Short communication

Comparative studies of nickel oxide films on different substrates for electrochemical supercapacitors

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Abstract

Thin nickel oxide (NiO) films were obtained by post-heating of the corresponding precursor films of nickel hydroxide (Ni(OH)$_2$) cathodically deposited onto different substrates, i.e., nickel foils, and graphite at 25 °C from a bath containing 1.5 mol L^{-1} Ni(NO$_3$)$_2$ and 0.1 mol L^{-1} NaNO$_3$ in a solvent of 50% (v/v) ethanol. The surface morphology of the obtained films was observed by scanning electron microscope (SEM). Electrochemical characterization was performed using cyclic voltammetrty (CV), chronopotentiometry (CP) and electrochemical impedance analysis (EIS). When heated at 300 °C for 2 h in air, the specific capacitance of the prepared NiO films on nickel foils and graphite, with a deposition charge of 250 mC cm^{-2}, were 135, 195 F g^{-1}, respectively. When the deposition charge is less than 280 mC cm^{-2}, the capacitance of both appears to keep the linear relationship with the deposition charge. The specific capacitance, cyclic stability of the NiO/graphite hybrid electrodes in 1 mol L^{-1} KOH solution were superior to those on nickel foils mainly due to the favorable adhesion, the good interface behavior between graphite and the NiO films, and the extra pseudo-capacitance of the heated graphite substrates.
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1. Introduction

Complementary to the double-layer capacitor of electrochemical capacitor (EC) technology is that based on redox pseudo-capacitance involving oxidation state changes in metal oxides, such as amorphous phase of hydrated ruthenium oxide (RuO$_2$·xH$_2$O) [1–3] and IrO$_2$ [4], NiO$_x$ [5–9], CoO$_x$ [10–12], and MnO$_2$ [13–16]. Similar capacitive behavior arises with electronically conducting polymers [17–19]. Since the cost of the noble metal oxides is inherently prohibitive, much attention has been paid to low cost metal oxides, e.g. NiO. Nickel oxide has thus been extensively prepared by thermal treatment of sol–gel-derived [5] or electrodeposited [6–8] Ni(OH)$_2$ thin films for pseudo-capacitor applications. Liu and Anderson [5] used the sol–gel method to fabricate a porous NiO electrode with a thickness of around 0.4 μm, in which nickel foil was withdrawn from the precursor Ni(OH)$_2$ sol and then heated at 300 °C to form NiO. The structure of this type of NiO is however uncontrollable and disordered, additionally, only a small amount of Ni(OH)$_2$

can be attached to the metallic nickel foil current-collector. In order to control the coating mass of the active material, Srinivasan and Weidner [6] utilized the cathodic precipitation method to fabricate NiO onto gold substrates, leading to a NiO film of 0.1–1 μm in thickness and of 7.0–70.0 μg in weight, correspondingly. This implies a critical consideration of the mass of loading NiO on a current-collector even though the specific capacitance was found to decrease dramatically with an increased loading mass [5–7]. In addition, there also exists a difficulty in controlling porous structure in favor of enhancing capacitive properties. Presumably, it is due to much mismatch in coefficient of thermal expending (CTE) between NiO phase and the metallic substrates employed. Consequently, when heated in air, the thicker NiO films cannot survive attaching tightly to the substrates, most badly, leading to NiO peering off. The effects of current collectors on the properties of RuOx·nH$_2$O and activated carbon–RuOx electrodes were investigated by Hu and Chen [20]. Actually, influences of contact resistance at the interface between current collectors and electro-active materials on the capacitive performance should be considered in the high-power applications of supercapacitors.

From the standpoint of commercial application, it is essential to use inexpensive metallic substrates of low density as current

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collectors. Activated carbon layers on aluminium foil [21,22], PANI coated stainless-steel electrodes [23], ruthenium oxide thin film precipitated on graphite fibres of carbon paper [24] or on titanium [3], and manganese oxide deposited on graphite [15,16], have been achieved the favorable aspects mentioned above. Moreover, as expected, the improved mechanical properties are obtained simultaneously because of overcoming the CTE mismatch between oxide phase and the metallic substrates to some extent. The objective of the present study is to comparatively evaluate nickel foil and graphite as substrates for coating NiO films and comprehensively investigate the effects of the employed substrates on the capacitive behaviors. This insight could be used to guide electrode development, which may make NiO more viable for commercial supercapacitors.

