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Effect of oxidant on the structural, morphological and supercapacitive properties of nickel hydroxide nanoflakes electrode films

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ABSTRACT

Nanostructured nickel hydroxide $Ni(OH)_2$ electrode films were synthesized using a chemical bath deposition (CBD) method at 80 °C. The effect of an oxidizing agent potassium persulfate ($K_2S_2O_8$) on the structural, morphological and supercapacitive properties of the $Ni(OH)_2$ electrode has been investigated. The structural and morphological studies revealed that randomly oriented $Ni(OH)_2$ nanoflakes are converted into vertically aligned dense $Ni(OH)_2 \cdot NiOOH$ nanoflakes after the addition of the $K_2S_2O_8$ oxidant. The specific capacitance of the $Ni(OH)_2 \cdot NiOOH$ electrode is found to be ~1257 F/g which is significantly larger than that of the $Ni(OH)_2$ electrode (~454 F/g). The oxidant-mediated $Ni(OH)_2 \cdot NiOOH$ electrode shows an improved capacitive retention. The significantly improved supercapacitor properties of the $Ni(OH)_2 \cdot NiOOH$ electrode are due to a combined effect of increased active area and enhanced electrical conductivity.

1. Introduction

Increasing energy demand and the limited availability of fossil fuels have resulted in the development of energy conversion and storages devices, which are the key technological challenges in the 21st century [1,2]. Supercapacitors or electrochemical capacitors have attracted considerable interest as energy storage devices due to their efficient energy delivery, high power density, and long life cycle [3–5]. In recent years, nickel hydroxide ($Ni(OH)_2$) and nickel oxide (NiO), have attracted much attention due to their high theoretical capacitance values (2584 and 2082 F/g), ready availability, environmentally benign nature and lower cost [6]. Nanostructured NiO or $Ni(OH)_2$ electrodes with different morphologies and their capacitive properties have been investigated [7–13]. Among various growth techniques, the chemical bath deposition (CBD) method is presently attracting considerable attention due to its simplicity and low cost as well as reasonably high-quality of deposited films [14].

It is known that a nanostructured, porous morphology with a large active surface area, good conductivity of the electro-active material and highly conducting current collector are key parameters for the development of high-performance supercapacitors [15–18]. $Ni(OH)_2$ nanoflakes electrode, deposited on ITO and stainless steel substrates using the CBD method showed a specific capacitance ranging between ~130 and ~460 F/g [11–13]. On the contrary, interconnected dense $Ni(OH)_2$ nanoflakes electrode synthesized on highly conducting Ni foam and carbon cloth showed much higher specific capacitances in the range of ~1416 to 1470 F/g [19–21]. It is also known that conductivity of the electrode materials plays an important role in determining supercapacitor performance. The charge/discharge processes for electrically non-conducting materials can be localized only in a finite volume near the current collector, causing a sudden drop in specific capacitance [17]. Thus, to enhance the supercapacitive performance of electrodes, it is desirable to improve the conductivity of electrode materials or to design a nanostructured morphology of the electrode materials with an increased chemically-active surface area.

In this work, we have synthesized $Ni(OH)_2$ electrode films using the CBD method with the addition of potassium persulfate ($K_2S_2O_8$) as an oxidant, and investigated the effect of oxidant on the structural, morphological and supercapacitive properties of the $Ni(OH)_2$ electrode films. We demonstrate that the $Ni(OH)_2$ electrode film prepared using the oxidant shows significantly improved supercapacitive properties. We argue that these improved properties are due to the combined effects of a modified dense morphology with an increased chemically-active area and enhanced conductivity.

2. Experimental details

$Ni(OH)_2$ electrode films were synthesized using a conventional CBD method. An alkaline bath was prepared using 0.1 M $NiSO_4$ as a source of nickel and aqueous ammonia was added under constant

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stirring. The $Ni(OH)_2$ electrode films were grown on glass and stainless steel substrates immersed vertically in the solution. The pH of the solution was maintained at ~12 and the bath was heated. When the bath reached a temperature of 80 °C, precipitation started in the bath. During the precipitation, a heterogeneous reaction occurred and $Ni(OH)_2$ was deposited on the substrate. To modify the morphology and chemical composition of the $Ni(OH)_2$ electrode films, the same growth procedure was repeated by adding 0.1 M potassium persulfate ($K_2S_2O_8$) as an oxidizing agent. After the deposition, the substrate was washed thoroughly with deionized water to remove loosely bound particles.

The weight of the deposited electrode films were measured using a conventional weight difference method with a sensitive microbalance. The structural analysis of the films were carried out using a high-resolution X-ray diffractometer (X pert PRO, Philips) with a copper target of wavelength 1.54056 Å. Their surface morphologies were investigated using field emission scanning electron microscopy (FE-SEM Model: JSM-6701F). The electrical conductivity of the electrode films were measured using a standard two-probe measurement technique with a Keithley 4200 parameter analyzer.

The electrochemical supercapacitor properties of the electrode films were measured using a potentiostat (Princeton Applied Research, VersaSTAT 3) with a specially-designed three electrode system in a 1 M KOH electrolyte at room temperature. A Pt wire and a saturated calomel electrode (SCE) were served as the counter and reference electrodes, respectively. The electrochemical performance of the supercapacitor electrode films was evaluated by performing standard cyclic voltammetry (CV) measurements in the potential range between 0 and 0.6 V (vs. SCE).

