



Bismuth nanosheets grown on carbon fiber cloth as advanced binder-free anode for sodium-ion batteries



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ABSTRACT

The bismuth nanosheets grown on carbon fiber cloth were designed. For sodium-ion batteries, the Bi/CFC electrode exhibited a high reversible capacity of 350 and 240 mAh g⁻¹ after 300 cycles at 50 and 200 mA g⁻¹, as well as a good rate capability. Besides, the electrode displayed two flat potential profiles during the charge/discharge process. The results suggest that the Bi/CFC electrode has excellent potential as an anode for sodium-ion batteries.

1. Introduction

Lithium-ion batteries (LIBs), as one of the most appropriate and promising electrical energy storage (EES) systems, have a wide range of applications such as in electric vehicles, portable devices, and smart grids [1,2]. However, overexploitation and exhaustion of lithium resources has seriously affected the sustainable development of LIBs in the longer term [3,4]. Therefore, sodium-ion batteries (SIBs), as supplement or alternative to LIBs, have attracted lots of attention in recent years due to the greater abundance and lower cost of sodium resources, as well as the analogous energy storage mechanism [5,6]. Up to now, the commercialization of SIBs has not been realized [7]. Graphite, which is the most commonly used commercial anode material for LIBs, is not suitable for SIBs since the large sodium atoms cannot be embedded into the graphite layers [8]. Thus, research focused on applicable anode materials for SIBs is imperative.

In general, there are several different categories of anode materials for SIBs such as alloy-based materials [9,10], carbon-based materials [11], titanium-based composites [12,13], and metal oxides and sulfides [14,15]. Among them, the alloy-based materials, such as Sn [16], Ge [17], P [18], and Sb [19–21], are considered promising anode owing to their high theoretical capacity. However, the main challenge for alloy-based materials is the enormous volume expansion which can cause pulverization of the electrode material during the repeated sodium deinsertion/insertion processes [22,23]. Therefore, an efficient approach is to use composites of carbon materials [12], as they can partially reduce the volume expansion, simultaneously improving the conductivity of the electrode.

Recently, bismuth (Bi) is expected to be a viable anode material for SIBs due to its unique layered crystal structure [24]. Importantly, it is different from the above alloys in that the mechanism of Na-ion embedding is *via* intercalation instead of the alloying process [25]. However, bismuth anodes for SIBs are rarely reported. Carbon fiber cloth (CFC), as one of the conductive carbon substrates, is usually used to prepare flexible electrodes [26]. The potential of such flexible electrodes in wearable devices is enormous [27,28].

In this paper, the synthesis and electrochemical properties of Bi/CFC are reported. For SIBs, the Bi/CFC electrodes exhibited a high capacity of 350 mAh g⁻¹ after 300 cycles at 50 mA g⁻¹ (capacity retention ~ 93.2%) and 240 mAh g⁻¹ after 300 cycles at 200 mA g⁻¹ (capacity retention ~ 74%), as well as a good rate capability.

2. Experimental

0.233 g Bi₂O₃ (Sigma-Aldrich, purity > 99.0%) was added into a mixed solution of 35 mL ethylene glycol and 10 mL ethanol. After sonication for 30 min, the suspension was transferred into a 50 mL autoclave liner, and a piece of CFC (CeTech, Taiwan, cut into 2 cm × 2 cm, cleaned using acetone, ethanol and deionized water in turn, then treated using concentrated nitric acid by refluxing at 70 °C for 2 h) was placed into it. The assembly was sealed in a stainless steel autoclave, and the reaction was carried out at 200 °C for 12 h. After naturally cooling down, the CFC was soaked in diluted hydrochloric acid (2 mol L⁻¹) for 12 h in order to remove excess Bi₂O₃, and then washed several times with ethanol and distilled water. The final product was obtained by drying the CFC at 60 °C over night.

