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Preparation and Electrochemical Properties of Hollow Nickel Oxide Fibers

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In order to make better use of nano-nickel oxide particles, hollow nickel oxide fibers (HNOFs) were prepared by electroplating nickel particles on the surface of mesophase pitch based carbon fibers (MPCFs) and then burned off the carbon fibers under air atmosphere. Scanning electron microscopy showed that the HNOFs had hollow holes in center with diameter about 10 μm and the HNOFs fiber wall were made up of nickle oxide nanoparticles whose sizes ranged from 10 to 500 nm. The thickness of HNOF fiber wall can be controlled from tenths of micrometer to tens of micrometer. Thermogravimetric analysis and X-ray diffraction indicated that the nickel coated on MPCF surface was oxidized to nickel oxide when the heat treatment temperature was higher than 400 ℃ and the MPCF substrate decomposed when the temperature was higher than 600 ℃. Moreover, the nickel oxide had a high crystallinity when the heat treatment temperature was higher than 700 ℃. To be used as electrode for supercapacitor, the HNOFs showed well electrochemical properties. The specific capacitance of HNOFs with 0.8 μm fiber wall was 480 F/g with the current of 50 mA/g.

Keywords: Nanoparticles; Nickel oxide; Hollow fiber; Electrochemical properties

1. INTRODUCTION

NiO nanoparticles are very prosperous material with small dimension, high specific surface area and well chemical activity. Due to these advantages, NiO nanoparticles have extensively attracted interests in many applications, especially in catalyst [1] and supercapacitors [2, 3]. There are many methods to prepare NiO nanoparticles, including thermal treatment of electrodeposited or sol-gel prepared nickel hydroxide [4-6], liquid-phase process [7, 8], spray pyrolysis method [9, 10] and rotating ring-disk electrode method [11]. Carbon paper, carbon nanotubes [12] and stainless steel [13] have been used as current collector substrate, and nickel hydroxide was deposited on substrate surface. Thin NiO film formed after the as-deposited nickel hydroxide was heated in air at 300 ℃ and exhibited well electrochemical properties. To enhance the specific capacitance of NiO capacitor, it is necessary to augment the surface area of NiO film and improve the operability of the prepare process.

Compared to plate and film, the shape of hollow fiber has larger surface area. So, it is useful to prepare the NiO film into a shape of hollow fiber. Moreover, electroplating has been commonly used in industries. The particles plated on roughness substrate have a size in nanometer scale [14]. MPCFs possess high electric conductivity and have many grooves along fiber axis which make metallic ions can be electroplated onto MPCF surface easily. Therefore, nickel oxide nanoparticles could be facilely prepared by electroplating method. The particle size and the thickness of coating could be controlled by the electroplating current density and time.

In this paper, HNOFs were successfully prepared by electroplating nickel particles on the surface of MPCFs. The structure of carbon fibers was too dense, therefore, there was not enough pores in carbon fibers to store electric charge. In order to enhance the specific capacitance, the carbon fiber substrate was burn off under air atmosphere. The generation process, structure and specific capacitance of HNOFs were studied.

2. EXPERIMENTAL

2.1. Preparation of MPCFs

Naphthalene-based AR mesophase pitch produced by the Mitsubishi Gas-Chemical Company was used. The mesophase pitch was melt-spun at 320 ℃ and extruded through a spinneret under the press of nitrogen gas. The as-spun fibers were oxidatively stabilized in air at 260 ℃ and then carbonized in pure N_2 gas at 1000 ℃. The MPCFs prepared have average diameter about 10 μm and electrical resistivity about 19 μΩ·m (The main properties of MPCFs are similar to Thornel-P25).

