Energy materials

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A facile synthetic method and electrochemical performances of nickel oxide/carbon fibers composites

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ABSTRACT

The uniform and completed nanofilms of nickel oxide (NiO) were electrodeposited on the carbon fibers (CFs) by a facile method of cyclic voltammetric. The as-prepared NiO/CFs composites can be used as a flexible electrode for electrochemical supercapacitors. Electrochemical measurements showed that 1.0-NiO/CFs had a good redox process and reversibility, and displayed the specific capacitances as high as 929 F g^{-1} at a current density of 1 A g^{-1}. After 5000 cycles of charge and discharge, the 1.0-NiO/CFs composite materials could retain more than 88% of initial capacitance and show an excellent cyclability. Meanwhile, this supercapacitor exhibited a higher energy density of 20.8 Wh kg^{-1} at a power density of 200 W kg^{-1}. The carbon fibers acting as active substrate for the composite electrode are a good conductor and have a larger capacitance of electrical double layer. The nanofilm structure of NiO could facilitate the contact of the electrolyte with the active materials, thus increasing the Faradaic pseudo-capacitance.

Introduction

Supercapacitor has caused widespread attention to the potential applications in the electronic equipment, medical apparatus and instruments, transportation and portable batteries [1]. But as an energy storage device, a supercapacitor which has many problems such as a large volume, heavyweight and rigid structure is difficult to meet the special requirements of flexible electronics. For realizing the energy requirements of the modern products including the wearable design, crimp display screen and flexible mobile phone, we need to develop flexible material—flexible supercapacitor which has a lightweight, high electrochemical capacitance and strong mechanical properties [2, 3].

At present, the materials used in supercapacitors mainly include carbon, conductive polymer and metal oxide [4, 5]. Among them, carbon materials possess a large specific surface area, long cycle life, good mechanical properties and electrochemical electric double layer (EDLC) at the interface of electrode/electrolyte effect, e.g., graphene (GR), carbon nanotube (CNT) and carbon fiber (CF) [5–7]. In numerous carbon materials, the carbon fibers (CFs), which reveal a good prospect of the application in flexible supercapacitors, have a low cost, good chemical stability and power density, at the same

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time with both the soft workability and mechanical strength of textile fiber. However, its energy density and specific capacitance are low, while the effects of practical application are poor [8]. Zhou et al. [7] using a simple method of acid oxidation obtained the carbon fibers with porous core–shell structure and made into the flexible electrochemical supercapacitors, which specific capacitance is only 20.4 F g^{-1} (at current density of 1 A g^{-1}). As the important materials of improving the performance of specific capacitance and others for supercapacitor, metal oxide with a low cost, environmental-friendly nature and ideal electrochemical pseudo-capacitance performance is considered to be the most promising supercapacitor materials, for instance RuO_2, MnO_2 and NiO [5–7, 9]. Hydration RuO_2 has high theoretical specific capacity and electrical conductivity, but its nominal battery voltage is limited and the cost is expensive. Hence, it is difficult to widely use in commerce [10, 11]. While the prices of MnO_2 and NiO are cheaper and its pseudo-capacitance is perfect [12, 13], but almost all the previous reports are that the two oxides made of a powder base or a non-flexible, this hampers the flexible application of supercapacitor [14–17]. Thus, it can be seen that when the pure application of carbon fiber is as a flexible supercapacitor electrode, the EDLS's contribution to the capacity is limited, and in most cases the carbon fiber is used as the carrier of loading other active material. The pseudo-capacitance materials of metal oxide are needed to deposit on the high conductivity and flexibility of carbon fiber material for increasing the capacitance in order to form a superior electrochemical performance, including a high power density and energy density of composite materials [3, 17]. Wang et al. [14] introduced a chemical deposition method for forming nano-MnO_2 on the carbon fiber, resulting in the composite structure of MnO_2/carbon fiber, which obtained the volume capacitance up to 2.5 F cm^{-3} and its energy density of 2.2×10^{-4} Wh cm^{-3}. Zhao et al. [18] showed α-MnO_2 nanowires growth on the reclaimed carbon fibers (RCFs) surface through a one-step hydrothermal process, and the MnO_2/RCF composite prepared at 150 °C got the special capacitance of 228 F g^{-1} at 1 A g^{-1}. Zhou et al. designed the core–shell nanowires of WO_{3-x}@Au@MnO_2 growing on the nanocarbon fiber (NCF). A specific capacitance of the composite was as high as 1195 F g^{-1} (current density is 0.75 A g^{-1}), and their power density and

energy density were 30.6 kW kg^{-1} and 78.1 Wh kg^{-1}, respectively [19]. Nickel oxide (NiO), which has a wide range of sources, good environmentally friendly and high electrochemical performance, is considered to be a promising candidate for a pseudo-capacitance. However, the small potential window (0.5 V) of Ni limits the energy density of these Ni-based electrodes [20]. Wang et al. [21] illuminated that the device capacitance of the hierarchical porous nickel oxide and carbon was up to 38 F g^{-1}, which was attributed to the Faradaic charge conversion. Al-Enizi et al. [15] studied the composites of carbon nanofibers with NiO which were prepared by chemical deposition and heat treatment, and its highest specific capacitance was 738 F g^{-1} at a calcinations temperature of 400 °C.

