

Cyclic voltammetry study on electrochromic copper(I) oxide thin films

Ratka Neshkovska¹, Mimoza Ristova² and Julijana Velevska²

Abstract – Electrochromic copper(I) oxide thin films were deposited onto conductive glass substrates using two different methods: chemical bath and low vacuum deposition. The coloring/bleaching processes of the films were investigated by cyclic voltammetry.

Keywords – Copper(I) oxide, Thin films, Electrochromism, Cyclic voltammetry.

I. INTRODUCTION

A. Electrochromism

Electrochromic materials are able to vary their optical properties (color, transparency, absorbance, etc.) in a reversible manner, upon electrically induced oxidation and reduction when they are subjected to a small electric field (1–5 V) [1]. They can be colored in a reduced state and bleached in an oxidized state, or vice versa.

The concept of electrochromism originated in the 1960s. In the early 1980s, the electrochromic materials were a subject of great interest and were extensively studied due to their possible use in displays and watches. Due to durability issues and manufacturing problems, another type of chromogenic material, liquid crystals, was chosen for displays. Furthermore, liquid crystals were able to switch from a transparent state to an opaque one faster, within fractions of a second. The interest in EC materials had a new impetus in the early 1990s, particularly in the aerospace and aviation sectors [1]. They are currently being used in the automotive industry as glare-free automotive rear view mirrors and sunroofs. The great interest of researchers during the last decades in the optical, electrical and mechanical properties of electrochromic materials, as reflected by the large number of studies developed worldwide, is due to the fact that the most promising electrochromic device use is "smart windows" - all-solid-state electrochromic devices used for modulating of incident solar radiation. They change their optical properties (transmittance, reflectance, absorbance, etc.) in their colored and bleached state, thus achieving energy efficiency and human comfort in buildings. The technology has recently been implemented in large-area glazing (windows and glass

facades) in order to create buildings which combine energy efficiency with good indoor comfort [2].

A number of materials, both inorganic and organic, liquids, solids and polymers exhibit electrochromism, but the main materials with electrochromic properties are metal oxides of some transition elements, in particular WO₃, MoO₃, IrO₂, NiO, and V₂O₅.

Major techniques for analyzing electrochromic oxide films include techniques for studying their crystal structure and elemental composition, optical properties, electronic structure, ion intercalation and deintercalation. The processes of ion intercalation and deintercalation are studied by:

- Chronoamperometry
- Coulometric titration
- Cyclic voltammetry
- Impedance spectrometry
- Beam deflectometry
 - Mirage effect
 - Beam bending
- Nuclear magnetic resonance (NMR)
- Microbalance measurements [3].

B. Cyclic voltammetry

Cyclic voltammetry is a very important analytical method of characterization in the field of electrochemistry. Any process that includes electron transfer can be investigated with this characterization. Cyclic voltammetry is a potentiodynamic method of tracking the current flowing in the circuit, caused by the change in the potential of the working electrode [4, 5]. This method permits the investigation of the redox and transport properties of a given system in a solution. Most often for this purpose, three electrode systems consisting of a working, reference and counter electrode are used, in which the working electrode can be exposed to a single or multiple linear change in the potential, relative to the reference electrode. The large impedance between the reference and the working electrode forces the resulting current to flow through the counter electrode. The current flowing through the opposite electrode is measured. The potential is measured between the working electrode and the reference electrode, while the current is measured between the working electrode and the counter electrode.

The velocity variation of the potential between the electrodes depends on the type of the process and can have a value from millivolts per second, to a few volts per second. When the potential of the working electrode is positive, there is an oxidation of the material applied to it, i.e. the electrons move from the solution to the working electrode and give an anode current. Similar, when the potential is changed in the opposite direction, the potential of the working electrode becomes more negative than the reduction potential, and

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reduction occurs (i.e. the electrons "flow" from the electrode). Thus, the cathode current is obtained. In order to transfer electrons, the molecules in the solution should be brought to the electrodes. In cyclic voltammetry, the solution is not mixed, so the mass flow occurs only because of the diffusion (due to the concentration gradient) around the surface of the electrode. The signal size is a function of the diffusion characteristic of the system. The intensity of the current is dependent on the size of the surface of the working electrode, the concentration of the electroactive components and on the speed of the potential change (scan rate). On the diagram which gives the dependence of the current density on the potential between the electrodes, a maximum (or peak) occurs, when a certain reaction on some of the electrode's surface begins to occur. The current in the peak has a different value for reversible and irreversible processes and, among other things, depends on the square of the velocity of the potential change, the molar concentration of the electroactive component in the solution and the surface of the electrode. The peak current in a reversible system at 298 K is given by the Randles-Sevcik equation:

$$I_p = (2.69 \cdot 10^5) n^{3/2} A D^{1/2} \nu^{1/2} C \quad (1)$$

where n is the number of exchanged electrons during the redox process, A (cm^2) is the active surface of the working electrode, D ($\text{cm}^2 \cdot \text{s}^{-1}$) and C ($\text{mol} \cdot \text{cm}^{-3}$) are the coefficients of diffusion and the concentration of the electroactive components in the solution, respectively, and ν (Vs^{-1}) is the scan rate (the velocity of the voltage change).

