

The Preparation of C/Ni Composite Nanofibers with Pores by Coaxial Electrospinning

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ABSTRACT

PAN/Nickel acetate/PVP composite nanofibers were prepared by coaxial electrospinning and porous C/Ni composite nanofibers as anode materials for Li-ion battery were produced via peroxidation and carbonation. XRD, FE-SEM and TEM were used to investigate the morphology of the composite nanofibers. Results showed that fiber surface had obvious porous structure. Ni was cubic crystalline and the particle size was 20-90 nm. The electrochemical cycling performance was tested in the current density of 50mA/g. The first charge capacity of the porous composite nanofibers was 605mAh/g. The reversible specific capacity of the nanofibers was 435mAh/g after the 20th cycle, and the charge-discharge efficiency was 97.44%.

INTRODUCTION

Because of the excellent performance of nanomaterials, they have been widely applied in the field of lithium ion battery [1]. At present, carbon nanofibers are the dominant anode materials for lithium ion battery. However, a passivation film would form on the fiber surface after the first charge-discharge cycle, resulting in high capacity loss [2]. The application of Ni nanoparticles in carbon nanofibers can

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improve the conductivity, thus retard the formation of passivation films and reduce the irreversible capacity effectively. Ji et al [3] produced the C/Ni composite nanofibers as the anode materials for lithium ion. The first lithium specific capacity was up to 1020 mAh/g. The first cycle efficiency in Kulun was 77.9%, and the 20th and 40th time specific capacity was 565 mAh/g and 540 mAh/g, respectively.

Electrostatic spinning method has the advantages of simple process and low cost, which is currently the only method to prepare continuous Nano carbon fiber [4]. In this study, polyacrylonitrile (PAN)/nickel acetate/polyvinyl pyrrolidone (PVP) composite nanofibers were prepared by coaxial electrospinning, and porous C/Ni composite nanofibers were obtained after preoxidation and carbonization. Finally, the electrochemical performance of the C/Ni composite nanofibers was investigated systematically.

EXPERIMENTAL

Preparation of The PAN/Nickel acetate/PVP Composite Nanofibers

PAN/nickel acetate solutions (weight ratios of PAN and nickel acetate were 10:0, 9:1, 7:3, 5:5) were prepared in DMF with a stirring process for 10h. Therefore, the solutions to construct the cortex layer were got. Next, 30wt% PVP solution was prepared by dissolving PVP chips in DMF with stirring for 10h, so as to make solutions for the core layer. The PAN/nickel acetate solutions PVP solutions were loaded into the 20 ml syringes. The grounded stainless roller covered with aluminum foil was the receiving device with a tip-to-collector distance of 15 cm. The flow rate was 0.4 ml/h for the PAN/nickel acetate solutions and 0.2 ml/h for the PVP solutions, respectively. The spinning voltage was set at 15kv.

Preparation of The Porous C/Ni Composite Nanofibers

Preoxidation of the PAN/nickel acetate /PVP composite nanofiber mats was as follows: Raise the temperature from room temperature to 250 °C at a 5 °C/min increasing rate; then hold the temperature at 250 °C for 6 h. Increase the temperature from 250 °C to 800 °C at the rate of 2 °C/min and then last for 8 h in the nitrogen protection atmosphere. Finally, the porous composite nanofibers and the solid composite nanofibers were produced, respectively.

Characterization of The Nanofiber Structure and Morphology

XRD analysis was performed on the D8 Advance X ray diffraction ($\text{CuK}\alpha$, $\lambda=0.15406$ nm). Sol-X solid state detector was used to measure the intensity of the X-ray. The scanning speed was 4° /min and the step length was 0.02°. Morphologies of the porous C/Ni composite nanofibers and the solid C/Ni composite nanofibers

were analyzed by S-4800 FE-SEM. Microstructures of the porous C/Ni composite nanofibers were examined by JEM-2100 TEM.

