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The electrochromic behavior of nickel oxide films sprayed at different preparative conditions

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Abstract

Nickel oxide films have been prepared onto transparent conducting-coated glass at different substrate temperatures using spray pyrolysis technique. Electrochromic characterizations of the prepared films have been studied by cycling between their coloured and bleached states using a three-electrode cell containing 1 M KOH electrolyte. The influence of substrate temperature as well as film thickness on the electrochromic (EC) performance has been investigated. The substrate temperature (T_{sub}), film thickness, and the colouration and bleaching potentials have been optimized as 275 °C, 140 nm, +0.7 and −1.0 V, respectively. With optimized coating and working parameters, the results yielded transmission solar modulation ΔT_s=0.35, visible modulation ΔT_v=0.51, injected charge=14 mC and colouration efficiency η=44 cm^2/C. In addition to the nominal bleaching state, a full bleaching state is newly assigned leading to higher optical modulation of 0.45 and 0.63 for ΔT_s and ΔT_v, respectively. An adequate potential pulse shape is suggested for operating the device. Different from some reported results, switching time measurements showed that colouration is faster than bleaching which may obscure different redox mechanisms of EC colouration. Infrared reflectance spectroscopy showed evidently the significance of water in the EC process. The results showed clear consistency with the view that a transparent film of $Ni(OH)_2$ is made absorbing through transformation to coloured NiOOH. Discussion of the results supports the colouration mechanism of double extraction of proton and electron.

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1. Introduction

The technology of the electrochromic (EC) thin films becomes more and more attractive for the researchers. The interest for electrochromic material is based on their potential applications to smart windows; glare free and variable reflectance mirror, gas sensors, and high contrast non-emissive information display system, devices for thermal control [1–10]. The potential advantages of the electrochromic device are its open-circuit memory and low power requirement. The electrochromic film is an important layer in an EC device. This film is generally composed of an amorphous or crystalline oxide deposited onto a transparent conducting oxide-coated glass or plastic sheet. Among various EC oxides of transition metals, nickel oxide is an interesting material due to, besides their potential use as a battery electrode, its rather high EC efficiency, large dynamic range, cyclic reversibility, durability and low material cost [11–15]. This material is stable in alkaline environments and colours and bleaches at potentials below the oxygen and hydrogen evolution potential. As an anodic electrochromic material, with grey colouration, nickel oxide can be used as a complimentary to tungsten oxide electrode in smart window application technique [16], where optical modulation increases due the simultaneous bleaching and colouring of both electrodes.

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Electrochromic nickel oxide can be prepared by various methods, thermal evaporation, electro-deposition, sputtering, chemical vapour deposition, spray pyrolysis, colloidal deposition, sol–gel route [17–27].

It was reported that annealing could remarkably improve the electrochromic characteristics of nickel oxide films deposited by chemical or electrochemical techniques [28]. In a previous work, cathodically deposited electrochromic nickel oxide films were characterized and the preparative parameters were optimised [14]. In another paper the dependence of the electrochromic as well as optical and structural properties of hydrated nickel oxide films on post deposition heat treatment was studied [29].

In a recent paper, [15], we reported the opto-structural, electrical and electrochromic properties of crystalline nickel oxide thin films. The samples were deposited by spray pyrolysis onto glass as well as Fluorine doped tin oxide (FTO) substrates maintained at 350 °C. The effect of solution molarity on their properties was studied and optimised as 0.1 M. Electrochromic cycling has been found to increase the solar and optical modulation whereas the amorphousity of the polycrystalline films increased. The heat treatment of the electrochromic film altered the water content and the crystalline nature of the film, which consequently changed the electrochromic properties. Using X-ray diffraction (XRD) and infrared (IR) reflectance spectroscopy, the influence of the substrate temperature on the structural properties was investigated. The variation of electrical conductivity with growth temperature was measured and has been interpreted assuming two phase model. Using corrected transmittance and reflectance, the optical constants are computed over the spectral range 300–2500 nm and the optical transitions are deducted.