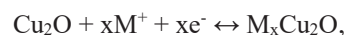
In electrochromic phenomena, cyclic voltammetry is used to investigate the processes of intercalation and deintercalation of ions into the electrochromic film. The voltage applied between the working electrode with electrochromic film and a counter electrode, is swept back and forth between two selected values. Often, the voltage is changed triangularly between the selected values, but it may also have a pulsating character between two specified voltage levels. With such a change in the voltage, the current flowing into and out of the film in conjunction with the ion intercalation/deintercalation is measured. The results of the cyclic voltammetry can be used to extract non-quantitative conclusions, such as: confirming that an electrochromic process takes place between the electrodes, to show the reversibility or irreversibility of the process, to determine the voltages that lead to the stable operation of the electrochromic system. Voltages outside the stability range lead to the release of gases, the covering of electrodes with metal, etc. Quantitative cyclic voltammetry is also possible, so one can measure the charge densities associated with intercalation/deintercalation (coloring/bleaching processes). However, it is often enough to see that the electrochromic process is reversible, i.e. the input current in each cycle is equal.

The electrochromic behavior of the films is influenced by some structural parameters, such as the crystallinity and morphology of the films. Various interpretations exist for their influence. These parameters strongly depend on the method of film preparation and the conditions of preparation in each

method. Therefore, the electrochromic properties of films prepared by different methods are studied.

The voltammograms (the current's dependence on the voltage) depend on the method of obtaining the film, the used electrolyte, the quantity of water in it, the voltage scan rate, the thickness of the film, the number of previous cycles of coloring/bleaching of the electrochromic film, its porosity, its age, etc. Cyclic voltammograms measured in various voltage scan rates can't be normalized to one universal curve. This also applies to the best electrochromic materials, including WO_3 [4, 5].

The coloring/bleaching of the copper(I) oxide thin film is related to the intercalation/deintercalation of ions and electrons in the film, according to the general reaction:



where M^+ is Na^+ , Li^+ , K^+ etc. cations and e^- are electrons.

The film is reversibly bleached with electrochemical oxidation, and is colored with reduction, in an electrolyte that contains light cations.

II. EXPERIMENTAL

It has been recently found that Cu_2O thin films exhibit cathode electrochromism [6-9].

Several methods for obtaining thin copper(I) oxide films have been developed, i.e. thermal oxidation, electrodeposition, sputtering, anodic and chemical oxidation, chemical oxidation, chemical deposition, sol gel technique, laser ablation, etc.

In this work electrochromic Cu_2O thin films were prepared by two different methods - chemical bath deposition and low vacuum deposition onto glass substrates precoated with fluorine-doped tin oxide (FTO) film. FTO film were deposited as proposed by other authors [10].

A. Deposition of Cu_2O thin films by chemical deposition method

Because the optical properties of copper(I) oxide depend on the methods and parameters of deposition, the prepared FTO substrates were subjected to the electroless chemical deposition method of Cu_2O films, which has been proposed by other authors [12] and low vacuum deposition. For that purpose, two beakers with aqueous solution: a cold and a hot one were used. The cold solution contained 200 ml of colourless complex mix of 1 M CuSO_4 and 1 M $\text{Na}_2\text{S}_2\text{O}_3$. The hot solution contained 2 M NaOH at 60-80° C. The FTO coated glass substrates were stuck together with a tweezer-like holder, with their conductive layers facing outwards, in order to be alternatively immersed into the hot and the cold solution. This procedure lasted until the desired thickness was obtained. The thickness was estimated by the number of immersions, since it was previously established that for a given concentration the film thickness is proportional to the number of successive immersions. Hence, each ten immersions

yielded an additional 0.1 μm in the film thickness [12]. Finally, the thin films were rinsed under a running tap water and distilled water. Subject of our studies were the films about 150-200 nm thick (fifteen and twenty successive immersions) [7-9, 11].

