

THE EFFECT OF MAGNETIC FIELDS ON CUPROUS OXIDE ELECTRODEPOSITION

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Introduction. Cuprous oxide thin films are non-toxic and suitable for numerous applications such as photovoltaic conversion [1]. Deposition of cuprous oxide by electrochemical technique from aqueous solutions has attracted much research interest because it is an inexpensive and convenient method [2, 3]. A magnetic field applied during metal growth can modify the growth process and the morphology [4]. We propose in this study to discuss the influence of a magnetic field on the electrochemical synthesis of the metal oxide Cu_2O .

1. Experimental. The electrochemical experiments were carried out in a conventional three-electrode cell. The reference electrode was a saturated mercury sulfate electrode (SSE), the counter-electrode was made of a platinum wire. The working electrode was a stainless steel substrate with an area of 1 cm^2 , polished before each experiment with Struers papers, down to 4000. The 100 cm^3 cell was plunged into a uniform horizontal magnetic field (up to 1 T) delivered by an electromagnet (Drusch EAM 20G), B being parallel to the upwards electrode surface. The redox method was used to produce copper (I) oxide. The electrolytic solution was a Cu(II) lactate solution (0.45 M Cu(II), 3.25 M lactate prepared by dissolving copper (II) sulphate pentahydrate in deionized water with stirring, then lactic acid was added, and finally the bath pH was adjusted to 8-9 by addition of NaOH pellets. The solution was stirred 8 hours, and then the pH was adjusted to its final value 9.5 with further addition of NaOH, a constant (70°C) temperature was maintained. The potential of the working electrode was controlled by means of a potentiostat-galvanostat (PGZ 100, Radiometer Analytical), interfaced with a PC. X-ray diffraction (XRD) experiments were carried out with a Bruker D8 diffractometer using the Cu $K\alpha$ radiation. The surface morphological studies were carried out using a Jeol JSM-6460 LA scanning electron microscope (SEM) operating at 15 kV.

2. Results. Linear sweep voltammograms of Cu_2O deposition on stainless steel from lactate solution at pH 9.5 are shown in Fig. 1 for various magnetic

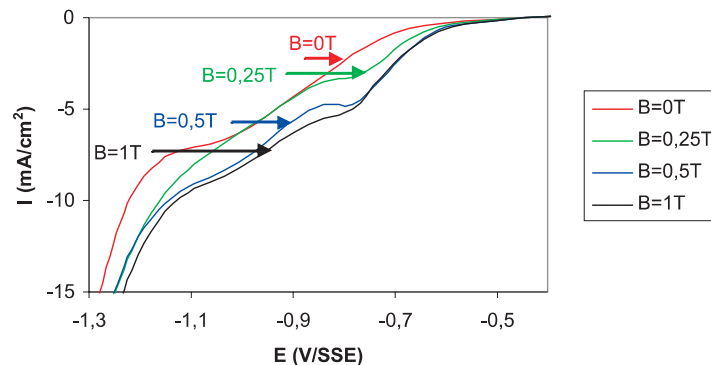


Fig. 1. Current density-potential curves for Cu(II) lactate reduction for different magnetic fields; scanning rate = 700 mV/s .

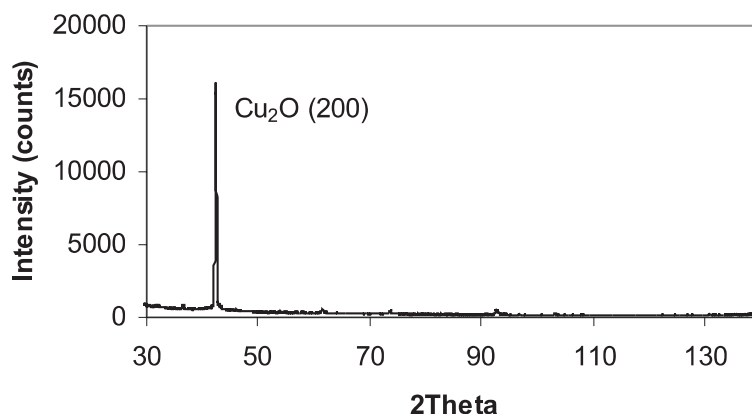


Fig. 2. X-ray diffraction pattern of cuprous oxide electrodeposited at a cathodic potential of -0.8 V/SSE during 1200s under a magnetic field value of 1T.

fields. The potential sweep started at an open circuit potential and was scanned cathodically at a 700 mV/s scan rate. The effect of B is intricate because several phenomena as diffusion, convection and germination are mixed, notwithstanding transient phenomena due to scanning potential. In all cases, a change of bend is observed around potential values between -0.8 V/SSE, and -0.9 V/SSE, corresponding to the deposition of Cu_2O [5].