In this paper, we have used the facile methods of cyclic voltammetry (CV) electrochemical deposition and heat treatment in preparation for the electrode materials of NiO nanofilm/carbon fibers (CFs). The energy storage performance of NiO/CFs electrodes was tested by the method of AC impedance (EIS), cyclic voltammetric curves (CVs) and galvanostatic charge/discharge. The results show that 1.0-NiO/CFs in alkaline electrolyte (KOH) has a strong electrical conductivity and large electrochemical capacitance, and its specific capacity is as high as 929 F g^{-1} at a current density of 1 A g^{-1}. The electrodes also show a high electrochemical stability and reversibility.

Experimental

## Synthesis of NiO/CFs electrodes

1. Coarsening carbon fibers

The surface of the commercial carbon fibers whose diameter was about 6 μm was smooth and contains a lot of colloids. The deposition layers were difficult to firmly combine with carbon fibers and easy to falloff. The carbon fibers were put into the mixed solution of 200 g L^{-1} of chromic acid and 200 mL L^{-1} of sulfuric acid (98%) and were coarsened at a certain conditions. After many experiments, we found that the best condition of surface coarsening was the temperature of 50 °C and the time of 30 min.

2. Preparation of NiO/CFs composite materials
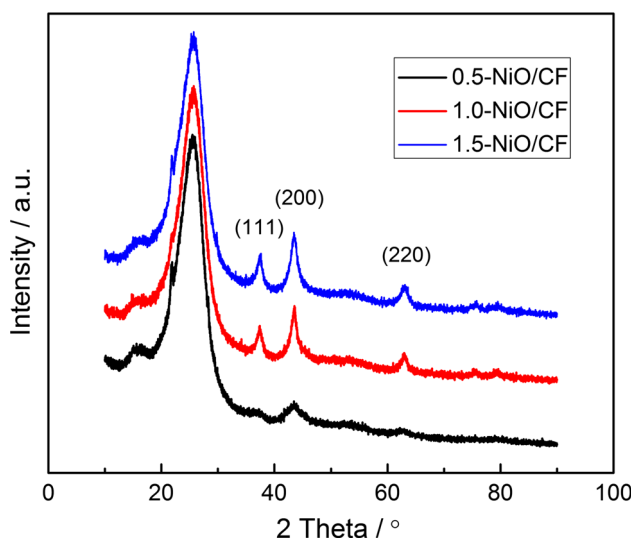
Figure 1 X-ray diffraction (XRD) pattern of NiO/CFs composites.

The electrochemical deposition on carbon fibers was used by cyclic voltammetry (CV) in 0.5, 1, 1.5 M of Ni(NO₃)₂ solution. The deposition layers of Ni(OH)₂ were formed through the reaction Eqs. (1) and (2).

$$NO_3^- + 7H_2O + 8e^- \rightarrow NH_4^+ + 10\,OH^- \tag{1}$$

$$Ni^{2+} + 2OH^- \rightarrow Ni(OH)_2 \tag{2}$$
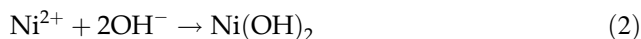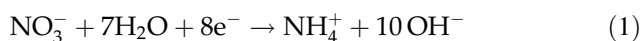
The prepared composite materials of Ni(OH)₂/CFs were put into the muffle furnace, heated to 300 °C at the rate of 5 °C s⁻¹ and then kept at this temperature for 1 h. According to the reaction of Eq. (3), the NiO/CFs composites were obtained and cooled in the furnace to room temperature. The electrode materials in this experiment according to the concentration of reaction solution were numbered to 0.5-NiO/CFs, 1.0-NiO/CFs and 1.5-NiO/CFs.

$$2Ni(OH)_2 \xrightarrow{\text{heat}} 2NiO + H_2O. \tag{3}$$
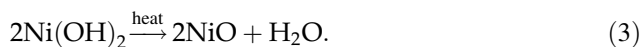
Performance testing of the composite electrode

1. Characterization of electrode materials

The structure, phase composition and morphology of the as-prepared samples were investigated by X-ray diffraction (XRD, Rigaku D/max-2500, Cu Kα radiation) and a field-emission scanning electron microscopy (FE-SEM, SU-70). X-ray energy-dispersive spectrometry (EDS) was used in SU-70. X-ray photoelectron spectroscopy (XPS) measurements of the electrode materials were taken in a Thermo Scientific ESCALAB250 spectrometer equipped with a hemispherical electron analyzer and a Mg Kα (hy1/4 1253.6 eV) X-ray source for analyzing the chemical composition and the valence state.

