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Electrospun carbon–cobalt composite nanofiber as an anode material for lithium ion batteries

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Carbon–cobalt (C/Co) composite nanofibers with diameters from 100 to 300 nm were prepared by electrospinning and subsequent heat treatment. They were characterized by X-ray diffraction, scanning electron microscopy, galvanostatic cell cycling and impedance spectroscopy. As a lithium storage material, these fibers exhibit excellent electrochemical properties with high reversible capacity (>750 mA h g^{-1}) and good rate capability (578 mA h g^{-1} at 1 C rate). These composite fibers are a promising anode material for high-power Li-ion batteries.

Keywords: Electrospinning; Polymer matrix composite; Fibers; Electrochemistry

Owing to their unrivalled energy density and long cycle life, Li-ion batteries are widely regarded as the most promising power sources for electric vehicles and power tools. To fabricate better Li-ion batteries, it is very important to explore novel materials for battery components, including cathode, anode and electrolyte [1]. As the most widely used anodes, conventional carbon materials require high-temperature treatment (usually >2000 °C) to form a graphitic layered structure yet their capacity for lithium storage is limited to less than 372 mA h g^{-1}. Thus, new carbon materials with lower costs and improved electrochemical properties are desirable. During recent years, various kinds of carbonaceous materials including particles [2,3], fibers [4–6] and nanotubes [7,8] have been investigated as potential anode materials. As a result of their high specific surface area, carbon nanofibers were found to be able to effectively reduce the distance of Li-ion diffusion and lead to low resistance and high capacity of the electrode at a large current rate [9,10]. Ortiz et al. used a chemical vapor deposition process to synthesize a carbon fiber at 1000 °C that could achieve a reversible capacity of up to 350 mA h g^{-1} [9]. Recently, Kim et al. fabricated carbon fibers by electrospinning at room temperature followed by heating at 1000 °C [10]. Their carbon fibers attained a reversible capacity of up to 500 mA h g^{-1}. However, it should be noted that these carbon materials are all synthesized or annealed at a relatively high temperature of >700 °C since carbons obtained at a low temperature usually have a rather high resistance and a large irreversible capacity. On the other hand, a carbon material obtained at a low temperature can usually store more lithium [11,12]. Thus, in this work, a new strategy is adopted to retain the high capacity of the low-temperature carbons and improve the electrical conductivity by introducing a metallic second phase. Specifically, a carbon–cobalt (C/Co) composite nanofiber is fabricated via electrospinning and a subsequent low-temperature thermal treatment. These C/Co composite fibers exhibit a discharge capacity of over 800 mA h g^{-1} even after 50 cycles.

Four grams of polyacrylonitrile (PAN, Mw ≈ 86,000) was dissolved in 50 ml dimethylformamide to form a polymeric precursor solution. In another precursor solution, 5 g of $Co(CH_3COO)_2 \cdot 4H_2O$ was also added to the above solution (i.e. its composition was 0.02 mol Co in 4 g PAN). Each of the solutions was transferred into a 1 ml syringe with a stainless steel needle (0.6 mm diameter) to prepare a nanofiber. A positive direct current (DC) voltage of 10–11 kV was applied between the needle tip and a flat copper foil which was 12 cm away and was used as a fiber collector. A syringe pump controlled the flow rate of the precursor solutions to 2.5 μl min^{-1}. Under these conditions, a pure PAN nanofiber and a

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cobalt-containing PAN-based nanofiber were separately generated and collected on the copper foil. Then they were pre-oxidized at 230 °C in air for 6 h, causing the color of the fibers to change from white to brown. They were then treated at 600 °C under a high-purity argon atmosphere for 10 h to cause them decompose into carbon or carbon-based nanofibers. To determine the carbon yield after the heat treatment, the pure PAN fiber was dried at 80 °C for 12 h and then weighed before the pre-oxidation and after the 600 °C heat treatment.

The structures of the fibers were examined by X-ray diffraction (XRD) (Philips X'Pert Pro Super; Cu K_α radiation, $\lambda = 0.15405$ nm). The fiber morphology was observed under a scanning electron microscope (SEM) (Hitachi X-650). The electrochemical properties of the nanofibers were characterized using 2032 coin cells. The carbon-based fibers were adhered onto a copper foil with a polyvinylidene difluoride (PVDF) binder (C:PVDF = 10:1 w/w) to make working electrodes. A lithium metal sheet was used as the counter electrode. The electrolyte was 1 M $LiPF_6$ in ethylene carbonate/diethyl carbonate (1:1 v/v). A few C/Li and C(Co)/Li half-cells were assembled in an argon-filled glovebox (M. Braun Labmaster130) with moisture and oxygen levels less than 1 ppm. These cells were cycled in the voltage range between 3.0 and 0 V on a multichannel battery cycler (Neware BTS-610). At the end of discharge in the 30th cycle, the impedance spectra of the cells were measured with an electrochemical workstation (CHI 604B) in the frequency range 0.01–100 kHz.

