Electrochemically Deposited 3D Honeycombnetwork-Like NiO Films with Its High-Power Pseudocapacitive Properties

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Citation

Abstract
In this work, we reported that three-dimensional (3D) honeycomb-like NiO nanoflakes can be directly deposited on nickel foam via a facile electrodeposition method. The effects of electrodeposition conditions including the deposition potential and deposition mass on structure and pseudocapacitive performance are systematically studied. The results show that the 3D honeycomb-like NiO film can be obtained at a potential of -0.7 V (vs. SCE) and a mass loading about 0.83 mg per square centimeter, thus providing superior electrochemical performance. For example, this 3D honeycomb-like NiO film can yield an extremely high specific capacitance of 1308 F g⁻¹ at 3 A g⁻¹ and still deliver 950 F g⁻¹ at an ultra-high current density of 36 A g⁻¹. The present work elaborates on a profound understanding for designing high-performance metal oxide electrodes for supercapacitors.

1. Introduction

Electrochemical capacitors (ECs) have attracted enormous attention in recent years due to the unique characteristics of the high power density, the excellent reversibility, and the longer cyclic life in comparison with batteries. ECs have been widely used for practical applications such as power hybrid electric vehicles and camera flash bulbs, where they are expected to work in conjunction with a conventional battery. Therefore, a lot of research works have been done in the past few years to improve the performances of the electrochemical capacitor electrodes. Most commercially ECs are based on electrochemical charge accommodation at two catalogues, (i) the electric double layer capacitors (EDLCs) arising from the charge separation at the electrode/electrolyte interface and (ii) the faradaic pseudocapacitors arising from fast, reversible electrosorption or redox processes occurring at or near the solid electrode surface [1]. Generally, the faradaic pseudocapacitors have been reported many times because it has been recognized that the energy density based on pseudo-faradaic processes is of many times greater than that of the traditional EDLCs.

Carbon materials [2], transition metal oxides [3] and conducting polymers [4] are widely used as the supercapacitor electrode materials. Among these materials, transition metal oxides and conducting polymers are regarded as the candidate electrode materials for pseudocapacitors. However, electrically conducting polymers (ECPs) have a defect of the typical volumetric shrinkage during ejection of counterions (doped ions). Furthermore, the
conductivity of ECPs was very low at dedoped state, which would result in high ohmic polarization of supercapacitor. Consequently, transition metal oxides (ruthenium oxides, manganese oxides, nickel oxides and others) generally turn out to be the most promising candidates, because of their higher specific capacitance, rate capability and availability. Among the available metal oxides, nickel oxide is one of the potential candidates for EC electrode materials due to its energy storage performance in basic electrolytes, environment compatibility and chemical stability. Generally, the capability of electrode material is significantly influenced by its surface area and morphology. The electrode material with high surface area and a uniform, ordered pore network of nanometer dimension would be expected to exhibit superior performance in supercapacitor system. Thus, nanostructured nickel oxides display higher electrochemical activities and excellent capacitive performance than their bulk counterparts.

In order to effectively improve the desired functionality, a variety of preparation methods, such as chemical precipitation [5, 6], thermal decomposition [7, 8], hydrothermal process [9, 10], surfactant template [11, 12], polymer template [13, 14], sol-gel method [15], and electrodeposition [16] have been explored to fabricate nanostructured nickel oxides. Among these synthetic approaches, the electrochemical deposition method is a relatively easy method to deposit the active material directly onto the substrate at room temperature without templates. We can accurately control the surface microstructure, mass and thickness of the deposited films by changing deposition variables, such as electrolyte, deposition potential and bathing temperature. Moreover, it has been shown that the nickel oxide synthesized by electrodeposition exhibits superior electrochemical performances compared to others. Thus, electrochemical technique attracts considerable attention. Presently, a lot of research work has been done to prepare the nanostructured NiO films by electrochemical deposition and expected to get better performances. Cao et al. [17] have reported the hierarchical porous NiO nanotube arrays and showed the maximum value of specific capacitance of 675 F/g. Aghazadeh et al. [18] have prepared the porous NiO nanostructure which had a specific capacitance as high as 1056.4 F/g. It showed that the network-like NiO film possess a maximum specific capacitance of 1308 F/g and a high-power pseudocapacitive performance, which shows great potential as the electrode materials for ECs. In addition, the effect of deposition potential and deposition mass on the surface morphology and capacitance property of the deposited films were also studied in detail.

