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Electrochemical capacitance characterization of NiO with ordered mesoporous structure synthesized by template SBA-15

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Abstract

In this paper, NiO with ordered mesoporous structure was synthesized by replicating template SBA-15 and its electrochemical capacitance characterization was for the first time studied in 2 M KOH electrolyte solution. Electrochemical tests results indicated the ordered mesoporous structure can greatly increase the utilization of NiO, which is attribute to a large effective surface area due to the mesoporous structure. The capacitance of NiO with order mesoporous structure was about 120 F/g, about four times larger than that of NiO prepared by direct calcining Ni(NO₃)·6H₂O at 550 °C. On the other hand, the mesoporous NiO showed a good rate capability, which is due to that the ordered mesopores did not limit the ion motion within the pores.

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Keywords: Supercapacitor; NiO; Mesoporous structure

1. Introduction

Electrochemical capacitors combining the advantages of high power of the dielectric electric capacitors and high specific energy of rechargeable batteries, has found an increasingly important role in power source applications such as hybrid electric vehicles, short-term power sources for mobile electronic devices, etc. [1–3]. Nowadays, many researches on the electrochemical capacitors aim to increase power and energy density as well as lower fabrication costs while using environmental friendly materials.

On the basis of electrode materials used and the charge storage mechanisms, electrochemical supercapacitors are classified as: (a) electrical double-layer capacitors (EDLCs) that employ carbon or other similar materials as blocking electrodes [4,5], and (b) redox supercapacitors in which electroactive materials such as insertion type compounds (e.g.RuO₂, NiO, etc.) or conducting polymers are employed as electrodes [6–9]. Some of transition metal oxides, such as RuO₂ and IrO₂ exhibit prominent properties as pseudocapacitive electrode materials.

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However, despite the remarkable performance of this material, high cost of these materials limits it from wide application. A major breakthrough in electrochemical capacitor electrodes is the development of various alternatives as a replacement for RuO₂, e.g. NiO_x [10–13], CoO_x [14], MnO₂ [15–17], etc. However, comparing with RuO₂, these cheap transition metal oxides exhibit lower electrochemical capacitance performance. Thus, improving the capacitance performance of these materials is the next logical step.

Recently, the synthesis of ordered metal oxide nanoarrays was reported [18]. These ordered mesostructured metal oxide nanoarrays generally have uniform pore size of 3–7 nm. It is well-known that the pore size at the rang of 2–50 nm (mesopores) is considered to be highly desirable for the electrochemical supercapacitors, and the ordered mesopores facilitate ionic motion easy compared conventional mesoporous material in which the pores are randomly connected [19]. However, no any attempts have been made to test their electrochemical activity.

In this work, crystallized NiO nanoarrays with ordered mesoporous structure were synthesized by replicating template SBA-15 and its electrochemical capacitance performance was for the first time evaluated in 2 M KOH electrolyte solution. The electrochemical capacitance performance of ordered mesoporous NiO was extensively investigated by the means

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of cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS) and galvanostatic charge–discharge tests compared with that of conventional NiO prepared by direct calcining $Ni(NO_3)$ · $6H_2O$ at 550 °C.

2. Experimental

2.1. Synthesis and characterization of electrode materials

Crystallized NiO with ordered mesoporous structure were prepared by calcining Ni(NO₃)·6H₂O at 550 °C within the template of SBA-15. SBA-15 is a kind of silica material with high ordered porous structure and can be used as hard template [20,21]. In our experiment, the SBA-15 is purchased from Chang Chun Jilin University High-Tech. Co., Ltd., China. In a typical synthesis, 5 g Ni(NO₃)·6H₂O was dissolved in 25 g of distill water, and then 0.6 g SBA-15 sample was added to the above solution. After stirring for several hours at vacuum conduction, the solution was transferred to clean petri dish and the solvent was evaporated at 50 °C in air atmosphere. The hybrid samples were calcined at 550 °C for 5 h. The crystallized NiO with ordered mesoporous structure were obtained by the solution etching of the silica framework by 2 M NaOH solution. The final products were separated by centrifugation, followed by washing with distilled water and ethanol. The conventional NiO was prepared by direct calcining Ni(NO₃)·6H₂O at 550 °C. The prepared NiO was characterized by X-ray diffraction (XRD, Bruker D8), scanning electronic microscope (SEM, Philip XL30), transmission electron microscopy (TEM, Jeol JEM-2010) and BET surface area measurement (Micromeritics Tristar).