B. Deposition of Cu_2O thin films by low vacuum deposition method

Cu_2O thin films were deposited onto the prepared FTO substrates using low vacuum evaporation method [11, 14].

The melting temperatures of Cu, CuO and Cu_2O are 1083°C , 1326°C and 1235°C respectively. The temperature difference between elemental and oxides' melting points makes the evaporation technique attractive for depositing copper oxide thin films. Stable copper oxides can be deposited over a source temperature region of $1090\text{--}1350^\circ\text{C}$. In general, the oxidation rate and the evaporation rate of the source material define the deposition rate of the product grown on the substrate surface. Copper oxide thin films were deposited on glass substrates pre coated with FTO by the low vacuum evaporation technique, using granulated (0.3mm) copper with 99.8 % purity as a starting material. The deposition was performed in a Balzers Automatic BA 510 apparatus. The distance between the source (copper) and the substrates was about 50cm. The evaporation pressure was 0.67Pa. During evaporation the transparency of the substrates changed by 50 %. The deposition lasted several minutes, until all of the starting material from the tungsten boat was evaporated. If the vacuum in the chamber is very high, pure copper will be deposited on the glass substrates. In our case, the vacuum was not so high, so the evaporated copper reacted with the gasses in the chamber. As a result of that reaction cuprous oxide thin films were obtained on the substrates.

The deposited films were yellowish in appearance. The film thickness, measured by weight difference method was about 130nm [11, 14].

Cyclic voltammograms of the deposited copper(I) oxide electrochromic films obtained by the two different methods were recorded with a computer-controlled three-electrode system, part of the Modular electrochemical instrument (AUTOLAB) apparatus. The working electrode of the cell was the electrochromic film of copper(I) oxide deposited on the FTO glass substrate, platinum wire was the counter electrode and Ag/AgCl was used as a reference (nonpolarized) electrode. In all cases, the voltage was changed from +1 V to -1 V and back to +1 V. 0.1 M solution of NaNO_3 in deionized water was used as an electrolyte. The surface of the working electrode was about 1 cm^2 .

III. RESULTS AND DISCUSSION

The prepared Cu_2O films revealed cathode electrochromism. They were colored at a negative potential of

-4V and were bleached at a positive potential of +4V in the constructed electrochromic test devices (ECTD) consisting of a glass supstrate/FTO/ Cu_2O film as a working electrode, a 0.1 M NaOH aqueous solution as an electrolyte and an FTO/glass substrate as a counter electrode. The films are transparent to visible light in their oxidized state and almost black in their reduced state (Fig. 1) [7].

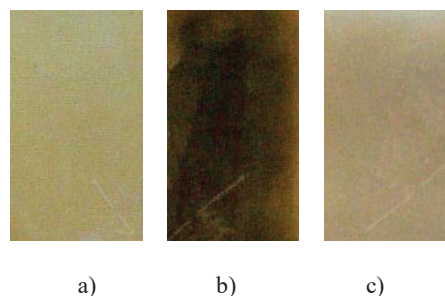


Fig. 1. Photos of electrochromic copper(I) oxide thin film: a) as prepared; b) in colored state; c) in bleached state.

The cyclic voltammogram of the chemically deposited film in 0.1 M aqueous solution of NaNO_3 is given on Fig. 2. The peak potential values of intercalation/deintercalation of ions are -500 mV, -180 mV and 600 mV.

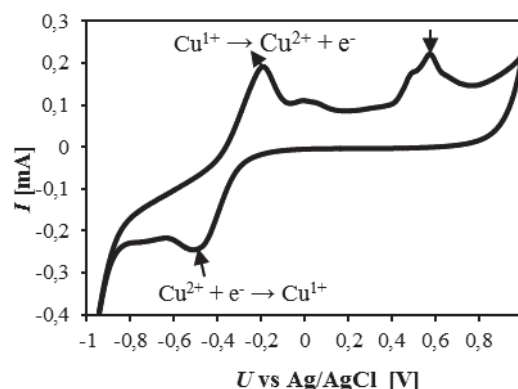


Fig. 2. Cyclic voltammogram of chemically deposited thin Cu_2O film in 0.1 M NaNO_3 at scanning rate 10 mV/s.

Fig. 3 shows five consecutive voltammograms of chemically deposited film in the same electrolyte at the same voltage scan rate [7].

Fig. 4 and Fig. 5 present one and five consecutive cyclic voltammograms of Cu_2O thin films deposited by low vacuum evaporation method, in 0.1 M NaNO_3 electrolyte. The cycling was carried out within a potential range from -1 to +1V and back to -1V vs. the counter electrode. The voltage scan rate was 25 mV/s, and the film working area was 1 cm^2 .

