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# Porous NiO/Ag composite film for electrochemical capacitor application

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#### 1. Introduction

Electrochemical capacitors (ECs) have been widely investigated due to their interesting characteristics in terms of high power capability, excellent reversibility and long cycle life [1,2]. Generally, ECs are classified into two types depending on the charge storage mechanism: (1) "Electrical double-layer capacitors", arising from a nonfaradaic reaction with accumulation of charges through electrostatic interactions at the electrode–electrolyte interface and (2) "Pseudocapacitors", resulting from fast and reversible surface or near-surface faradaic reactions for charge storage [3,4]. Various materials such as transition metal oxides, metal hydroxides, NaxMnO<sub>2</sub>, KxMnO<sub>2</sub> and polymeric materials have been explored for pseudocapacitor application [5–9]. Among them, NiO is an attractive pseudocapacitive material due to its high specific capacitance, good capability retention and low cost [3].

The pseudocapacitive performance of active material mainly depends on two factors: morphology and conductivity. It is well accepted that pseudocapacitance is an interfacial phenomenon tightly related to the morphology of electroactive materials. The pseudocapacitive process of NiO is a reversible electrochemical reaction NiO/NiOOH associated with double injection (extraction) of ions and electrons. Unfortunately, the rate of redox interconversion in NiO bulk materials is usually slow leading to low electrochemical activity because of the slow transport of counterions into the NiO layer to balance charge. In recent years, research about pseudocapacitance of NiO heavily focused on nanostruc-

## ABSTRACT

A highly porous NiO/Ag composite film is prepared by the combination of chemical bath deposition and silver mirror reaction. The as-prepared NiO/Ag composite film has an interconnecting reticular morphology made up of NiO flakes with highly dispersed Ag nanoparticles of about 6 nm. The pseudocapacitive behavior of the NiO/Ag composite film is investigated by cyclic voltammograms (CV) and galvanostatic charge–discharge tests in 1 M KOH. The NiO/Ag composite film exhibits weaker polarization, higher specific capacitance and better cycling performance as compared to the unmodified porous NiO film. The specific capacitance of the porous NiO/Ag composite film is 330 F g<sup>-1</sup> at 2 A g<sup>-1</sup> and 281 F g<sup>-1</sup> at 40 A g<sup>-1</sup>, respectively, much higher than that of the unmodified porous NiO film (261 F g<sup>-1</sup> at 2 A g<sup>-1</sup> and 191 F g<sup>-1</sup> at 40 A g<sup>-1</sup>). The enhancement of pseudocapacitive properties is due to highly dispersed Ag nanoparticles in the composite film, which improves the electric conductivity of the film electrode.

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tured porous films. These highly porous structures can provide a very short diffusion pathway for ion as well as large active surface area, leading to improved pseudocapacitive properties [2,3]. For example, more recently, Wu et al. reported several electrodeposited porous NiO films and their superior pseudocapacitances to bulk counterparts [10,11]. Thus, fabrication of NiO film with porous structures is an effective way to enhance the pseudocapacitive performance. By far, several methods have been developed to prepare porous NiO film. Wu et al. [12] developed anodic electrodeposition methods for fabricating nanoporous NiO film with net-like structure and investigated their pseudocapacitive properties systematically. Additionally, Tu's group pioneered a robust chemical bath deposition (CBD) for preparing nanoporous NiO film with huge porosity [13,14]. This CBD technique is an advantageous technique due to its low cost, low temperature, easy processing and convenient for large-area deposition.

On the other hand, the conductivity of active material has a great influence on the pseudocapacitance. Pseudocapacitive material with good conductivity would show low polarization resulting in high utilization of materials and high pseudocapacitance. NiO is a p-type semiconductor with low conductivity. In order to enhance the pseudocapacitance of NiO, it is suggested to fabricate NiO/metal hybrid film. The introduction of metal improves the intrinsic conductivity of NiO and increases utilization of NiO. It is reported that Ag particles can effectively enhance the electronic conductivity of the active materials [15]. Hence, it would be interesting to combine porous NiO film and Ag particles into one single electrode. To date, there is little literature into the pseudocapacitive properties of NiO/Ag composite film. In the present work, a nanoporous NiO/Ag composite film is prepared by the combination of chemical bath deposition and a modified silver mirror reaction. Remarkably, the

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Fig. 1. Effect of Ag content on the discharge specific capacitance at 2 A g<sup>-1</sup>.

as-prepared nanoporous NiO/Ag composite film exhibits superior performance with high specific capacitance and excellent capacitance retention during cycling and thus promising application.