Battery Charge-discharge Performance Test

The porous C/Ni composite nanofiber mats, acetylene black and PTFE emulsion were mixed in a mass ratio of 8:1:1. The mixture was pressed to 0.05 mm thick membrane and cut to 1.4 cm circular sheets. The metallic lithium pieces were used as the counter electrode and the electrode, and the Celgard 2400 membrane was the separator. 1 mol/l LiPF₆/EC+DMC+EMC (volume ratio of 1:1:1) was electrolyte. The simulated battery was assembled in the glove box filled with argon. Charge-discharge performance of the battery was tested in the BTS-5V1mA battery test system with the current of 50 mA/g and voltage of 0.01 ~ 3 V.

RESULTS AND DISCUSSION

SEM Analysis

Figure 1 showed the SEM images of the C/Ni composite nanofibers. When the nickel acetate content was low, there were no pores in the fibers in Figure 1(a) and Figure 1(a). As the nickel acetate content increased, porous structure can be found in Figure 1(c) and Figure 1(d). The fiber diameter was about 100nm~300nm, and the average aperture was about 30nm. With the increase of nickel acetate content, the cortex solution viscosity decreased and conductivity of the cortex solution increased, and the surface tension of the cortex solution decreased, too. As a result, more core layer solutions diffused into the cortex solutions. After the cortex constituent dissipated during the calcination process, the fiber surface formed a porous structure.

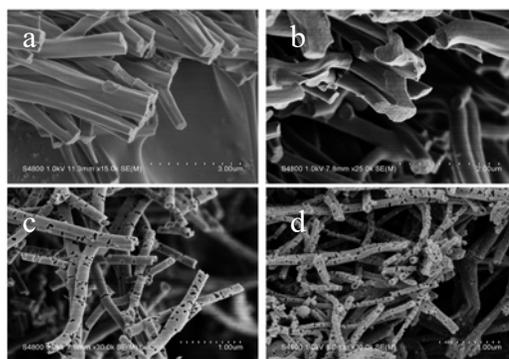


Figure 1. SEM images of the C/Ni composite nanofibers with different solution concentrations. (a) $m_{\text{PAN}}:m_{\text{nickel acetate}} = 10:0$, (b) $m_{\text{PAN}}:m_{\text{nickel acetate}} = 9:1$, (c) $m_{\text{PAN}}:m_{\text{nickel acetate}} = 7:3$, (d) $m_{\text{PAN}}:m_{\text{nickel acetate}} = 5:5$.

TEM Analysis

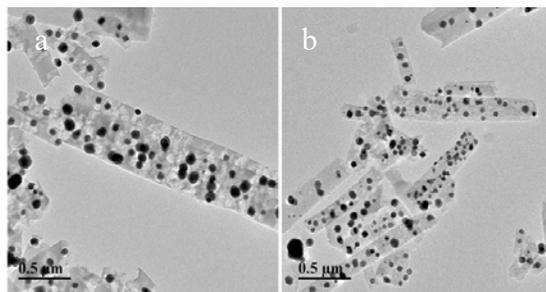


Figure 2. TEM pictures of the porous C/Ni composite nanofibers.

(a) $m_{\text{PAN}}:m_{\text{nickel acetate}} = 7:3$, (b) $m_{\text{PAN}}:m_{\text{nickel acetate}} = 5:5$

TEM pictures of the porous C/Ni composite nanofibers were shown in Figure 2. It can be seen that Ni dispersed uniformly in the porous C/Ni composite nanofibers. The average particle size of Ni was about 45nm. The amount of Ni particles in Figure 2(b) was more than that in Figure 2(a), which was because that the mass ratio of nickel acetate nickel in Figure 2(b) was higher than that in Figure 2(a).

X-ray Diffraction Analysis

Figure 3 was the XRD analysis result of the C/Ni composite nanofibers after calcination with different solution concentrations. It can be seen that the characteristic peaks was at about 25° , which was corresponding to the peak of C generated during fiber carbonation. However, the peak intensity was weak. When the nickel acetate content was 10%, the characteristic peak of Ni was weak. On the contrary, characteristic peaks appeared at 44.4° , 51.7° and 76.3° when the nickel acetate content was 30% and 50%, respectively, corresponding to the crystal face of (111), (200) and (220).