2. Experimental

A graphite disc electrode (6 mm in diameter) was prepared via a method described before [16]. The nickel foils (10 mm × 10 mm × 1 mm) were degreased in a chemical detergent solution, rinsed in distilled water, and then electrochemically cleaned. $Ni(OH)_2$ thin films were electrochemically precipitated onto the above two substrates, respectively, at room temperature (ca. 25 °C) from a bath containing 1.5 mol L^{-1} $Ni(NO_3)_2$ and 0.1 mol L^{-1} $NaNO_3$ in a solvent of 50% (v/v) ethanol at a cathodic current density of 5.0 mA cm^{-2} via a procedure described in detail by Streinz et al. [25,26]. The deposition process was run for specified time to achieve different thickness of films. The deposited $Ni(OH)_2$ films were washed in distilled water and delicately heated in air at specified temperatures for 2 h, to obtain NiO films [5]. And then the samples were automatically allowed to cool to room temperature. For an encapsulated graphite electrode, the epoxy coating was removed from the electrode before being heated in air, and after heating, the graphite electrode was re-insulated with epoxy coating but the electroactive NiO film.

The surface morphology of the nickel oxide films was observed on a JEOL JSM-5800LV scanning electron microscope. The as-obtained electrodes were electrochemically characterized in an electrolyte of 1.0 mol L^{-1} potassium hydroxide (KOH) solution with a saturated calomel electrode (SCE) as a reference electrode and a platinum gauze as a counter electrode. CV, CP, and EIS were performed with a CHI760B computer-controlled electrochemical workstation driven by a CHI760B electrochemical analysis software. All of the electrochemical measurements were conducted at room temperature. The average specific capacitance of the NiO films were estimated from the CVs by integrating the area under the current (per gram of the sample)–potential curve and then dividing by the sweep rate, and the potential window according to the following equation:

$$C_q = \text{voltammetric charge}/(\text{potential} \times \text{sample loading})$$

$$= q/(\Delta V m) = \frac{1}{0.35mv} \int_0^{0.35} i(V) \, dV$$

$$= \frac{1}{0.35v} \int_0^{0.35} \frac{i(V)}{m} \, dV = \frac{1}{0.35v} \int_0^{0.35} i'(V) \, dV \quad (1)$$

where v is a constant of sweep rate applied for the CV measurements, i.e. $\frac{dV}{dt}$, $i(V)$ is a current response depending on sweep voltage, and voltammetric charge is thus estimated as $q = \int_0^{0.35} \frac{i(V)}{v} \, dV$ within a potential window (ΔV) of 0–0.35 V. The charge–discharge behaviors of the NiO films were examined by CP. The specific capacitance can be calculated from the following equation [13]:

$$C_{CP} = \frac{i}{|(dE/dt)m|} \approx \frac{i}{[(\Delta E/\Delta t)m]} \quad (2)$$

where i is the charge–discharge current applied, (dE/dt) indicates the slope of the charge–discharge plot of the CP curves, and m is the mass of the NiO film. The deposition efficiency was considered to be similar to that by Srinivasan and Weidner [6,7], and accordingly the mass of the prepared NiO films were estimated.

3. Results and discussion

It is well known that the conversion of $Ni(OH)_2$ to NiO [5–8] arises when the precursor $Ni(OH)_2$ is heated at or above 250 °C
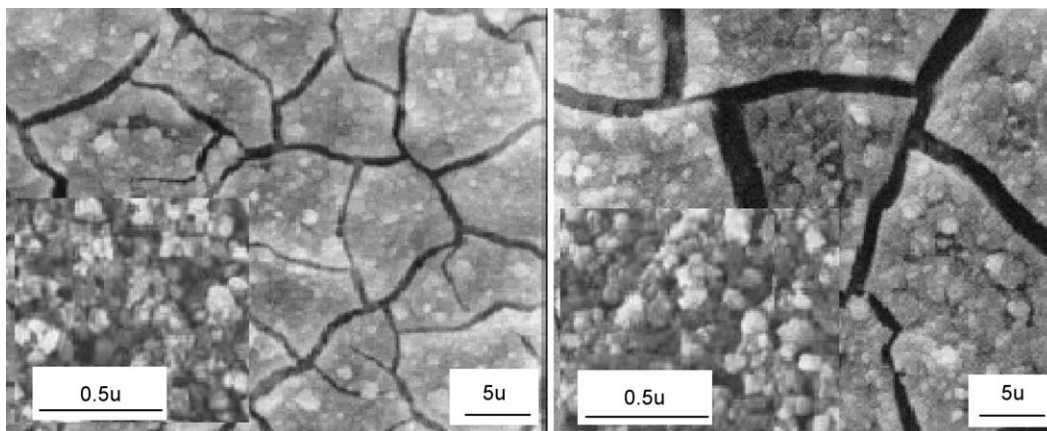