2. Testing of electrochemical performance

Electrochemical performance was conducted on a CHI660E electrochemical station with a three-electrode system, using a Pt sheet as the counter electrode, SCE (saturated calomel electrode, in saturated KCl) as the reference electrode and 2 M of KOH as the electrolyte. The preparation process of the working electrode was provided in the description section above. The electrochemical impedance spectroscopy (EIS) measurements of the samples were taken under open-circuit potential with an excitation signal of 5 mV in a frequency range of 10 kHz ∼ 100 mHz in 2 M of KOH solution. The impedance data were fitted to an appropriate equivalent circuit using ZSimpWin 3.0 software (Echem Software). The cyclic voltammogram (CV) curves were recorded by an electrochemical station in a potential range from 0.0 to 0.8 V at different scanning rates. The galvanostatic charge/discharge capacitance (C_s) was measured by using a Program Testing System (produced by China-Land Com. Ltd., China). Charge and discharge voltages ranged between 0.0 and 0.8 V.

Results and analysis

Structure and phase analysis

Figure 1 shows the X-ray diffraction (XRD) pattern for NiO/CFs composites. It can be seen that the diffraction angles (2θ) are 37.23°, 43.29° and 62.82°, and the corresponding crystal face is (111), (200) and (220), respectively. All peak values agree with the peaks of NiO in 65-6920 standard card of PDF. At the same time, 0.5-NiO/CFs can be also seen the obvious peak at (200), but there are no obvious diffraction peaks appeared at other positions. While 1.0-NiO/CFs and 1.5-NiO/CFs have high diffraction intensity, the diffraction peaks of NiO and C are obvious. It indicates that the Ni(OH)₂ films on the surface of carbon fiber have been completely transformed into NiO after the deposition and heat treatment and have formed NiO/CFs electrode materials.
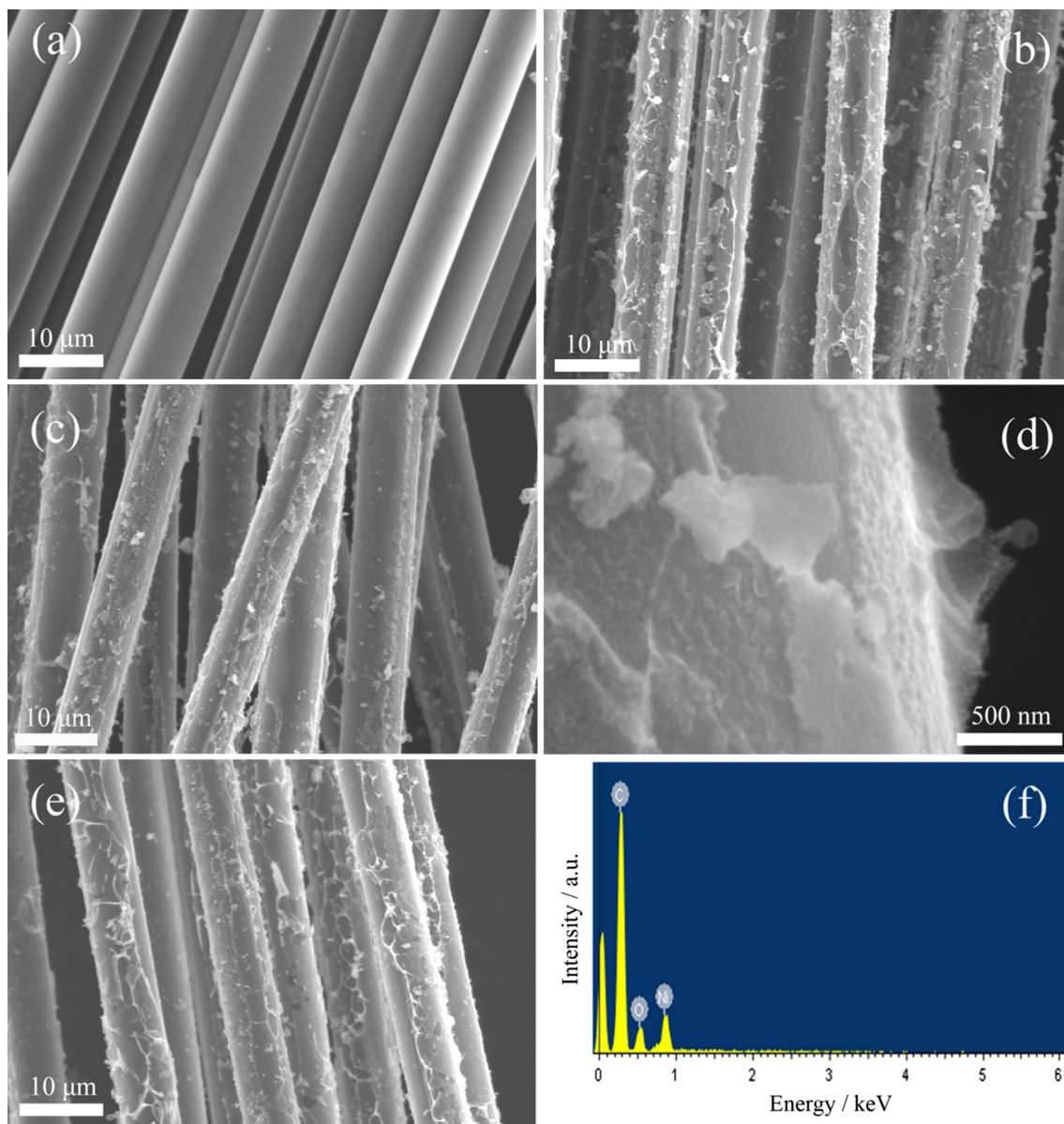
Figure 2 Scanning electron microscope (SEM) morphology and energy spectrum (EDS) of the carbon fibers after unprocessed (**a**), electrodeposited and heat treatment. Unprocessed CFs, **b** 0.5-NiO/ CFs, **c** 1.0-NiO/CFs, **d** amplification (**c**), **e** 1.5-NiO/CFs, **f** EDS of 1.0-NiO/CFs.

