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STUDY ON THE ELECTRODEPOSITION OF MOLYBDENUM OXIDES ON COPPER SUPPORT

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ABSTRACT. Transition metal oxides (WO_3, MoO_3, V_2O_5) are intensively studied for applications in batteries, catalysis and energy storage. There are several methods for thin films preparation of these materials, including electrodeposition from aqueous electrolyte solutions. In this paper it is studied the electrochemical deposition of molybdenum oxides at different electrodeposition potentials using peroxo-polymolybdate and ammonium molybdate as precursors in a 0.05 M solutions at pH = 2.3 and 5.5. Metallic copper was used as a support. The obtained thin films have been characterized by cyclic voltammetry, optical microscopy and differential scanning calorimetry.

Keywords: *electrodeposition, thin film, cyclic voltammetry.*

INTRODUCTION

Molybdenum oxides are very promising materials for the construction of high power density accumulators for energy storage [1]. In 1987, Auborn and Barberio [2] reported the possible utilisation of MoO_2 as anode material in lithium-based batteries.

The morphological and structural characteristics of the molybdenum oxides prepared by different methods have significant influence on the batteries charging-discharging cycles, stability and lifetime. Nanostructured oxides having high specific surface areas enable a more easy diffusion of lithium ions during the charging-discharging process.

Molybdenum oxides are also useful in the construction of gas sensors for CO detection [3], ion-selective sensors [4] or thin film catalysts for different processes [5, 6].

There are several methods for the preparation of molybdenum oxides thin films, among which are spray-pyrolysis (SP), Metal-Organic Chemical Vapour Deposition (MOCVD), Pulsed Laser Deposition (PLD) [7-9]. In the case of spray-pyrolysis, the precursor (an aqueous solution of molybdenum

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pentachloride, ammonium molybdate, etc.) is sprayed in oxidizing atmosphere (air) onto heated glass where it decomposes with the formation of a thin layer of MoO_3 [7]. Oxide layers can also be deposited on conductive supports by electrochemical procedures using aqueous electrolyte solutions of $(NH_4)_6(Mo_7O_{24})$, $Li_6Mo_7O_{24}$, or Na_2MoO_4 [10,11]. If aqueous peroxo-polymolybdate solutions are used, oxide layers with different molybdenum oxidation states can be obtained [12-14].

In a former paper [15], we reported some of our results related to the preparation of molybdenum oxides thin films by a comparative study concerning their electrochemical deposition on platinum and copper. In the present work, new experimental results on electrodeposition of molybdenum oxides on copper are presented, with the aim to complete the characteristics of deposited layers.

RESULTS AND DISCUSSION

Dissolution of molybdenum

According to ref. [13], the reactions taking place during the dissolution of the Mo powder in H_2O_2 (diluted aqueous solution; pH < 3) are:

$$2Mo_{(s)} + 10[H_2O_2] \rightarrow [Mo_2O_3(O_2)_4(H_2O)_2]^{2-} + 2[H_3O^+] + 5H_2O \quad (1)$$

$$2[Mo_2O_3(O_2)_4(H_2O)_2]^{2-} + 2[H_3O^+] \leftrightarrow [Mo_4O_9(O_2)_4]^{2-} + 4[H_2O_2] + 3H_2O \quad (2)$$

As illustrated by Eq. (1), H_2O_2 acts both as an oxidizing agent and as ligand. At pH < 3, in solutions with low peroxide amounts and containing higher molybdate concentration, the initially formed peroxomolybdate species can polymerize as it is shown in - Eq. (2).

Cyclic voltammetry

In order to establish the potential range, inside which stable thin oxide layers can be obtained by potentiostatic cycling, voltammograms have been registered in the working solutions.

In Figure 1 the voltammogram obtained by scanning the potential from +200 mV to –900 mV vs. Ag/AgCl, with a rate of 10 mVs^{-1}, is presented. The peak with the maximum value at around -100 mV vs. Ag/AgCl is due to the reduction of Mo(VI) ions adsorbed at the electrode surface as a complex species. In the same time, in the close vicinity of the electrode, the solution color becomes blue – proving the Mo(VI) reduction to Mo(V).

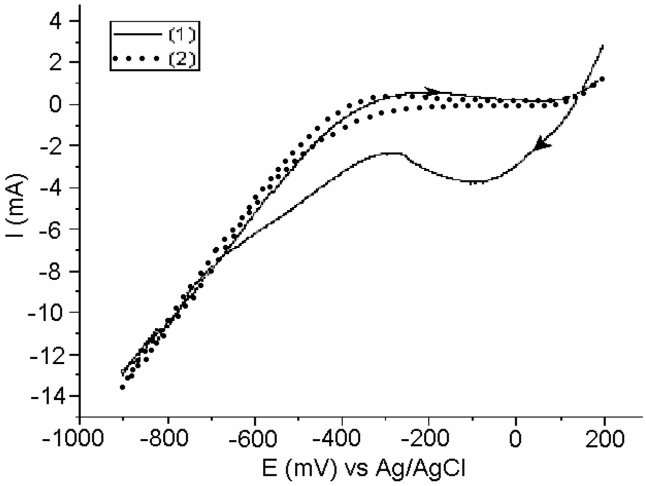

Figure 1. Cyclic voltammograms obtained for peroxo-polymolybdate solution on copper support (surface area 1 cm^2). Continuous line–cycle 1; dashed line–cycle 2.

