Synthesis of Novel NiFe$_2$O$_4$/Fe$_3$O$_4$ Nanotube arrays as flexible negative electrodes for Supercapacitor Applications

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Abstract. Electrode materials with specific morphologies and microstructures can help to speed up the charge transfer to a certain extent and provide more electrochemically active sites in electrochemical reactions. In this work, NiFe$_2$O$_4$/Fe$_3$O$_4$ nanotube arrays were synthesized on the stainless steel mesh through an ion-exchange reaction involving Zn(OH)$_2$ nanorods under the hydrothermal condition. By analyzing the electrochemical performances of the supercapacitor electrodes, the optimal electrode could be obtained by the hydrothermal process at 160 °C. It has a specific capacity of 258.8 F g$^{-1}$ at a current density of 1.25 A g$^{-1}$ as a negative electrode. This work provides a new strategy to prepare nickel-iron oxide as negative electrode materials in supercapacitor applications.

1. Introduction

Frequent industrial activities have triggered a shortage of traditional fossil fuels and continued global warming, which has forced scientists to develop new, clean, and renewable energy technologies to reduce the use of traditional fossil energy[1]. To utilize the energy generated by intermittent sustainable resources, energy storage systems are essential. Among all kinds of new energy technologies, electric energy storage systems are considered to be the most feasible, environmentally friendly, and sustainable[2, 3]. Compared with common energy storage devices such as batteries and fuel cells, supercapacitors have the advantages of high power density, long operating life, and wide operating temperature range[4, 5]. Therefore, compared with batteries, supercapacitors are regarded as more promising and safer alternative devices.

It is worth noting that nickel-iron oxide has a popular application in the field of supercapacitor electrode materials because it has ideal specific capacitance, low cost, and environmental protection[6, 7]. NiFe$_2$O$_4$ as a representative substance of nickel-iron oxide can provide high-density electrons in a fast and reversible redox reaction, which is mainly due to the redox pairs of Ni$^{2+}$/Ni$^{3+}$ and Fe$^{2+}$/Fe$^{3+}$[8]. Meanwhile, iron oxide (Fe$_2$O$_3$, Fe$_3$O$_4$), as a common negative material for supercapacitors, also has a high theoretical specific capacity and a large potential window[9, 10]. This makes it possible to further try to synthesize nickel-iron oxide as a negative material.

The outline of our thesis is the material structure design of nickel-iron oxide. We successfully converted Zn(OH)$_2$ nanorods on the stainless steel mesh (SSM) into nickel-iron oxide nanotube arrays through a hydrothermal ion-exchange reaction. we obtained NiFe$_2$O$_4$/Fe$_3$O$_4$ composite with excellent electrochemical properties by adjusting different hydrothermal synthesis temperatures. The as-synthesized sample displays a specific capacity of 258.8 F g$^{-1}$ at the current density of 1.25 A g$^{-1}$. 
2. Experimental Details

2.1. Sample preparation

2.1.1. The preparation of Zn(OH)₂ nanorods on the SSM substrate

The synthesis of Zn(OH)₂ nanorods were conducted by a common wet-chemical process. Firstly, a piece of SSM (2 × 3 cm) was soaked in 4 M HNO₃ solution for 4 h at 60 °C and sonicated for 20 min in ethanol and deionized (DI) water sequentially, then dried in the oven to act as the substrate in the following steps. 2.082 g Zn(NO₃)₂·6H₂O as a zinc source was dissolved in 200 mL DI water, and 6 M NH₃·H₂O was added drop by drop until the solution was clear completely. The as-prepared substrate was immersed in the transparent zinc precursor solution and then transferred to a sealable glass container. The sealed container was heated at 70 °C for 12 h. After cooling to the room temperature, Zn(OH)₂/SSM was rinsed sequentially with ethanol and DI water, and dried in an oven at 60 °C for 12 h.