2. Experimental

2.1. Preparation of NiO Films

Nickel hydroxide films were deposited directly on a 1 cm² nickel foil at room temperature by electrochemically deposition in a bath containing 0.1 M Ni(NO₃)₂ and 0.075 M NaNO₂ in a solvent of 50% ethanol mixture. All chemicals were analytical grade and were used without further purification. The electrodeposition of nanostructured Ni(OH)₂ film was conducted using an electrochemical working station (CHI660C, Shanghai, China) in a three-electrode cell at room temperature (RT). A piece of nickel foil (1 cm² in area) was used as the working electrode, a platinum foil (area 1 cm²) was used as the counter electrode, and a saturated calomel electrode (SCE) as reference electrode, respectively. Prior to electrochemical deposition, nickel foil was soaked with acetone and ultrasonically vibrated for 15 min to wash away any contaminants from their surface, and finally treated with de-ionized water. Cathodic deposition of nanostructured NiO films was carried out at different deposition potentials, viz., -0.70, -0.90, -1.10, and -1.30 V versus SCE. After deposition, the as-prepared Ni(OH)₂ electrode was washed with a copious amount of distilled water several times. Nickel oxide films were formed on the substrates by heating the as-deposited Ni(OH)₂ films at different temperature in air for 3h, viz., 100, 200 and 300°C (without special denotation, the NiO film is referred to the deposition potentials of -0.7 V, mass of 0.83 mg and heated temperature of 300°C).

2.2. Structure Characterization

The obtained NiO films were characterized by field-emission scanning electron microscope (JEOL, JSM-6701, Japan), X-ray diffraction measurements (Rigaku, D/MAX-2400, Japan) and Thermogravimetric-differential scanning calorimeters analysis (TG-DSC) (Netzsch, STA-449C, Germany).

2.3. Electrochemical Measurements

Electrochemical capacitive behaviors of the nickel oxide electrode were determined by using an electrochemical working station in a three electrode cell with a 2 M KOH electrolyte. The freshly prepared NiO film on nickel foam was used as the working electrode, a platinum foil (area 1 cm²) was used as the counter electrode, and a saturated calomel electrode (SCE) as reference electrode, respectively. The CV curves were recorded in the potential range between -0.1 and 0.55 V (vs. SCE) at different scan rates and the galvanostatic charge/discharge were carried out in the potential range of 0 ~ 0.4 V at different
constant current densities. AC impedance spectroscopy measurements were performed under open circuit potential in an a.c. frequency range from 10 kHz to 0.01 Hz with an excitation signal of 5 mV. All electrochemical experiments were carried out at room temperature (about at 20 ± 1°C).

3. Results and Discussion

3.1. Film Formation Mechanism

In electrochemical deposition method, Ni(OH)$_2$ film formation is observed from aqueous Ni(NO$_3$)$_2$ solutions, which may involve as follows:

When electric current passes the electrolyte containing Ni(NO$_3$)$_2$, nitrate ions can be reduced on the cathodic surface to produce hydroxide ions. The generation of OH$^-$ at the cathode raises the local pH, resulting in the precipitation of Ni(OH)$_2$ at the electrode surface according to the following reactions [19]:

$$\text{NO}_3^- + 7\text{H}_2\text{O} + 8e^- \rightarrow \text{NH}_4^+ + 10\text{OH}^- \quad (1)$$

$$\text{Ni}^{2+} + 2\text{OH}^- \rightarrow \text{Ni(OH)}_2 \quad (2)$$

References in Baes and Mesmer [20] have shown that the predominant species of soluble complexes in concentrated Ni(NO$_3$)$_2$ aqueous solutions (ca. 0.1 M in our work) is the polymeric Ni$_4$(OH)$_4$$^{4+}$. The polymeric species Ni$_4$(OH)$_4$$^{4+}$ then combines with more OH$^-$ to form Ni(OH)$_2$ deposit as given in eq 4: [21]

$$4\text{Ni}^{2+} + 4\text{OH}^- \rightleftharpoons \text{Ni}_4(\text{OH})_4^{4+} \quad (3)$$

$$\text{Ni}_4(\text{OH})_4^{4+} + 4\text{OH}^- \rightarrow 4\text{Ni(OH)}_2 \quad (4)$$