Figure 2 shows the scanning electron microscope (SEM) morphology and energy spectrum EDS of the carbon fibers after unprocessed, electrodeposited and heat treatment. Figure 2a shows the surface of unprocessed carbon fibers is smooth, the thickness of carbon fibers is uniform, and its size is about 6 μm. Figure 2b–e shows the surface topography of the carbon fibers modified by the electrochemical deposition and heat treatment, respectively. The composite electrode material of 1.0-NiO/CFs after heat treatment has a relatively uniform surface layer on

the carbon fiber, and its thickness of deposition nanofilm is about 100 nm. There are the surface sheets crystals of about 300 nm and the needlelike NiO crystals of smaller size. Due to the coarsening process at 50 °C for 30 min, the surface of the carbon fibers appears rough, as shown in Fig. 2d. The surface sediments of 0.5-NiO/CFs and 1.5-NiO/CFs composites have different degrees of loss. It is mainly because the Ni contents in 0.5 M of solution are low, which makes it difficult to form a complete electrochemical deposited layer on the surface of CFs and

cause a lot of naked places. On the contrary, 1.5 M of solution is a high concentration, the formation of sediment is thick, and the combination degree of deposited nanofilm with CFs is poorer. Therefore, it is prone to falloff (Fig. 2e). The composition of 1.0-NiO/CFs was tested by the spectrometer (EDS), as shown in Fig. 2f. There are three elements (C, O and Ni) on surface, and measured atomic percentage was 82.05% of C, 18.26% of O and 18.26% of Ni. This proves the formation of Ni oxide on the surface of CFs.

Elemental composition and oxidation state of electrochemical constitute of 1.0-NiO/CFs are decided by the spectral line of XPS (X-ray photoelectron spectroscopy), as shown in Fig. 3. Fitting by Gauss, the electronic states of NiO can be analyzed by Ni 2p3 and Ni 2p1 spectrum. Ni 2p3 peak is located at 854.4 eV, and its satellite peak is at 861.5 eV. While the Ni 2p1 peak is located at 871.9 eV, its satellite peaks are 879.1 and 881.8 eV (Fig. 3a). These binding energies are consistent with Ni^{2+}, confirming the formation of NiO at this time [22, 23]. In Fig. 3b, O 1s is divided into two convolution peaks of 531.6 ($O_{2\ I}$) and 533.5 eV ($O_{2\ II}$). $O_{2\ I}$ peak attributable to oxygen in the lattice, and the $O_{2\ II}$ peak is considered to be hydroxyl groups or oxygen atoms similar to Ni [O/def] vacancies in the oxide [24]. All of them contribute to the formation of Ni oxides, which are in good agreement with the results of EDS and XRD.

Electrochemical performances

Figure 4 shows the AC impedance (EIS) spectra of 0.5-NiO/CFs, 1.0-NiO/CFs and 1.5-NiO/CFs samples. All of them have similar electrochemical impedance characteristics. Usually, the EIS impedance spectrum in the Nyquist diagram is composed of a high-frequency semicircle and a low-frequency oblique line. The high-frequency semicircle attributed to the charge transfer or electrochemical reaction resistance and determined by R_{ct}. The carbon/electrolyte interface is parallel to the electric double-layer capacity, which expresses CPE. The linear slope of the low-frequency oblique line is more than 45°, which is related to the process of kinetics and diffusion and is Warburg impedance (W) [25]. Randles equivalent circuit of the fitting curve is shown in Fig. 4 inset. EIS spectra (R_{ct}) of 0.5-NiO/CFs, 1.0-NiO/CFs and 1.5-NiO/CFs are 11.78, 4.53 and 7.86 $\Omega\ cm^2$, respectively. It can be seen that the impedance R_{ct} of 1.0-NiO/CFs electrode material is the lowest, which is conducive to the diffusion and migration of electrons and electric charges on their surface, showing a higher electrochemical conductivity.