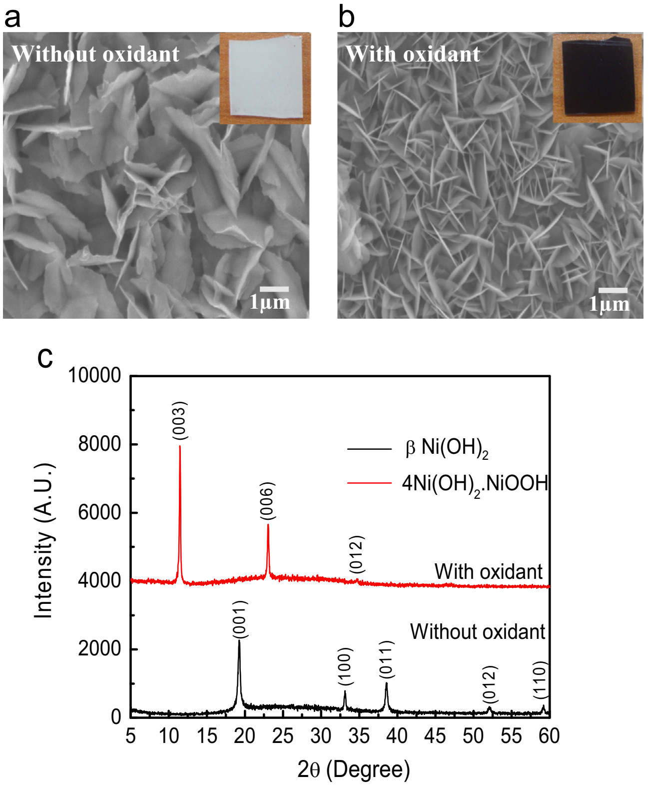

Fig. 1. (a and b) SEM images and (c) XRD patterns of the $Ni(OH)_2$ and oxidant-mediated $Ni(OH)_2 \cdot NiOOH$ films on the glass substrate.

3. Results and discussion

The nickel cations (Ni^{2+}) and hydroxyl group anions (OH^-) from the precursor solution in the supersaturated state, undergo homogeneous nucleation and form a resistive gray $Ni(OH)_2$ thin film (inset in Fig. 1(a)). The corresponding growth procedure is described by the following equation:

$$NiSO_4 + 2NH_4OH \rightarrow Ni(OH)_2 + (NH_4)_2SO_4 \tag{1}$$

However, in case where the oxidant $K_2S_2O_8$ is added in the precursor solution, $Ni(OH)_2$ nanoparticles are firstly formed on the substrate via the same homogeneous nucleation. These nanoparticles then react with the oxidant through a molecular level heterogeneous reaction forming a conducting black $Ni(OH)_2 \cdot NiOOH$ thin film (inset in Fig. 1(b)). This growth is a two-step chemical process described as follows: [22]

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

$$Ni(OH)_2 + S_2O_8^{2-} \rightarrow 2NiOOH + 2SO_4^{2-} + 2H^+ \tag{3}$$

Fig. 1(a) shows SEM images of the $Ni(OH)_2$ and oxidant-mediated $Ni(OH)_2 \cdot NiOOH$ thin films. The $Ni(OH)_2$ film is well-covered, macroporous, randomly oriented nanoflakes with a thickness of about 20 nm whereas the oxidant-mediated $Ni(OH)_2 \cdot NiOOH$ film shows interconnected microporous nanoflakes with a thickness of 40 nm and vertically aligned to the substrate. The density of the oxidant-mediated nanoflakes are increased more than twice and their size becomes smaller accordingly. The oxidant-mediated film is dense with a large chemically active surface area. Hence it provides a less contact resistance and effective ion/electron transfer between the electrolyte, electro-active material and current collector, which are necessary for the Faradic surface reaction [23]. The electrical conductivity of the oxidant mediated film is about 5×10^{-8} S/cm whereas that of the $Ni(OH)_2$ film is about 1×10^{-9} S/cm.

Fig. 1(c) shows the XRD patterns of the without and with oxidant-mediated $Ni(OH)_2$ thin films. The film prepared without oxidant shows a pure single phase β-$Ni(OH)_2$ with (0 0 1), (1 0 0), (0 1 1), (0 1 2) and (1 1 0) diffraction peaks. However, the oxidant-mediated film shows a $Ni(OH)_2 \cdot NiOOH$ mixed phase with diffraction peaks (0 0 3), (0 0 6) and (0 1 2) [JCPDS file No.: 01-0768990 and 01-08990]. This confirms that the oxidant plays an important role in determining the morphology as well as crystal structure.

The cyclic voltammogram (CV) curves for the electrodes are shown in Fig. 2(a and b). The appearance of anodic and cathodic peaks corresponding to the $Ni(OH)_2$/NiOOH redox reaction in the CV curve is according to the following electrochemical reaction:

$$Ni(OH)_2 + OH^- \leftrightarrow NiOOH + H_2O + e^- \tag{4}$$

The anodic peak is due to the oxidation of $Ni(OH)_2$ to NiOOH and the cathodic peak is due to the reverse process. The cathodic peak current density of the oxidant-mediated $Ni(OH)_2$ electrode is much larger than that of the $Ni(OH)_2$ film. This increased current density is attributed into the combined effect of the NiOOH conducting phase along with the $Ni(OH)_2$ phase [24] and the much larger chemically active surface of the oxidant-mediated electrode.

Specific capacitance of the electrodes calculated from the CV curves is shown as a function of scan rate in Fig. 2(c). The specific capacitance (C) of both electrodes can be calculated using following equation [10]

$$C = \frac{1}{mv(V_c - V_a)} \int_{V_a}^{V_c} I(V)dV \tag{5}$$

where υ is the potential scan rate (mV/s), $(V_c - V_a)$ is the potential range, I denotes the response current and m is the weight of the