These reactions are likely to occur simultaneously during the electrodeposition process. While numerous researchers used Faraday's law to predict the mass of the deposited films as the necessary first step in determining the specific capacitance, relatively few have provided the experimental verification of the exact film mass. For example, MacArthur [22] used Faraday’s law to calculate film thickness but gave no experimental evidence other than electrochemical capacity. Of particular interest, Streinz et al. [23-26] observed that at low concentrations (e.g., 0.2 or 0.1 M) the utilization efficiency of electrochemically generated OH$^-$ was nearly 100%, whereas at high concentrations (e.g., 1.0 or 2.0 M) the utilization efficiency of OH$^-$ was significantly less than 100%. On the basis of the above discussion, Faraday’s law was used to calculate the mass of the deposited films at low concentrations (such as 0.1 M in our work). Consequently, $Q$, the quantity of electrical charge during electrodeposition, could be estimated by Faraday’s law $Q = mFn / M$, where $m$ and $M$ are the mass and molecular weight of the deposited film, respectively, and $n$ is the number of electrons in the electrodeposition reaction per atom of Ni (see eqs 1 and 2).

In order to improve crystallinity and remove hydroxide phase, films were annealed for 3 h at 300°C. Pure NiO film is formed after annealing by following mechanism:

$$\text{Ni(OH)}_2 \xrightarrow{\Delta} \text{NiO + H}_2\text{O} \quad (5)$$

In other words, depositing a Ni(OH)$_2$ film of about 1.0 mg, the corresponding deposition charge quantity is approximately 1.665 C, and the 1.0 mg film remains 0.83 mg after heating to 300°C according to TG-DSC (elaborating on later).

3.2. Structural Characterization of NiO Films

TG-DSC was conducted on electrochemically precipitated nickel hydroxide to investigate the thermal behavior of the deposited films and to estimate the mass of the heat-treated films. As seen in Figure 1, TG-DSC of the Ni(OH)$_2$ in this study indicates two weight loss regions: (i) removal of the water of hydration and absorbed water below 125°C; (ii) removal of water due to the decomposition of the Ni(OH)$_2$ to the NiO over 250°C. When the temperature is above 300°C, the TG curve becomes flat, which indicates that no phase transformation occurs, and further heating could only make the structure of the products more crystalline, which goes against the increasing of specific capacitance. Thermogravimetric analysis showed that the mass of the heat-treated NiO at 300°C is 83% of that of the initial material, excluding the weight of absorbed water. Therefore, the 1.0 mg film remains 0.83 mg after heating to 300°C.

![Figure 1. TG and DSC curves for the decomposition of Ni(OH)$_2$ under a dynamic air environment.](image-url)

In order to study crystalline nature of the as-prepared and annealed thin films, the XRD patterns were recorded in the 2θ range 5-75°. Figure 2 shows the XRD patterns of the as-deposited Ni(OH)$_2$ and the corresponding nickel oxide heated at different temperatures for 3 h in air. The XRD pattern of the precursor Ni(OH)$_2$ corresponds to the layered α-Ni(OH)$_2$ structure with low crystallinity. Being heated at 100°C for 3h, the product remains the α-Ni(OH)$_2$ structure, however, its (001) peak shifted slightly to higher angles, leading to a decrease of the “c” spacing of the unit cell. This is due to water removal from planes perpendicular to the c axis.
of Ni(OH)$_2$ crystals [27]. A conversion of nickel hydroxide to nickel oxide took place as the temperature increased to 200°C. The diffraction peaks of the nickel oxide heated at 200°C are broad, which indicates the low degree of crystallization of the products. For the deposits treated at 300°C, all these diffraction peaks, including not only the peak positions but also their relative intensities, can be perfectly indexed into the standard cubic NiO spectrum (PDF, card no 44-1159). This result is in agreement with that of the TG-DSC.