The objectives of the present work, therefore, is to study the influence of the film grown temperature of nickel oxide on its electrochromic properties such as solar and visible optical modulation, colouration efficiency and switching time. The prepared amorphous and polycrystalline nickel oxide films are cycled in 1 M KOH electrolyte using three electrode cell. The effect of film thickness and the dependence of solar and visible modulation and electrochromic efficiency on colouration potential are also investigated aiming to optimise the preparative as well as performance parameters.

The type of ion species (H^+ or OH^-) transported upon colouration is extensively discussed in the literatures. Therefore, part of this work deals with the changes observed in the infrared reflectance spectra during colouring and bleaching reactions. In addition, response time measurements are reported and discussed to throw more light on the colouration and bleaching mechanism with the significant colouration ion species, in such anodic EC material.

2. Experimental details

Nickel oxide thin films were deposited from 0.1 M aqueous solution of nickel chloride [15], by conventional spray pyrolysis technique. The layers have been deposited onto indium doped tin oxide (ITO)-coated and/or FTO-coated glass substrates which are chemically and ultrasonically cleaned before deposition. The overall reaction process can be expressed as heat decomposition of nickel chloride to clusters of nickel oxides in the presence of water and air oxygen. The deposited films may have disordered $Ni(OH)_2$ structure or nano-crystalline NiO structure according to the following reactions:

$$\begin{aligned} NiCl_2 + 2H_2O &\xrightarrow{\text{heat}} 2HCl + Ni(OH)_2 \\ NiCl_2 + 2H_2O &\xrightarrow{\text{heat}} 2HCl + NiO + H_2O \end{aligned} \quad (1)$$

In order to optimise the deposition temperature, the flow rate, virgin solution concentration, deposition time, the nozzle to substrate distance are kept constant at 15 cm^3/min, 0.1 M, 40 s and 40 cm, respectively. The film thickness of the prepared samples was measured using multiple beam Fizeau fringes at reflection using either white light or a monochromatic light (Hg, λ_g=546 nm). The coloured interference fringes enable the determination of the integer number of the fringe shift, while using the monochromatic light, fringe shift as a fraction of order separation, is measured using an eyepiece micrometer.

To investigate the EC properties of the samples, a three-electrode cell was employed with nickel oxide as working electrode. The counter electrode is being a platinum sheet and a saturated calomel electrode is used as a reference electrode.

The solar transmittance T_s and visible transmittance T_v in the colouration and bleached states were obtained by integrating the measured transmittance $T(\lambda)$ weighted by the solar spectrum at air mass 2 (AM2).

$$T_s = \frac{\int_{\lambda_1}^{\lambda_2} T(\lambda).G(\lambda)\mathrm{d}\lambda}{\int_{\lambda_1}^{\lambda_2} G(\lambda)\mathrm{d}\lambda}, \qquad T_v = \frac{\int_{\lambda_1}^{\lambda_2} T(\lambda)V(\lambda)\mathrm{d}\lambda}{\int_{\lambda_1}^{\lambda_2} V(\lambda)\mathrm{d}\lambda} \quad (2)$$

where $G(\lambda)$ is the solar spectrum at AM2 and $V(\lambda)$ is the photopic luminous efficiency function defining the eye sensitivity. For solar transmittance the limits of integration are taken as λ_1=300 nm and λ_2=2400 nm while for visible transmittance the limits are λ_1=380 nm and λ_2=780 nm.

The optical transmittance and reflectance of the films were recorded in the wavelength range from 300 nm to 2500 nm using SHIMADZU UV 3101 PC: UV–VIS–NIR double beam spectrophotometer. Infrared investigation has been performed in the wave-number range 400 to 4000 cm^{-1} for films deposited onto FTO glass substrates (as an IR reflector) and using a Perkin-Elmer 1460 IR recording spectrophotometer. Those spectra were recorded ex situ.