

Preparation and electrochemical performance of cellular structure Ni(OH)₂ thin film



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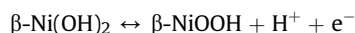
ABSTRACT

Cellular structure Nickel Hydroxide Ni(OH)₂ thin film grown on indium-tin oxide (ITO) substrate was synthesized by a two-step hydrothermal method. The crystal structure and morphology of Ni(OH)₂ thin film was investigated by means of X-ray diffraction (XRD) and scanning electron microscopy (SEM), respectively. The electrochemical performance was investigated by a cyclic voltammetry (CV) method. The results indicated that the thin film consisted of plate-like β-Ni(OH)₂ grains growing on the substrate vertically and connecting each other to form a kind of multilayer cellular structure, which formed a large number of stable three-dimension pores and facilitated electrolyte diffusion and penetration to the inside of thin film. Thus, the specific capacitance of Ni(OH)₂ thin film capacitor was 980 F/g at a low scan rate of 10 mV/s; and the better reversibility and stability indicated that the cellular structure Ni(OH)₂ thin film should be a kind of promising capacitor electrode material.

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1. Introduction

Nickel hydroxide is a kind of important functional material, which has been widely used in catalytic, battery electrode material and electrochemistry capacitor et al. Two polymorphic forms of nickel hydroxide, α-Ni(OH)₂ and β-Ni(OH)₂, have caused concern. Despite the lower theoretical special capacitance of β-Ni(OH)₂ compared with that of α-Ni(OH)₂, β-Ni(OH)₂ is considered as a promising electrochemistry capacitor material due to its high density and charge–discharge stability [1–4]. Researches show the fact that active substances are transformed between β-Ni(OH)₂ and β-NiOOH during the charge and discharge of β-Ni(OH)₂ electrode, that is to say, the protons and electrons transform during phase transition. The reaction can be described as following:



However, the specific capacitances reported are still much lower than the corresponding theoretical values (2082 F/g for Ni(OH)₂) which limits the electrochemical utilization of Ni(OH)₂. For example, Liu et al. [5] synthesized coin-like β-nickel hydroxide

nanoplates via a simple coordination homogeneous precipitation method, which had a specific capacitance value of ~1532 F g^{−1}. Dai et al. [6] synthesized Ni(OH)₂ nanoplate grown on grapheme via a two-step hydrothermal method, which had a specific capacitance value as high as ~1335 F g^{−1} based on mass of Ni(OH)₂ and ~935 F g^{−1} based on total sample mass at a charge and discharge current density of 2.8 A g^{−1}. The above-mentioned Ni(OH)₂ capacitors were prepared by traditional slurry-coating method using powder active material on current collector. Therefore, a large portion of active surface of materials was prohibited from contacting the electrolyte. To greatly improve the performance of active materials, Ni(OH)₂ thin films growing directly on a current collector with an open and porous nanocrystal arrays as a capacitor, being free from using acetylene conductivity and polytetrafluoroethylene binder, have recently attracted increasing attention. The properties of Ni(OH)₂ thin films depend not only on the particle size, specific surface area and morphologies, but also on the electrode/electrolyte contact area. And the higher electrode/electrolyte contact area rests on the formation of thin film with a large number of stable three-dimensional porous structure. Among various liquid phase methods, the sol–gel [7], electrodeposition [8,9] and Chemical bath deposition (CBD) method [10–12] are widely used for preparation the nickel hydroxide thin film. CBD method is presently attracting considerable attention due to its simple and economic setup, less energy consumption as well as reasonably high-quality of deposited film. The nucleation and growth of thin

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film could be controlled by dominating the ionic concentration, pH value and deposition temperature. U.M.Patil [13] synthesized a macroporous and interconnected honeycomb-like $\text{Ni}(\text{OH})_2$ thin films via a simple CBD method; the microstructure could accommodate electro active species in the solid bulk electrode material and the specific capacitance of $\beta\text{-Ni}(\text{OH})_2$ was 398 F g^{-1} . The $\text{Ni}(\text{OH})_2 \cdot \text{NiOOH}$ nanoflakes electrode films, adding $\text{K}_2\text{S}_2\text{O}_8$ oxidizing agent, had been synthesized using a conventional CBD method by Hyunsik Im team [14], and the specific capacitance of $\text{Ni}(\text{OH})_2 \cdot \text{NiOOH}$ nanoflakes electrode films was found to be $\sim 1257 \text{ F g}^{-1}$ which was significantly larger than that of $\text{Ni}(\text{OH})_2$ electrode ($\sim 454 \text{ F g}^{-1}$). Furthermore, the state of substrate surface should affect the process of nucleation and growth of metal hydroxide directly, i.e., the morphology and electrochemistry performance of thin film also depended on the state of substrate surface. It was reported in ref. [15], the carboxylation pretreatment of glass substrate could form carboxylic groups, as an important template in the $\text{Ni}(\text{OH})_2$ thin film growth process, which was the key to the cellular structure of $\text{Ni}(\text{OH})_2$ thin film.

In this article, multilayer cellular structure $\text{Ni}(\text{OH})_2$ thin film with a large number of stable three-dimension porous structure obtained by a two-step hydrothermal method. The influences of hydrothermal growth time on the morphology of $\text{Ni}(\text{OH})_2$ thin film and the electrochemistry performances were investigated.

