

KINETICS OF THE ELECTROREDUCTION OF Ag_2CrO_4 SALT FILMS ELECTRODEPOSITED ON SILVER

Brunetti, V.; Villullas[#], H.M.; López Tejelo^{*}, M.

INFIQC - Departamento de Fisicoquímica, Facultad de Ciencias Químicas, Universidad Nacional de Córdoba, Pabellón Argentina, Ala derecha, 2do. Piso, Ciudad Universitaria. 5000 Córdoba, Argentina.

Fax: +54 351 4334188. e-mail: mlopez@fisquim.fcq.unc.edu.ar

[#] Present address: Laboratorio Interdisciplinar de Eletroquímica e Cerâmica. Departamento de Química, Universidade Federal de Sao Carlos, CMDMC-LIEC, CP 676, CEP 13565-905, Sao Carlos-SP, Brazil.

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Dedicated to Professor Dr. A.J. Arvia on occasion of his 75th Anniversary

Abstract

The electroreduction of silver chromate films prepared by anodic polarization of polycrystalline silver in solutions containing chromate was studied. The potentiodynamic current-potential behavior as well as the potentiostatic current-time dependence is adequately described by using the layer-pore resistance model. The electroreduction of the Ag_2CrO_4 films occurs mainly under ohmic control. The properties of the Ag_2CrO_4 films are dependent on the formation conditions. A current contribution of reversible kinetic characteristics attributed to the reduction of a gel-like structure is also obtained.

Resumen

Se estudia la electroreducción de películas de cromato de plata preparadas por polarización anódica de plata policristalina en soluciones de cromato. El comportamiento corriente-potencial potenciodinámico y la dependencia corriente-tiempo potencioestática se interpretan en términos del modelo de resistencia de una capa porosa. La electroreducción de las películas de Ag_2CrO_4 ocurre principalmente bajo control óhmico. Las propiedades de las películas dependen de las condiciones de formación, obteniéndose una contribución de corriente de características cinéticas reversibles que se atribuye a la reducción de una estructura tipo "gel".

Introduction

Anodic salt films formation and their electroreduction are of importance in relation to second-class reference electrodes, applications to galvanic cells, seawater batteries, corrosion and passivation in different media. The kinetics of growth of silver anodic films is determined by the chemical, electrical and structural properties of the new phase [1-6].

The dissolution and passivation of silver electrodes in solutions containing chromate have been studied by cyclic voltammetry and potential steps [7-9]. The active to passive transition involves the active dissolution of silver followed by precipitation of a poorly conducting Ag_2CrO_4 film. A three-dimensional progressive nucleation process with diffusion-controlled growth initially controls the rate of formation of the passivating layer. To produce the precipitation of the salt film, a critical concentration of Ag^+ in the vicinity of the electrode surface has to be reached, resulting in an induction time, which depends on potential. At high coverage, the current is lower than that expected from the model. The deviations are associated to the resistance of the electrolyte in the pores of the passivating layers that begins to contribute to the rate control [8]. The passivating layer of Ag_2CrO_4 grows and spread across the surface until only small pores in the layer remain and the overall rate is controlled by the resistance of the electrolyte in the pores and later by diffusion in the pores [9].

The electroreduction of the silver chromate layer proceeds mainly under ohmic resistance control but a direct interpretation of the fit parameters with the Layer Pore Resistance Model (LPRM) [10-13] is not straightforward. Further work on the model is necessary in order to take into account that the passive layer structure seems to depend upon the formation conditions, probably involving variations in the hydration of the salt layer and/or the formation of a duplex layer [8,9].

In this work, the kinetic characteristics of the electroreduction of Ag_2CrO_4 films electroformed on polycrystalline silver in sodium chromate aqueous solutions are studied. The data obtained by potential sweep and potential steps are compared with the theoretical curves for the layer-pore resistance model to demonstrate that the cathodic process is mainly controlled by ohmic resistance.

