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Electrochromic iridium oxide films: Compatibility with propionic acid, potassium hydroxide, and lithium perchlorate in propylene carbonate



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ABSTRACT

Porous thin films of Ir oxide were prepared by reactive dc magnetron sputtering onto unheated substrates. The crystallite size was ~ 5 nm, and a small amount of unoxidized Ir was present. The electrochromic performance was studied by optical transmittance measurements and cyclic voltammetry applied to films in aqueous and non-aqueous electrolytes, specifically being 1 M propionic acid, 1 M potassium hydroxide (KOH), and 1 M lithium perchlorate in propylene carbonate (Li-PC). Cyclic voltammetry measurements indicated that the films had a fractal surface structure. Good electrochromism, with mid-luminous transmittance modulation between ~ 55 and $\sim 90\%$ in ~ 100 -nm-thick films, was documented in all of the electrolytes.

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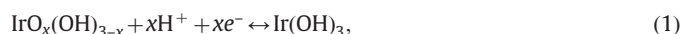
1. Introduction

Electrochromic (EC) thin films show reversible and persistent changes of their optical properties under charge insertion/extraction [1–3] and have many applications in contemporary technology such as for energy saving and comfort-enhancing “smart” windows and glass facades in buildings [4–7], high-performance information displays, “anti-dazzling” rear-view mirrors for cars, variable-emittance surfaces for thermal control, etc. The most widely studied EC device incorporates five superimposed layers: an electrolyte is in the middle and connects an EC film to an ion-storage film (ideally also with EC properties), and this three-layer configuration is embedded between transparent and electrically conducting films. Optical changes are effected when a voltage is applied between the transparent conductors and are related to joint insertion of electrons from the transparent electrodes and ions from the electrolyte into the EC film(s).

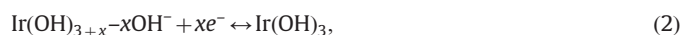
There are two types of EC thin films: one is called “cathodic” and colors under ion insertion and the other is called “anodic” and colors under ion extraction. Oxides based on W, Mo, Nb, and Ti are examples of the first type, and oxides of Ir, Ni, and Co belong to the second type. Combinations of one cathodic and another anodic EC film are favorable from an optical point of view, and devices incorporating W oxide, Ni oxide, and an intervening polymer electrolyte have been studied in particular detail during the last decade [8,9].

The purpose of this paper is to lay the foundation for in-depth studies of Ir-oxide-based films, which are interesting from a fundamental perspective and also for special applications requiring EC devices with particularly good optical performance and/or durability. Ir oxide has been studied in this context at least since 1978 [10,11], and sputter deposited EC films were reported in 1979 [12]; the early literature has been reviewed in detail [1]. The research field maintains its vitality [13–20]. Concerning durability, we notice that Ir oxide films have undergone EC cycling for up to 7×10^6 ion insertion/extraction cycles without significant degradation [21]. Ir is a rare element in the earth’s crust and available only at a few geographical locations, which gives obvious restrictions for applications. However, it should be noticed that significant electrochromism prevails in Ir oxide even after dilution with less costly Ta [16,19] and Sn [17,18,20].

Specifically, we report below on the compatibility of porous Ir oxide films with three electrolytes: 1 M propionic acid ($\text{CH}_3\text{CH}_2\text{COOH}$; aqueous and acidic), 1 M KOH (potassium hydroxide; aqueous and basic), and 1 M lithium perchlorate in propylene carbonate (LiClO_4 in $\text{C}_4\text{H}_6\text{O}_3$, denoted Li-PC; non-aqueous). The electrochemical reactions underlying the electrochromism in these types of electrolytes have been the subject of much interest over the years [1]. Thus, for aqueous electrolytes, a cation (proton) process is expected to progress according to



whereas an anion (hydroxyl) process can be described as



where e^- denotes electrons and x can be as large as unity. Reaction (2) is highly schematic, and the reason for the electrochromism

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may in fact be the splitting of water molecules and ensuing insertion and extraction of protons. $\text{Ir}(\text{OH})_3$ represents the transparent state; it can be written alternatively as $\text{HlrO}_2 \cdot \text{H}_2\text{O}$ or $\text{IrOOH} \cdot \text{H}_2\text{O}$. At $x=1$, the colored oxide can be written as $\text{IrO}_2 \cdot \text{H}_2\text{O}$ for the cation process and $\text{IrO}_2 \cdot 2\text{H}_2\text{O}$ for the anion process. With regard to the Li-containing electrolyte, the corresponding reaction is



Our present study can be viewed as a counterpart to our earlier investigation on the compatibility of Ni oxide with different electrolytes [22].

2. Experimental

2.1. Thin film deposition

Thin films of Ir oxide were prepared by reactive dc magnetron sputtering in a deposition system based on a Balzers UTT 400 unit. The substrates were unheated $5 \times 5 \text{ cm}^2$ glass plates pre-coated with transparent and electrically conducting layers of $\text{In}_2\text{O}_3:\text{Sn}$ (known as ITO) with a sheet resistance of 60Ω . Some films were deposited also onto carbon plates. The target was a 5-cm-diameter cylindrical plate of metallic Ir (99.95%). Pre-sputtering took place in argon (99.998%) for 3 min, and oxygen (99.998%) was then introduced so that the O_2/Ar gas-flow ratio remained at a constant value within the $0.5 \leq \gamma \leq 2$ range. The target-substrate separation was 13 cm. The total pressure during sputtering was set to 30 mTorr, and the power at the target was 200 W.