#### 2. Experimental

The synthesis route of porous NiO film has been already described in detail elsewhere and thus will be briefly described here [13]. Nickel foam substrate was placed vertically in the freshly deposition solution containing 80 ml of 1 M nickel sulfate, 60 ml of 0.25 M potassium persulfate and 20 ml of aqueous ammonia (25–28%). After stirring for 1 h, the substrate was removed from the solution and washed with distilled water. Finally, the as-prepared sample was annealed at 300 °C for 1.5 h. The thickness of the NiO film was approximately 1  $\mu$ m, determined with an Alphastep 200 profilometry. NiO/Ag film was prepared by immersing the nickel foam-support NiO film in a mixture containing 50 mL of freshly prepared 0.01 M [Ag(NH<sub>3</sub>)<sub>2</sub>]<sup>+</sup> and 50 mL of ethanol dissolved 1.0 g polyvinylpyrrolidone (molecular weight = 40,000). The mixture was sealed and then placed in a water bath at 70 °C for 24 h, and finally the substrate was washed with water and dried in air.

The structure and morphology of the products were characterized by X-ray diffraction (XRD, Philips PC-APD with Cu K $\alpha$ radiation), field emission scanning electron microscopy (FESEM, FEI SIRION) and transmission electron microscopy (TEM, JEM 200 CX 160 kV). The content of Ni and Ag elements in the NiO/Ag film was analyzed by inductively coupled plasma mass spectrometry (Thermo PQ3). It was calculated from the result that the content of Ag in the film was 8 wt.%.



Fig. 2. XRD patterns of (a) NiO film and (b) NiO/Ag composite film deposited on nickel foam substrates.



Fig. 3. SEM images of (a and b) porous NiO film and (c and d) NiO/Ag composite film.

The electrochemical measurements were carried out in a three electrode electrochemical cell containing 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). CV measurements were carried out at a scanning rate



Fig. 4. TEM images of (a and b) porous NiO film and (c and d) NiO/Ag composite film.

of  $10 \text{ mV s}^{-1}$  between 0 V and 0.6 V at  $25 \circ \text{C}$ , NiO/Ag film as the working electrode, Hg/HgO as reference electrode and a Pt foil as counter-electrode. EIS tests were made with a superimposed 5 mVsinusoidal voltage in the frequency range of 100 kHz to



**Fig. 5.** CV curves of both film electrodes in the potential region of 0–0.6 V at a scanning rate of  $10 \,\text{mV} \,\text{s}^{-1}$  at the first cycle.

0.01 Hz. 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 specific capacitance is calculated according to the following equation:

$$C = \frac{I\Delta t}{M\Delta V} \tag{1}$$

where  $C(Fg^{-1})$  is specific capacitance, I(mA) represents discharge current, and M(mg),  $\Delta V(V)$  and  $\Delta t(s)$  designate mass of active materials, potential drop during discharge and total discharge time, respectively.

## 3. Results and discussion

Effect of Ag content on discharge specific capacitance is given in Fig. 1. Notice that the porous NiO/Ag composite film with 8 wt.% Ag exhibits the highest discharge specific capacitance. It is indicated that the optimum content of Ag is 8 wt.% and we select this composite film as a testing electrode in the following work.

Fig. 2 shows the XRD patterns of NiO and NiO/Ag composite films deposited on nickel foam substrate. Excluding three strong peaks from the nickel foam substrate, both films show typical diffraction peaks at  $37.3^{\circ}$ ,  $43.3^{\circ}$  and  $62.9^{\circ}$ , which correspond to (111), (200) and (220) crystal planes of cubic NiO phase (JCPDS 47-1049), respectively. For the NiO/Ag film, the peaks at  $38.1^{\circ}$  and  $64.4^{\circ}$  correspond to (111) and (220) reflections of Ag (JCPDS 89-3722).