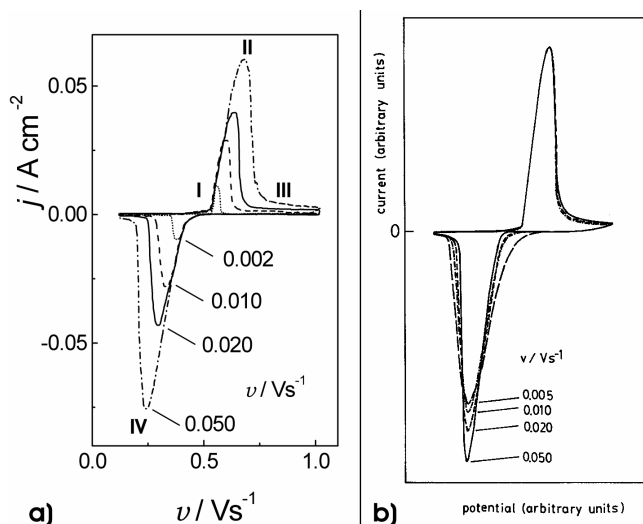


Figure 1: a) Potentiodynamic j/E profiles of silver at different potential sweep rates in $0.1 \text{ M Na}_2\text{CrO}_4 + 0.1 \text{ M borax (pH 9.3)}$ solutions. b) Normalized j/E profiles of the data of Fig. 1a.

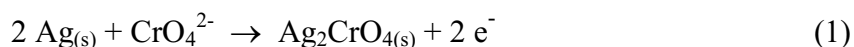
Experimental

The working electrode consisted of a polycrystalline silver rod (Koch-Light, 99.999% purity) of 2 mm diameter mounted in a Teflon holder, which exposes a circular area of 0.031 cm^2 . Before the experiments the electrode surface was abraded with emery paper and then polished mechanically with alumina (1, 0.3 and $0.05 \mu\text{m}$) on a polishing cloth (Microcloth, Buehler). Then the electrode was cleaned repeatedly with purified water, immersed in the electrolyte and cathodized at -0.135 V for 5 min before the experiments. The electrochemical measurements were performed in a three-compartment electrolysis cell using a gold sheet as counter electrode and a $\text{Hg}/\text{Hg}_2\text{SO}_4/\text{Na}_2\text{SO}_4$ (1M) as reference electrode. Nevertheless, all potentials are referred to the standard hydrogen electrode (SHE). Solutions of Na_2CrO_4 of different concentration were prepared from AR chemicals and purified water (Milli Ro-Milli Q system). 0.1 M Borax was added to maintain pH ~ 9.3 in order to ensure that the change in CrO_4^{2-} concentration by formation of $\text{Cr}_2\text{O}_7^{2-}$ can be neglected and to avoid interference by the silver oxide formation [8]. Measurements were performed at 25°C under nitrogen gas saturation.

Electrochemical measurements were done by applying single or repetitive triangular potential sweeps between preset lower ($E_{s,c}$) and upper ($E_{s,a}$) switching potentials at different scan rates (v). Moreover, the *triangularly modulated triangular potential sweep (TMTPS) technique* was also used. This method is a powerful tool for studying reaction intermediates produced during the electrochemical reactions [14, 15] and consists essentially of a triangular potential sweep at a low scan rate (base signal, v_b) and a superimposed triangular potential modulation at a faster scan rate (modulation signal, v_m). The amplitude of the modulation signal (ΔE_m) is smaller than the amplitude of the base signal. Potentiostatic current transients were also employed. Potential steps were applied from an initial potential value $E_{in} = 0.115 \text{ V}$ to a formation potential E_f where anodic film formation takes place ($0.575 \text{ V} < E_f < 0.915 \text{ V}$) and then to a potential value to produce the layer electroreduction ($0.275 \text{ V} < E_r < 0.435 \text{ V}$).

