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Nickel foam-supported porous $Ni(OH)_2$/NiOOH composite film as advanced pseudocapacitor material

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ABSTRACT

A porous net-like β-$Ni(OH)_2$/γ-NiOOH composite film is prepared by a chemical bath deposition. The as-prepared porous composite film shows a highly porous structure built up by many interconnected nanoflakes with a thickness of about 20 nm. The pseudocapacitive behavior of the porous composite film is investigated by cyclic voltammograms (CV) and galvanostatic charge–discharge tests in 1 M KOH. The porous β-$Ni(OH)_2$/γ-NiOOH composite film exhibits a noticeable pseudocapacitance with 1420 F g^{-1} at 2 A g^{-1} and 1098 F g^{-1} at 40 A g^{-1}, respectively, much higher than those of the dense $Ni(OH)_2$ film (897 F g^{-1} at 2 A g^{-1} and 401 at 40 A g^{-1}). The porous architecture is responsible for the enhancement of the electrochemical properties, and it increases electrochemical reaction area, shortens ions diffusion paths and relaxes volume change caused by the electrochemical reactions.

1. Introduction

Electrochemical capacitors (ECs), also called supercapacitors, are considered as a promising candidate for energy storage due to their high power performance, long cycle life and low maintenance cost [1–3]. These devices store energy using either ion adsorption (electrochemical double layer capacitors) or fast surface redox reactions (pseudocapacitors) [4,5]. Various materials such as transition metal oxides, metal hydroxides and polymeric materials have been explored for pseudocapacitor application [6–8]. Among them, $Ni(OH)_2$ is an attractive pseudocapacitive material because of its high specific capacitance, well-defined electrochemical redox activity and good capability retention [9,10].

In recent years, extensive research has been launched into the development of nanostructured porous pseudocapacitive films because of their high surface-to-volume ratio and short path length for ion transportation [2,3]. Recently, Yang et al. reported a electrodeposited α-$Ni(OH)_2$ film with porous-wrinkle structure and its ultrahigh capacitance [11]. It is well accepted that pseudocapacitance is an interfacial phenomenon tightly related to the morphology of electroactive materials. The porous structure can provide a very short diffusion pathway for ion as well as large active surface area, leading to enhanced electrochemical properties. Therefore, it is believed that the porous $Ni(OH)_2$ film could exhibit superior pseudocapacitor performance. To date, despite several $Ni(OH)_2$ films being synthesized and applied for pseudocapacitors, all these researches focused on films grown by electro-deposition [8,11–14], and there are few reports devoted to pseudocapacitive characteristics of porous $Ni(OH)_2$ films except for that prepared by Yang et al. [11]. However, the film prepared by Yang et al. is stacked by small grains resulting in low porosity. Furthermore, the grains filled in the pores will block electrolyte diffusion and decrease reaction surface area.

In the present work, a facile chemical bath deposition (CBD) method is put forward for the large-area growth of highly porous nanowall β-$Ni(OH)_2$/γ-NiOOH film on nickel-foam substrate. The as-prepared porous composite film shows a unique interconnected net-like porous structure made up of nanowall flakes. Its pseudocapacitor performances are investigated deeply. The as-synthesized β-$Ni(OH)_2$/γ-NiOOH film exhibited superior pseudocapacitor applications with high capacitance capabilities.

2. Experimental

Porous $Ni(OH)_2$/NiOOH composite film was prepared by a chemical bath deposition (CBD) technique as follows [15–17]: solution for the CBD process contained 40 mL of 1 M $NiSO_4$, 30 mL of 0.25 M $K_2S_2O_8$, 10 mL of aqueous ammonia (25–28% NH_3), and 20 mL of deionized water. Clean nickel foam with a size of 3 cm × 4 cm was used in this work. Nickel foam as the substrate was placed vertically in the freshly reaction solution. The deposition process was

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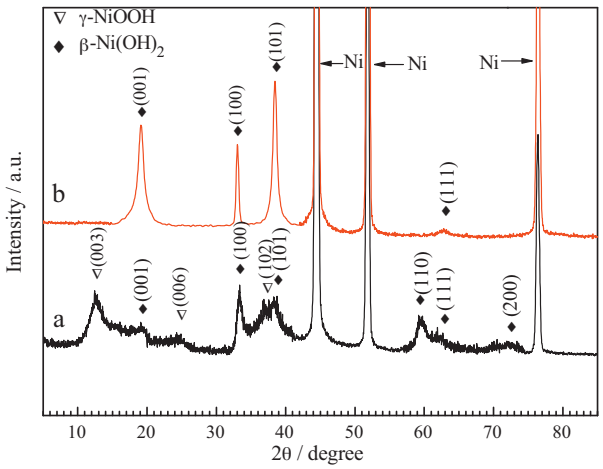

Fig. 1. XRD patterns of films prepared by (a) CBD and (b) electrodeposition methods.

carried out by stirring the solution at 300 rpm for 1 h at 20 °C. The nickel foam was afterwards taken out, washed and dried.