2.2. Preparation of HNOFs

The plating process was as shown in Fig.1. The prepared MPCFs were cut into 10 cm long. A cluster of cut fibers were dispersed by hand and immersed into plating solution. One ends of fiber cluster was connected to cathode of power. The plating solution was consisted of nickel sulfate hexahydrate (270 g/L), nickel chloride hexahydrate (70 g/L), boric acid (40 g/L) and frother (0.1~0.5 g/L). Nickel sheet was used as anode. The nickel particles were deposited on the surface of carbon fibers under a constant current for a certain time. Two current densities were used: 1 A/m^2 for 2 hours and 10 A/m^2 for 0.5 hours. HNOFs electroplated with 1 A/m^2 and 10 A/m^2 current density were named as HNOF-1 and HNOF-10 respectively. After deposition, the deposited fibers were rinsed several times with de-ionized water and then dried at 100 ℃ for 6 h. The HNOFs were generated by burning off the carbon fibers in air at 900 ℃ for 2 h.

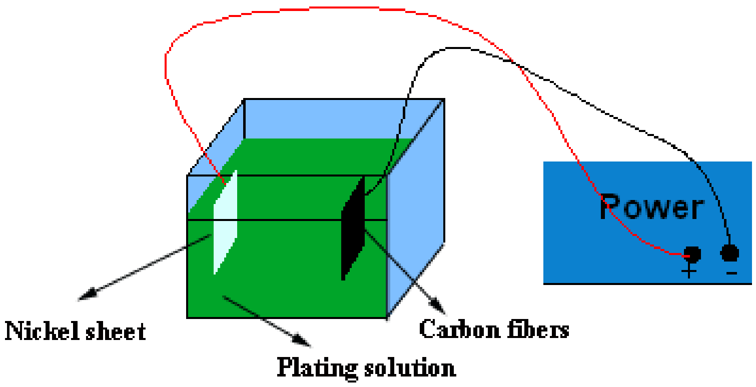

Figure 1. The sketch map of plating process

2.3. Characterization of HNOFs

The surface patterns of HNOFs were characterized by S-4800 field emission scanning electron microscopy (SEM, Hitachi, Japan). The components of hollow fibers were analyzed by X-Ray diffraction (XRD, D8 Advace, Germany) using copper K_α X-rays ($\lambda = 0.1541$ nm). Thermogravimetric (TG) analysis and differential thermogravimetry (DTG) were carried out on a STA 409PC (Netzsch, Germany). The thermograms were acquired between 30 and 900 ℃ at a heating rate of 5 ℃/min. Nitrogen and air were used as the gas at a flow rate of 10 and 60 mL/min respectively.

2.4. Electrochemical measurement

Electrodes were prepared by mixing the active materials with 10 wt% acetylene black and 10 wt% polytetrafluoroethylene (PTFE) of the total electrode mass. A small amount of alcohol was then added to this composite to make more homogeneous mixture, which was pressed on nickel foam to fabricate the electrodes. Electrochemical characteristics of the HNOFs were determined by galvanostatic charge and discharge method and cyclic voltammetry method in a three-electrode cell with 6 M KOH electrolyte, a platinum foil was used as the counter electrode and a saturated Hg/HgO electrode as the reference electrode.

3. RESULTS AND DISCUSSION

3.1. TG analysis of nickel coated MPCFs

The TG and DTG curves of nickel-coated MPCFs show the weight change of the materials as it is heated. The weight of nickel-coated MPCFs begins to increase at temperature about 400 ℃ as shown in Fig.2. The weight increase should be due to the oxidization of nickel coated on MPCFs. The weight of nickel-coated MPCFs continuously increases with the temperature increasing until 600 ℃.

At 600 ℃, the MPCFs will decompose under air atmosphere and this leads to a weight loss of the sample. It can be observed a broad peak of DTG curve in the temperature ranging from about 600 to 900 ℃. This may be ascribed to the decomposition of MPCFs. The nickel-coated MPCFs must be heated at temperature higher than 400 ℃ so that the nickel could be oxidized to nickel oxide. And a temperature higher than 600 ℃ was necessary for complete decomposition of MPCFs.