Fig. 1. The SEM images of NiO films on graphite (a), and on nickel foil (b), heated at 300 °C for 2 h in air.

according to the reaction as follows:

$$Ni(OH)_2 \rightarrow NiO + H_2O \qquad (3)$$

Additionally, heating at a temperature above 300 °C may cause the increase in crystal size, and accordingly the decrease in specific surface area, and also possibly its reactivity for surface chemical process. These critical factors for high capacitance have been estimated [6–8]. Fig. 1 illustrates the difference of the morphology of NiO films on different substrates heated at 300 °C for 2 h in air. It is clear that the NiO film on nickel foil is of much crack, but that on graphite is more uniform although the highly magnified seems very similar, as shown in the insect. It can be concluded that the use of different substrates may lead to different microstructure and surface morphology of NiO films. Consequently, the substrate in deed plays some role on the surface nature of NiO films. Moreover, it is very understandable that this effect will be highlighted with the increase in thickness of the NiO films. It could be ascribed to much mismatch of the CTE between the NiO film and the metallic nickel foil. Even though good pretreatment of substrate and delicate heating process can offer a remedy to some extent, the thicker NiO films on metallic substrate may suffer the risk of peering off. However, the use of graphite as a substrate can improve attaching NiO film to the substrate, especially upon heating at high temperature. Furthermore, the carboxyl groups possibly present on the surface graphite at high temperature may not only offer anchors for oxide to the substrate, but also can exhibit adsorption pseudo-capacitance [27].

To compare the capacitive behaviors of the resulting NiO films on different substrates, the NiO films from corresponding Ni(OH)$_2$ precursors with identical deposition charge were evaluated by CV running in 1 mol L^{-1} KOH solution. As shown in Fig. 2 are typical CVs of NiO films on different substrates, heated at 300 °C for 2 h in air. It can be seen that very similarly shaped CV comes with the two different NiO films, but the film on graphite can get charged approximately 30% more, namely, ~195 and ~135 F g^{-1} with the NiO/graphite electrode
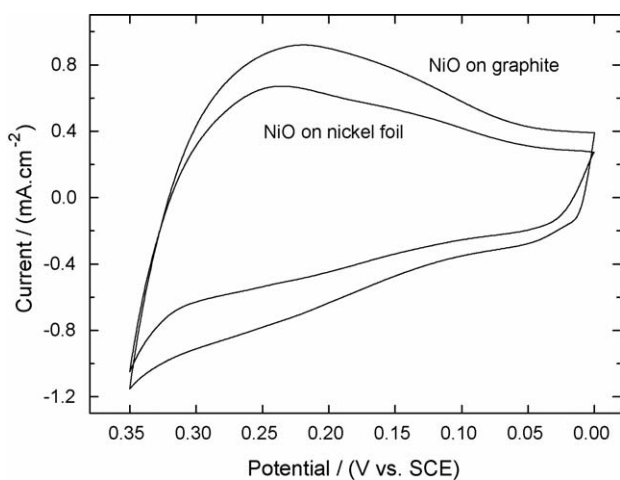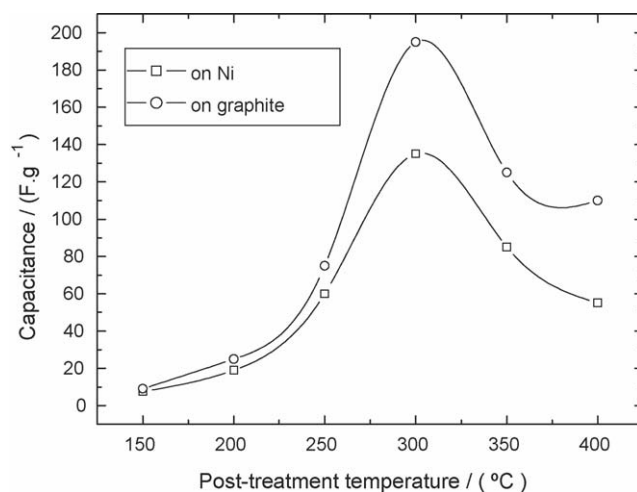

