



Short communication

Chemically grown, porous, nickel oxide thin-film for electrochemical supercapacitors

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ABSTRACT

A porous nickel oxide film is successfully synthesized by means of a chemical bath deposition technique from an aqueous nickel nitrate solution. The formation of a rock salt NiO structure is confirmed with XRD measurements. The electrochemical supercapacitor properties of the nickel oxide film are examined using cyclic voltammetry (CV), galvanostatic and impedance measurements in two different electrolytes, namely, NaOH and KOH. A specific capacitance of $\sim 129.5 \text{ F g}^{-1}$ in the NaOH electrolyte and $\sim 69.8 \text{ F g}^{-1}$ in the KOH electrolyte is obtained from a cyclic voltammetry study. The electrochemical stability of the NiO electrode is observed for 1500 charge–discharge cycles. The capacitive behaviour of the NiO electrode is confirmed from electrochemical impedance measurements.

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1. Introduction

Electrochemical supercapacitors attract much attention due to their application in electronic devices. Many research groups have made considerable efforts to increase their specific power and specific energy, as well as to lower fabrication costs by using environment-friendly materials. Electrochemical supercapacitors are classified into two types on the basis of their charge storage mechanisms, namely: (i) electrical double-layer capacitors (EDLCs) and (ii) redox supercapacitors [1–3]. RuO₂ and IrO₂ are well studied materials used as pseudocapacitive electrode materials with remarkable performance. The use of these materials, however, is limited due to their high cost. Alternative materials, such as NiO_x [4–8], CoO_x [9,10], and MnO₂ [11,12], have been fabricated by various groups [4–12] in order to overcome the cost factor. Among these materials, nickel hydroxide and nickel oxide are commonly employed in rechargeable batteries and supercapacitors, owing to their low cost, easy availability, and comparable electrochemical behaviour [4–8]. Their morphology plays an important role in capacitance enhancement. In general, a porous structure with a large surface area significantly improves the charge transfer and capacitance of an electrode [1,4,13–17]. The capacitance of NiO films was found to be 128, 60 and 146.3 F g^{-1} for films synthesized by the template method [1], precipitation synthesis [18] and

the electrodeposition technique [19], respectively. A capacitance of up to 1000 F g^{-1} for an electrodeposited nickel hydroxide film is possible, but the potential window for this electrode is small [20].

This study proposes the synthesis of porous NiO thin-films using a chemical bath deposition (CBD) technique for supercapacitor applications.

2. Experimental

Nickel oxide thin films were prepared by means of the CBD technique. The films were deposited onto indium doped tin oxide (ITO) ($25\text{--}27 \Omega \text{ cm}^{-2}$) coated conducting glass substrates. Prior to deposition, the ITO substrates were ultrasonically cleaned consecutively in acetone, methanol, and deionized water. The reaction bath for the deposition of NiO contained 0.25 M nickel nitrate, and 0.25 M urea. The pH of the precursor solution was 5. The cleaned ITO glass substrates were immersed vertically in the deposition bath. Deposition was carried out at 80 °C for 90 min. After the deposition, the films were immersed in deionized water and then dried in air. Finally, the films were air-annealed at 350 °C for 2 h in order to improve the structural quality and adherence of the films.

The structural properties of the NiO films were examined using high-resolution X-ray diffraction (XRD) with Ni-filtered Cu K α radiation [$k\alpha = 1.54056 \text{ \AA}$] (X pert PRO, Philips, Eindhoven, Netherlands). Surface morphology was observed with a field emission scanning electron microscope (FE-SEM; Model: JSM-6701F, JEOL, Japan) attached to an energy-dispersive X-ray (EDAX) analyzer. Electrochemical measurements of the NiO films were performed