**Figure 2.** XRD patterns for as-deposition Ni(OH)$_2$ and heated films at different temperatures for 3h.

### 3.3. Surface Morphology of NiO Films

In order to investigate the effect of the deposition mass on the surface morphology of deposited films, SEM measurement was performed to the nickel films with different masses, the results were shown in Figure 3a, b and c for the 0.41, 0.83 and 1.66 mg NiO films, respectively. As shown in Figure 3a, only loosely packed particles can be seen in the NiO film with an extremely low deposited mass of 0.41 mg. It is noteworthy that the highly porous network-like structure, which consists of interconnected nano-flakes in nanometer scale, can be found in Figure 3b and Figure 3c. However, comparing these micrographs of both films, it can be seen that the 0.83 mg NiO film reveals a smoother surface of the interconnected nano-flakes, whereas the nano-flakes in the 1.66 mg NiO film are relatively dense and aggregate to some extent. These results show that NiO films of three-dimensional network-like structure can be obtained at the optimum deposition mass. For this reasons, the mass of deposited films on nickel foams with an exposed area of 1 cm$^2$ was controlled to be about 0.83 mg in our work. The correlation between the surface morphology of deposited films and their specific capacitance is discussed later in this paper, because the surface morphology of the electrode materials significantly affected the capacitance of an electrochemical capacitor [28].

**Figure 3.** SEM image of the deposited nickel oxide films in 20,000 magnifications (50,000× is shown in the inset) as a different deposited mass on the nickel foam: (a) to a 0.3 mg film and (b) to a 0.75 mg film (c) to a 1.5 mg film.

### 3.4. Supercapacitive Behaviors of NiO Films

In order to determine electrochemical capacitive properties of the NiO films, CV and chronopotentiometry measurements were performed on the NiO films in 2 M KOH solution at RT. The effects of electrodeposition potential, deposited mass and current density on the specific capacitance were studied in detail. Generally, the specific capacitance (C) of an electrode during galvanostatic test can be calculated by the following equation:

$$C = \frac{i\Delta t}{w\Delta v}$$  \hspace{1cm} (6)

where $w$ is the mass of nickel oxide(g), $\Delta v$ is the potential window (V), $i$ is the discharge current (A) applied for time $\Delta t$ (s).

#### 3.4.1. Effects of Deposited Potential on Specific Capacitance of Nickel Oxide Film

Figure 4a shows the discharging curves of NiO films deposited at different potentials in the potential range of 0-0.40 V vs. SCE in 2 M KOH at a current density of 3.0 A g$^{-1}$. The mass of the NiO films was about 0.83 mg. According to Eq. (4), the specific capacitance values of the NiO films deposited at -0.7, -0.9, -1.1, -1.3 V were 1308, 1093, 906, 637 F g$^{-1}$.
respectively. The maximum specific capacitance is the highest report of NiO for supercapacitors. Obviously, the specific capacitance of film deposited at -0.7 V (1308 F g\(^{-1}\)) is much higher than that of deposited at -1.3 V (637 F g\(^{-1}\)). This reflects that more ordered nanoporous network structure within a nickel oxide deposited at -0.7 V are more suitable for electrolyte penetration, which can increase the faster electrochemical accessibility of the electrolyte and OH\(^{-}\) ions to the bulk of the NiO phase. This phenomenon may be explained that: with increasing deposited potential, the deposition speeding gradually accelerates, the deposition at higher potential may cause the increase in pore diameter, and accordingly the decrease in specific surface area and, also possibly, its reactivity for surface chemical process, thereby leading to a decreased capacitance [29]. Therefore, we select an optimum electrodeposition potential of -0.70 V vs. SCE in this study.