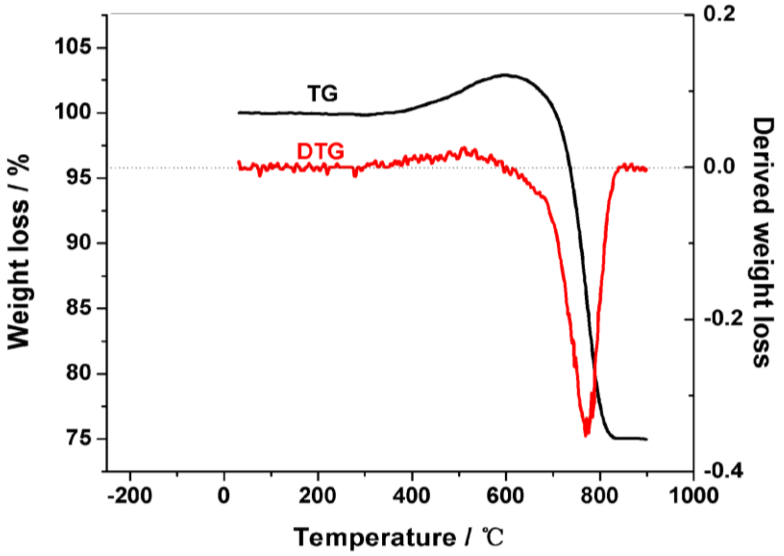

Figure 2. TGA-DTG curve of nickel-coated MPCFs

3.2. Generation process of nickel oxide

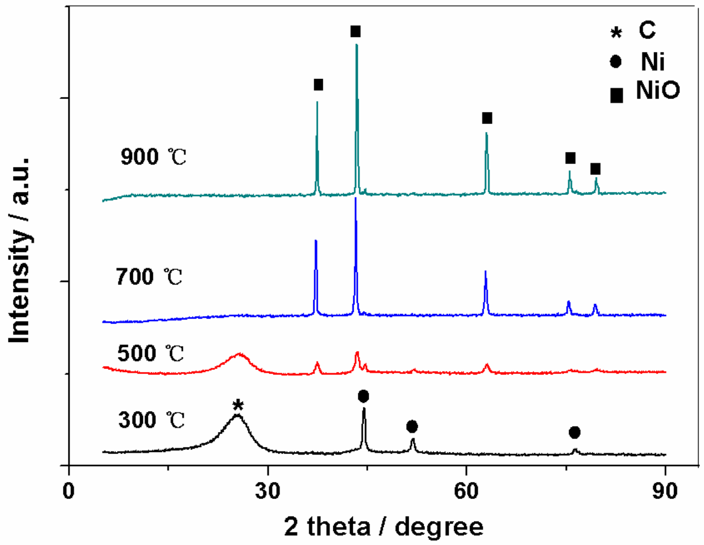

Figure 3. XRD patterns of nickel-coated MPCFs heat treated at different temperature

Fig. 3 shows the XRD patterns of nickel-coated MPCFs burned in air at 300, 500, 700 and 900 ℃. Analysis of the diffraction patterns reveals that nickel-coated MPCFs heat treated at 300 ℃ consist of two sets of peaks, which are corresponding to carbon and Ni respectively. A new diffraction peak belonged to NiO appears after a heat treatment at 500 ℃. It shows that the Ni coated on MPCF substrate has been oxidized to NiO when the sample was heat treated at 500 ℃. The diffraction peaks of carbon and Ni become weaker as the treatment temperature increases. When the treatment temperature was higher than 700 ℃, the diffraction peaks of carbon and Ni had disappeared. It shows that the carbon fibers have burn off and the Ni has oxidized into NiO under 700 ℃. Moreover, the characteristic peaks of NiO heat treated at 700 and 900 ℃ are narrower than that heat treated at 500 ℃. This indicates a high crystallinity of NiO heat treated at higher temperature than 500 ℃. The average particle size can be calculated using Scherrer formula [15], the average particle size of samples heat-treated at 700 and 900 ℃ are 41 and 83 nm respectively. It shows that the size of NiO particles grows with the heat treatment temperature increasing. So, the NiO particle size and crystallinity can be controlled by the heat treatment temperature.