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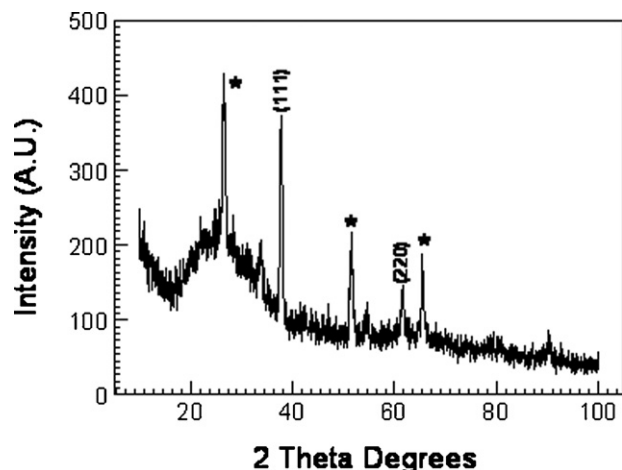


Fig. 1. X-ray diffraction pattern of chemically grown NiO thin films, showing rock salt NiO structure.

with a three-electrode electrochemical cell containing 1 M NaOH (or KOH) as the electrolyte, a saturated calomel electrode (SCE) as the reference electrode, and graphite as the counter-electrode. Electrochemical impedance measurements were performed with a potentiostat (Princeton Applied Research, Versastat 3) using Versa studio software.

3. Results and discussion

The X-ray diffraction pattern of chemically grown, porous, NiO films annealed at 350 °C in air is shown in Fig. 1. The XRD pattern depicts reflections at 2θ values of 37.74° and 61.5°. The peaks are characteristic of NiO peaks, which agrees well with the reported values [19]. This indicates the presence of a rock salt NiO structure in the film. The peaks, indicated by stars, are due to reflection from the substrates. According to the literature, annealing beyond 250 °C converts Ni(OH)₂ to crystalline NiO [19]. Scanning electron microscopy (SEM) measurements were carried out in order to determine the morphology of the chemically deposited NiO films; an image is shown in Fig. 2. It can be seen that the film consists of a porous structure with flakes and this provides easy access for ions to access the electrode|electrolyte interface, which is a very important factor for the faradic surface reaction.

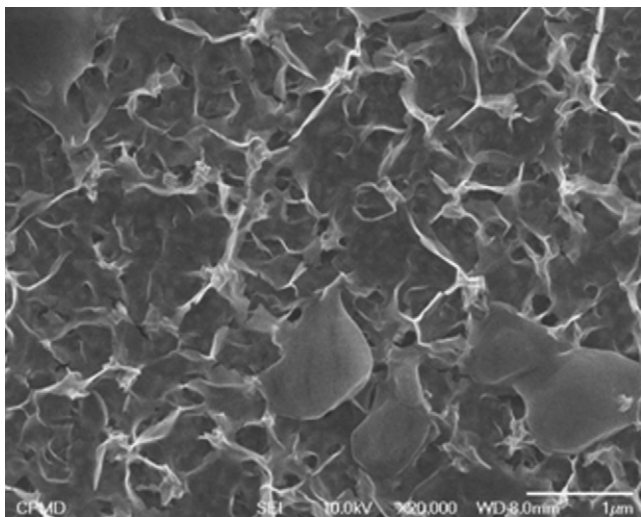


Fig. 2. Scanning electron micrograph of NiO thin film, showing its porous nature.