Results and discussion

The electroformation and electroreduction of silver chromate films in alkaline solutions was studied by applying repetitive triangular potential sweeps. Figure 1a shows the general potentiodynamic j/E behavior of silver electrodes in 0.1 M Na_2CrO_4 solutions at different sweep rates. The positive scan shows a potential region from 0.3 V up to *ca.* 0.6 V where the current density increases slightly (region I) followed by a sharp anodic current peak (II) which corresponds to the formation of a poorly conducting silver chromate film according to the overall anodic reaction:



After the sudden drop of current produced by the formation of the silver chromate layer, the current decreases smoothly (region III). The negative sweep shows a main cathodic current peak (IV) attributed to the electroreduction of the Ag_2CrO_4 anodic film.

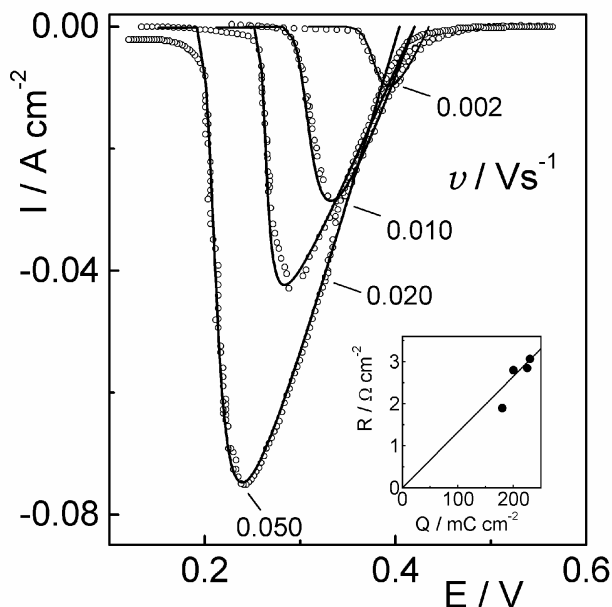


Figure 2: Potentiodynamic j/E curves for the electroreduction of Ag_2CrO_4 films at different sweep rates. (—) Calculated curves with the LPRM. Inset: Cathodic charge (Q) and resistance (R) values corresponding to the simulations. $0.1 \text{ M Na}_2\text{CrO}_4 + 0.1 \text{ M borax (pH 9.3)}$.

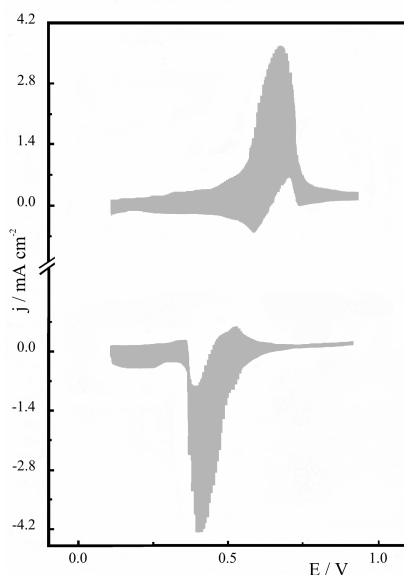


Figure 3: j/E response of silver electrodes obtained by applying TMTPS. $v_b = 0.010 \text{ V s}^{-1}$; $v_m = 0.500 \text{ V s}^{-1}$. Upper curve: positive scan; lower curve: negative scan. $0.1 \text{ M Na}_2\text{CrO}_4 + 0.1 \text{ M borax (pH 9.3)}$.

In the potential region prior to the anodic and cathodic peaks, the current varies linearly with potential and all curves lay along the same line. Furthermore, peak current density (j_p) and peak potential (E_p) change linearly with $v^{1/2}$ for both the anodic and the

cathodic processes. As previously described [9], this type of behavior is characteristic of the growth of a layer under ohmic resistance control. The overall electroformation of the passivating salt layer occurs through a sequence of different processes starting with the active silver dissolution (region I). This produces a continuous increase in the concentration of silver ions near the electrode surface until a critical value is reached and the precipitation of the salt layer that passivate the electrode takes place. The growth of the salt film takes place under ohmic resistance control until the surface is almost completely covered. According to the LPRM, the ohmic behavior is produced by the spread of the reaction product on the electrode surface, which acts as a mechanical barrier to the current flow until only small pores in the layer remain [11].