3.3. Surface patterns of MPCF and HNOFs

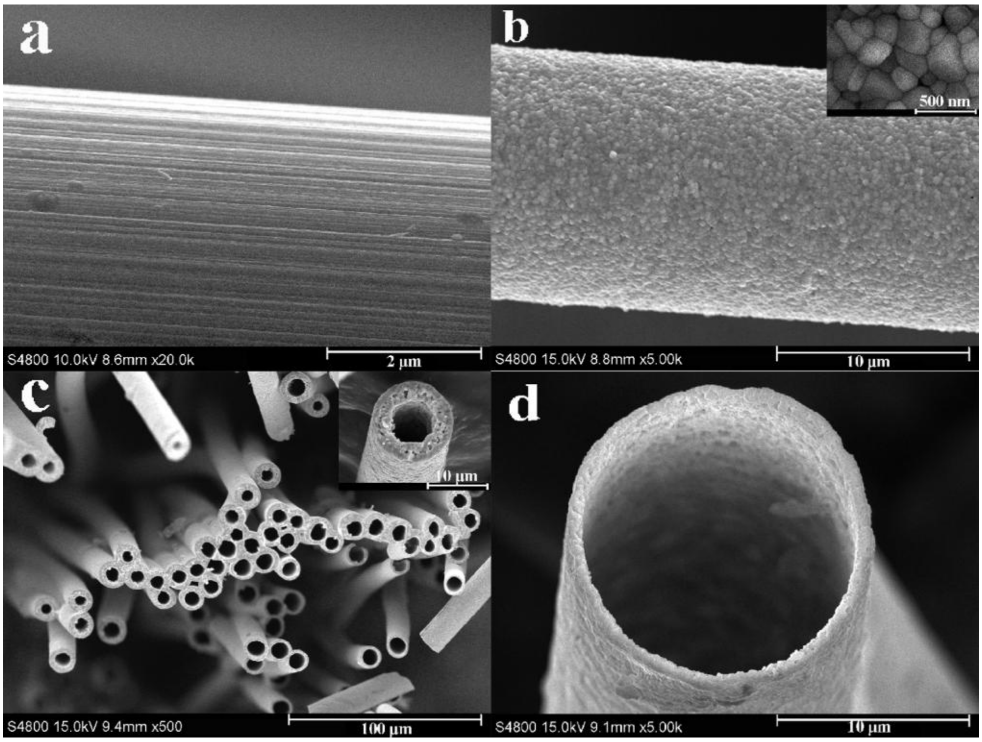

Figure 4. SEM image of MPCF (a), SEM image along HNOF-10 axis (b), cross-section texture of HNOF-10 (c) and HNOF-1 (d)

There are many grooves on the surface of MPCFs as shown in Fig. 4a. Thereby, MPCFs have high surface energy and well wettability. The nickel particles could be electroplated on MPCF surface easily. Fig. 4b is the SEM image of nickel oxide fibers along fiber axis. As can be seen, the nickel oxide fibers are consisted of nanoparticles in a shape of granular with size ranging from 10 to 500 nm. Fig. 4c shows the cross-section texture of HNOF-10. The nickel oxide fiber has a hollow hole in centre inherited from the carbon fiber substrates. Fig. 4d shows the cross-section texture of HNOF-1. The plating process is feasible, so HNOFs with desirable fiber wall thickness could be obtained easily by adjusting the electroplating current density and time. From Fig. 4c and Fig. 4d, the thickness of HNOF-10 and HNOF-1 fiber wall is about 2.8 and 0.8 μm respectively. The thickness of fiber wall plated at 1 A/m^2 current density is thinner than that of plated at 10 A/m^2 current density.