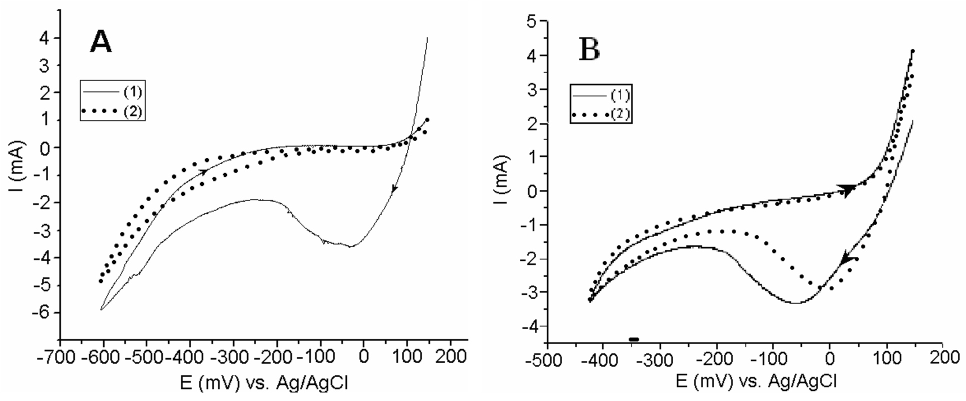

Figure 2. Cyclic voltammograms obtained using peroxo-polymolybdate as precursor solution. The potential was scanned between +0.15 and – 0.60 V *vs.* Ag/AgCl (A), respectively, between +0.15 and - 0.42 V *vs.* Ag/AgCl,KCl_{sat} (B).

At a potential value around -250 mV, a Mo(VI) diffusion limiting current appears. At potentials more negative than -350 mV, the cathodic current rises due to H_3O^+ ions discharge; this process occurs simultaneously with the metal ions reduction.

The potential, at which theoretically the hydrogen evolution is possible, at the actual value of pH, is – 0.33 V *vs.* Ag/AgCl,KCl_{sat}. At a potential value around -650 mV, the reduction curve slope increases, due to the formation of a molybdenum oxide layer on the cathode surface. In the second cycle (dashed line), the current observed is that corresponding to hydrogen evolution. This fact is due to the formation of a stable oxide layer that confers passivity to the cathode surface. The formation of this layer is probably influenced also by the fact that alkalinity of the medium in the close vicinity of the interface increases.

Taking into account that in the diffusion layer the molybdenum concentration diminishes and the HO^- ions concentration increases (due to H_3O^+ ions discharging), in the proximity of the charge transfer surface there may coexist the following species [13]:

$[Mo_2O_3(O_2)_4(H_2O)_2]^{2-}$ pH < 5 and (H_2O_2):Mo = 2 : 1 ; $C_{Mo} < 10$ mM

$[Mo_4O_9(O_2)_4]^{2-}$ pH < 5 and (H_2O_2):Mo = 2 : 1 ; $C_{Mo} < 10$ mM

$[Mo_7O_{23}(O_2)]^{6-}$, $[Mo_7O_{22}(O_2)_2]^{6-}$ pH ~ 4 at low $C_{H_2O_2}$

Figure 2 shows the cyclic voltammograms recorded using the same precursor solution, but different ranges of potential scanning, in order to determine the least negative potential for which the layer becomes stable in the working solution. It has been observed that the stability of the oxide layers deposited on copper by potentiostatic cycling depends on the minimum value of the potential attained during the scanning.

If the cathode potential is more negative than –0.55 V *vs.* Ag/AgCl,KCl_{sat}, one can obtain a stable oxide layer (Figure 1 and 2 A). For potentials more positive than the above value, at each cycle, one can observe the Mo(VI) reduction without the formation of a stable oxide layer (Figure 2B).

Because the working solution is acid and oxidant at the same time, the copper support may be dissolved with the formation of Cu^{2+} ions. Consequently, the anodic current observed at potentials more positive than +100 mV *vs.* Ag/AgCl,KCl_{sat} was attributed to copper oxidation. The copper ions as formed will be again reduced to metallic copper, which can be integrated in the deposited oxide layer.

The polarization curves obtained in solution 2 using copper as substrate were presented in a previous paper [14].