The cyclic voltammetry curves (CV) of 0.5-NiO/CFs, 1.0-NiO/CFs and 1.5-NiO/CFs electrodes at different scanning speeds and the potential range of 0.0–0.8 V are obtained in 2 M of KOH solution, as shown in Fig. 5. From Fig. 5a, we can see that the CV
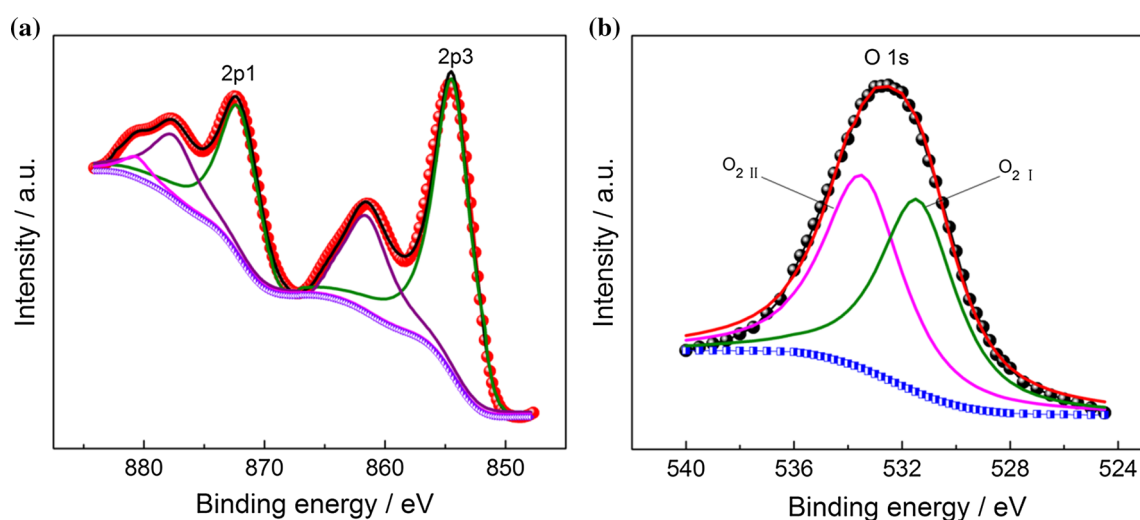

Figure 3 XPS spectrum of 1.0-NiO/CFs composites **a** Ni 2p3, **b** O 1s.
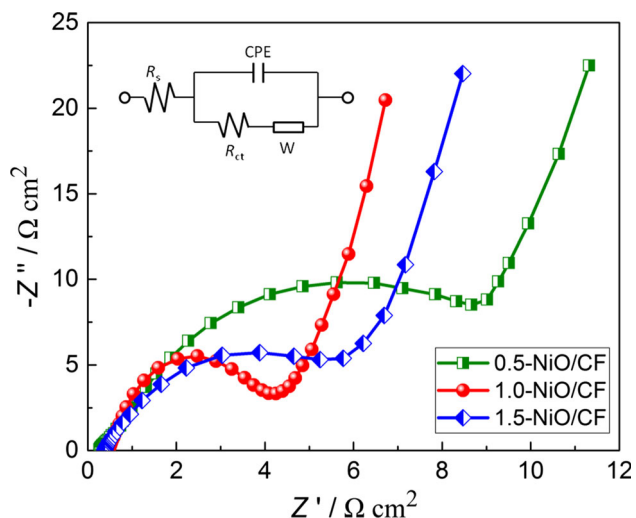
Figure 4 EIS Nyquist diagram of NiO/CFs electrode in 2 M of KOH solution. *Inset* shows the electrical equivalent circuit used for the fitting impedance spectra.

