Nanostructured nickel oxide ultrafine nanoparticles: Synthesis, characterization, and supercapacitive behavior

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ABSTRACT

Well-dispersed NiO nanoparticles were prepared via cathodic electrodeposition followed by a heat-treatment method. The supercapacitive performance of the prepared nanoparticles was analyzed by means of cyclic voltammetry (CV) and galvanostatic charge–discharge tests at -0.2–0.5 V potential windows in 1 M KOH. The nanoparticles exhibited high specific capacitance ($1623.1 \, \mathrm{F \, g^{-1}}$ at the scan rate of $5 \, \mathrm{mV \, s^{-1}}$) and good long-term cycling stability (9.6% capacity decay after 1000 cycling at the current density of $2 \, \mathrm{A \, g^{-1}}$).
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1. Introduction

Nanostructured nickel oxide (NiO) has received increased interest because of its potential applications in rechargeable alkaline batteries [1], supercapacitors [2,3], sensors [4], electrochromic films [5,6] and solar cells [7]. As a result, different synthesis methods such as chemical precipitation [8], decomposition [9], hydrothermal [10–12], surfactant template [13], solid state [14], solvothermal [15] and sol–gel [16] have been developed for preparation of NiO nanostructures with various shapes and sizes. Furthermore, electrochemical methods (i.e. anodic [17–21] and cathodic [3,22–24] electrodeposition) have been applied for the preparation of nanostructured NiO and demonstrated that electrolytic NiO exhibits better supercapacitive behavior, which can be employed in electrochemical supercapacitors. For example, in a comparative study, the nanostructured electrolytic NiO has proven to be superior in

electrochemical performance compared to those synthesized via conventional methods [12]. However, the reported specific capacitances for nanostructured NiO prepared by various methods are in the range of 100–$1500 \, \mathrm{F \, g^{-1}}$ which are still far from its theoretical value ($3228 \, \mathrm{F \, g^{-1}}$ within 0.4 V). Therefore, it is necessary to optimize the microstructure of NiO through appropriate strategies to enhance both the energy density and power density.

Cathodic electrodeposition followed by heat-treatment can be applied for the preparation of NiO with desired physico-chemical properties. In this method, the hydroxide precursor is firstly deposited on the cathode surface via base (OH^-) electrogeneration. The structure and morphology of the deposited hydroxide can be easily tuned by controlling the base electrogeneration and the deposit formation steps. The prepared deposit is then heat-treated to obtain final oxide. However, this easy and powerful technique has been rarely used in the preparation of nanostructured NiO [22–24]. Notably, most efforts in the electrochemical preparation of NiO have been performed in the anodic regime [17–21]. Notably, only one report is available on the cathodic electrodeposition of NiO particles

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and investigation of their supercapacitive performance. In that report [25], nanoparticulate NiO has been prepared via potentiostat (-0.90 V vs. SCE) deposition on Ni foil from 0.08 M Ni(NO$_3$)$_2$ aqueous solution and high specific capacitance of 1478 F g^{-1} has been observed for film calcined at 250 °C [25]. In the previous work [3], NiO nanocapsules were prepared by cathodic electrodeposition followed by heat-treatment at 300 °C for 3 h. The hydroxide precursor was galvanostatically deposited ($i=0.1$ mA cm^{-2}) onto the steel substrate from low-temperature 0.005 M Ni(NO$_3$)$_2$ bath (10 °C). The selection of the annealing temperature (300 °C) was based on Ref. [24], which has obtained smallest crystal size and high capacitance at this temperature. In this letter, we report NiO ultrafine nanoparticles prepared by galvanostatic deposition ($i=0.1$ mA cm^{-2}) from 0.005 M Ni(NO$_3$)$_2$ bath ($T=25$ °C) followed by heat-treatment at 300 °C for 3 h. The supercapacitive performance of the nanoparticles was evaluated by cyclic voltammetry (CV) and charge–discharge techniques.

2. Experimental procedure

2.1. Chemicals

Ni(NO$_3$)$_2 \cdot$6H$_2$O (Merck), polytetrafluoroethylene (PTFE, Merck), acetylene black and KOH (Merck) were used as were used as received. All solutions were prepared by using purified water by UHQ Elga System. Aqueous solution of 5 mM Ni(NO$_3$)$_2 \cdot$6H$_2$O was prepared for electrodeposition.