Optical microscopy and Differential Scanning Calorimetry (DSC) study

Micrographs for layers deposited by cyclic voltammetry (3 cycles) in the potential range of -600 ÷ -610 mV *vs.* SCE using solution 1, are presented in Figure 3. The potential scanning rate was 50µV/s. In all cases, the micrographs have been registered after a heat treatment of the samples.

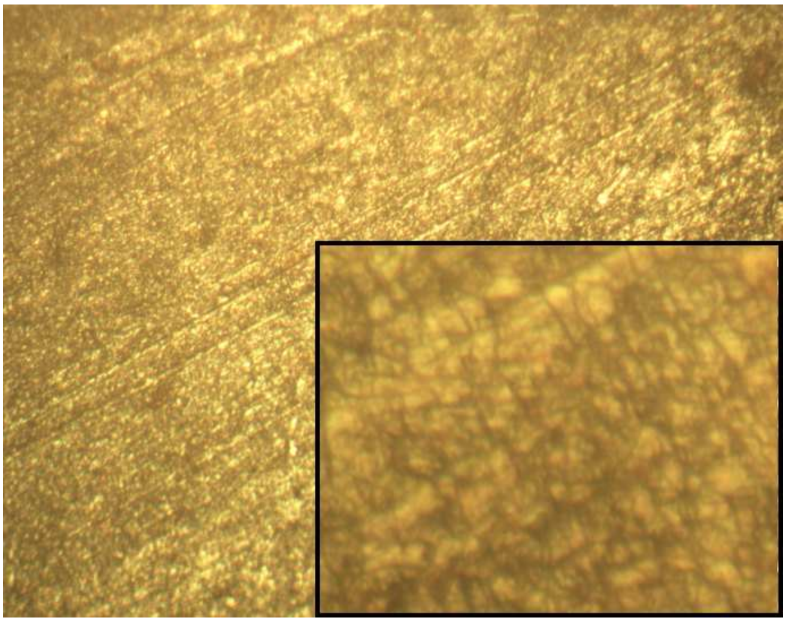

Figure 3. Micrographs of the layers deposited on copper support by cyclic voltammetry and heat-treated; potential range of -600 ÷ -610 mV *vs.* SCE.

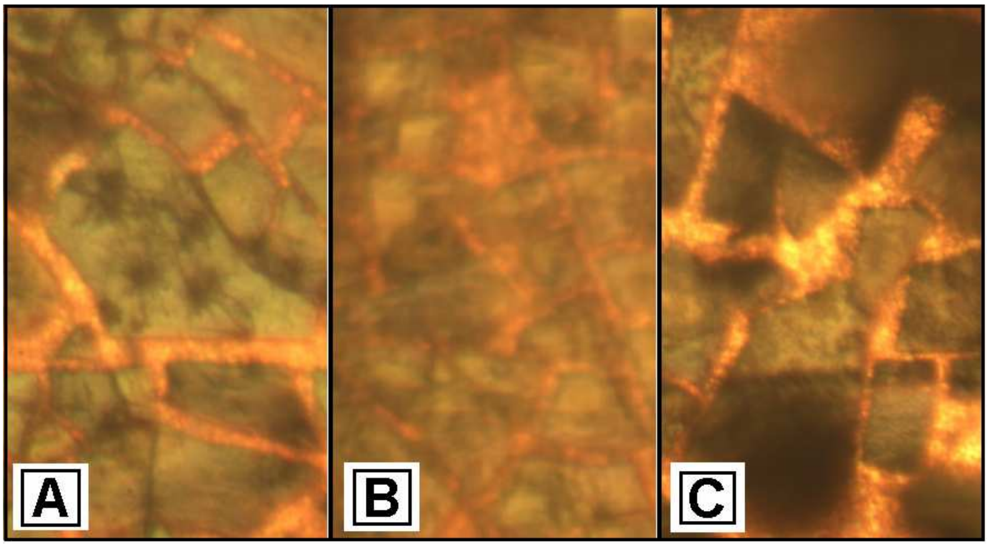

Figure 4. Micrographs of the layers deposited on polished (mirror-like) copper support by cyclic voltammetry and heat-treated; potential range -700 ÷ -710 mV (A) ; -800 ÷ -810 mV (B) ; -900 ÷ -910 mV (C) *vs.* SCE.

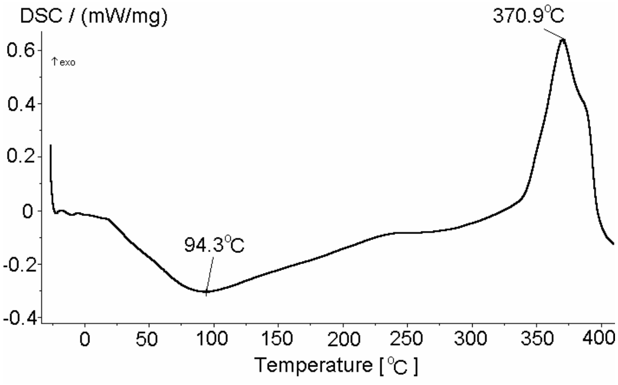

Figure 5. DSC curve of the powder (resulted from scraping away thin films deposited on copper support). Temperature range: -25 ÷ 420 °C.