of 0.5-NiO/CFs is more complete rectangular in shape and mainly shows typical behaviors of electric double-layer capacitor because a complete deposition layer of NiO cannot be formed and produce less redox process. In Fig. 5b, c, CVs of 1.0-NiO/CFs and 1.5-NiO/CFs composite appear redox peaks at the potential range of 0.2–0.6 V under guaranteeing the conditions of a certain rectangle. It illustrates that 1.0-NiO/CFs and 1.5-NiO/CFs electrodes not only have an electric double-layer capacitance of carbon fiber, but also keep the existence of the metal oxide pseudo-capacitor. Relatively, the NiO layer on the surface of 1.0-NiO/CFs electrode material with a suitable thickness and uniform distribution can provide more active sites for the redox reaction with KOH electrolyte solution. Therefore, the greater current densities are formed in a certain voltage range. With the increase in the scanning speed, the electrodes keep in
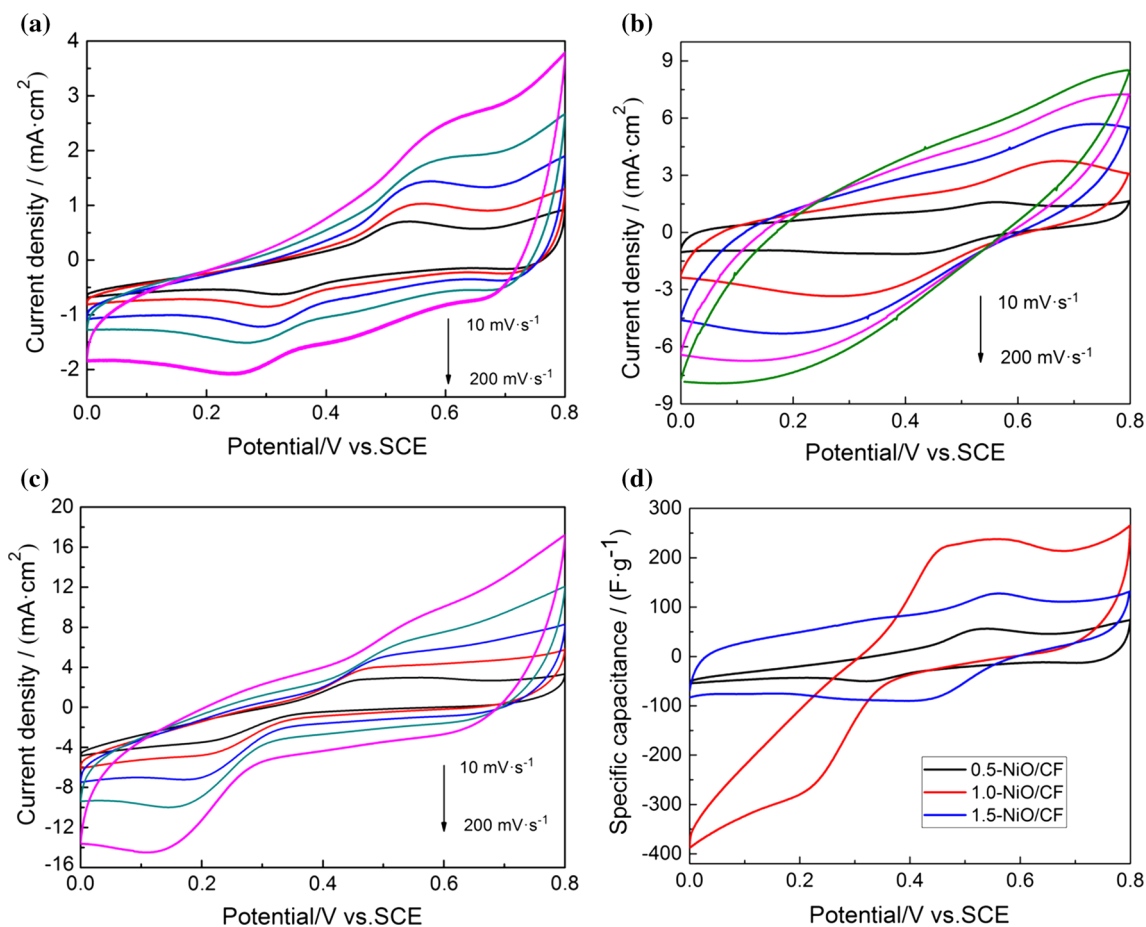
Figure 5 CV of **a** 0.5-NiO/CFs, **b** 1.0-NiO/CFs and **c** 1.5-NiO/CFs at different scan speeds (10, 50, 100, 150 and 200 mV s^{-1}) in 2 M of KOH solution, **d** specific capacitance of 0.5-NiO/CFs, 1.0-NiO/CFs and 1.5-NiO/CFs at a scanning speed of 10 mV s^{-1}.
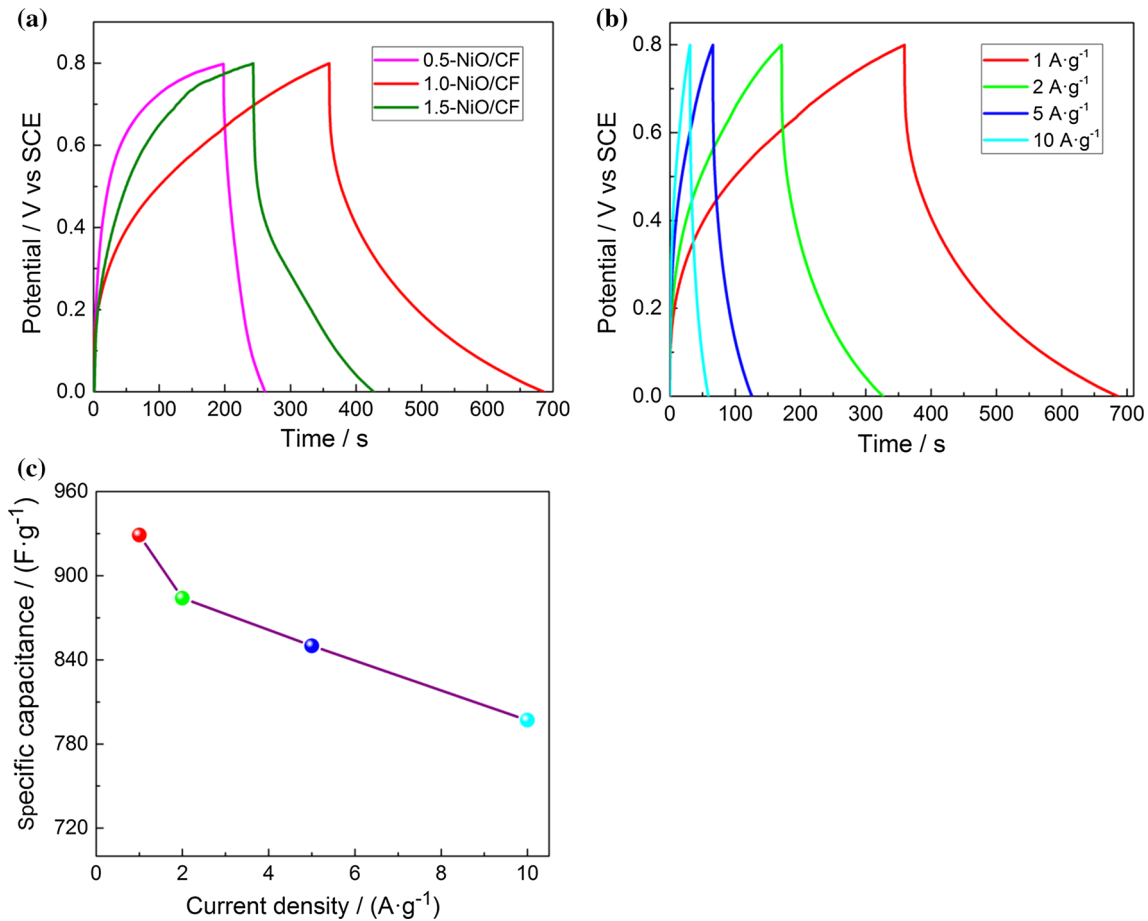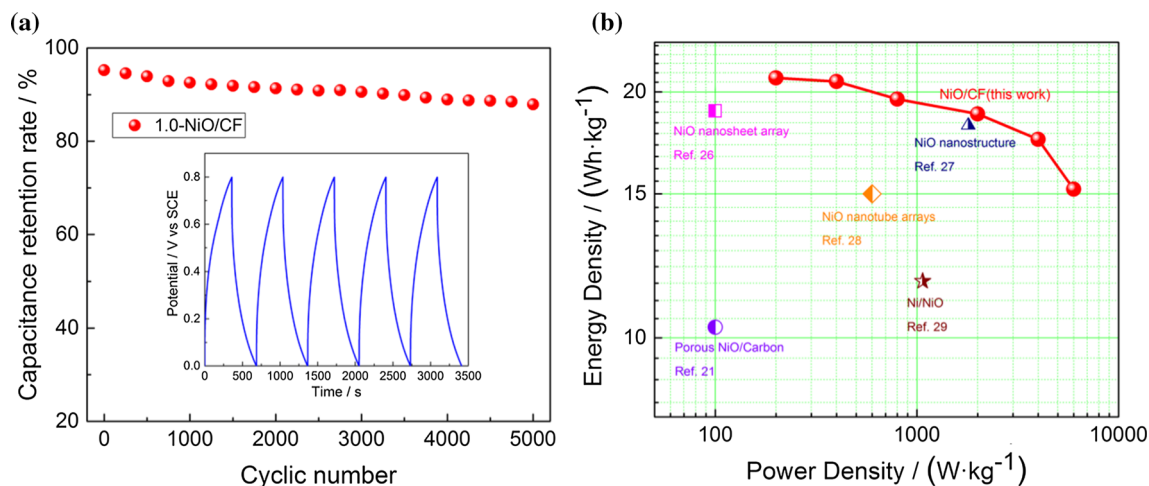
Figure 6 Galvanostatic charge–discharge plot recorded of 0.5-NiO/CFs, 1.0-NiO/CFs and 1.5-NiO/CFs in 2 M of KOH solution at a current density of 1 A g^{-1} (**a**), 1.0-NiO/CFs tested at current density of 1, 2, 5 and 10 A g^{-1} (**b**), the specific capacitance of 1.0-NiO/CFs at various current densities (**c**).