The film thickness was determined by surface profilometry using a DektakXT instrument and lay in the $30 \leq d \leq 700 \text{ nm}$ range.

2.2. Structural and compositional characterization

Film structures were determined by X-ray diffraction (XRD) using a Siemens D5000 instrument operating with $\text{CuK}\alpha$ radiation at a wavelength $\lambda_x = 0.154 \text{ nm}$. Specific assignments and inferences about preferred orientations were obtained by comparison with the Joint Committee on Powder Diffraction Standards (JCDPS) data base.

The grain size D was determined from Scherrer's formula [23], i.e.,

$$D = \frac{k\lambda_x}{\beta \cos \theta} \quad (4)$$

where $k \sim 0.9$ is a dimensionless "shape factor", β is the full width at half-maximum of an X-ray diffraction peak, and θ is the diffraction angle.

The morphology of the Ir oxide films was characterized by scanning electron microscopy (SEM) using a LEO 1550 FEG Gemini instrument with an acceleration voltage of 10 to 15 kV.

Elemental compositions and atomic concentrations were determined by Rutherford Backscattering Spectroscopy (RBS) at the Uppsala Tandem Laboratory, specifically using 2 MeV ^4He ions back scattered at an angle of 172 degrees. The RBS data were fitted to a model of the film-substrate system by use of the SIMNRA program [24].

The film density ρ was computed from

$$\rho = \frac{M \times N_s}{n_{\text{atoms}} \times N_A d} \quad (5)$$

where M is molar mass, N_s is thickness in atoms/cm², n_{atoms} is number of atoms in a molecule, N_A is Avogadro's constant, and d is thickness in centimeters.

2.3. Electrochemical and optical measurements

Cyclic voltammetry (CV) was performed in a three-electrode electrochemical cell by use of a computer-controlled ECO Chemie Autolab/GPES Interface. The Ir oxide film served as working electrode and was electrochemically cycled in three electrolytes: 1 M propionic acid, 1 M KOH, and 1 M Li-PC. For propionic acid and KOH, the counter electrode was a Pt foil and the reference electrode was Ag/AgCl; the voltage ranges were chosen as -0.5 to 1.25 V vs Ag/AgCl for propionic acid and -1.2 to 0.5 V vs Ag/AgCl for KOH, in order to get the same anodic and cathodic charge density while avoiding electrolyte decomposition. The pH value is 2.2 and 14 for propionic acid and KOH, respectively. In the case of Li-PC, both counter and reference electrodes were Li foils, and the voltage range was 2.0 to 4.7 V vs Li. The low voltage limit was chosen to avoid irreversible formation of Li_2O and LiOH [25] as well as electro-activity in ITO [25,26]; the high voltage limit was set to avoid oxidation of PC [27,28]. The voltage sweep rate lay in the $2 < \nu < 50 \text{ mV/s}$ range.

Optical transmittance measurements were recorded in situ during electrochemical cycling of Ir oxide films at the fixed wavelength $\lambda = 550 \text{ nm}$ by use of a fiber-optical instrument from Ocean Optics. The electrochemical cell was positioned between a tungsten halogen lamp and the detector, and the 100%-level was

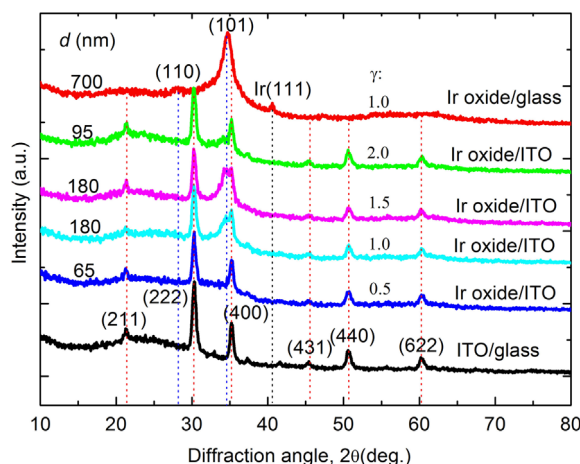


Fig. 1. X-ray diffractograms taken for films of Ir oxide and ITO, and for four Ir oxide films on ITO. Thickness d and O_2/Ar ratio γ during sputtering are given for the Ir oxide films. All films were backed by glass. The diffraction peaks are assigned to the shown reflections, and their locations are indicated by vertical dotted lines.

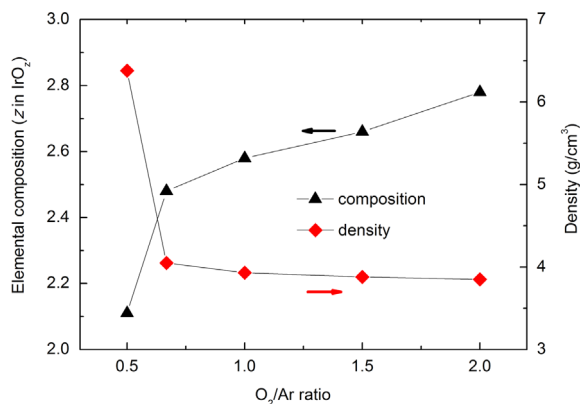


Fig. 2. Elemental composition, given as z in IrO_z , and density for Ir oxide films sputter deposited at the shown O_2/Ar ratios. Data points are connected by lines for convenience. Arrows indicate the pertinent vertical scale.

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