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The crystal structure and phase of Bi/CFC were characterized by XRD measurements, which were performed on a D/max 2500 X-ray diffractometer with Cu/K α radiation ($\lambda = 1.54178 \text{ \AA}$). The morphology was analyzed by field emission scanning electron microscopy (FESEM, FEI Nova NanoSEM 230, 20 kV). Detailed structural information was further obtained by transmission electron microscopy (TEM) and high-resolution TEM (HRTEM, FEI Tecnai G2 F20, 200 kV) characterization.

The flexible Bi/CFC was cut into pieces of $0.8 \text{ cm} \times 0.8 \text{ cm}$ and used as working electrodes (the calculation of the capacity was based on the loading mass of Bi nanosheets $\sim 1.2 \text{ mg cm}^{-2}$ and the side of more load was in the face of sodium foil). The electrolyte was 1 M NaPF $_6$ in ethylene carbonate, dimethyl carbonate, and ethyl-methyl carbonate (EC/DMC/EMC + 5% FEC, volume ratio of EC:DMC:EMC was 1:1:1), and a glass fiber (Whatman GF/D) was used as the separator. CR2016 coin cells were assembled in an Ar-filled glovebox, and their galvanostatic charge/discharge measurements were carried out on a LAND battery tester (Land CT2001A, China), while the cyclic voltammetry (CV) tests were carried out on a CHI 660C electrochemistry workstation. The electrochemical impedance spectrometry (EIS) were performed on a ZAHNER-IM6ex electrochemical workstation (ZAHNER Co., Germany).

3. Results and discussion

Fig. 1a schematically illustrates the synthesis route of the composites. After hydrothermal reaction, the hexagonal bismuth nanosheets disorderly grew on the smooth surface of the CFC. The XRD patterns of Bi/CFC and pure Bi powder (the remaining powder in the autoclave liner) are shown in Fig. 1b. The diffraction peaks in both the patterns can be well indexed to a hexagonal structure (JCPDS No. 44-1246). However, unlike the pure Bi powder, the Bi/CFC pattern shows a broad peak at about 26° that can be assigned to the characteristic peak of carbon.

The morphology and crystal structure of Bi/CFC are shown in Fig. 2. As shown in Fig. 2a, each carbon fiber is completely covered by sheet-like Bi. The high magnification SEM images (Fig. 2b and c) show that the Bi sheets are disordered, with many small nanosheets stacked together. Fig. 2d and e show a hexagonal morphology for Bi nanosheets, with an average size of about 200 nm. The inset of Fig. 2e displays the SAED image, which reveals that the nanosheets grew in six directions ($\pm [110]$, $\pm [010]$, and $\pm [-100]$) at an almost constant speed. The HRTEM image (Fig. 2f) shows the d-spacing of the lattice fringe as 0.2285 nm, corresponding to the (110) plane of Bi. The energy dispersive spectroscopy (EDS) elemental mapping images show the composition of Bi and C in Bi/CFC (Fig. 2g).

Fig. 3 shows the electrochemical performance of the Bi/CFC anode

for SIBs. As shown in Fig. 3a, the CV curves of the Bi/CFC electrode exhibit two sets of peaks at a scan rate of 0.1 mV s^{-1} within the voltage range of 0.01–2.0 V (vs. Na/Na $^+$). In the cathodic process (the insertion of sodium ions), two peaks are observed around 0.5 and 0.3 V, corresponding to the two peaks around 0.7 and 0.77 V in the anodic process (the de-insertion of sodium ions), which is consistent with previous reports [24,25,29]. The well-overlapped CV curves in the 2nd and 3rd cycles reveal the reversibility of the electrode reaction. The inset in Fig. 3a shows the CV curves of the CFC at 0.1 mV s^{-1} . It reveals that the CFC contributes very little to the capacity of Bi/CFC.