2.1.2. The synthesis of nickel-iron oxide nanotube arrays (NFO)

The sample marked NFO was prepared by a hydrothermal ion exchange process. Typically, 0.808 g Fe(NO₃)₃·9H₂O, 0.398 g FeCl₂·4H₂O, 0.582 g Ni(NO₃)₂·6H₂O, 1.8 g urea, and 0.222 g NH₄F were dissolved in 80 mL DI water in turn. The homogeneous solution containing the immersed Zn(OH)₂ deposited on the substrate was transferred to a 100 mL Teflon-lined stainless steel autoclave, and the reactor was heated to the specific temperatures (120 °C, 140 °C, 160 °C, and 180 °C) and kept for 8 h. Finally, the samples marked as NFO-120, NFO-140, NFO-160, NFO-180 were cleaned with ethanol and DI water and dried in a vacuum oven at 60 °C for 12 h.

2.2. Material characterization

X-ray diffraction (XRD) spectrum analysis was used to obtain the structure and composition information of nickel-iron oxide by using a Philips X’pert X-ray diffractometer. A field-emission scanning electron microscopy system (Inspect F, FEI Co., USA) was used to observe the morphologies. The data of N₂ adsorption-desorption was measured at 77 K using a JW-BK112 Surface Area Analyzer (Beijing JWGB, China).

2.3. Electrochemical measurement

The electrochemical test of nickel-iron oxide was carried out under the three-electrode system based on 2 M KOH solution as the electrolyte on a CHI 760E electrochemical workstation. A sample with a size of 1 × 1.5 cm was cut and used as a working electrode. The platinum titanium mesh is used as the auxiliary electrode, and the Hg/HgO electrode was used as the reference electrode. Electrochemical data of electrodes mainly include cyclic voltammetry (CV), Galvanostatic charge-discharge (GCD), and electrochemical impedance spectroscopy (EIS).

3. Results and discussion

As shown in Figure 1, the XRD result of SSM manifests that three diffraction peaks are corresponding to (111), (200), (220) characteristic crystal planes (PDF#33-0397) in order at diffraction angles of 43.6°, 50.8°, and 74.7°. The characteristic peaks of cubic NiFe₂O₄ (PDF#89-4927) are observed in the XRD spectra of the four NFO samples. The characteristic crystal plane (311) corresponding to the diffraction angle of 35.5° has the highest intensity, which proves the formation of the NiFe₂O₄ spinel structure. Other peaks are also observed at the diffraction angle positions of 30.3°, 43.4°, 57.4°, and 63.0°, corresponding to (200), (400), (511), and (440) crystal planes in turn. Comparing the XRD results of NFO-120, NFO-140, and NFO-160, it can be seen that the intensity of the characteristic peak at near 34.5° gradually increases, indicating that monoclinic Fe₂O₄ is synthesized and gradually crystallizes. However, the Fe₂O₄ phase is not found in the XRD spectra of NFO-180. The inconsistency could be attributed to a higher water oxidation environment in the 180 °C hydrothermal system, and the divalent
Iron is more easily oxidized to trivalent iron in the condition [11]. Overall, these results indicate that NiFe$_2$O$_4$/Fe$_3$O$_4$ composite with a high degree of crystallinity is successfully fabricated via a 160 °C hydrothermal progress.

Figure 1 XRD pattern of SSM, NFO-120, NFO-140, NFO-160, and NFO-180

The morphologies of the samples during the synthesis of electrode materials were identified with a field emission scanning electron microscope (FESEM). The SEM images indicate the nanorod structure of Zn(OH)$_2$ and the nanotube structure of the NFO-160 (Figure 2). According to the image shown in Figure 2 (c), ordered arrays of nanotubes are observed at the bottom layer. It can be seen from the high-resolution image in Figure 2 (d) that the diameter of the nanotubes is 200-400 nm, and the thickness of