Fig. 3. Dependence of specific capacitance of the NiO films on the post-treatment temperature. Deposition charge: 250 mC cm^{-2}; CV electrolyte: 1 mol L^{-1} KOH.

and NiO/Ni electrode, respectively. As for the possibility of the NiO crystallizability affecting their capacitance, the similar studies were conducted to indicate any difference when the graphite substrate is utilized in this paper. As indicated in Fig. 3, the dependence of capacitance on the heating temperatures was therefore obtained. Obviously, there presents a dramatic increase in specific capacitance for both of the samples when the Ni(OH)$_2$ precursors are heated from 150 to 300 °C but a slow drop when heated above 300 °C. It is generally believed that the faradaic capacitance is of interfacial phenomena. It is well accepted that the capacitance of the NiO films may be determined by specific surface area and surface reactivity [5–7]. It can be thereby easily understood that the Ni(OH)$_2$ heated below 200 °C exhibits poor capacitive behavior, and the difference in capacitance for both of the two electrodes seems not too much. The capacitive behavior otherwise improves with the increase of the heating temperature up to 300 °C, and the difference also becomes more and more, with an ultimate value of around 30%. It is not only very likely due to the less accessibility of the mass of NiO on nickel foil due to its poor adhesion to the substrate, but also because of the capacitance attribution from the functionalized graphite active sites. However, the specific capacitance appears a drop with the increase of the heating temperature above 300 °C. It is mainly because that the NiO crystallite phase becomes inert to the electrolyte with increasing crystallization degree. Fig. 3 clearly indicates an optimal heating temperature of 300 °C to achieve the largest specific capacitance, and it is well justified the advantages of using graphite as substrate in this work.

As mentioned above, the pseudo-capacitance is restricted on the surface of electro-active material. However, more loading of the electro-active material is favorable for high charge storage, and the thickness of films is thus one another important factor of much consideration [2]. Therefore, investigations were made to examine the dependence of capacitive performance on the thickness of NiO films. We did not have a try to measure the thickness of the NiO films, but controlled the deposition charge to obtain NiO films of different thickness. Shown in Fig. 4 is a clear dif-
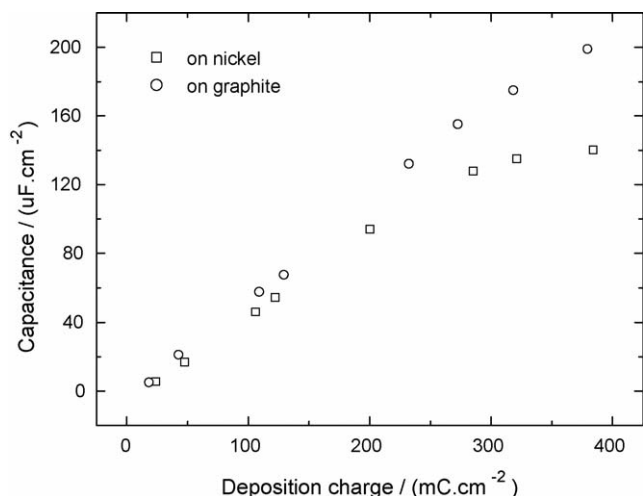

Fig. 2. Typical CVs of the NiO films heated at 300 °C for 2 h in air. Deposition charge: 250 mC cm^{-2}; CV electrolyte: 1 mol L^{-1} KOH; potential sweep rate: 10 mV s^{-1}.

Fig. 4. The relationship between specific capacitance and deposition charge for NiO films. CV electrolyte: $1 \, mol \, L^{-1}$ KOH.

Fig. 6. Comparison of cycling behaviors of NiO films on different substrates. Deposition charge: $250 \, mC \, cm^{-2}$, cycling between 0 and 0.35 V (vs. SCE) in $1.0 \, mol \, L^{-1}$ KOH at $5 \, mA \, cm^{-2}$.

ference of the dependence of specific capacitance on deposition charge. When the deposition charge is more than $280 \, mC \, cm^{-2}$, the capacitance of both films appears to not still keep the linear relationship with the deposition charge, and comparatively, worse case goes with the NiO films grown on nickel foils.