SEM images of NiO and NiO/Ag composite films are shown in Fig. 3. The NiO film has a porous structure with pore diameters ranging from 30 to 250 nm. The interconnecting network is made up of flaky NiO with thickness of 20-40 nm, similar to those reported by Xia et al. [13,14]. After the loading of Ag, the morphology of NiO/Ag composite film does not change much and maintains the highly porous net-like structure. This randomly porous structure is believed to be beneficial for the enhancement of pseudocapacitance because of its huge porosity and large surface area. The porous morphological characteristics would lead to fast ion/electron transfer, sufficient contact between active materials and electrolyte, and enhanced electrochemical properties with higher specific capacitance and better cycling stability, especially for high discharge/charge current density. Further insight into the microstructure of the nanoflake is obtained by TEM. It is noticed that two nanoflakes have distinct surface morphology (Fig. 4a and b). The nanoflake from the porous NiO film is thin and flat with lowroughness, while the nanoflake after silver reaction has a rough



**Fig. 6.** (a) First charge–discharge curves for both film electrodes at a current density of 2 A g<sup>-1</sup>; (b) discharge curves of porous NiO/Ag composite film at different discharge current densities; (c) discharge curves of porous NiO film at different discharge current densities; (d) specific capacitances at various discharge current densities.

appearance covered by highly dispersed Ag nanoparticles with a size of about 6 nm (Fig. 4c and d).

Fig. 5 shows the CV curves of the porous NiO and NiO/Ag composite films at a scan rate of  $10 \text{ mV s}^{-1}$ . Both films exhibit a redox couple corresponding to the conversion between NiO and NiOOH, represented by the following reaction [13,16]:

$$NiO + OH^- \leftrightarrow NiOOH + e^-$$
 (2)

The porous NiO/Ag composite film exhibits an oxidation peak at 0.471 V before the oxygen evolution reaction (OER), and a reduction peak at 0.389 V. For the unmodified porous NiO film, the oxidation and reduction peak shift to higher (0.502 V) and lower potentials (0.374 V), respectively. Apparently, the porous NiO/Ag composite film exhibits smaller potential separations between the oxidation peak and the reduction peak. It is well-known that the peak potential separation is used as a measure of reversibility. It indicates that the porous NiO/Ag composite film has better reaction reversibility. In addition, the cathodic and the anodic peak currents of the porous NiO/Ag composite film are higher than those of the unmodified NiO film, indicating that the NiO/Ag composite film has higher electrochemical activity. The highly dispersed Ag nanoparticles loaded on the NiO flake improve the electrical conductivity of the film and also enhance the electrical contact among the substrate, the film, and the electrolyte, resulting in lower polarization with higher electrochemical activity.

Fig. 6a compares the first charge–discharge curves of the porous NiO and NiO/Ag composite films between 0 and 0.55 V (*vs.* Hg/HgO) at a galvanostatic current density of  $2 \text{ Ag}^{-1}$ . The porous NiO/Ag composite film exhibits much lower charge voltage plateau and higher discharge voltage plateau than the unmodified porous NiO

film, indicating that the porous NiO/Ag composite film has smaller polarization during the charge–discharge processes. The specific capacitance of the porous NiO/Ag composite film is calculated to be  $330 \text{ Fg}^{-1}$  at  $2 \text{ Ag}^{-1}$ , much higher than that of the unmodified porous NiO film ( $261 \text{ Fg}^{-1}$  at  $2 \text{ Ag}^{-1}$ ). Discharge curves of both film electrodes at different discharge current densities are shown in Fig. 6b and c, and the specific capacitances verse discharge current densities are presented in Fig. 6d. The corresponding calculated pseudocapacitances are listed in Table 1 in detail. As shown in Table 1, the porous NiO/Ag composite film possesses quite good pseudocapacitance at different discharge current densities. As



**Fig. 7.** Cycling performances of both film electrodes at  $2 \text{ Ag}^{-1}$ .

Та	bl	e	1

Pseudocapacitances at different o	discharge current densities (	(corresponding to Fig. 6b an	d c)
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	Discharge current densities (Ag <sup>-1</sup> )						
	2	4	8	10	20	40	
Pseudocapacitance for NiO/Ag composite film (Fg <sup>-1</sup> ) Pseudocapacitance for NiO film (Fg <sup>-1</sup> )	330 261	328 247	322 225	308 221	287 203	281 191	

we can see that when the discharge current density increases to 40 A g<sup>-1</sup>, the pseudocapacitance for the porous NiO film decreases to 191 Fg<sup>-1</sup>, while that for the porous NiO/Ag film maintains a high level of  $281 \text{ Fg}^{-1}$ . The enhancement of pseudocapacitance is due to the conductive network formed by the highly dispersed Ag nanoparticles. The integrated conductive network helps to improve the charge efficiency and diminish the polarization with lower charge voltage plateau and higher discharge voltage. Thus, the reaction NiOOH  $\rightarrow$  NiO can proceed to a higher extent with higher specific capacitances.

