



Electrochromic and electrochemical properties of amorphous porous nickel hydroxide thin films

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ABSTRACT

Nickel hydroxide films were prepared using the chemical bath deposition (CBD) technique. The amorphous nature of the films was confirmed by X-ray diffraction measurements. X-ray photoelectron spectroscopy (XPS) measurements showed that the films exhibited nickel hydroxide nature. The porosity of the films was studied using optical measurements. The electrochromic properties of the porous nickel hydroxide layers were investigated, using cyclic voltammetry, chronoamperometry, in situ transmittance, UV–vis spectroscopy, and impedance spectroscopy. The change in the optical density (ΔOD) was found to be 0.79 for the as-deposited nickel hydroxide films, whereas it is 0.53 and 0.50 for the films annealed at 150 °C and 200 °C, respectively. The in situ transmittance and chronoamperometry curves revealed that the annealed films had a very fast colouration ($t_c < 290$ ms) and decolouration ($t_d < 130$ ms). The measured colouration efficiencies range between 30 and 40 cm²/C. The impedance measurements revealed the faster colouration and good electrochromic properties for the annealed nickel hydroxide films.

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1. Introduction

Electrochromic (EC) materials are able to change their colours reversibly and persistently under an applied electric field. EC materials are divided into two general classes: transition metal oxides and organic materials. The inorganic materials exhibit two types of colouration processes: cathodically colouring and anodically colouring. Fig. 1 shows the schematic of an electrochromic device consisting of a transparent electrically conducting layer, electrochromic cathodically (or anodically) colouring materials, ion storage layer and an ion conducting electrolyte. An electrical potential causes redox reactions to take place in the electrochromic and ion storage layers, a process that is accompanied by ion migration across the ion-conducting layer in order to achieve charge compensation (i.e., charge transfer). A good electrochromic device has a long-term stability and a reversibility of the colour/bleach processes, and its response (i.e. the time required to colour the device) should be as fast as possible.

The transition metal oxides have attracted much attention in recent years, due to their low power consumption, high colouration efficiency (CE), and their memory effect under open circuit conditions [1–3]. Among these electrochromic materials, the most commonly studied is WO₃, due to its large colouration efficiency (CE) value. However WO₃ has a slow response time compared to any of the other electrochromic materials. In contrast, nickel oxide is an anodically colouring material. Upon oxidation, the charge transfer results in a colour change from transparent (Ni²⁺) to brownish (Ni³⁺) (Ni²⁺ → Ni³⁺). However, despite promising features such as high electrochromic efficiency, good cycling reversibility, cost effectiveness [4,5], and a gray colouration, useful for smart window technology [6], nickel oxide is the least understood of the electrochromic materials. The electrochromism in NiO thin films is rather complicated, although it is generally accepted that the transition from a coloured to a bleached state is related to a charge transfer process between the (Ni²⁺) and (Ni³⁺) states [7].

A variety of methods have been used to prepare electrochromic NiO films, among them, the CBD method is an advantageous technique due to its low cost and, low temperature, and it is convenient for large-area deposition. However, the films deposited by this chemical technique showed a different stoichiometry, structure,

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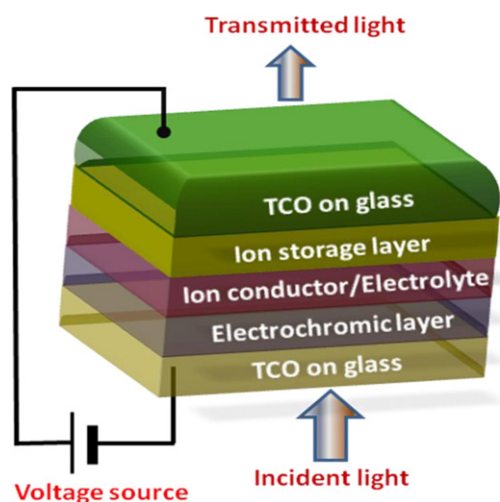


Fig. 1. The schematic of the electrochromic device.

crystallinity, and crystallite size. In addition, chemically deposited films require a thermal treatment in order to improve the adhesion to the substrate and to ensure structural stability. This is an important factor for improving the performance of EC devices. According to Surca et al. [8,9], a high temperature thermal treatment lowers the EC effect; on the other hand, thermally untreated films are optically inactive. The highest colouration efficiencies, in the range of 24–42 cm²/C, were reported in CBD grown porous NiO thin films by Xia et al. [10] and Ristova et al. [11]. According to these reports, the porous structure was helpful for good reaction kinetics with a fast switching speed. When we surveyed the literature, we noted that morphology plays a key role in the electrochromic and electrochemical properties of NiO thin films.

In this study, we examined the effect of porosity on the electrochromic and electrochemical properties of chemical bath-deposited nickel oxide thin films.