3.4. Electrochemical properties of HNOFs

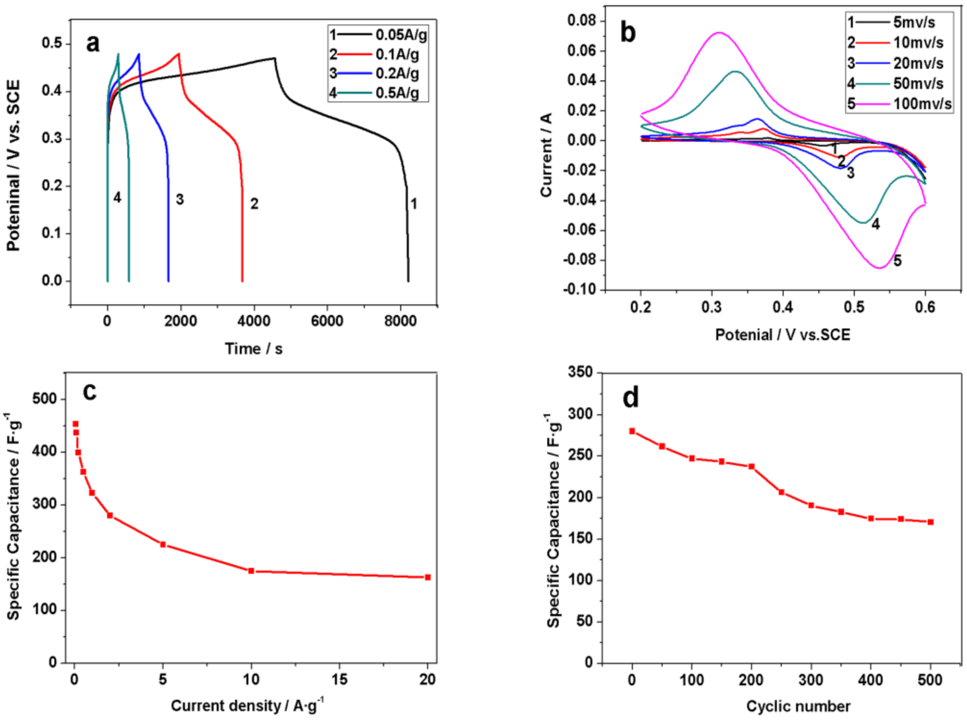

Figure 5. Charging and discharging curve of HNOF-1 (a), cyclic voltammetry curves of HNOF-1 (b) and specific capacitance curve of HNOF-1 (c), cycle test of specific capacitance of HNOF-1 at 2A/g (d)

The specific capacitance was calculated by the following equation:

$$C = i\Delta t / m\Delta v$$

where C is the specific capacitance (F/g), i is the discharge current (A), $\triangle t$ is the discharge time (s), m is the mass of active material (g), and $\triangle v$ is the potential interval (V). The specific capacitance of HNOF-1 is 480 F/g at a current of 50 mA/g according to the charging and discharging curve in Fig. 5a. Fig. 5b shows the cyclic voltammetry curves of HNOF-1 at different scanning rate. As a transition metal oxide, NiO has large pseudocapacitance so the redox peaks can be observed clearly. Fig. 5c shows that the specific capacitance of HNOF-1 decreases with the increasing of charge-discharge current density. The diffusion resistance of electrolyte increases with the current density increasing. This is the main reason for the deamplification of specific capacitance. Fig. 5d shows that the specific capacitance of HNOF-1 decreased about 30 % after 500 cycles. The swell and shrink of NiO in electrolyte will cause the decrease of specific capacitance. Additional, the stability of specific capacitance of HNOFs during 100 to 200 cycles might related to the formation of $Ni(OH)_2$ on the surface of the NiO electrode. It has been shown that the specific capacitance of NiO electrode will increase due to the formation of $Ni(OH)_2$ in many researches [12,16,17].

The surface area of HNOF-1 in this study is 56 m^2/g according to BET test. The high surface of HNOFs leads to high specific capacitance of HNOF electrode.

4. CONCLUSIONS

HNOFs were successfully prepared by electroplating nickel particles on the surface of MPCFs and then burned off the MPCFs. The obtained HNOFs are made up of nano-sized nickel oxide particles and the size of nickel oxide particle grows with the heat treatment temperature increasing. Moreover, electroplating process is controllable that the thickness of HNOF fiber wall could be tuned easily by adjusting the electroplating current density and time. The HNOFs have high specific surface area which make HNOFs show well electrochemical properties when it was used as electrode of capacitor.

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