



Controllable *in situ* synthesis of Ni(OH)₂ and NiO films on nickel foam as additive-free electrodes for electrochemical capacitors



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ABSTRACT

Nickel hydroxide nanosheet films are prepared *via* a hydrothermal treatment of nickel foam at a low temperature using Fe(NO₃)₃ as an oxidant without any templates and nickel salts. The as-formed Ni(OH)₂ nanosheets are vertically self-grown on the Ni foam substrate. They are inter-connected and free-standing to form a homogeneously porous coating on the substrate with a thickness about 1 μm. The mass loading of Ni(OH)₂ film on nickel foam can be precisely determined by thermogravimetric analysis on base of phase transformation from nickel hydroxide to oxide. The mass loading of Ni(OH)₂ is strongly related with the concentration of Fe(NO₃)₃. The Ni(OH)₂ film grown on nickel foam can directly serve as additive-free electrodes and display a much high specific capacitance, 1100 F g⁻¹ at 0.5 A g⁻¹, excellent rate-capability performance owing to fast electron and ion transport. The Ni(OH)₂ film can transform into NiO by annealing under a moderate temperature. However, the NiO film shows a low specific capacitance of 79 F g⁻¹ at 0.5 A g⁻¹. The preparation method concerns limited chemicals and produces little residual, implying a green chemical process to fabricate Ni(OH)₂ and NiO films on Ni substrate.

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1. Introduction

Due to their high power performance, long cycle life and low maintenance cost, electrochemical capacitors (ECs), (or supercapacitors) have recently attracted increasing attention [1]. Their electrode materials can commonly be carbon materials, transition metal compounds, as well as conducting polymers [2]. The charge storage of pseudocapacitor is based on surface red–ox reactions when using the latter two kinds of electrode materials, usually leading to a much higher specific capacitance than carbon materials. Developing cheap pseudocapacitive materials with excellent performances is very important for the practical applications of ECs [3].

The compounds of nickel, such as Ni(OH)₂ [4–13], NiO [14–16], layered double hydroxide containing Ni [17–20], and Ni_xS [21,22], are deemed as very promising electrode materials for high-performance ECs owing to their high specific capacitance, low cost, environmental friendliness and natural abundance. The common electrode of ECs is polymer-binder-enriched that are prepared by traditional slurry-coating method using powder active

material on current collector [23]. Therefore, a large portion of active surface of materials is prohibited from contacting the electrolyte. Meanwhile, the polymer binder will reduce the electrical conductivity of the electrode material, thus deteriorating its electrochemical performance. Therefore, these powder nickel compounds usually show poor cycling performance and low rate capability due to the low electrical conductivity and surface area.

To greatly improve the performances of electrode material, an efficient method is directly combining it with a current collector to form a film of nanostructured compounds with an open and porous architecture, *i.e.* forming a thin film of nanocrystal arrays [3]. Thus, each block of electrode material will have a good chance to contact with electrolyte during electrochemical reaction and a low electrical conductivity with the current collector, facilitating the diffusion of electrolyte in the inner region of the electrode [24]. Thin films of transition metal compounds deposited on conductive substrates can be used as EC electrodes straightforward, in which any polymer binders and conducting agents are thus not necessary, resulting in a high specific capacitance and good rate capability [25]. As nickel foam is a commonly used current collector and has a low conductivity with a three dimensional porous architecture and large surface area. A lot of reports have been published on the direct growth of porous active materials on nickel form as a film

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[4–6,24,26–33].

It is generally believed that the performance of film electrode is greatly sensitive to the mass of active material. Thus, it is quite important for researchers to accurately determine the mass loading of film material on the surface of nickel foam. For a conventional method, researchers can straight obtain the mass loading by the weight difference of nickel foam before and after the growth of active material, if a very high-accuracy balance is available and the nickel foam is not corroded. For these cases when nickel foam is involved in the chemical reaction for the deposition of active materials [12,14,31,32,24–36], above strategy is not accurate due to the losing of elemental nickel. For example, Ni S.B. *et al.* applied an electrochemical corrosion and subsequent annealing method to prepared NiO nanowalls directly on nickel foam [34]. Lei J. L. group developed a method to *in situ* fabricate Ni(OH)₂ hexagonal platelets on Ni foam as a binder-free electrode by hydrothermal treatment of Ni foam in 15 wt% H₂O₂ solution [35]. Sun and co-workers prepared Ni(OH)₂ nanoflake arrays on nickel foam by hydrothermal treatment of nickel foam in an acidic medium without using extra nickel salts [32,36]. Zhao's group prepared reduced graphene oxide/Co₃O₄/Ni(OH)₂ composite on nickel foam using nickel foam as both reductant of GO and nickel source [31]. In above cases, nickel foam is applied as a chemical source of nickel compounds. Thus, it is necessary to use a substitute method to precisely determine the mass loading of the nickel compounds on the nickel foam.

In this work, we applied thermogravimetric (TG) analysis method to accurately determine the mass loading of Ni(OH)₂ nanosheet arrays on the surface of nickel foam, where stable β -Ni(OH)₂ nanosheets were prepared by oxidizing nickel foam in a solution containing Fe(NO₃)₃ as an oxidant under a low temperature. Then, a dense Ni(OH)₂ nanosheet film was covered on nickel foam, which could be directly used as electrodes of ECs without polymer binder and conductive additive. The mass loading of electroactive material (*i.e.* Ni(OH)₂) on nickel foam is related to the concentration of Fe(NO₃)₃, which can be quantitatively determined by TG method. After annealing at a moderate temperature, porous NiO film was obtained from Ni(OH)₂ precursor. The electrochemical properties of Ni(OH)₂ and NiO films were studied as additive-free electrodes for ECs and they displayed excellent performances.