Figure 2 SEM micrograph. (a) Zn(OH)$_2$ at the low magnification; (b) Zn(OH)$_2$ at the high magnification; (c) NFO-160 at the low microstructure; (d) NFO-160 at the high microstructure.
the nanotube wall is less than 100 nm. The aforementioned morphology can effectively demonstrate the acquisition of samples with large specific surface areas. And the analysis of BET results further reveals that the specific surface area of the NFO-160 on the SSM (39.54 m² g⁻¹) is significantly increased compared to the SSM substrate (2.45 m² g⁻¹) (Figure 3). In Figure 3 (a), it is observed that there is a hysteresis loop in the N₂ adsorption-desorption isotherms of NFO-160 at a relative pressure of 0.4-1.0, which can confirm that there is an irregular mesoporous structure in the sample[12]. The existence of the mesoporous structure can be further confirmed by the results of the pore size distribution in Figure 3 (b) (average pore size: 2.78 nm). Mesoporous structure and large specific surface area are effective features of high electrochemical performance of electrode materials from the perspective of the energy storage mechanism of supercapacitors[13].

![Figure 3](image)

Figure 3 (a) N₂ adsorption-desorption isotherms of SSM and NFO-160; (b) pore size distributions of SSM and NFO-160

Figure 4 demonstrates the overall electrochemical measurement results of the NFO sample as the negative electrode of supercapacitors. As shown in Figure 4 (a), the CV curves have obvious redox peaks, which proves that the type of electrode is battery-type[14]. By comparing the CV curves of NFO samples synthesized at different hydrothermal temperatures, we can observe that the appearance of oxidation peaks at -0.4 V and -0.1 V related to the electrochemical reactions of nickel ion and iron ion in NiFe₂O₄ (Equation 1), and the oxidation peak near -0.7 V is due to the conversion of Fe²⁺ to Fe³⁺ in the monoclinic Fe₃O₄ phase. The sample NFO-160 has the biggest CV curve integral area, which indicates the NFO-160 has the best energy storage performance. A possible explanation for this result might be that the presence of the Fe₃O₄ phase introduced more active sites on the electrode surface[15].

\[
\text{NiFe}_2\text{O}_4 + 2\text{H}_2\text{O} + 2e^- \longrightarrow \text{NiO} + \text{FeO} + 2\text{OH}^-
\]  

(1)

The CV curves at different scan rates are shown in Figure 4 (b). The same three oxidation peaks as before can be observed. Through the analysis of the GCD curve in Figure 4 (c), we can obtain the specific capacity of the electrode under different current densities. The specific capacity (C, F g⁻¹) of the electrodes in the three-electrode system is calculated according to Equation (2);

\[
C = \frac{i \times \Delta t}{m \times \Delta U}
\]

(2)

where \(i\) is the set current, \(\Delta t\) is the discharge time, \(m\) is the mass of the electroactive materials in the electrode. As a result, we obtain the specific capacity of NFO-160 electrode in 2 M KOH electrolyte as follows: 258.8 F g⁻¹ (1.25 A g⁻¹), 210 F g⁻¹ (2 A g⁻¹), 178.5 F g⁻¹ (2.5 A g⁻¹), 145 F g⁻¹ (5 A g⁻¹), and 104 F g⁻¹ (10 A g⁻¹). Combining the results of Figure 4 (c) and (d), it can be observed that the voltage drop (IR) in the GCD graph and the charge transfer resistance in the high-frequency region of the EIS impedance graph are both very small, indicating that NFO samples on the SSM as the self-supporting electrodes have superior conductivity. The Nyquist plots of NFO-160 compared with other samples have an inclination angle between 45° and 90° at the low-frequency region, which demonstrates that the surface of the NFO-160 electrode can effectively carry out the electrochemical adsorption and diffusion process[16].
4. Conclusion

Nickel-iron oxide nanotubes on the SSM substrate were obtained through ion-exchange progress in the hydrothermal condition. We studied the difference of electrode materials prepared under different hydrothermal temperatures. NiFe₂O₄/Fe₃O₄ nanotube arrays synthesized at 160 °C have the highest electrochemical activity and superior conductivity. The maximum specific capacity of the NFO-160 as the negative electrode is 258.8 F g⁻¹ at the current density of 1.25 A g⁻¹. These experiment results confirmed that NFO-160 with the mesoporous structure and the large specific surface area is a promising candidate for the negative materials of supercapacitors. The electrochemical performance of NFO-160 as a positive electrode can be further studied, and we can try to assemble symmetric supercapacitor devices by using NFO-160 in the future.

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