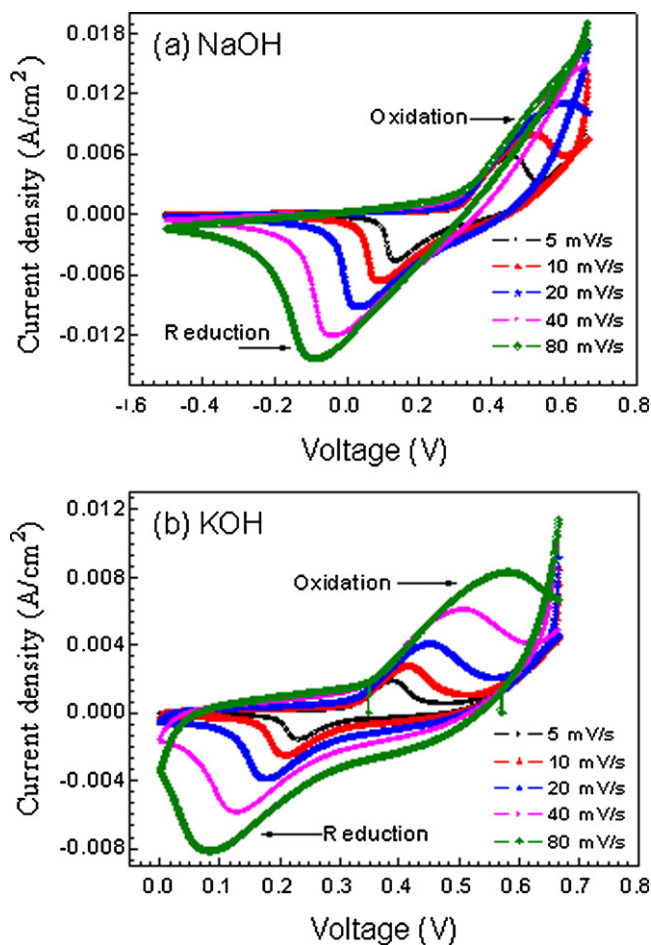
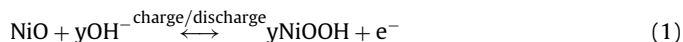


Fig. 3. CV curves of NiO film at different scan rates: (a) in NaOH electrolyte within potential window of –0.5 to 0.67 V vs. SCE, and (b) in KOH electrolyte within the potential window of 0.0–0.7 V vs. SCE.

The cyclic voltammograms (CVs) of the NiO film were recorded at different scan rates using two different types of electrolyte, namely, NaOH and KOH, see Fig. 3(a) and (b). The CVs were cycled between two different voltage ranges: 0.67 to –0.5 V vs. SCE in NaOH electrolyte, and 0.67–0 V vs. SCE in KOH electrolyte. During the scans, reduction and oxidation peaks (marked with arrows in the figure) are observed, in which nickel hydroxide (Ni(OH)₂/NiOOH) is formed at the surface of the nickel oxide during the cycling in the NaOH/KOH aqueous solutions. Here the capacitance is mainly based on the redox reaction because the shape of the CVs is distinguished from that of electric double-layer capacitance, which is normally close to an ideal rectangular. The general chemical reaction mechanism for NiO electrode in the NaOH (or KOH) electrolyte is



where y represents Na or K metal ions. The redox reaction depends on the rate of oxidation of H₂, and the Na, K metal ions present in the electrolyte. During the redox reaction, nickel oxide is oxidized to metal nickel hydroxide, i.e. to NaNiOOH or KNiOOH. The CV spectra show different behaviours in NaOH and KOH electrolytes and this suggests that different redox reactions are taking place. The reaction in both electrolytes starts with a similar redox process producing metallic Na, K ions and the metal nickel hydroxide (NaNiOOH or KNiOOH). The reaction proceeds further, however, with the intercalation of Na or K metal ions into the electrode surface and this exerts an important influence on the reaction mechanism.

Table 1
Specific capacitance values calculated from CV and charge–discharge curves.

Specific capacitance calculated from CV (F g^{-1})		Specific capacitance calculated from charge–discharge measurements (F g^{-1})		Average specific capacitance (F g^{-1})	
NaOH	KOH	NaOH	KOH	NaOH	KOH
129.48	69.79	104.2	51.79	116.84	60.79

According to the voltammograms, the current density with NaOH electrolyte is higher than that with KOH electrolyte and suggests a higher intercalation rate of Na metal ions into the electrode surface leading to a higher rate of hydroxide and oxide formation. This is a main difference between the redox reaction in NaOH and KOH electrolytes.