2.2. Electrochemical tests

The electrode of NiO was prepared according to the following steps. The mixture containing 80 wt.% NiO and 15 wt.% acetylene black and 5 wt.% polytetrafluoroethylene (PTFE) was well mixed, and then was pressed onto nickel grid $(1.2 \times 10^7 \text{ Pa})$ that serves as a current collector (surface is 1 cm²). The typical mass load of electrode material is 10 mg. The used electrolyte was 2 M KOH solution. The electrochemical behavior of NiO was characterized by cyclic voltammetry, electrochemical impedance spectroscopy and charge-discharge tests. The experiments were carried out in a three-electrode glass cell. Platinum foil was used as a counter electrode, and SCE as a reference electrode. CV and EIS measurements were performed using a Solartron Instrument Model 1287 electrochemical interface and 1255B frequency response analyzer controlled by a computer. The frequency limits were typically set between 1000 kHz and 0.01 Hz. The AC oscillation was 10 mV.

3. Results and discussion

3.1. Characterization of materials

Fig. 1 shows X-ray diffraction pattern of NiO prepared by template method. The diffraction peaks at 37.2° , 43.3° , 62.9° , 75.4° and 79.4° are the typical character diffraction peaks of



Fig. 1. X-ray diffraction pattern of NiO prepared by the template method.

NiO, which is agreed with that of the standard values (ICDD-JCPDS card no. 14-0117). Fig. 2 shows the SEM and TEM image of the NiO synthesized by template method. SEM image shown in Fig. 2a indicates that the prepared NiO is aggregate and does not have regular shape. TEM images shown in Fig. 2b and c clearly feature highly ordered NiO nanowires viewed from the their mother mold SBA-15. The diameter of the ordered NiO nanowires is about 9–10 nm, which is consistent with the channel diameter of the SBA-15 host, and the pore size produced from the ordered interspaces between these nanowires which are due to the removing of SBA-15 is about 4 nm, indicating the ordered crystallized NiO nanoarrays had a ordered mesoporous structure (hereafter it defined as the ordered mesostructured NiO).

 N_2 sorption measurement shows that BET surface areas are 47 and $6 \text{ m}^2/\text{g}$ for the ordered mesostructured NiO and the conventional NiO prepared by direct calcining Ni(NO₃)·6H₂O, respectively. Fig. 3 shows the N₂ adsorption–desorption isotherm of the ordered mesostructured NiO. As shown in Fig. 3, the profile of the hysteresis loop indicates an adsorption–desorption characteristic of the porous materials. The pore size distribution shown in Fig. 3 as an insert suggests that the ordered mesostructured NiO has a narrow pore size distribution centered at about 4 nm.

3.2. Electrochemical tests

3.2.1. Cyclic voltammetry tests

CV curves of the ordered mesostructured NiO and conventional NiO prepared by direct calcining Ni(NO₃)· $6H_2O$ are compared in Fig. 4. As shown in Fig. 4, the curve shapes of both samples reveal that the capacitance characteristics are very distinguished from that of electric double-layer capacitance in which the shape is normally close to an ideal rectangular shape, indicating that the capacity mainly results from the pseudocapacitive capacitance which is based on redox mechanism. A couple of redox peaks were observed within potential range 0.1–0.3 V (versus SCE), which can be considered to according to the fol-



Fig. 2. SEM and TEM images of NiO prepared by the template method. (a) SEM image; (b) TEM image seen from (001) direction; (c) TEM image seen from (111) direction.



Fig. 3. The N_2 adsorption-desorption isotherm and pore size distribution (the insert) of NiO prepared by the template method.

lowing redox reaction:

$$NiO + OH^{-} \rightleftharpoons NiOOH + e$$
 (1)

Comparing the curves (a) and (b) in Fig. 4, the redox current intensity of ordered mesostructured NiO is much higher than that of conventional NiO prepared direct calcining Ni(NO₃)· $6H_2O$. This can be interpreted in terms of that the ordered mesostructured NiO has many mesopores in its bulk which can provide more surface for fast, reversible faradaic reactions, thus increasing the utilization of NiO greatly.

3.2.2. Electrochemical impedance spectroscopy tests

The electrochemical impedance measurements were carried out on both electrodes at 0.25 V (versus SCE). The typical results are shown in Fig. 5. Two distinct regions which are dependent on the frequency range are shown in Fig. 5a and b. From the point intersecting with the real axis in the range of high frequency (shown as a insert), the internal resistances R_i of both electrodes are about 0.7 Ω . It includes the total resistances



Fig. 4. CV curves of NiO at a scan rate of 5 mV/s within potential window of -0.1 to 0.35 V vs. SCE: (a) ordered mesostructured NiO; (b) conventional NiO prepared by direct calcining Ni(NO₃)·6H₂O at $550 \,^{\circ}$ C.