To be sure to deposit only Cu_2O and not a mixture of $\text{Cu} + \text{Cu}_2\text{O}$, we propose to study cuprous oxide electrodeposition at a fixed potential of -0.8 V/SSE. As can be seen on XRD pattern in Fig. 2, only Cu_2O peaks are identified [in accordance with the JCPDS (05-0667) data] for all magnetic fields at a potential of -0.8 V/SSE. We obtain the same (100) preferential orientation as Switzer *et al.* [6]. So the chronoamperometry was carried out at a potential low enough to ensure that only Cu(I) was obtained on the working electrode. Effectively, as reported by Mahalingam *et al.* , a first peak corresponding to copper reduction at -0.6 V/SSE may correspond to the reaction:



and as the potential is increased further, a second cathodic peak at -0.76 V/SSE may be attributed to the formation of Cu_2O on the substrate according to the reaction:

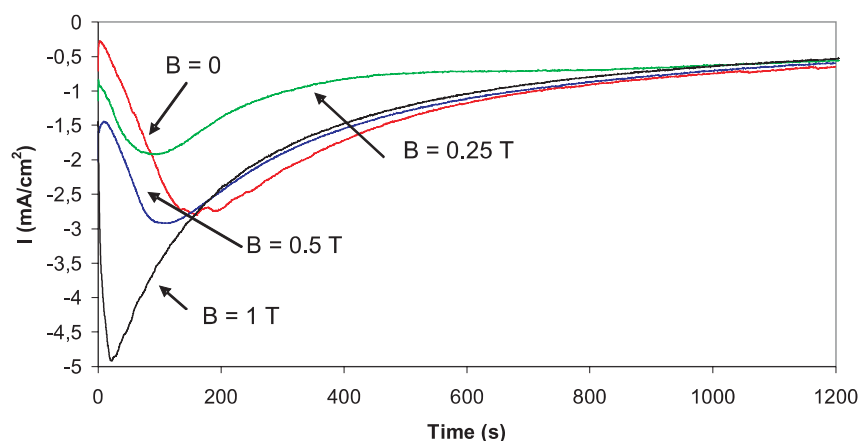
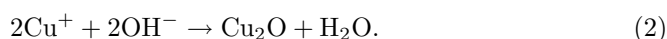


Fig. 3. Cathodic current density during copper oxide electrodeposition on a stainless steel substrate for different magnetic fields.

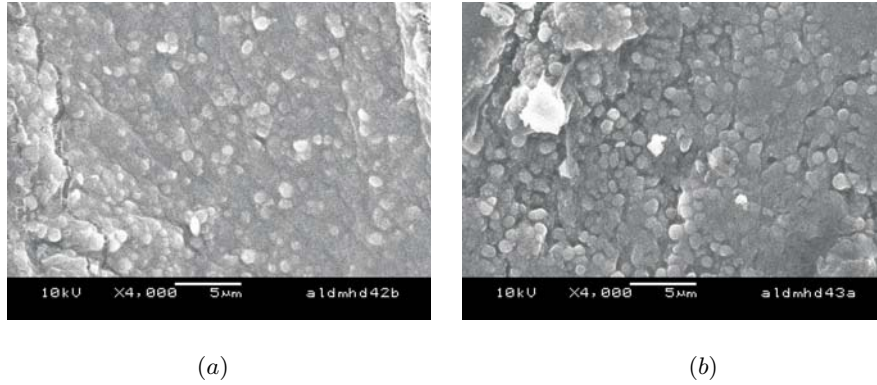


Fig. 4. SEM micrographs of Cu_2O electrodeposited at -0.8 V/SSE during 1200 s under (a) $B = 0$ and (b) $B = 0.5$ T.

Table 1. Value of the exponent n (Eq. 3) according to the mechanism of the electrodeposition [7].