An increment in the area of the CVs and its current response with increasing scan rate were observed. This indicates that porous NiO provides more surfaces for fast reversible faradaic reactions. There is a set of redox reaction peaks at higher scan rates which demonstrate the high kinetic reversibility of the electrode. As the sweep rate becomes high, the CV curves deviate from their original shape; the anodic and cathodic peak current densities are relatively similar, indicating that charge and the discharge occur reversibly at the electrode|electrolyte interface [19]. The similarity in the shape of the CVs for all scan rates suggests a high efficiency in the capacitive characteristics at the electrode|electrolyte inter-

face. These results indicate that the measured capacitance is mainly based on the redox mechanism. In addition, the CV peak current densities of the NiO film in the NaOH electrolyte are much larger than those found in the KOH electrolyte. These results indicate that the capacitive properties of the NiO film in the NaOH electrolyte can be improved. The specific capacitance of the NiO electrode can be calculated from the CV curves according to following equation [21]: $C_{sp} = \frac{i}{sm}$ where i is the average cathodic current; s is the scan rate; m is the mass of the active electrode. The specific capacitance of the NiO electrode is 129.48 F g^{-1} in the NaOH electrolyte, whereas it is 69.79 F g^{-1} in the KOH electrolyte. The values of the specific capacitance are presented in Table 1.

The charge–discharge (CD) characteristics of the porous NiO film in the NaOH and the KOH electrolytes were investigated using chronopotentiometry from 0 to 0.46 V at 1 mA cm^{-2} . The corresponding results are shown in Fig. 4(a) and (b), respectively. With the KOH electrolyte, the CD curve deviates in a non-linear fashion

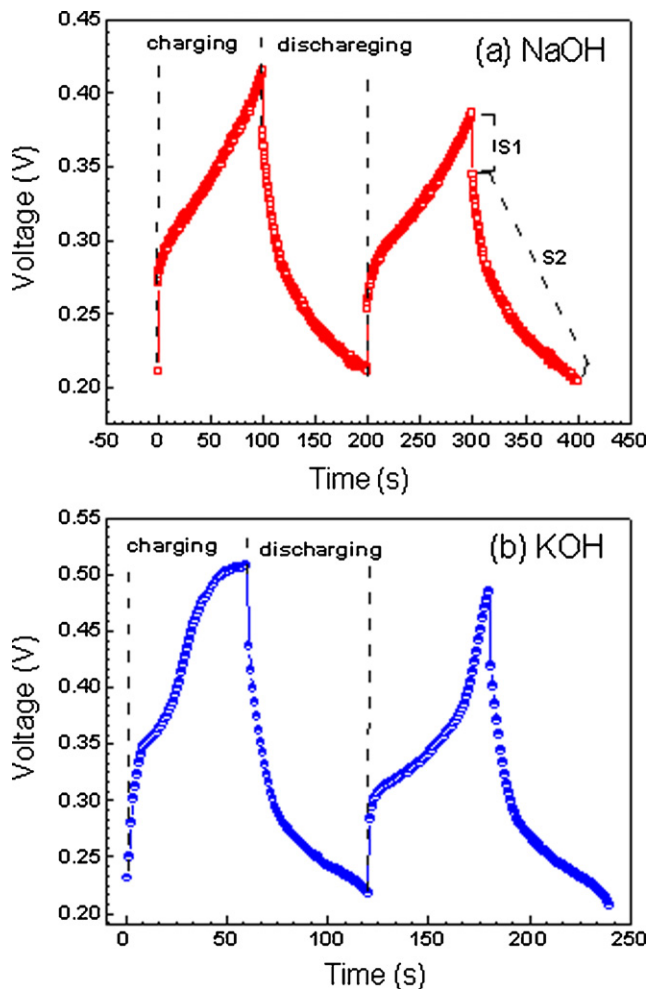


Fig. 4. Chronopotentiograms of porous NiO electrodes; (a) 1 M NaOH, between 0 and 0.43 V at 1 mA cm^{-2} , and (b) 1 M KOH, between 0 and 0.52 V at 1 mA cm^{-2} .