2. Experimental details

Nickel oxide thin films were prepared using the CBD technique at room temperature. The films were deposited onto indium doped tin oxide (ITO) (25–27 Ω/cm²) coated conducting glass substrates. Prior to the deposition, the ITO substrates were consecutively ultrasonically cleaned in acetone, methanol, and deionized water. The reaction bath for the deposition of the NiO_x contained 20 ml of 1.0 M nickel sulphate, 30 ml of 28% ammonia, and 50 ml of water. The pH of the dark blue precursor solution was 2.5. The cleaned ITO glass substrates were immersed vertically in the deposition bath. The deposition was carried out under vigorous stirring (800 rpm) for 24 h using a magnetic stirrer. After the deposition, the films were immersed in deionized water and dried in air. Finally, the films were air-annealed at 150 °C and 200 °C for 2 h in order to improve the structural quality and adherence of the films. The films annealed at 150 °C and 200 °C were denoted as N₂ and N₃, respectively, whereas the as-deposited film was denoted as N₁.

The structural and morphological properties of the samples were studied using x-ray diffraction (XRD) and scanning electron

microscopy (SEM), respectively. The porosity of the films was measured using an optical microscope (Carl Zeiss, model-AXIOVERT 40 MAT) equipped with BioVis software. The cyclic voltammetry (CV), chronoamperometry (CA), and chronocoulometry (CC) measurements of the NiO_x films were performed in a three-electrode electrochemical cell containing 0.5 M LiClO₄ with propylene carbonate (PC) as the electrolyte, a saturated calomel electrode (SCE) as the reference electrode, and platinum wire as counter-electrode, using an electrochemical workstation (CH-Instruments, model CHI400A). The electrochemical impedance measurements were made by using a potentiostat (Princeton applied research, versastat 3) with Versa studio software. The optical absorption and transmittance were recorded with a UV–vis–NIR spectrophotometer, (Systronic-119) over 350–850 nm. The response times were also deduced from in situ transmittance measurements at 630 nm. The variation of the transmittance with time was recorded with an X–Y recorder.

3. Results and discussion

Fig. 2(a)–(c) and (d)–(f) shows the XPS spectra of the nickel oxide films for the nickel and oxygen binding states, respectively. The presence of nickel hydroxide was evidenced by nickel Ni 2p_{3/2} peaks and oxygen O 1s XPS peaks. Fig. 2(a)–(c) show a Ni 2p_{3/2} peak of as-deposited and annealed films at 150 °C and 200 °C respectively. The deconvoluted Ni 2p_{3/2} peaks at 856.18 eV (NiOOH), [12], 858.03 eV, (NiO₂), 861.16 eV (NiO), and 863.58 eV (NiOOH) are attributed to the presence of Ni²⁺, Ni³⁺ and Ni⁴⁺ oxide phases [13,14]. The existence of the Ni-hydroxide phases is also reflected in the O 1s core level spectra shown in Fig. 2(d)–(f). The three different peaks deconvoluted as O 1s spectra are attributed to the three different binding states of Ni, which are related to the Ni–O–Ni bond (530.5 eV) for the divalent and tetravalent oxide, the NiO–OH bond (531.63 eV) for a trivalent oxide, and the H–O–H bond (532.94 eV) for the residual water [15]. All the as-deposited and annealed films contained mixed phases of Ni²⁺, Ni³⁺ and Ni⁴⁺ ions. The atomic concentration ratio between Ni and O (Ni/O) atoms has been estimated by using the measured XPS spectra. The concentration ratio was found to be 0.675, 0.680 and 0.706 for the as-deposited and annealed films at 150 °C and 200 °C respectively. It seems that the relative OH concentration of the films was reduced with annealing, resulting in the formation of stoichiometric films. From the XRD and XPS measurements, we note that the as-deposited films and films annealed at 150 °C and 200 °C are made of amorphous nickel hydroxide nature.

The SEM and optical images of the nickel oxide films are shown in Fig. 3(a)–(c) and (d)–(f), respectively. The as-deposited film was rather homogeneous and was yellowish in colour. After annealing, the films were nearly transparent and found to be strongly adhered to the ITO substrate. All three types of nickel hydroxide films are porous in nature. The degree of porosity was calculated using the optical images shown in Fig. 3(d)–(f). The values of the porosity are shown in Table 1. Well-defined clusters (Fig. 3(a)) were observed for the as-deposited film. The films annealed at 150 °C and 200 °C showed a porous structure with cracks (Fig. 3(b)–(c)). These surface cracks may be due to the stress relaxation in the film involving a volume change from nickel to nickel oxide during the thermal oxidation process [16].

Table 1
The electrochromic and electrochemical parameters in the NiO_x films.

Sample	Porosity (%)	Response time		T_b (%)	T_c (%)	$(\Delta OD)_{630\text{nm}}$	Colouration efficiency (cm ² /C)
		t_b (ms)	t_c (ms)				
N ₁	15.66	130	290	53.45	8.61	0.79	41
N ₂	21.41	120	240	37.49	10.82	0.53	37
N ₃	25.60	120	190	41.68	13.16	0.50	32

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