For comparison reasons, a dense $Ni(OH)_2$ film was also prepared by a cathodic electrodeposition method as follows. The electrodeposition was performed in a standard three-electrode glass cell at 20 °C, nickel foam with a size of 3 cm × 4 cm as working electrode, saturated calomel electrode (SCE) as reference electrode and a Pt foil as counter-electrode. The electrolyte was composed of 1 M $Ni(NO_3)_2$ and 0.075 M $NaNO_3$. The electrodeposition was carried out at a constant cathodic current of 3 mA cm^{-2} for 750 s. Finally, the sample was immersed into 1 M KOH for 48 h.

The thickness of both samples was approximately 1 μm, determined with an Alpha-step 200 profilometry. The loading weight for CBD and electrodeposited films is 1.4 and 1.7 mg cm^{-2}, respectively. The morphology and microstructure of two films were characterized by a field emission scanning electron microscopy (FESEM, Hitachi S-4700), X-ray diffraction (XRD, Philips PC-APD with Cu Kα radiation).

The electrochemical measurements were carried out in a three electrode electrochemical cell with 1 M KOH aqueous solution as the electrolyte. Cyclic voltammetry (CV) measurements and electrochemical impedance spectroscopy (EIS) tests were performed on a CHI660c electrochemical workstation (Chenhua, Shanghai). Cyclic voltammetry (CV) measurements were carried out at a scanning rate of 10 mV s^{-1} between 0 V and 0.75 V at 25 °C, Hg/HgO as reference electrode and a Pt foil as counter-electrode. The galvanostatic charge–discharge tests were conducted on LAND battery program-control test system. The as-prepared electrodes, together with a nickel mesh counter electrode and an Hg/HgO reference electrode were tested in a three-compartment system. The film electrodes with 0.5 cm × 1.0 cm in sizes were used for electrochemical impedance spectroscopy (EIS) measurements, which were made with a superimposed 5 mV sinusoidal voltage in the frequency range of 100 kHz to 0.01 Hz. The EIS obtained experimentally were analyzed using a nonlinear least squares fitting program EQUIVCRT.

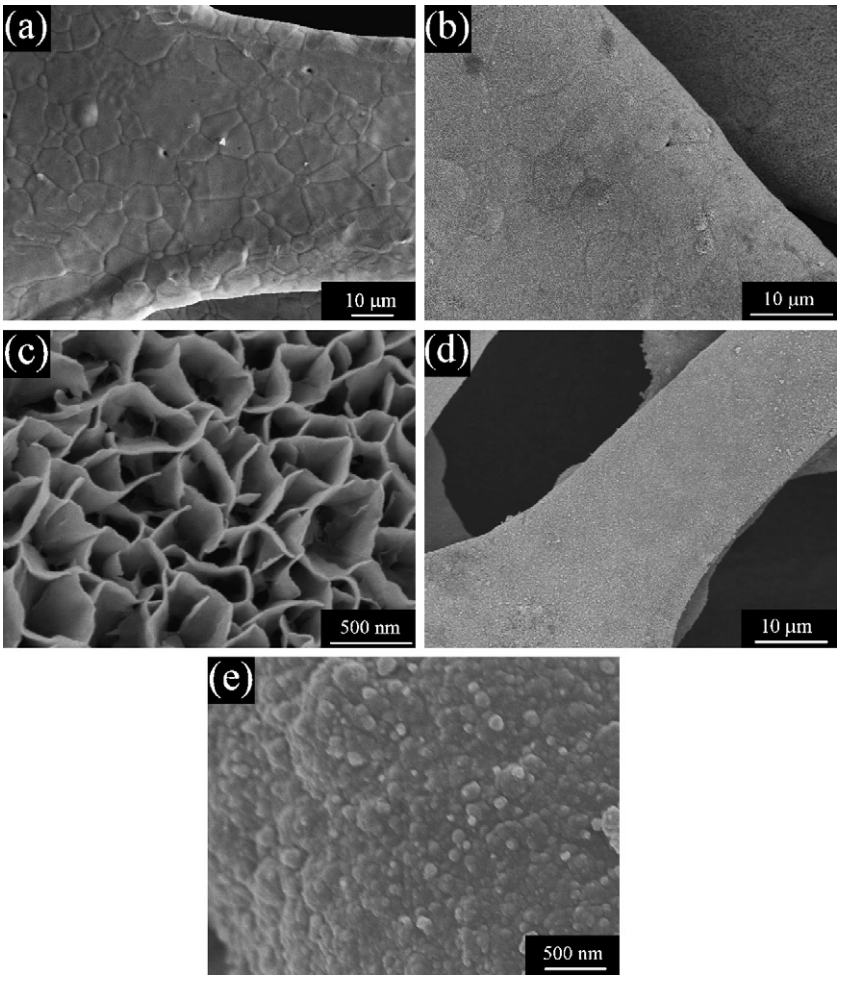

Fig. 2. SEM images of (a) nickel foam substrate; (b), (c) porous $Ni(OH)_2$/NiOOH composite film; (d), (e) dense $Ni(OH)_2$ film.