2. Experimental procedure

2.1. Carboxylation pretreatment of ITO substrates

The carboxylation pretreatment of ITO substrates was similar to that of glass substrate reported in our previous work [15], and the procedure was shown as following. Firstly, the ITO substrates were washed cleanly by deionized water and absolute ethanol, respectively. To protect the conducting layer of ITO substrate from damaging, the cleaned ITO substrates were placed in an intermixture solution of 98 wt% sulfuric acid and 30 wt% hydrogen peroxide (volume ratio of H_2SO_4 and H_2O_2 was 7:3) and then treated by ultrasonic for 10–15 min, which differed from the treatment process applied to glass substrate mentioned in ref. [15]. After being rinsed by deionized water, the hydroxylated ITO substrates obtained. Subsequently, the hydroxylated substrates were placed in an oleic acid and heated in a water-bath at 70°C for 3 h, after that, rinsed by absolute ethanol in an ultrasonic washer to eliminate the residual oleic acid. Finally, the ITO substrates were dipped into a potassium permanganate solution (10 mg/ml) at room temperature for 6 h and washed by deionized water to eliminate the remained KMnO_4 solution. Thus, the carboxylated ITO substrates formed.

2.2. Preparation of $\text{Ni}(\text{OH})_2$ thin film

The preparation method of $\text{Ni}(\text{OH})_2$ thin film grown on ITO substrate was similar to that on glass substrate reported in our previous work [15], and the procedure was divided into two parts, seed presetting and film growing. Seed presetting, ammonia water (25 wt%) was added dropwise into a 20 mM of nickel acetate and ethanol mixed solution until the pH value reached 8. Then the mixed solution was stirred continuously at room temperature to form $\text{Ni}(\text{OH})_2$ colloid solution. After that, the carboxylated ITO substrate was immersed in $\text{Ni}(\text{OH})_2$ colloid solution for 8 min and pulled out with a pulling rate of 2 mm s^{-1} , then dried at 120°C for 10 min, which was repeated for a total three times to preset $\text{Ni}(\text{OH})_2$ seeds on the substrate surface. Film growing, nickel nitrate solution (5 mM) and hexamethylenetetramine (HMTA) solution (5 mM) were mixed and heated with vigorous stirring until the temperature of the water bath reached 70°C to synthesize $\text{Ni}(\text{OH})_2$ growth

solution. Significantly, to decrease the ratio of the large grains deposited on the thin film surface, the concentration of nickel nitrate solution and HMTA was lower than those used in our previous work. Then the growth solution and ITO substrate deposited with $\text{Ni}(\text{OH})_2$ seeds were placed in a 50 ml hydrothermal reactor with a filling rate of 80%. A two-step hydrothermal method was used. Step one, the hydrothermal reactor was put in an oven at 70°C for 2 h. Step two, the hydrothermal temperature was increased to 170°C and maintained for 6 h. After cooling, the cellular structure $\text{Ni}(\text{OH})_2$ thin film self-assembly grew on the surface of ITO substrate, and the sample was named NTF1. To investigate the effect of hydrothermal growth time on morphology and electrochemical performance of $\text{Ni}(\text{OH})_2$ thin film, the film growing procedure was repeated directly on the surface of NTF1 for one and two times again, and the corresponding obtained $\text{Ni}(\text{OH})_2$ thin film was labelled as NTF2 and NTF3, respectively.

2.3. Performance characterization

The crystal structure of $\text{Ni}(\text{OH})_2$ thin film was characterized by an X-ray diffractometer (XRD) (model: D/max-RB with an accelerating voltage 40 kV) with $\text{Cu K}\alpha$ radiation ($\lambda = 1.54059 \text{ nm}$) and a scan rate of $8^\circ/\text{min}$ at room temperature. The morphology of $\text{Ni}(\text{OH})_2$ thin film on substrate surface was scanned using a FEI Sirion 200 scanning electron microscopy (SEM). Electrochemical analysis of the films deposited on the ITO substrates was investigated by cyclic voltammetry (CV) using a LK2006A electrochemistry work station and a typical three-electrode system was used. The nickel hydroxide films were used as the working electrode. The counter electrode was a carbon electrode and the reference was a Hg/HgO electrode. The electrolyte was 30 wt% KOH solution.

3. Results and discussion

3.1. Microstructure of $\text{Ni}(\text{OH})_2$ thin film

The XRD patterns of $\text{Ni}(\text{OH})_2$ thin films with different growth times were shown in Fig. 1. It could be observed that all the characteristic peaks at 19.40° , 33.22° , 38.76° , 51.78° and 59.4° , corresponding to the reflecting planes of (0 0 1), (1 0 0), (0 1 1), (0 1 2) and (1 1 0), were found, and could be indexed as $\beta\text{-Ni}(\text{OH})_2$ phase with lattice parameters from the JCPDS card (no. 74-2075), without any impurity phase. However, the characteristic peaks intensity of NTF1 was lower and the effect of substrate on diffraction result was

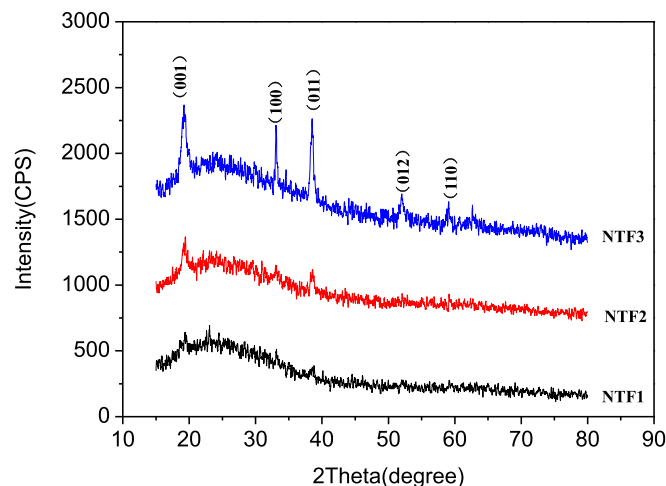


Fig. 1. XRD patterns of $\text{Ni}(\text{OH})_2$ films grown on ITO.

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