$n = \frac{\partial \ln(\mathbf{I})}{\partial \ln(\mathbf{t})}$	Nucleation type	Growth type	Regime control
1	gradual	1D	kinetic
1	instantaneous	2D	kinetic
2	gradual	2D	kinetic
2	instantaneous	3D	kinetic
3	gradual	3D	kinetic
1	gradual	2D	diffusion
1/2	instantaneous	3D	diffusion
3/2	gradual	3D	diffusion

For all magnetic fields we obtain the same (100) preferential orientation. No change in orientation is noted.

Chronamperometric experiments were carried out in order to investigate the copper oxide nucleation/growth process. Typical current-time transients resulting from such experiments are shown in Fig. 3. These transients exhibit the classic shape of a nucleation process. After the rapid decay of the double-layer charging current, the current increases due to the nucleation/growth of copper oxide nuclei. The rising current reaches quickly a maximum (i_m) as the discrete diffusion zones for each of the growing crystallites begin to overlap at a time t_m .

After the maximum current has been reached, the current decays as the diffusion layer, to reach a stationary value. By superimposition of the magnetic field (0.25 to 1 T), t_m decreases, while i_m reaches a maximum for $B = 1$ T. It seems that the magnetic field presence modifies the deposition kinetics. For longer times, we do not notice modifications of the stationary current with the magnetic field. Polished and etched microstructure of Cu_2O obtained for $B = 0$ and $B = 0.5$ T are presented in Fig. 4. The average grain size does not change with the B value.

In a potentiostatic regime and for discrete germs without coalescence, a set of current-time relations for a nucleation independent from the substrate surface state and a growth of germs controlled either by the mass transport, or by the

Table 2. n values (Eq. 3) for various magnetic field.

$B(\text{T})$	0	0.25	0.5	1
n	0.83	0.80	0.55	0.27

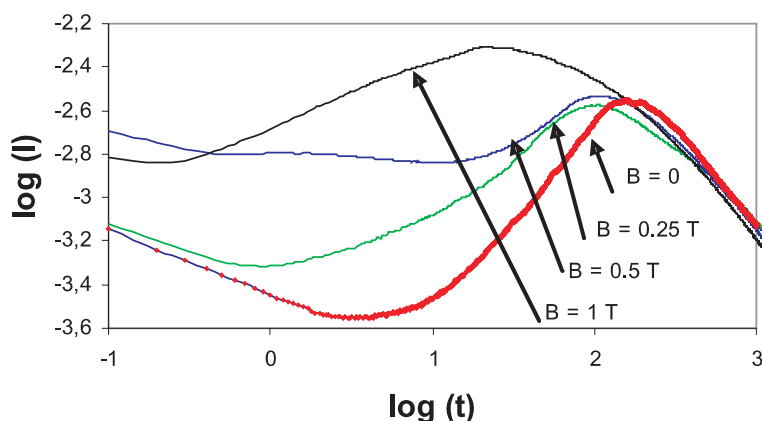


Fig. 5. $\ln I$ vs. $\ln t$ for various magnetic fields.

electronic transfer kinetics, has been proposed by Thirsk and Harrison [7]. The general expression of the current that depends only on the reaction mechanism takes then the following shape:

$$I = kt^n, \quad (3)$$

where k is a constant that depends on the deposited material characteristics and on the reduction mechanism, n depends on the nucleation/growth type, and on the electrochemical regime control as presented in Table 1. The plots of $\ln(I)$ vs $\ln(t)$ (Fig. 5) display linear parts corresponding to the n value of Eq. 3. The obtained values are reported in Table 2. They vary from a value close to $3/4$ for $B = 0$ to $1/4$ for $B = 1$ T. These n values do not correspond to a pure regime but to a mixed regime that is certainly controlled by diffusion. The value of $1/4$ determined for $B = 1$ T is quite unusual. Another mechanism of electrocrystallization nucleation and growth phenomenon can thus be expected. Nevertheless, it is obvious that the magnetic field exerts an influence on the kinetic electrodeposition of oxide.

3. Conclusion. The initial stages in the electrochemical oxide deposition have been modified by the presence of magnetic fields. In our experiment, electrodeposited material is less conductive than the substrate, so the growth mode previously presented [7] could not be used to explain such a mechanism. A further study on nucleation and growth is thus necessary to undertake oxide deposition under magnetic fields.

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