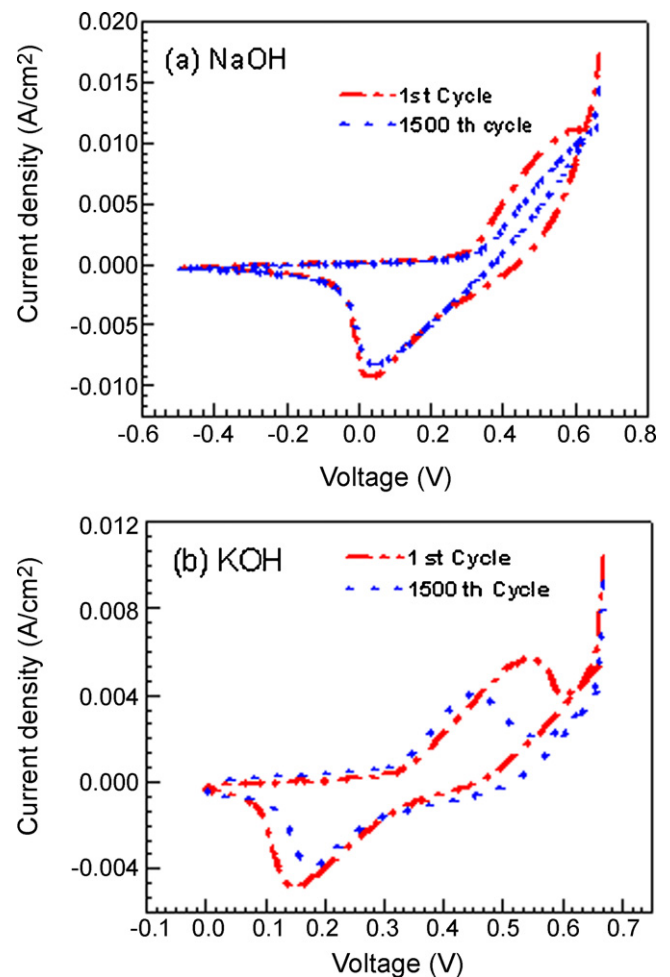


Fig. 5. CV curves of NiO film after 1500 cycles: (a) in NaOH electrolyte, and (b) in KOH electrolyte at scan rate of 100 mV s^{-1} .

during charging, where-as it is linear with the NaOH electrolyte. The charge process occurs above 0.27V for the NaOH electrolyte and 0.34V for the KOH electrolyte, due to the oxidation reaction of the NiO electrode [22]. The discharge curve contains two slopes: one (S1) is parallel to the y-axis and represents the voltage change, whereas the second (S2) is related to a capacitive component (Fig. 4). The slope variations of the time dependence discharge curve suggest a typical pseudo-capacitive behaviour, which is the result of the electrochemical redox reaction at the electrode|electrolyte interface [23]. The specific capacitance of the electrode can be evaluated according to:

$$C_s = \frac{I \times t}{\Delta V \times m} \quad (3)$$

where C_s is the specific capacitance of the electrode based on the mass of the active materials (Fg^{-1}); I is the current during the discharge process; t is the discharge time; ΔV is the potential window; m is the mass of the active electrode materials. C_s values of 104.2 and 51.79 Fg^{-1} were obtained at 1 mA cm^{-2} in the NaOH and the KOH electrolytes, respectively. The charge–discharge curves exhibit reversible characteristics without apparent deviation in each cycle; this suggests that the NiO electrode has good electrochemical stability. The average supercapacitor values for the NiO electrode calculated from the CVs and charge–discharge curves are presented in Table 1. These results suggest that the NaOH electrolyte delivers better supercapacitor performance. The redox

reactions occurring at the electrode|electrolyte interface through faradaic charge-transfer between the electrolyte and the electrode results in the enhancement of the specific capacitance in a metal oxide.