To further confirm the advantage of graphite over nickel foil as a substrate in this work, electrochemical impedance analysis and charge–discharge cycling were performed with the results shown in Figs. 5 and 6, respectively. The resistance of the NiO/graphite related to the conductivity of the electrode and electrolyte is less than $3 \, \Omega$ while the counterpart of the NiO/Ni is near $5 \, \Omega$. Moreover, the knee frequency is 5.5 and 0.5 Hz, respectively. The significantly enhanced electric properties should be attributed to the graphite improving electron conducting. Presumably, it is mainly owing to good contact between graphite substrate and NiO films. The cycling test indicates that the electro-activity of the NiO/graphite electrode and the NiO/Ni electrode can maintain 93% and 90% after 2000 cycles, respec-
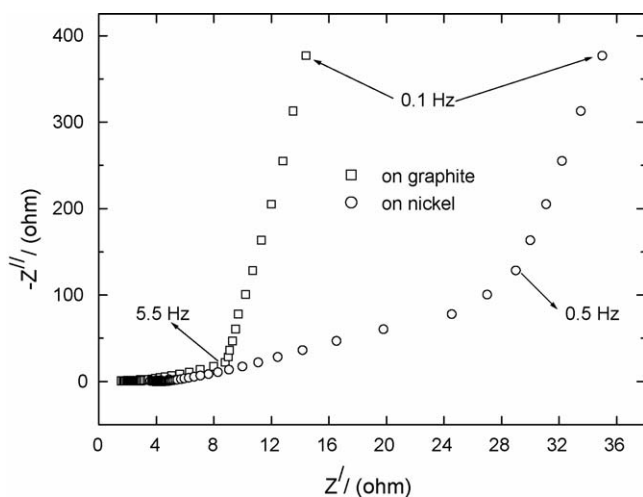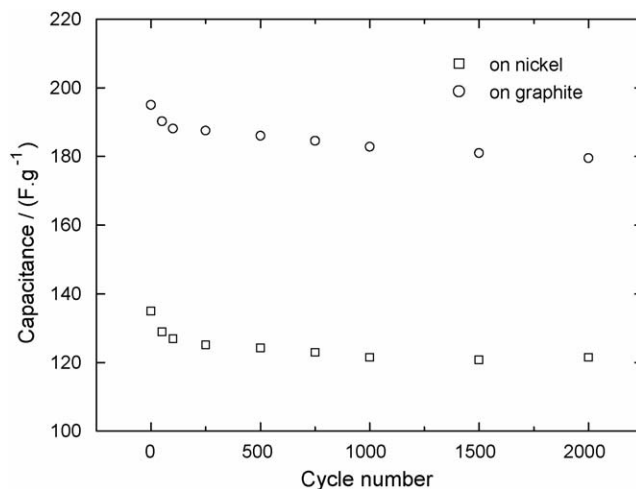
tively. Although there is not remarkable difference in cycling property, advantages mentioned above may make graphite more interesting and promising for such electrode systems for supercapacitors.

4. Conclusions

Nickel oxide films were prepared by electrochemical cathodic depositing hydroxide on graphite and nickel foil, respectively, and post-heating it at different temperature for 2 h in air to form the oxide. It is confirmed that post-heating temperature is critical factor in the optimization of the capacitance of all the deposits. When heated at $300 \, °C$ for 2 h in air, the specific capacitance of the prepared nickel oxide films on nickel foils and graphite, with a deposition charge of $250 \, mC \, cm^{-2}$, were 135, $195 \, F \, g^{-1}$, respectively. When the deposition charge is more than $280 \, mC \, cm^{-2}$, the capacitance of both appears to not still keep the linear relationship with the deposition charge, and comparatively, worse case goes with the NiO films grown on nickel foils. The specific capacitance, resistance, and cyclic stability of the nickel oxide/graphite hybrid electrodes in $1 \, mol \, L^{-1}$ KOH solution were superior to those on nickel foils mainly due to the favorable adhesion, good interface behavior between graphite and the nickel oxide films, and the extra pseudo-capacitance of the heated graphite electrodes. It is demonstrated that the cost-saving graphite is a very promising substrate for industrial applications of nickel oxide in electrochemical supercapacitors.

Fig. 5. Complex plane impedance plots of the NiO films heated at $300 \, °C$ for 2 h in air. Deposition charge: $250 \, mC \, cm^{-2}$; EIS electrolyte: $1 \, mol \, L^{-1}$ KOH; ac potential amplitude: 10 mV; frequency range: 50 kHz and 0.1 Hz.

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