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Electrochromism in spray deposited iridium oxide thin films

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Abstract

Electrochromic iridium oxide thin films were deposited onto fluorine doped tin oxide coated glass substrates from an aqueous iridium chloride solution by pneumatic spray pyrolysis technique. The as-deposited samples were X-ray amorphous. The electrochromic properties of thin films were studied in an aqueous electrolyte (0.5N H_2SO_4) using cyclic voltammetry (CV), chronoamperometry (CA) and spectrophotometry. Iridium oxide films show pronounced anodic electrochromism owing to $Ir^{+4} \leftrightarrow Ir^{+3}$ intervalency charge transition. The reversibility of cyclic process in Ir oxide films is found to be higher, which increases with increasing number of colour–bleach cycles.

Keywords: Spray pyrolysis; Thin films; Electrochromism; Iridium oxide

1. Introduction

Electrochromism is the process by which a material exhibits reversible and persistent colour change with applied electric current or applied field [1]. Electrochromic materials switch from the uncoloured state to the coloured state by simultaneous ion and electron injection and consequently have potential application in energy efficient “Smart Windows” [2], mirrors with variable reflectance and high contrast non emissive information displays [1].

Iridium oxide is a well-studied material due to its use in optical information storage [3], catalyst for O_2 evolution [4,5], micro-electronic devices and pH sensor. It was also used as an electrochromic material [6,7]. Iridium oxide/hydroxide films have desirable characteristics that include fast colouring and bleaching times (<50 ms), good open circuit memory, reversibility (>90%), stability ($\sim10^7$ cycles) and relatively sharp threshold voltage [6–8]. Thus, despite the problem of its high cost, it is useful for smart window technology and electrochromic devices.

Iridium oxide thin films have been prepared using different techniques that embrace thermal oxidation [9,10], anodic oxidation [6,11], reactive sputtering [12,13], electrodeposition [14] and sol–gel processing [15,16].

In this investigation, electrochromic Ir-oxide thin films were prepared probably for the first time using simple and inexpensive pneumatic spray pyrolysis technique (SPT) and have been investigated for their electrochromism in 0.5N H_2SO_4 electrolyte.

Iridium oxide films display pronounced electrochromism and bleach/colour, when ions are intercalated/deintercalated. The mechanism responsible for electrochromism has been subjected to considerable controversy over the years, but now it is generally accepted that the optical effects are connected with ion intercalation/deintercalation just as for W-oxide and Mo-oxide. Some early claims [6,8] that the electrochromism in Ir-oxide would be purely electronic nature have been convincingly disapproved. The ionic species involved in the intercalation and deintercalation reaction has been debated at length and in essence two mechanisms have been put forward

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to account for electrochromism of anodic films in aqueous electrolytes. These are:

(a) cation mechanism requiring colouration via proton extraction;
(b) an anion mechanism requiring colouration via hydroxide ion insertion.

It is seen that extraction of protons and electrons from the film leads to colouring and insertion of protons and electrons into the film leads to bleaching. In these reactions, the presence of free hydroxyl ions and absorbed water in iridium oxide film play a key role in stimulating their electrochromic activity.

2. Experimental

Iridium oxide thin films were prepared by spraying 0.01 M, 25 ml aqueous iridium chloride ($IrCl_3 \cdot 3H_2O$) solution in doubly distilled water onto conducting fluorine doped tin oxide (FTO) coated glass substrates (sheet resistance was 10 Ω/□), maintained at a temperature of 250 °C. Process parameters (e.g. spray rate, nozzle to substrate distance, solution quantity, etc.) have been optimized to obtain good quality films. Table 1 shows various process parameters, their range and optimized values. Further details are reported in our earlier work [17].

The electrochromic (EC) cell was a conventional three-electrode cell. The iridium oxide thin film deposited onto FTO coated glass substrate was used as working electrode (area ≈ 1 cm^2). The counter electrode was a graphite plate and a saturated calomel electrode (SCE) was used as a reference electrode. The electrolyte used was 0.5N H_2SO_4 solution.