The long-term electrochemical stability of the porous NiO electrode was examined using a cyclic voltammetry test. The CVs of the NiO electrode after 1500 cycles in NaOH and the KOH electrolytes are given in Fig. 5(a) and (b), respectively. The NiO film is stable after 1500 or more cycles. Small changes in the CV shape and area under the curve are observed for NaOH electrolyte (Fig. 5(a)). By contrast, small change only in the area is observed from the curves recorded for the KOH electrolyte (Fig. 5(b)). This indicates that the repetitive cycling in either the NaOH or the KOH electrolyte does not induce noticeable degradation of the NiO microstructure.

Electrochemical impedance spectroscopy (EIS) measurements were carried out for both the electrolytes at different applied potentials in the frequency range from 1 GHz to 1 Hz. Fig. 6 (a) and (b) presents the impedance spectra for the NiO samples in NaOH and KOH electrolytes with different applied potentials, respectively. The spectra show vertical lines in the low-frequency region, which are characteristic of supercapacitive behaviour, and the inclined Warburg-like curves at the high frequencies, indicating a typical electric double-layer behaviour. It is obvious that as the frequency increases, the more inclined features for the spectra (inset of Fig. 6(a) and (b)) are observed, due to the more pronounced surface redox reactions at the electrode–electrolyte interface.

4. Conclusions

Porous NiO thin films are successfully synthesized, by means of a chemical bath deposition technique, for electrochemical supercapacitor applications. The formation of a NiO rock salt structure is confirmed by the XRD analysis. The electrochemical measurements are performed using two different electrolytes, namely, NaOH and KOH, employing cyclic voltammetry and electrochemical impedance techniques. Average electrochemical supercapacitors of 116.84 Fg^{-1} in NaOH electrolyte and 60.79 Fg^{-1} KOH electrolyte are obtained. It is found that the NiO electrode is more electrochemically stable up to 1500 charge–discharge cycles in the NaOH and KOH electrolytes.

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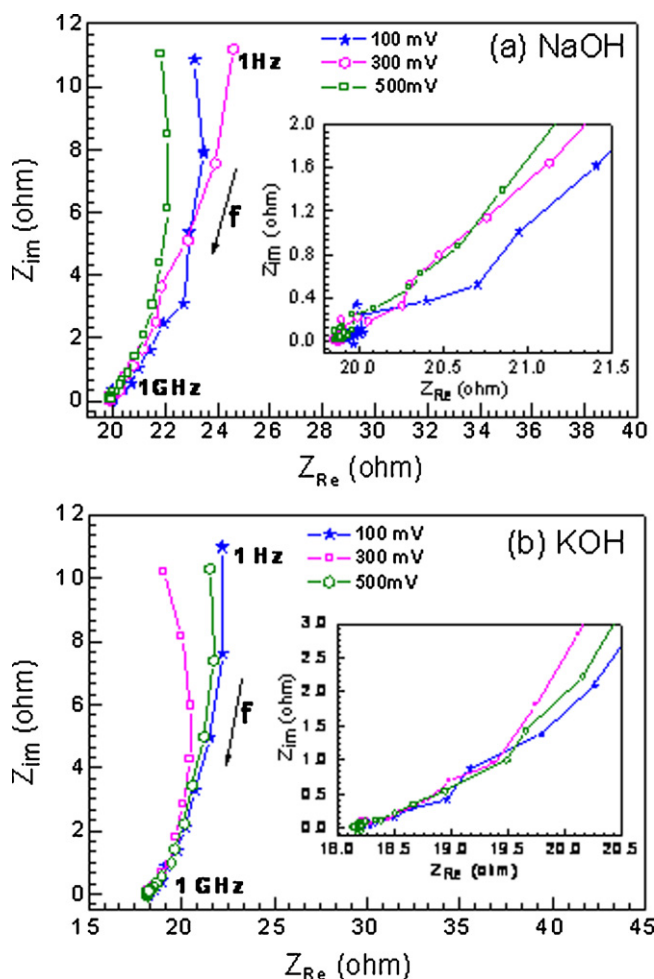


Fig. 6. Nyquist plots of NiO thin films at different potentials (a) in NaOH electrolyte, and (b) in KOH electrolyte.

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