For an insulating film, the resistance of the overall layer-pore system is determined by the coverage degree of the surface (θ), the specific conductivity of the electrolyte (κ) and the thickness of the layer (d_0) and is given by [11]:

$$R(\theta) = d_0 \theta^{1/2} / \kappa A (1 - \theta) \quad (2)$$

where A is the geometric area of the electrode.

On the other hand, the j/E curves have the same general shape at the different sweep rates (Figure 1a). This behavior is also predicted by the LPRM. Figure 1b shows the normalized j/E curves obtained by dividing the current and potential scales for the experiments in Figure 1a by the square root of sweep rate. It can be seen that the same shape of the j/E profiles is obtained for the anodic silver chromate film in region II while slight differences in the normalized scale are seen within region III. This indicates that the anodic growth of the passivating film takes place under ohmic control, while the differences found in region III have been attributed to the further growth of the passive film controlled by the diffusion of chromate ions within the pores of the Ag_2CrO_4 layer [9]. On the contrary, the normalized j/E profiles for the electroreduction process exhibits a different shape and a variation of the resistance value for the different values of v . Nevertheless, the electroreduction curves can also be simulated adequately using the LPRM (Figure 2), indicating that the electroreduction of the Ag_2CrO_4 film also takes place under ohmic control. The change of the value of resistance for the different sweep rates is explained taken into consideration that the anodic film, after formation in region II, continues its growth in region III through a process controlled by the diffusion of chromate ions into the pores [9]. The increase of the overall charge (increase of thickness) is larger at lower sweep rates, producing an increase of R (equation. 2) as v decreases (inset ion Figure 2). Also, the resistance values for the electroreduction process are higher than the corresponding value found for the anodic process at every sweep rate (ca. $1.89 \Omega \text{ cm}^2$ for the experiments in Figures 1 and 2) that includes only the charge involved in the process in the region II of potential.

Furthermore, the different rate-controlling processes in regions II and III could produce a duplex structure of the film. Impedance spectra obtained for films formed potentiodynamically at different sweep rates exhibit variations attributed to differences in the structure of the porous layers. Films formed at lower scan rates exhibit larger

resistance values attributed to the formation of low porosity films that reach greater coverage values [16].

In order to obtain the kinetic response of the different phenomena as well as to detect reaction intermediates, the electroreduction of the silver chromate films were also studied employing the TMTPS technique. Figure 3 shows the potentiodynamic j/E response obtained by applying a slow scan ($v_b = 0.010 \text{ V s}^{-1}$) modulated with a superimposed faster triangular scan ($v_m = 0.500 \text{ v s}^{-1}$). During the positive scan, a potential region of low constant anodic and cathodic current associated with double layer charging is obtained. At potentials more positive than *ca.* 0.3 V, the anodic as well as the cathodic current increase and both are similar in value indicating that the corresponding faradaic process is highly reversible. The kinetic characteristics agree with previous results obtained by potential steps and ring-disk experiments [8] indicating that in this potential region the active silver dissolution takes place. On the contrary, the j/E response obtained at potentials more positive than *ca.* 0.6 V shows only an anodic current contribution and exhibits an irreversible kinetic behavior associated with the film growth under ohmic control [9].

