adequate carbon introduced, the cycling performances of the BCF@SnO₂@C composite obtains great improvement. As shown in Fig. 6d, though the second discharge capacity decays to 815 mAh g⁻¹, the BCF@SnO₂@C₂ composite shows a stable cycling

performance after the first cycle. A high reversible discharge capacity of 627.1 mAh g^{-1} is retained even after 100 cycles with high coulombic efficiency close to 100%. The good cycling performance of BCF@SnO₂@C₂ composite can be attributed to the sandwich-like structure with good conductivity and buffer effect to restrict volume change generated by SnO₂ in the charge/discharge process. Compared with the pure BCFs, there is a huge increase as high as 351.7% in discharge capacity. Furthermore, the discharge capacity of the BCF@SnO₂@C₂ composite displays almost five times as high as the T300 fiber (130 mAh g^{-1} at 10 cycles) in the application as anode material for SLIBs [12]. In consideration of the comparable capacity (as list in Table S1, Supporting Information) [6, 12], the 1D BCF and its composite show tremendous application prospect for SLIBs.

The high rate discharge abilities of the as-prepared products are shown in Fig. 7 measured at current densities of 100-1000 mA g^{-1} . As shown in Fig. 7a, the BCFs exhibit good rate discharge ability with average discharge capacities of 236.7, 181.5, 158.4 and 137.5 mAh g^{-1} at current densities of 100, 200, 500 and 1000 mA g^{-1} , separately. It cannot be ignored that the capacity of the BCF at a high discharge condition of 1000 mA g^{-1} is also higher than that of the reported PAN-based carbon fiber measured at a normal condition. However, although with high specific capacity, the BCF@SnO₂ presents poor rate discharge ability. Therefore, much improvement is still need to the enhancement of rate discharge ability. This barrier can be broken by introducing the glucose-derived carbon coated onto the surface of the SnO₂ layer. As shown in Fig. 7d, it can be seen that the BCF@SnO₂@C₂ composite electrode shows more decent rate capability in comparison with the BCF@SnO₂ and BCF@SnO₂@C₁ composites. Average discharge capacities of 758.8, 628.8, 499.8 and 409.1 mAh g^{-1} at current densities of 100, 200, 500 and 1000 mA g^{-1} are delivered, separately. Importantly, when the current density is lowered to 100 mA g^{-1} , the discharge specific capacity resumes well to 657 mAh g^{-1} and maintains at the value of 624.5 mAh g^{-1} even after 120 cycles. These enhanced capacity and cycling stability indicate a wonderful application prospect of the as-prepared products in SLIBs.

After the above-mentioned analysis, the splendid electrochemical performances of the BCF@SnO₂@C₂ composite can be attributed to the synergistic effect of SnO₂ active material and the bio-inspired conductive BCF matrix as well as the coated glucose-derived amorphous carbon. Firstly, the inner bamboo carbon fibers backbone functions as the robust scaffold and electric cables for electrons transfer, which can improve the cycling performance of composite. Secondly, the ion channel in the BCFs for ion transmission for bamboo may be the electronic transmission channel, and thus

enhancing the conductivity of BCFs and the BCF@SnO₂@C composites. Thirdly, the coated carbon layers on the outer surface of SnO₂ are responsible for positive mechanical protections, which can also contribute to improve conductivity of the BCF@SnO₂@C composites and buffer the volume change in charge/discharge process. Because of the comprehensive impacts of the above-mentioned factors, the BCF@SnO₂@C₂ composite exhibits enhanced electrochemical performances and are deemed as a promising candidate anode material for future SLIBs.

4. Conclusions

In summary, a scalable approach is developed to fabricate the bioinspired BCF and its composites with sandwich-like structure. In the composite, the BCFs are transformed from the bamboo chopsticks waste in hot alkaline solution as a carbon resource and a template for synthesis. Owing to the peculiar sandwich-like structure and the synergistic effect between the SnO₂ active material and the bio-inspired carbon matrix to accommodate volume variations during repeated charge/discharge cycles, the as-prepared BCF@SnO₂@C composite exhibits superior lithium storage performances in terms of discharge capacity, cycling stability and rate discharge ability. Based on the excellent electrochemical performances, the BCF@SnO₂@C composite is considered as one of promising candidate anode materials for future SLIBs. This work provides an effective way to combine the advantages of SnO₂ with high theoretical specific capacity and bioinspired bamboo carbon fiber with good conductivity and buffer effect. Also, point out an effective solution to solve the urgent issue that the limitation of capacity in current structural lithium-ion batteries when use commercial carbon fibers as anode materials.

Supporting Information

The supporting information is available free of charge via the Internet at <http://xxxxxxxxxxxxx>.

Acknowledgements

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Figures

Fig. 1. The XRD pattern of the as-prepared products, (a) BCFs, (b) BCF@SnO₂, (c) BCF@SnO₂@C₁ and (d) BCF@SnO₂@C₂ composites.

Fig. 2. The SEM images of the as-prepared products, (a-b) BCFs, (c-d) BCF@SnO₂, (e) BCF@SnO₂@C₁ and (f) BCF@SnO₂@C₂ composites.

Fig. 3. (a) The TG curves of the as-prepared products, the TEM images of the (b) BCF@SnO₂, (c) BCF@SnO₂@C₁ and (d) BCF@SnO₂@C₂ composites.

Fig. 4. The CV curves of the as-prepared products, (a) BCF and (b) BCF@SnO₂ composite.

Fig. 5. The charge/discharge curves of the as-prepared products, (a) BCFs, (b) BCF@SnO₂, (c) BCF@SnO₂@C₁ and (d) BCF@SnO₂@C₂ composites.

Fig. 6. The galvanostatic charge/discharge capacities vs. cycles number curves of the as-prepared products at a current density of 100 mA g^{-1} , (a) BCFs, (b) BCF@SnO_2 , (c) $\text{BCF@SnO}_2\text{@C}_1$ and (d) $\text{BCF@SnO}_2\text{@C}_2$ composites.

Fig. 7. The rate charge/discharge capacities vs. cycles number curves of the as-prepared products at different current densities ranging from 100 to 1000 mA g^{-1} , (a) BCFs, (b) BCF@SnO_2 , (c) $\text{BCF@SnO}_2\text{@C}_1$ and (d) $\text{BCF@SnO}_2\text{@C}_2$ composites.