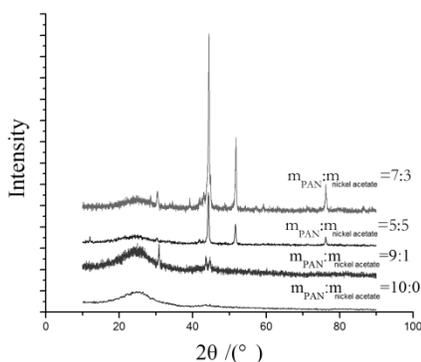


Figure 3. XRD analysis of the C/Ni composite nanofibers after calcination.

Electrochemical Performance Analysis

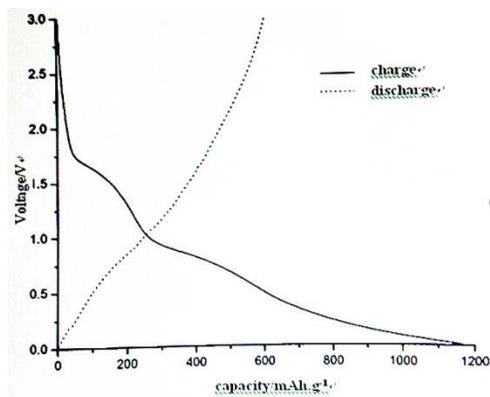


Figure 4. First charge-discharge curves of the porous C/Ni composite nanofibers.
(mPAN:m nickel acetate = 7:3)

As shown in Figure 4, the voltage quickly reduced to 1.75 V in the initial charge process; then the charge speed gradually slowed down until the specific capacity reached 1162 mAh/g. For the first discharge capacity, the initial irreversible capacity was 605 mAh/g, and the first charge-discharge efficiency was only 52.06%. This was mainly because that the porous C/Ni composite nanofibers had large specific surface area, the SEI films generated in the first cycle of 0.01 V ~ 1 V consumed the majority of lithium ions. The irreversible capacity occupied almost 50% of the charge capacity.

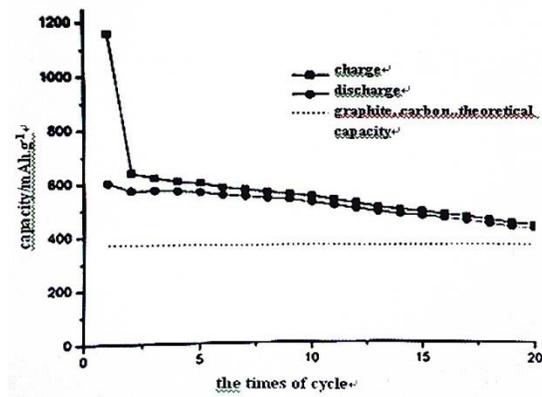


Figure 5. Cycle performance curves of the C/Ni porous composite nanofibers.
(mPAN:m nickel acetate = 7:3)

Figure 5 showed the cycle performance curves of the C/Ni porous composite nanofibers. As can be seen, the capacity of the porous composite nanofibers drop significantly during the first two cycles. The discharge specific capacity changed from 605 mAh/g to 575 mAh/g. However, the capacity decreased slowly during the third cycle. There was 435 mAh/g discharge specific capacity remained after the 20th cycle, which was higher than that of the theoretical capacity of graphite carbon (375mAh/g). Charge and discharge efficiencies increased from the second cycle, and the efficiency reach 92% in the third cycle. Moreover, the irreversible capacity gradually reduced. Therefore, the porous C/Ni composite nanofibers possessed good cycle performance and low discharge capacity reduction. Except that the first charge-discharge irreversible capacity was high and the first cycle efficiency was low, cycle performance of the C/Ni porous composites nanofibers during the following charge-discharge cycles were excellent.

CONCLUSIONS

PAN/Nickel acetate/PVP composite nanofibers are prepared by coaxial electrospinning and porous C/Ni composite nanofibers as anode materials for Li-ion battery are produced via preoxidation and carbonation. The first charge capacity of the C/Ni porous composite nanofibers is 605mAh/g and the reversible specific capacity of the nanofibers is 435mAh/g after the 20th cycle. It can be found that the porous C/Ni composite Nano materials have good charge-discharge performance, but their large capacity reduction needs further study.

ACKNOWLEDGEMENTS

This work was supported by the Science and Technology Research Projects of Hebei Universities (QN2016225) and the Five Platform Open Funds of Hebei University of Science and Technology (2015PT60).

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