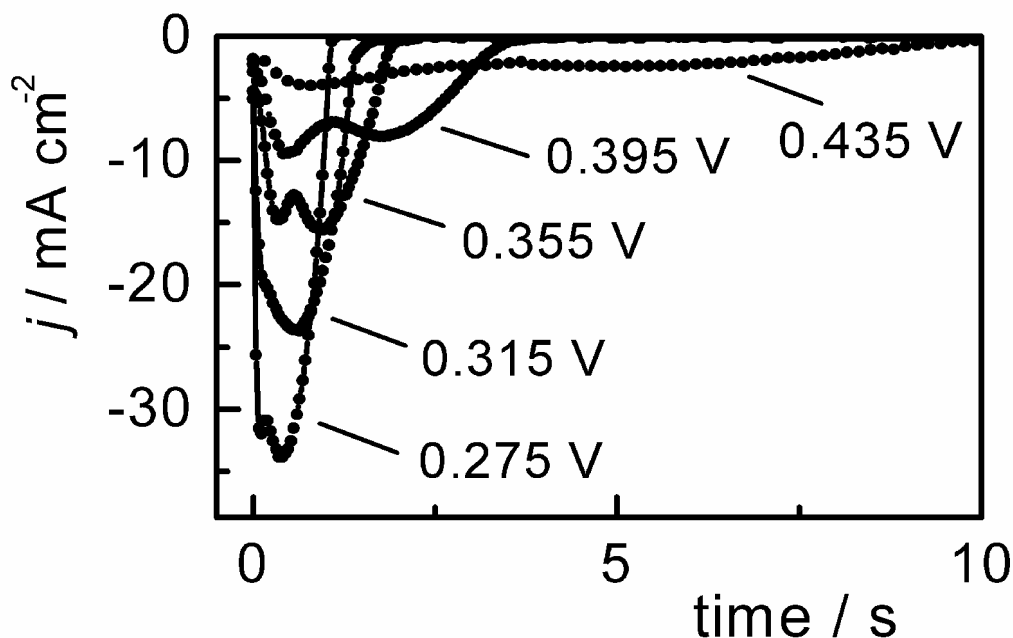


Figure 4: Potentiostatic current transients at different potentials for electroreduction of Ag_2CrO_4 films grown on polished silver electrodes at $E_f = 0.575 \text{ V}$ ($t_f = 20 \text{ s}$). $0.1 \text{ M Na}_2\text{CrO}_4 + 0.1 \text{ M borax}$ (pH 9.3).

During the negative scan the current is very low up to *ca.* 0.6 V, where an increase of the anodic and cathodic current showing a reversible kinetic behavior is obtained. At potentials lower than *ca.* 0.5 V the j/E profiles show a cathodic contribution of irreversible characteristics, which is associated with the film electroreduction under ohmic control. The reversible response obtained in the 0.6 V to 0.5 V can be associated

with the presence of silver (I) species in a gel-like silver chromate matrix. Similar results have been reported for chemically precipitated silver oxide/hydroxide layers on vitreous carbon [17].

The electroreduction of the silver chromate films was also studied by applying potentiostatic methods according to the procedure described in the experimental section. The j/t response is noticeably dependent on the pre-treatment of the silver surface employed before growing the anodic films. The current transients obtained at different potentials for the electroreduction of Ag_2CrO_4 grown on mechanically polished silver surfaces are shown in Figure 4. The j/t curves exhibit two current maxima strongly dependent on the applied reduction potential, indicating that the film electroreduction presents two contributions. For lower reduction potentials the current values are higher and the maxima appear at shorter times. Also, the overall cathodic charge is similar to the anodic charge and is independent of the applied potential.