a better electric double-layer and pseudo-capacitance process and maintain a good change shape of CV. Due to the high concentration content of Ni, the deposition thickness formed on the surface of carbon fiber is larger and is prone to falloff. This is not conducive to electron transport. Because there is the large presence of pseudo-capacitor, the capacitance of 1.5-NiO/CFs is greater than that of 0.5-NiO/CFs, but lower than that of 1.0-NiO/CFs. Figure 5d shows that the specific capacity of 1.0-NiO/CFs electrode is significantly higher than that of 1.5-NiO/CFs and 0.5-NiO/CFs. The suitable thickness and reasonable organization size of NiO deposition layer will provide more active sites of the metal oxides and a better electrical conduction for 1.0-NiO/CFs. Therefore, 1.0-NiO/CFs electrode materials expand the electrochemical capacitance of supercapacitor.

The galvanostatic charge–discharge plots recorded through the different electrodes at a current density

of 1 A/g and 1.0-NiO/CFs at the different current density are shown in Fig. 6. Figure 6a shows that the charge and discharge time of 1.0-NiO/CFs is the longest time up to 686 s, the charging time and discharge time are similar in 2 M of a KOH solution, and at a current density of 1 A/g. 0.5-NiO/CFs electrode has a long charging time and a short discharge. It is related to the deposition layer falling from the surface of carbon fibers. The more NiO off, the less space of charge storage, the worse pseudo-capacitance performance, and the shorter discharge time. Figure 6b shows that the charge and discharge times of 1.0-NiO/CFs electrode material are shorten with the increase in the current density, the specific capacitance of the composite material will have a corresponding change, and the ratio of value change of special capacitance can be calculated by the relevant formula [13]. Therefore, with different degree of NiO deposition on the surface of carbon fibers, the

Figure 7 Cycling performance and capacitance retention for 1.0-NiO/CFs in 2 M of KOH solution (**a**), *inset* galvanostatic charge–discharge curve of 5th cycles at 1 A g^{-1} of current density. Ragone plots (energy density/power density) for the as-prepared 1.0-NiO/CFs, and the values reported previously for other NiO-based composites are given here for a comparison (**b**).

available special capacitance of 1.0-NiO/CFs at the current density of 1 A/g is 929 F g^{-1}. That special capacitance is about 3.0 and 1.8 times of 0.5-NiO/CFs and 1.5-NiO/CFs (279 and 520 F g^{-1}), respectively. The specific capacities of 1.0-NiO/CFs are 929, 884, 850 and 797 F g^{-1} at the current density of 1, 2, 5 and 10 A g^{-1}, as shown in Fig. 6c.

In order to measure the electrochemical cycle stability and repeatability of the active electrode materials, the charge–discharge tests are carried out using the galvanostatic charge–discharge method for NiO/CFs composites in 2 M of KOH solution. As illustrated in Fig. 7a inset, the 5th cycles of charge and discharge of 1.0-NiO/CFs electrode are exhibited in this process, and each cycling curve shows a symmetrical triangle, showing that this kind of electrodes has a good symmetry and capacitance properties. With the increase in charge–discharge cycles (Fig. 7a), the overall attenuation of the specific capacity of 1.0-NiO/CFs electrode is slow. The capacitance value of this electrode tends to be stable after 2000 circles, and its specific capacitance value is still 88% of the initial value after 5000 circles. Galvanostatic charge and discharge data at different current density are calculated according to references [4, 9, 11], and the energy density and power density of the 1.0-NiO/CFs electrode material (Ragone diagram) were obtained. In Fig. 7b, at a power density of 200 W kg^{-1}, the energy density of 1.0-NiO/CF composite is as high as 20.8 Wh kg^{-1}. When a power density increases to 200 W kg^{-1}, the energy density

will decrease gradually. And at a power density of 6000 W kg^{-1}, its energy density is only 15.2 Wh kg^{-1}. The energy density of the electrodes decreases from 20.8 to 15.2 Wh kg^{-1} as the power density increases from 200 to 6000 W kg^{-1}, which are much higher than that of NiO-based composite materials, such as porous NiO/carbon [21], NiO nanosheet array [26], Ni nanostructure [27], Ni nanotube [28] and Ni/NiO [29]. Although the energy density and power density of the NiO/CFs electrode materials are lower than those of some other materials, such as WO$_{3-x}$@-Au@MnO$_2$/NCF [19], NiO/rGO [20, 30, 31], the NiO materials have great advantage of the low-cost, environmental-friendly and easily prepared traits. Therefore, the composite structure of NiO and carbon fibers can effectively promote the migration of ions, while NiO redox reaction can increase the electrochemical capacitance performance of electrode materials and improve the generation and transport of charge. On the premise of an excellent power density, 1.0-NiO/CFs composites have a higher energy density of supercapacitors.

Conclusions

NiO nanofilms were deposited on the surface of CFs (carbon fibers) by CV (cyclic voltammetry method), and the NiO/CFs electrode material with compact and complete deposition layer was prepared. This method is very simple and practical. The cyclic

voltammetry curves of NiO/CFs have better double-layer rectangular structure and obvious redox peak in 2 M of KOH solution. The specific capacity of 1.0-NiO/CFs electrode at the current density of 1A g^{-1} is 929 F g^{-1}. After the galvanostatic charge–discharge tests for 5000 cycles, the 1.0-NiO/CFs composites kept 88% of the capacitance retention rate. The electrode materials show a good cycling and at the time exhibit a high energy density (20.8 Wh kg^{-1}) and a power density (200 W kg^{-1}). The 1.0-NiO/CFs composite material, which not only has the advantages of carbon fiber—electric double-layer capacitance, but also has a better NiO—pseudo-capacitance properties, obtained a high electrochemical capacitor.

Acknowledgements

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