**Figure 4.** The effects of electrodeposition conditions on specific capacitance of nickel oxide film in 2 M KOH at a current density of 3.3 A g\(^{-1}\): (a) discharging curves of the NiO films deposited at -0.7 V, -0.9 V, -1.1 V, -1.3 V potentials on nickel foam substrates measured in the potential range from 0 to 0.40 V versus SCE; (b) the plot of various of specific capacitance with deposited mass of anneal NiO films.

### 3.4.2. Effects of Deposited Mass on Specific Capacitance of Nickel Oxide Films

The effect of deposited mass on specific capacitance was investigated by chronopotentiometry at a current density of 3.0 A g\(^{-1}\) in 2 M KOH solution and the corresponding results are shown in Figure 4b. As seen in Figure 4b, the specific capacitance increases significantly with increasing the deposited mass, and a maximum value of the specific capacitance can be obtained for the 0.83 mg NiO sample; however, the specific capacitance decreases with increasing the deposited mass when the mass is over 0.83 mg. The maximum specific capacitance of 1308 F g\(^{-1}\) was obtained for 0.83 mg cm\(^{-2}\), which shows a capacitance approximately two times that of a 1.66 mg film. This can be explained that the interconnected network-like structures of electrode materials were not formed, when the deposited masses are lower at the beginning of deposition (shown in Figure 3a). With the increase of deposited masses, some NiO films gradually grew into the interconnected network-like structure, which can facilitate the penetration of electrolytes into the whole active material and shorten the proton diffusion distance, providing an important morphological foundation for an ultrahigh specific capacitance (shown in Figure 3b). However, it can be found that the deposited films are relatively dense and have some agglomerates in surface of nickel foams at the higher masses (shown in Figure 3c). This results showed that lower or higher deposited mass may cause the decrease in specific surface area and, also possibly, its reactivity for surface chemical process, thereby leading to a decreased capacitance. It can be therefore easily understood that the 0.83 mg NiO films exhibits the best capacitive behavior than other samples.

**3.4.3. Cyclic Voltammetry and Discharge Tests of Nickel Oxide Films**

The charge-storage mechanism of NiO for a pseudocapacitor electrode in alkaline solution has been represented as a simple OH\(^{-}\) participating reaction, which is described by the following reaction [30]:

\[
\text{NiO + OH}^- \xrightarrow{\text{charge}} \text{NiOOH + e}^- \quad (7)
\]

Figure 5a shows the CV curves of the deposited NiO films at different scan rates within a potential range of -0.1 to 0.55 V. In general, scan rate merely influences the specific of an electrochemical capacitor rather than an ideal double-layer capacitor. When the potential is lower than 0.1 V, the CVs show a rectangular mirror image with respect to the zero-current line, which represents an electrical double-layer capacitive behavior and independent of scan rate. When the upper limit potential exceeds 0.1 V, redox capacitance, which depends on the scan rate, should be considered into the measured capacitance. The two strong redox reaction peaks are responsible for the pseudo-capacitive capacitance. The anodic peak may presumably come from the oxidation processes of nickel oxide (NiO/ NiOOH) and the cathodic peak is for the reverse process. So the results indicated that the
specific capacitance of nickel oxide electrode comes from both the electrical double-layer capacitances and the faradic. An electrochemical capacitor, due to the Faradaic reaction and Ohmic resistances, has a lower specific capacitance when the scan rate is high. High scan rate in CV scan corresponds to the high-rate charge/discharge.

Figure 5b shows the discharging curves of the NiO film electrode at different current densities in the potential range for 0 to 0.4 V. The shape of the discharge curves does not show the characteristic of pure double-layer capacitor, but mainly pseudo-capacitance, which is in agreement with the result of the CV curves [31]. The specific capacitance values are calculated to be 1308, 1193, 1132, 1066 F g\(^{-1}\) corresponding to the charge/discharge current densities of 3.0, 6.0, 12.0, and 24.0 A g\(^{-1}\), respectively. As the discharge current increases, the large voltage drop produces, and finally, the capacitance decreases. This phenomenon may be explained by referring to OH\(^-\) ions diffusion processes during the charging/discharging for the electrode. When the charging/discharging at high current density, massive OH\(^-\) ions are required to intercalate swiftly at the interface of electrode/electrolyte, but relatively low concentration of OH\(^-\) ions could not meet this demand and the processes would be controlled by the ion diffusion [32]. Therefore, the specific capacitance obtained at the low current density is believed to be closest to that of full utilization of the electrode material, which has a higher specific capacitance.