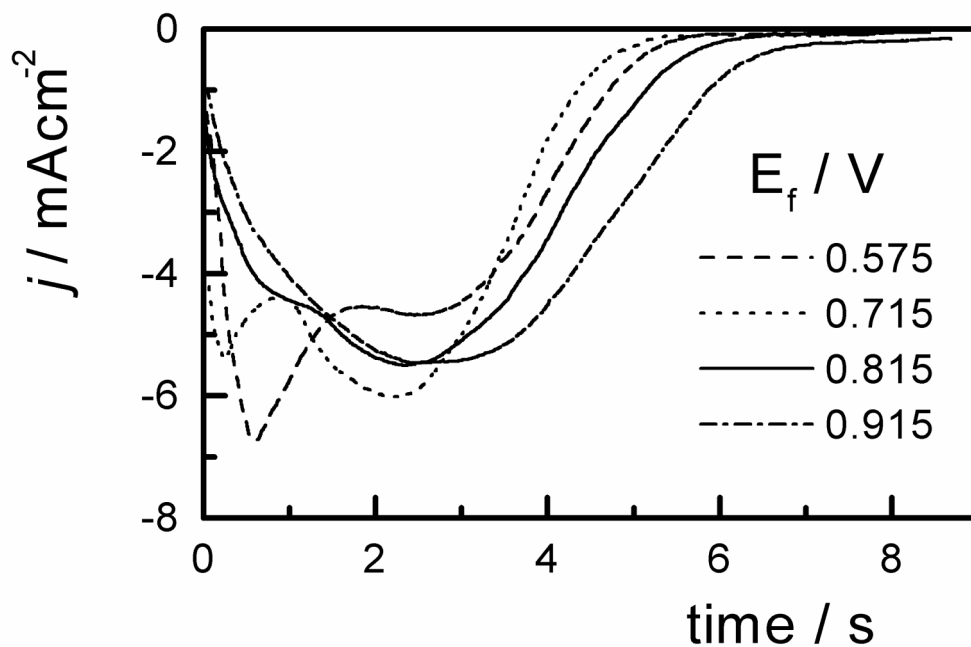


Figure 5: Potentiostatic current transients at $E_r = 0.415$ V for electroreduction of Ag_2CrO_4 films grown on polished silver electrodes at different E_f values ($t_f = 20$ s). 0.1 M $\text{Na}_2\text{CrO}_4 + 0.1$ M borax (pH 9.3).

Taking into account the porous structure of the anodic Ag_2CrO_4 film, the possibility of the contribution of the reduction of Ag^+ soluble species in the porous layer to the overall electroreduction process was considered. The estimation of the reduction charge corresponding to the process $\text{Ag}^+_{(\text{aq})} + \text{e}^- \rightarrow \text{Ag}_{(\text{s})}$ can be made on the basis of the volume of electrolyte in the pores and its concentration. The volume of electrolyte for a film of thickness d_0 is $d_0 A(1 - \theta)$. Taking conservative values of $d_0 \sim 100$ nm and $\theta \sim 0.9$ and considering a silver ion concentration ten times higher than the silver chromate saturation concentration, a charge value of $3 \mu\text{C cm}^{-2}$ is obtained. On the other hand, the

total reduction charge obtained from the j/t transients is about 1 mC cm^{-2} , indicating that the contribution of the Ag^+ soluble species in the porous layer to the overall cathodic current is negligible. In consequence, the two cathodic current contributions obtained in the potentiostatic transients could be related to different kinetic effects and/or distinct properties in different regions of the passive film. In the last case, the two current peaks would correspond to the electroreduction of a two-layer film composed by an inner layer and an outer layer of different properties.

Figure 5 shows the electroreduction transients obtained at $E_r = 0.415 \text{ V}$ for anodic Ag_2CrO_4 films formed at different potentials ($0.575 \text{ V} < E_f < 0.915 \text{ V}$). Depending on the potential of film formation, the j/t response on polished silver surfaces exhibits either one or two cathodic reduction maxima. For films electroformed at high potentials, the current transients show only the contribution obtained at high time values (*ca.* 2.5 s in the experiments in Fig. 5). On the contrary, for films formed at low potentials an increasing current contribution obtained at short time values, is clearly seen. This current contribution that is associated with the electroreduction of the inner layer with gel-like structure, decreases with the increase of the formation potential of the anodic film.