2. Experimental

The electrode of Ni(OH)₂ nanosheet film on nickel foam was prepared by hydrothermal method, similarly as previous reports [34,35]. Nickel foam with a size of 3 × 4 cm was washed with ethanol and distilled water using ultrasonic cleaner. Then, two pieces of them were vertically placed into a Teflon-lined autoclave filled with 50 mL water containing different amount of Fe(NO₃)₃ (0.1, 1 and 5 mmol). The autoclave was sealed and placed in an oven. After maintaining at 120 °C for 4 h, it was allowed to cool in air. The hydrothermal treated nickel foam was washed with abundant water by ultrasonic cleaner and then dried at 80 °C. The samples prepared using 0.1, 1 and 5 mmol Fe(NO₃)₃ were named as N1, N2 and N3, respectively. To obtain a NiO film, sample N2 was heated and kept at 350 °C for 1 h. The resultant NiO sample was called N2-NiO here.

The phase composition of the samples was characterized using X-ray diffractometer (Shimadzu, XRD-6000) using Cu K α irradiation (40 kV, 40 mA, $\lambda = 1.5406 \text{ \AA}$). The morphology and microstructure of the samples were characterized by a scanning electron microscope (SEM, Hitachi, S-4800). TG analysis (TGA) was carried out using a TA Q600 instrument with 100 mL min⁻¹ of nitrogen flow in a temperature range from 15 to 400 °C with a heating rate of 5 °C min⁻¹.

To evaluate the electrochemical performance of the as-prepared

Ni(OH)₂ (or NiO) film, a piece Ni foam covered by Ni(OH)₂ film with a size of (1.5 cm × 2 cm) was directly as a working electrode. Each working electrode contained about 4 mg of electroactive material according to their mass loading. The electrochemical measurements were conducted under a conventional three-electrode system in a 2 mol L⁻¹ KOH aqueous solution as electrolyte. A platinum foil and Ag/AgCl electrode served as the counter electrode and reference electrode, respectively. Cyclic voltammogram (CV), galvanostatic charge–discharge and electrochemical impedance spectroscopy (EIS) were carried out on a CHI660E electrochemical workstation. The cycling stability was characterized by a LAND CT2001A test system by galvanostatic charge–discharge techniques.

3. Results and discussion

3.1. Ni(OH)₂ and NiO films on Ni foam

The Ni(OH)₂ films grown on nickel foam were characterized by X-ray diffraction (XRD) to identify the phases. The XRD patterns of the Ni(OH)₂ films on Ni foam are shown in Fig. 1. Three intensive peaks correspond to metallic nickel in all the patterns can be easily seen, which is the substrate of Ni(OH)₂ films. Three weak diffraction peaks in the low angles at $2\theta = c.a. 19^\circ, 33^\circ$ and 38° can be indexed as (0 0 1), (1 0 0), and (0 1 1) reflections of β -Ni(OH)₂ phase (JCPDF: 74-2075), respectively. No peaks from other phases can be observed here, implying a pure β -Ni(OH)₂ phase formed on the Ni foam substrate. However, the diffraction peaks of Ni(OH)₂ can not be detected for sample N1, indicating a very low mass loading. From the diffraction peak intensity of Ni(OH)₂, we can find that the intensity of Ni(OH)₂ peaks is increased with the increasing amount of Fe(NO₃)₃.

The morphology and microstructure of Ni(OH)₂ on Ni foam were studied by SEM. Fig. 2a shows the surface morphology of pristine nickel foam, where a smooth surface and many nickel grains are observed. Fig. 2b shows a SEM image of sample N2 under a low magnification, where nickel hydroxide is homogeneously grown on the surface of Ni foam as a continuous film. Fig. 2c and d show sample N2 under high magnifications. From the SEM images, it can be clearly seen that the Ni(OH)₂ film for sample N2 is composed of a lot of hydroxide nanosheets with an average length of about 0.5 μm and thickness of approximately 10 nm. The film has a three-

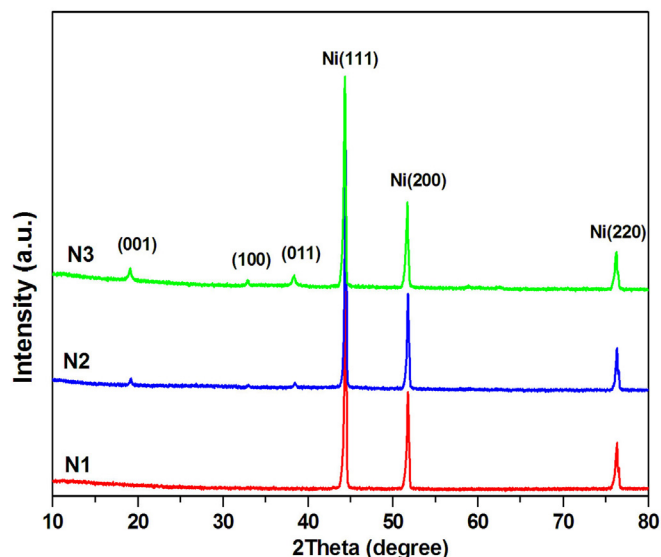


Fig. 1. XRD patterns of Ni(OH)₂ films on Ni foam substrate.

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