Generally, the ability to discharge at high-rate is crucial in capacitors. So it is necessary to investigate the relationship between specific capacitance and current density, and Figure 5c shows the results. Clearly, the deposited film has a higher capacitance at low discharge current than that at high discharge current. The initial specific capacitance at 3.0 A g\(^{-1}\) is 1308 F g\(^{-1}\), when the discharge current density increases from 3.0 to 36 A g\(^{-1}\), the specific capacitance decrease slightly to 950 F g\(^{-1}\), that remains 72.6% of the initial value. So the excellent rate capability of the sample makes it attractive particularly for a practical application. In this work we does not only aim to obtain a high specific capacitence, but also to develop an nickel oxide film with excellent rate capability.

**Figure 5.** Electrochemical properties of NiO in 2 M KOH solution: (a) cycle voltammograms (CVs) curves at different scan rates; (b) discharging curves at different discharging currents; (c) relationship between specific capacitances and discharge current densities; (d) complex-plane impedance plots of the NiO electrodes prepared at different deposition masses (0.21 V vs. SCE; electrolyte: 2M KOH).
3.4.4. AC Impedance Spectroscopy Tests of Nickel Oxide Film

The AC impedance measurements were carried out on the NiO electrodes at 0.21 V (vs. SCE). The typical results are shown in Figure 5d. The complex plane impedance plots for each sample can be divided into the high-frequency component and the low-frequency component. A distinct knee in the frequency can be observed in curves of Figure 5d. At very high frequencies, the intercept at real part (Z*) is a internal resistance of ionic resistance of electrolyte, intrinsic resistance of substrate, and contact resistance at the active material/current collector interface (Re). The internal resistances of the 0.83 mg NiO film and the 1.66 mg NiO film electrodes are 0.94 and 0.97 Ω, respectively. These results suggest that all the electrodes are not strongly controlled by the internal resistance. The semicircle in the high frequency range associates with the surface properties of porous electrode corresponds to the faradic charge-transfer resistance (Rct). It can be seen that all the NiO samples have small charge-transfer resistance. A major difference can be seen in the straight sloping line in the lower-frequency range, which represents to the diffusive resistance (Warburg impedance) of the electrolyte in electrode pores and the proton diffusion in host materials. The phase angle for impedance plots of 0.83 mg films were observed to be higher than the mass in 1.66 mg. This can be explained that with the increase of the deposition mass, some NiO nano-sheets grew to a stacking particles, which can weaken the diffusivity of the electrolyte iron in the NiO electrode and active zites. The higher the diffusive resistance, the lower the specific capacitance of the electrode. The nickel oxide electrode deposited in 0.83 mg has a lower charge-transfer resistance reflecting a higher specific capacitance due to the well-dispersed structure [33-34].

4. Conclusion

In conclusion, nickel oxide films were synthesized by electrochemical precipitation of the Ni(OH)₂ films and heating it to form oxide. Heat treatment causes phase change from Ni(OH)₂ to NiO as evidenced by XRD and TG-DSC. As revealed by SEM images, the as-prepared NiO films on nickel foam appear highly porous network-like structure, which consists of interconnected nano-flakes in nanometer scale. Electrochemical performances such as specific capacitance, high-rate charge/discharge, and impedance measurements of the deposited film are investigated in 2 M KOH electrolyte. The electrochemical studies showed that the network-like NiO film possess a maximum specific capacitances of 1308 F/g and a high-power pseudocapacitive performance, which is referred to the deposition potentials of -0.7 V, mass of 0.83 mg. In addition, the relatively small decrease in specific capacitance with increasing current density indicates the high-power characteristics of deposited nickel oxide electrode. To sum up, an excellent network-like NiO films with high specific surface area has been synthesized successfully, so it is suitable to be used as electrode material for electrochemical capacitors.

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References