The galvanostatic discharge/charge curves of the Bi/CFC electrode at 50 mA g^{-1} are shown in Fig. 3b. The first cycle delivers an initial discharge capacity of 737 mAh g^{-1} and a charge capacity of 451 mAh g^{-1} , with a coulombic efficiency of 61.2%. The theoretical capacity of Bi is about 385 mAh g^{-1} [24]. The excess Na-storage capacity and low coulombic efficiency of the initial cycle due to the formation of a solid electrolyte interface (SEI) film and some irreversible reactions [30]. The 20th, 50th, 100th, and 300th curves well coincide, demonstrating the stable structure of Bi/CFC. Moreover, there are two obvious voltage platforms located around 0.5 V and 0.3 V in the discharge cycle, which are consistent with the cathodic process in the CV curves. The voltage platforms at 0.67 and 0.77 V are in good agreement with the anodic process.

The rate performance of the Bi/CFC anode is presented in Fig. 3c. When the current density returned to 50 mA g^{-1} , the electrode could still deliver a discharge capacity of 346 mAh g^{-1} after 100 cycles. Fig. 3d shows the cycle performance of Bi/CFC and Bi powder. The Bi/CFC electrode maintains a reversible capability of 350 mAh g^{-1} at 50 mA g^{-1} after 300 cycles, with a capacity retention of 93.2% (compared to the 10th cycle). Even at a higher current density of 200 mA g^{-1} , it displays a discharge capacity of 240 mAh g^{-1} after 300 cycles (capacity retention $\sim 74\%$). In contrast, the Bi powder electrode shows a poor cycle performance with rapid decline of capacity. The inset in Fig. 3d shows the cycle performance of CFC at 200 mA g^{-1} , which again indicates the minor contribution of CFC to the Bi/CFC capacity. And the overall sheets-like morphology was partially retained after 100 and 300 cycles, respectively (insets in Fig. 3d), suggesting the good structural stability of Bi/CFC upon cycling.

In order to better comprehend the excellent electrochemical performance of the Bi/CFC electrode, EIS measurements of Bi/CFC and pure Bi powder electrodes are shown in Fig. 4. The R_{ct} of Bi/CFC is about 473Ω , which is significantly less than that of the pure Bi powder ($\sim 986 \Omega$). The results indicate that the CFC can highly improve the electronic conductivity and charge transfer reactions of the electrode.

There are only a few reports about bismuth anodes for SIBs. Su et al.

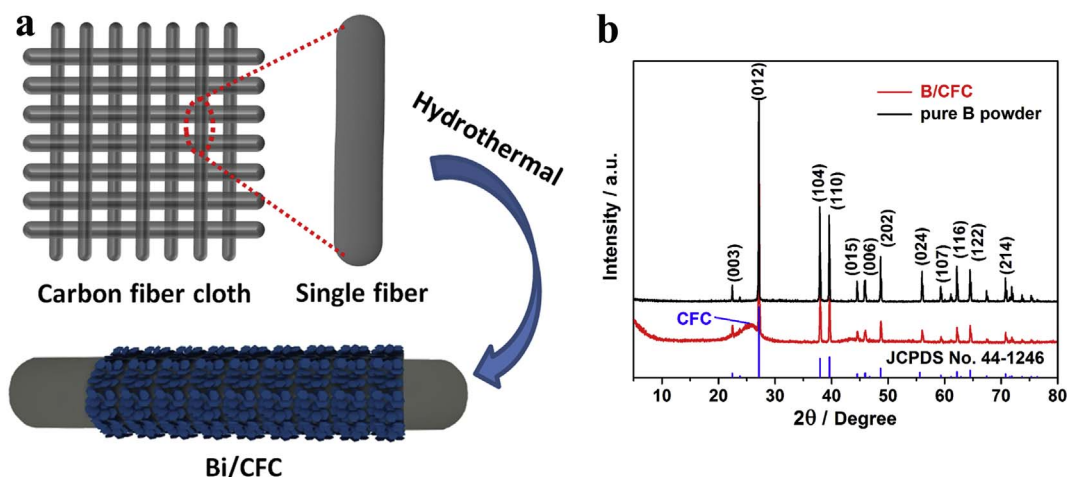


Fig. 1. (a) Schematic illustration of Bi/CFC, and (b) XRD patterns of Bi/CFC and pure Bi powder.

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