2.2. Synthesis procedure

Deposition experiments were conducted in the galvanostatic regime using a two-electrode system. The electrochemical cell included a cathodic stainless-steel substrate centered between two parallel graphite anodes. Prior to each deposition, the steel substrates were given a galvanostatically electropolishing treatment [3]. Deposition experiments were carried out at the constant current density of 0.1 mA cm^{-2} for 1 h at room temperature. After deposition, the steel electrode was brought out from the electrolyte and washed several time with the deionized water, and dried at RT for 48 h. The deposit was then scraped from the steel electrode and subjected to calcination at 300 °C for 3 h.

2.3. Instrumentation

The crystal structure of the prepared samples was determined by powder X-ray diffraction (XRD, Phillips PW-1800) using Cu $K\alpha$ radiation. These measurements were conducted in the range of diffraction angles (2θ) from 5 to 80° at 5°/min. The morphology of samples was examined using a scanning electron microscopy (SEM, LEO 1455VP) and transmission electron microscopy (TEM, Phillips EM 2085). Carbon, nitrogen, and hydrogen contents of the hydroxide powder were determined by CHN analysis (using Elementar Vario ELIII analyzer). Cyclic voltammetry (CV) and galvanostatic charge–discharge tests were performed using an Autolab workstation system (AUTOLAB®, Eco Chemie, PGSTAT 30).
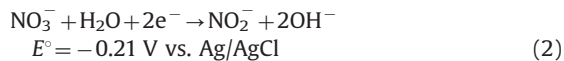
2.4. Electrochemical measurements

The electrochemical measurements were carried out in a three-electrode electrochemical cell containing 1 M KOH aqueous as electrolyte. An Ag/AgCl (1 M KCl, saturated) and platinum wire were used as the reference electrode and the counter electrode, respectively. The working electrode was prepared by mixing the prepared NiO, acetylene black, conducting graphite and polytetrafluoroethylene (PTFE) binder (with the weight ratios of 75:10: 10:5, respectively). The prepared mixture was pressed under 10 MPa into nickel foam current collectors (1 cm × 1 cm) and then dried in oven for 10 min at 70 °C. The CV was conducted in a potential range between -0.2 and 0.5 V versus Ag/AgCl at various scan rates of 2, 5, 10, 25 and 50 mV s^{-1}. The charge–discharge tests were carried out at different current densities of 1, 2, 5, 7 and 10 A g^{-1} within a potential range of -0.2 to 0.5 V.
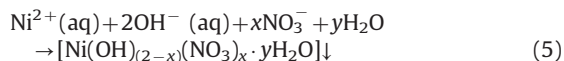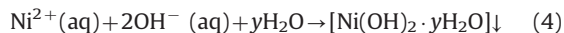
3. Results and discussion

3.1. Hydroxide formation mechanism

The formation of Ni(OH)$_2$ deposit on the cathode surface can be explained by the following steps [3]:

– *Electrochemical step*:

$$O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$$
$$E° = +0.26 \text{ V vs. Ag/AgCl} \tag{1}$$

$$NO_3^- + H_2O + 2e^- \rightarrow NO_2^- + 2OH^-$$
$$E° = -0.21 \text{ V vs. Ag/AgCl} \tag{2}$$

$$2H_2O + 2e^- \rightarrow H_2 + 2OH^-$$
$$E° = -1.08 \text{ V vs. Ag/AgCl} \tag{3}$$

– *Chemical step*:

$$Ni^{2+}(aq) + 2OH^-(aq) + yH_2O \rightarrow [Ni(OH)_2 \cdot yH_2O]\downarrow \tag{4}$$

$$Ni^{2+}(aq) + 2OH^-(aq) + xNO_3^- + yH_2O$$
$$\rightarrow [Ni(OH)_{(2-x)}(NO_3)_x \cdot yH_2O]\downarrow \tag{5}$$

Measuring the potential values during the deposition process (-0.94 V vs. Ag/AgCl) revealed that the reduction of water (Eq. (3)) has the major role in the base electrogeneration at our experiments. In fact, the electrochemical step is preceded via reaction (3) during the deposition process. The strings of gas bubbles are experimentally observed on the cathode surface, which completely confirmed the base electrogeneration via water reduction. Schematic viewing the formation of Ni(OH)$_2$ on the cathode surface is shown in Fig. 1. The electrochemical step includes water reduction and so production of OH$^-$ ions and H$_2$ gas on the cathode surface (step I in Fig. 1). This step results an increase of pH at the cathode surface. By establishing the pH conditions for Ni(OH)$_2$ formation, the chemical step is started and Ni(OH)$_2$ is sequentially