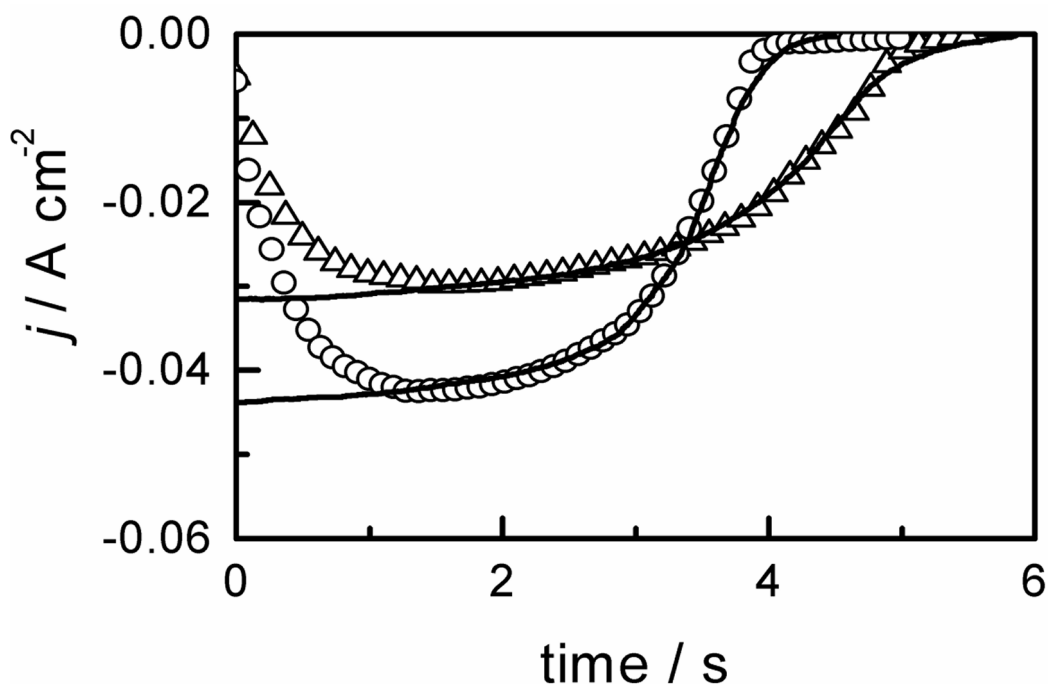


Figure 6: Potentiostatic current transients at different potentials for electroreduction of Ag_2CrO_4 films on cycled silver electrodes. $E_f = 0.575 \text{ V}$ ($t_f = 20 \text{ s}$). (Δ) $E_r = 0.305 \text{ V}$; (o) $E_r = 0.255 \text{ V}$; (—) calculated with the LPRM. $0.1 \text{ M Na}_2\text{CrO}_4 + 0.1 \text{ M borax}$ (pH 9.3).

On the other hand, the electroreduction transients obtained for Ag_2CrO_4 films electroformed on silver substrates under successive oxidation/reduction cycles show only one current contribution. Figure 6 shows the electroreduction j/t profiles at two different values of E_r . Initially, a rapid increase of current up to reach a potential region where current is nearly constant, is observed. The current in this region is dependent on

potential and is followed by a more or less abrupt current decrease due to the complete film electroreduction. For low values of E_r , the current values are higher and the current drop occurs at shorter time values. Figure 6 also shows the potentiostatic j/t response calculated from the model for a process controlled by the resistance of electrolyte in the pores [12,13]. The very good agreement of the experimental and calculated j/t curves indicates that the process takes place under ohmic control. In conclusion, the results indicate that films obtained by cycling are mainly constituted by the porous structure and the contribution of the inner gel-like part is negligible.

Conclusions

The analysis of the potentiodynamic and potentiostatic results as a whole indicates that the electroreduction of Ag_2CrO_4 films occurs mainly under ohmic control. The films are porous with structure and/or properties that are dependent on the formation conditions. In addition to the kinetic control of the film electroreduction by the resistance of the electrolyte in the pores, a second contribution of reversible kinetic characteristics attributed to the reduction of a layer with gel-like structure is obtained.

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