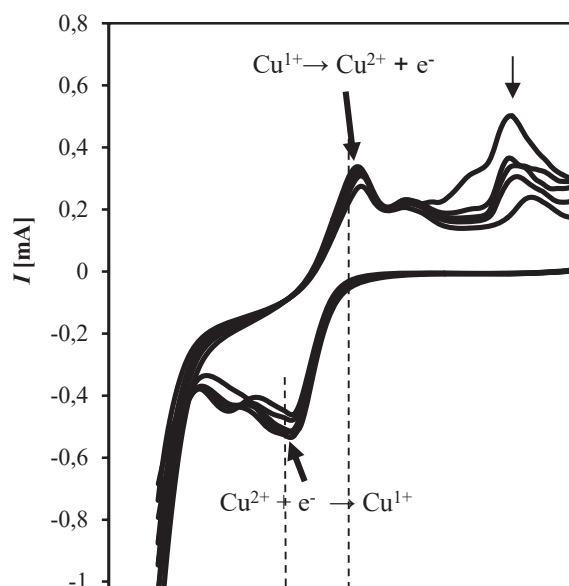


Fig. 3. Five consecutive cyclic voltammograms of chemically deposited thin Cu_2O film in 0.1 M NaNO_3 at scanning rate 10 mV/s.

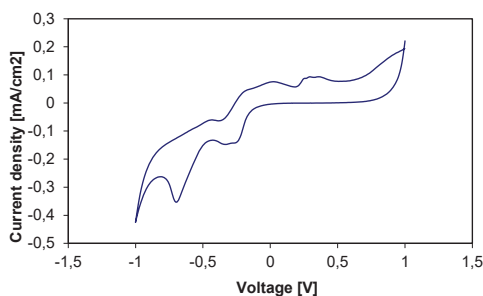
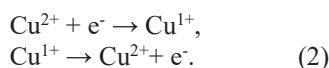


Fig. 4. Cyclic voltammogram of low vacuum deposited thin Cu_2O film in 0.1 M NaNO_3 at scanning rate 25 mV/s.

The above results confirm the electrochromic process between the electrodes in the electrochromic device in which the working electrode is made of copper(I) oxide film, deposited by the two methods. Also, they confirm the chemical reversibility of the processes of coloring and bleaching that occur in copper oxide electrochromic films deposited by the two methods. The cathode and anode peaks indicate that the coloring and the bleaching of the films are related to the reversible transition of Cu(II) in Cu(I) , respectively, according to the equations:



All voltammograms exhibit resolved cathode and anode peaks (corresponding to the reversible red-ox conversion of Cu_2O into CuO), the reversibility is fully established and could be provided by cycling within the voltage range between -800 mV and 500 mV.

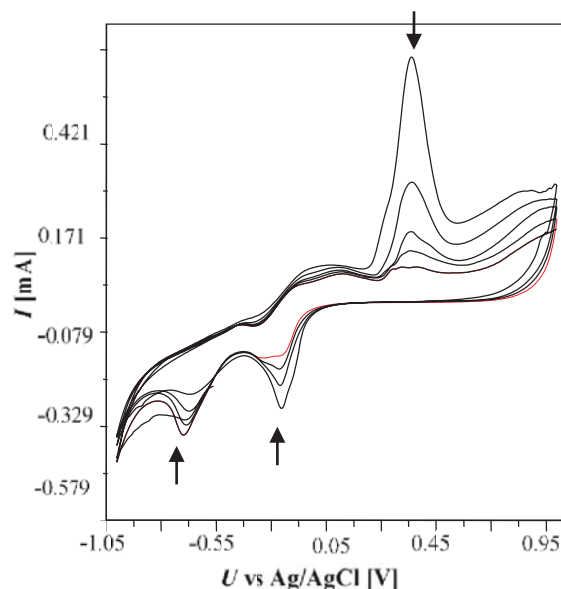


Fig. 5. Five cyclic voltammograms of low vacuum deposited thin Cu_2O film in 0.1 M NaNO_3 at scanning rate 25 mV/s.

IV. CONCLUSION

In this paper, the ion intercalation/deintercalation processes in thin electrochromic Cu_2O films, deposited by two different methods were studied with cyclic voltammetry. The results of the cyclic voltammetry were used to extract non-quantitative conclusions, such as: confirming that an electrochromic process takes place between the electrodes, to show the reversibility of the process, to determine the voltages that lead to the stable operation of the electrochromic system.

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