It has been observed that the most adherent layers obtained after the heat treatment are those deposited at the most positive potentials. At potentials above -700 mV *vs.* SCE, the deposited layers show multiple cracks and a poor adherence (Figure 4 A-C).

In the DCS curve (Figure 5) one can observe the presence of two important peaks related to two opposite thermal effects: one endothermic, in the 20 – 240°C range, followed by a strong exothermal process at temperatures above 340°C with a maximum at about 370°C. The endothermic process is attributed to the gradual elimination by a physical route of water from the oxide layer up to about 100°C, followed by the dehydration of the molybdenum hydroxy-oxides up to 240°C. The exothermal process may be due to the crystallization of the amorphous molybdenum oxide. This supposition is sustained by the mass-loss obtained by TG – DTG analysis and also by the XRD spectra obtained on samples heat treated in inert environment at different temperatures [15].

Our experimental data are in good agreement with those reported in the literature [16], where amorphous films of molybdenum hydroxy-oxide with Mo(IV) oxidation state, containing significant amounts of water, were electrodeposited on TCO (Transparent Conducting Oxide) using ammonium molybdate as precursor.

CONCLUSIONS

Thin films of molybdenum hydroxy-oxides can be electrodeposited on metallic copper using both diluted peroxo-polymolybdate and ammonium molybdate aqueous solutions as precursors. When peroxo-polymolybdate solution is used, stable layers can be deposited only for potentials more negative than –550 mV *vs.* Ag/AgCl,KCl_{sat}. The optical microscopy investigation of the thin films, heat treated at 350ºC in inert atmosphere, reveal the formation of multiple cracks in the oxide layer, which can be due to the shrinkage induced by water elimination. The so deposited films are amorphous in both cases. The hydroxy-oxide deposited from molybdate solution contains water and crystallization occurs by heat treatment at temperatures above 340ºC.

EXPERIMENTAL SECTION

Reagents and solutions

The experimental procedures used for the electrodeposition of molybdenum oxides thin films on copper are described hereinafter.

In the first step, two solutions are prepared (denoted "solution 1" and "solution 2"), as follows:

Solution 1: 0.05 M Mo(VI) concentration has been obtained by dissolving metal powder (Mo 99% , Carlo Erba) in 10 mL 30% H_2O_2, by continuous cooling. The so obtained yellow solution was completed to 250 mL with bidistilled water.

After storing for 24 h at room temperature in the dark, the concentration of H_2O_2 has been determined by titration with $KMnO_4$ 0.02 M in a strong acid medium. Hydrogen peroxide was added until the optimum value 1:1 of H_2O_2 : Mo ratio [13]. The pH solution was 2.3.

Solution 2: an appropriate quantity of $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$, 98% (Reactivul) was dissolved in bidistilled water resulting a solution with concentration 0.05 M and pH 5.5.

Electrodes and electrolysis cell

An electrolysis cell with 250 mL capacity has been used. $Ag/AgCl,KCl_{sat}$ was used as a reference electrode. High purity graphite (20 x 80 x 10 mm) was used as a counter electrode.

As working electrode Cu (foil 99.98%, Sigma–Aldrich) with a surface of 1 cm^2 has been used. The smooth Cu electrode has been prepared by polishing with different abrasive papers and then with alumina 50 nm (Buehler).

Thin films characterisation

The most adherent thin films deposited on Cu have been subjected to heat treatment at atmospheric pressure at 350ºC for 1 h in high purity argon (99.999 %, Linde Gas – Romania). The temperature was raised with a rate of 15 ºC/min.

Thin films were electrodeposited by cyclic voltammetry within a very narrow potential domain (10 mV) and using the same peroxo-polymolybdate solution. In these cases the support was metallic copper (4 cm^2), polished mirror-like. SCE was used as reference electrode. The so obtained thin layers have been heat treated under the same conditions and then studied by optical microscopy. From solution 2, oxide layers were electrodeposited on copper support for 2800 s, at a potential of –650 mV *vs.* Ag/AgCl,KCl$_{sat}$. After deposition, these films were washed with distilled water and scraped away from the copper support.

Differential Scanning Calorimetry (DSC) analysis (Netzsch DSC 204) was performed on samples prepared by scraping away the thin films from the copper support. Sample mass was 5.2 mg and nitrogen was used as inert atmosphere. The temperature increasing rate was 5 K min^{-1}.

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