The cyclic voltammetry (CV) and chronoamperometry (CA) were carried out using a VersaStat-II (EG&G) potentiostat/galvanostat, controlled by M270 software. All the potentials were measured with respect to SCE. The in situ optoelectrochemical study was carried out using a conventional laser source ($\lambda = 630$ nm) and a silicon detector. Optical transmission spectra of thin films before and after colouration were measured in the wavelength range 350–850 nm using a Hitachi-330 model spectrophotometer. For this measurement, the sample was removed from the electrolyte after bleaching or colouring, rinsed in distilled water, dried and then placed in the compartment of the spectrophotometer. The stability of iridium oxide thin film in 0.5N H_2SO_4 was tested by repeating colour–bleach cycles several times.

Table 1
Preparation conditions of film formation

S. no.	Process parameter	Range studied	Optimized value
1	Solution concentration (M)	0.0075–0.05	0.01
2	Solution quantity (ml)	10–50	25
3	Spray rate (cm^3/min)	3–20	5
4	Nozzle to substrate distance (cm)	15–30	25
5	Air pressure (kg/cm^2)	1.5–4.5	2.5
6	Substrate temperature (°C)	250	250
7	Deposition time (min)	2–10	2
8	Film thickness (μm)	–	0.12

3. Results and discussion

3.1. Formation of iridium oxide thin films

An aqueous iridium chloride solution was sprayed onto preheated FTO coated glass substrates. It undergoes a pyrolytic decomposition, resulting into the formation of a thin solid film. The chemical reaction that took place is as follows:

$$2IrCl_3 + 3H_2O \xrightarrow{250\,^{\circ}\mathrm{C}\ \text{(substrate temperature)}} Ir_2O_3 + 6HCl\uparrow \quad (1)$$

The resulting films were strongly adherent to the substrates.

As observed previously the infrared (IR) spectrum of the as-deposited iridium oxide films show residual chlorine in the film and were X-ray amorphous [17].

3.2. Electrochemical characterization

3.2.1. Cyclic voltammetry

The potential was cycled from +1.2 to −0.2 V (versus SCE) at potential sweep rate of 10 mV/s in 0.5N H_2SO_4. During the potential sweep the current resulting from ion intercalation and deintercalation was recorded and the variation is shown in Fig. 1(a). At the cathodic potential end (− 0.2 V), the film is in the bleached state and at the anodic potential end (+ 1.2 V) it becomes bluish black. The bleaching and colouration of Ir-oxide thin films is associated with intercalation and deintercalation of H^+ ions and electrons in the film. The CV spectrum exhibits an anodic current peak at a potential of + 0.7 V versus SCE, which is followed by a rapid increase of the current due to O_2 evolution. After reversal of the potential scan a cathodic peak is observed at + 0.67 V versus SCE, owing to Ir^{+4} to Ir^{+3} charge transfer. The iridium oxide electrode, thus, switches between bleached state and coloured state due to $Ir^{+4} \leftrightarrow Ir^{+3}$ intervalence charge transfer during the potential scan. The CV spectrum displays reversible charge transfer transition.

The CV spectrum is similar to that obtained for Ir-oxide thin films prepared by thermal decomposition [18], sputtering [13] and sol–gel [19] methods. However, the voltammogram of IrO_2 crystallites prepared by chemical vapour deposition on quartz at high temperature [20] differs from that of spray deposited Ir-oxide. The difference may be related to the degree of hydration and crystallinity of the oxide [18].

The following colouration and bleaching process is proposed for spray deposited Ir-oxide thin film:

$$Ir(OH)_3 - H^+ - e^- \underset{\text{bleach}}{\overset{\text{colour}}{\rightleftarrows}} IrO_2 \cdot H_2O,$$

$$\text{at } + 0.7\,\text{V (versus SCE)} \qquad (2)$$