The microimages of the electrospun PAN fiber and the carbon-based fibers are shown in Figure 1. The as-electrospun PAN fiber (Fig. 1a) exhibits a very long and straight fibrous morphology with smooth surface. The diameter of the fiber ranges from 100 to 250 nm. After the annealing at 600 °C, such a morphology remains virtually intact but the fiber tends to bend and thin somewhat (Fig. 1b) owing to a large weight loss, which is approximately 50% according the weight change before and after the heat treatment. Figure 1c shows the image of the cobalt-containing composite fiber after the 600 °C annealing. A similar fibrous morphology is obtained except that the fiber is thicker, with diameters from 100 to 300 nm.

Figure 2 shows the XRD patterns of 600 °C annealed carbon fibers. For the fiber containing no cobalt (Fig. 2a), the broad peaks near 25° and 55° correspond to the (002) and (004) diffraction peaks of graphite (JCPDS 75-1621), suggesting that the PAN fiber has been completely converted into disordered carbon. For the cobalt-containing fiber (Fig. 2b), three peaks near 44°, 52° and 75° are detected. They correspond to the (111), (200) and (220) diffraction peaks of cobalt metal (JCPDS 15-0806). Because cobalt acetate decomposes at a temperature of around 200 °C [13], cobalt oxide should be obtained in the composite when the pre-oxidation is carried out at 230 °C. As the temperature further increases in the annealing process, PAN decomposes gradually into carbon, which can also reduce the cobalt oxide into metal at the high temperature, i.e. $CoO + C \rightarrow Co + CO$ (g). Thus, the final product is a carbon–cobalt composite. Assuming the complete conversion of cobalt oxide into metallic cobalt and a fully

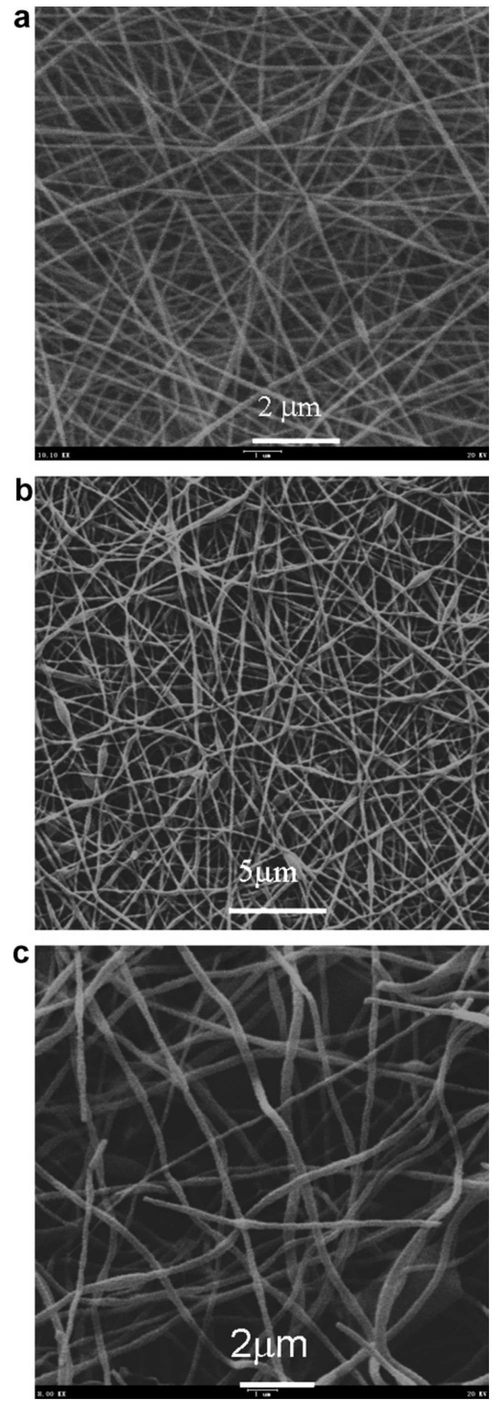

Figure 1. SEM images of the PAN fiber (a), carbon fiber (b) and C/Co composite fiber (c).

dense morphology of the fibers, the composition of the C/Co composite is C (60 wt.%)–Co (40 wt.%) or C (86 vol.%)–Co (14 vol.%). Based on the XRD pattern (Fig. 2b), the crystallite size of cobalt can be estimated from Scherrer's equation to be about 20 nm. It is much smaller than the diameter of carbon fibers, indicating that the cobalt particles can be easily dispersed in the fibers.

These two kinds of carbon-based fibers can be evaluated as potential lithium storage materials in C/Li half-cells. Figure 3 shows the electrochemical behavior of a