Fig. 7 shows the capacity retention properties of the porous NiO and NiO/Ag composite films at 2 A g<sup>-1</sup>. Similar cycling characteristics are observed for both films. Upon cycling, the porous NiO/Ag composite film exhibits higher specific capacitance and better cycling stability than the unmodified NiO film. The capacity deterioration of the porous NiO/Ag composite film is restricted to a very lower level, even after long-term cycling, while that of the NiO film diminishes quite quickly. The porous NiO/Ag composite film delivers a specific capacity of 312 F g<sup>-1</sup> after 3000 cycles, higher than that of the NiO film (206 F g<sup>-1</sup> after 3000 cycles). It is indicated that the introduction of Ag nanoparticles in NiO/Ag film is beneficial to the enhancement of cycling stability. The degradation mechanism of NiO film is a complex process mainly associated with two factors: a self-discharge phenomenon associated with a partial dissolution of NiO and oxygen bubbles striking [17]. It is well accepted that the pseudocapacitive process of NiO is a reversible reaction of NiO/NiOOH, which is accompanied by a spontaneous chemical conversion of NiO into Ni(OH)2 at the electrode/electrolyte interface. This side process leads to a progressive degradation of the NiO film. Besides, the oxygen evolution reaction (OER) is a competitive reaction with the electrochemical process of Ni(II)/Ni(III) couple during the cycle. The oxygen bubbles strikes the film accelerating the degradation process. As shown in CV result above (Fig. 5), the porous NiO/Ag composite film shows a potential of OER with 0.576 V. The potential difference between oxidation peak potential and OER potential is 0.105 V, while that for the porous NiO film is 0.084 V, meaning that the Ag in the composite film can suppress



Fig. 8. EIS plots of both film electrodes with 100% depth of discharge.

OER and ease the oxygen bubbles striking, leading to better cycling stability.

For pseudocapacitor application, the reaction kinetics is an important factor. The reaction kinetics has been evaluated by EIS (Fig. 8). The impedances of both film electrodes consist of a depressed arc in high frequency regions and a straight line in low frequency regions. Generally, the semicircle reflects the electrochemical reaction impedance of the film electrode and the straight line represents the diffusion of electroactive species [18,19]. Obviously, the NiO/Ag film exhibits a much smaller semicircle and slower slope. It is well accepted that bigger semicircle means larger charge transfer resistance and higher slope signifies lower ions diffusion rate. It is concluded that the NiO/Ag composite film has much lower charge transfer resistance and ion diffusion resistance than the NiO film, indicating the composite film is favorable for charge transfer and ion diffusion. The difference of reaction kinetics can be attributed to the introduction of Ag nanoparticles. The presence of Ag nanoparticles can keep the NiO flakes electrically connected, and offer conductive pathways among the NiO nanoflake, the substrate, and the electrolyte [15], leading to lower charge transfer resistance and ion diffusion resistance with fast reaction kinetics.

#### 4. Conclusion

A porous net-like NiO/Ag composite film is successfully prepared by combining chemical bath deposition and silver mirror reaction, successively. The as-prepared NiO/Ag composite film exhibits a highly porous cross-linked structure with diameter of pores ranging from 30 to 250 nm. Its high porosity and large surface area can facilitate the contact between electrolyte and the oxide surface and allow easy diffusion of ions among them. Compared to the unmodified porous NiO film, the NiO/Ag composite film exhibits better pseudocapacitive performance with weaker polarization, higher specific capacity, better reversibility and preferable cycling performance. The NiO/Ag composite film shows pseudocapacitances of  $330 \text{ Fg}^{-1}$  at  $2 \text{ Ag}^{-1}$  and  $281 \text{ Fg}^{-1}$  at 40 A g<sup>-1</sup>, respectively. The improved electrochemical performances are attributed to the introduction of Ag nanoparticles in the composite film, which improves the electric conductivity of the film electrode.

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