Fig. 5. Typical electrochemical impedance spectroscopy of NiO at applied potentials 0.25 V (vs. SCE) within frequency range $(10^6 \text{ to } 0.01 \text{ Hz})$. (a) Ordered mesostructured NiO; (b) conventional NiO prepared by direct calcining Ni(NO₃)·6H₂O at 550 °C.

of the electrode resistance, $R_{\text{electrode}}$, the bulk electrolyte resistance, R_{bulk}, and the resistance at electrolyte/electrode interface, R_{interface}. The phase angles for impedance plots of both electrodes were observed to be higher than 45° in the low frequencies clearly. These findings suggest that both electrodes are not controlled by diffusion process. It is quite different from the results reported by Li and co-workers very recently [22]. They detected a slop of near 45 °C in the low frequencies of impedance plots, and demonstrated that the electrochemical capacitance behavior of electrode based on mesoporous Co₃O₄ in which the pores are randomly connected is strongly controlled by the diffusive resistivity of the electrolyte within the pores of the electrode. The differences between two compounds may be attribute to that the ordered mesopores facilitate ionic motion easy compared conventional mesoporous material in which the pores are randomly connected [19].

3.2.3. Charge-discharge tests

The galvanostatic charge–discharge curves of ordered mesostructured NiO and conventional NiO prepared by direct calcining $Ni(NO_3)$ · $6H_2O$ within potential range 0.35–0 V (ver-



Fig. 6. Charge–discharge curves of NiO at a current density of 1 mA/cm^2 within the potential window of 0–0.35 V vs. SCE. (a) Ordered mesostructured NiO; (b) conventional NiO prepared by direct calcining Ni(NO₃)·6H₂O at 550 °C.

sus SCE) at current of 1 mA/cm² are shown in Fig. 6. The specific capacitance (C_m) can be calculated as follows:

$$C_m = \frac{C}{m} = \frac{It}{\Delta Vm} \tag{2}$$

where *I* is the current of charge–discharge, *t* the time of discharge, ΔV is 0.35 V, and *m* the mass of active materials in the work electrode. The evaluated specific capacitances of the ordered mesostructured NiO is 128 F/g whereas it is about 31 F/g for the conventional NiO. This result indicates the ordered mesoporous structure increases the utilization of NiO greatly, which is due to that the ordered mesoporous structure within the bulk of NiO provide more effective surface to create pseudocapacitance.

The capacitances of both electrodes are shown in Fig. 7 as a function of charge–discharge current densities. As shown in Fig. 7, the capacitance of ordered mesostructured NiO decreases from 128 F/g (at a current density of 1 mA/cm²) to 117 F/g (at a current density of 5 mA/cm²). The capacitance retention is about 91%. In the same process, the capacitance of conventional NiO prepared by direct calcining NiO(NO₃)·6H₂O at 550 °C was



Fig. 7. Capacitance vs. charge–discharge currents. (a) NiO prepared by template method; (b) NiO prepared by direct calcining Ni(NO₃)- $6H_2O$ at 550 °C.



Fig. 8. Cycle-life of NiO synthesized by different methods between 0 and 0.35 V (vs. SCE) at a current density of 2 mA/cm^2 . (a) Ordered mesostructured NiO prepared by template method; (b) conventional NiO prepared by direct calcining Ni(NO₃)·6H₂O at 550 °C.

reduce from 31 to 29 F/g. The capacitance retention is about 93%. So, this result can indicate that both electrodes can endure high current density.

Fig. 8 gives the charge–discharge cycling tests of the ordered mesostructured NiO synthesized by template method and conventional NiO prepared by direct calcining Ni(NO₃)· $6H_2O$ at a current density of 2 A/cm² between 0 and 0.35 V (versus SCE). As shown in Fig. 8a, the ordered mesostructed NiO exhibits a good cycle profile: the capacitance slightly decreases from 123 to 111 F/g over 2000 cycles, it still remains over 90% of initial capacity. Fig. 8b indicates that the capacitance of NiO prepared by direct calcining Ni(NO₃)· $6H_2O$ at 550 °C decreases from 30 to 28 F/g over 2000 cycles. The capacitance retention of conventional NiO prepared by direct calcining Ni(NO₃)· $6H_2O$ at 550 °C is about 93%.

4. Conclusion

In this paper, NiO with ordered mesoporous structure was synthesized by replicating template SBA-15, and its electrochemical capacitance performance was for the first time evaluated in 2 M KOH electrolyte solution. The capacitance of NiO synthesized by template method was about 128 F/g, approximately four times larger than that of NiO prepared by direct calcining Ni(NO₃).6H₂O at 550 °C, which is attribute to that the ordered mesoporous structure within the NiO bulk provide a larger effective surface area to produce nonfaradaic doublelayer capacitance as well as a peseudocapacitance of faradaic redox of NiO on the particle surface. Additionally, the ordered mesostructured did not affect the ionic motion within the pores, which is different from the porous electrode, especially for these with micropores (<2 nm) or randomly connected pores, in which both the charge storage and rate capability may be limited by diffusive resisitivity of the ion motion within the pores. The ordered mesostructured NiO also shows good rate capability and cycling life.

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