Kinetics of electrocrystallization of PbO₂ on glassy carbon electrodes. Influence of the electrode rotation.

J. González-García^a, F. Gallud^a, J. Iniesta^a, V. Montiel^{a*}, A. Aldaz^a and A. Lasia^b.

^aGrupo de Electroquímica Aplicada. Departamento de Química Física.

Universidad de Alicante. Ap. Correos 99. 03080 Alicante. Spain.

^bDépartement de Chimie, Université de Sherbrooke, Sherbrooke, P. Q., J1K 2R1, Canada

ABSTRACT

Electrodeposition of PbO₂ on glassy carbon electrodes was studied in the stationary conditions and on the rotating disk electrode using chronoamperometric technique. The kinetics of electrodeposition was significantly retarded by the hydrodynamic mass transport flow. This observation is in agreement with the mechanism involving formation of soluble Pb(III) or Pb(IV) species, which may, subsequently, form PbO₂. The kinetics of the nucleation and crystal growth was determined by the analysis of the initial part of the transients and of the whole curves. This process proceeds through the 3 dimensional progressive nucleation and crystal growth mechanism with an induction time. The growth rate constant is strongly affected by convection while the nucleation process and the induction time are much less influenced.

* Corresponding author. Tel.: +34965903628; fax:+34965903537;e-mail:vicente.montiel@ua.es

Key words: lead dioxide, glassy carbon electrode, nucleation and crystal growth, rotating disk electrode, electrodeposition.

INTRODUCTION

In our recent studies preparation and characterization of various anodic materials such as C/PbO₂ [1], Ti/PbO₂ [2,3], and Ti/Pt [4] was carried out. These materials may be used in different electrochemical applications such as the treatment of wastewater [5], purification of high value-added organic products via electrodialysis [6] and organic electrosynthesis [7]. In the preparation of films onto a substrate by means of electrodeposition, it is important to understand the process of nucleation and growth of the deposit and its relationship with the properties of coating.

Cathodic stripping voltammetry (CSV) of metal ions is the least commonly used of the three main electrochemical stripping techniques, which is surprising considering its potential benefits: sensitivity, selectivity, and attractive approach to the analytical determination of trace metals that eliminates intermetallic interferences, which sometimes plague anodic stripping voltammetry (ASV). This technique involves first electrooxidation (electrodeposition) of the corresponding ions from aqueous solution followed by the stripping step, which provides the analytical information [8]. Both processes can be carried out in quiescent solution, however, for many applications it is important that the electrode is located within a flow system to permit continuous monitoring and to enhance the speed of the analysis. Nowadays, different approaches to increase the mass transport to the surface electrode are being investigated: ultrasonic field [9], wall-jet [10] and channel electrode [11] geometries. Accordingly, the question arises as to whether the introduction of convection as a dominating contribution to the transport leads to significant changes in the process.

The electrodeposition of lead dioxide from aqueous solutions of Pb(II) has been extensively studied and its thermodynamic and kinetic behavior was analyzed. This process was first studied by Fleischmann et al. [12-15] who proposed a mechanism involving intermediate adsorbed species. However, other authors [16, 17] detected soluble species and modified mechanisms are nowadays being proposed, such as these proposed by Velichenko et al. [18-20]

or by Chang and Johnson, [21, 22] involving $\text{Pb}(\text{OH})_2^{2+}$ or PbO^{2+} intermediates.

The electrodeposition of lead dioxide on electrodes of glassy carbon is being studied in our laboratory, both in static and sonicated solutions [23]. In the latter, a strong influence of the effects of the ultrasound field has been found in the electrodeposition mechanism. In literature, many effects of the ultrasound field on the electrode processes have been described [24, 25]. One of the most relevant is increased mass transport towards the electrode [26, 27].

Various studies found in the literature, focused on the study of the electrocrystallization of lead dioxide in convection-diffusion conditions, employing almost exclusively disk or disk-ring electrodes [16-22, 28-31], but no quantitative determination of the kinetics of the process (N_o , A , k) was made in these conditions.

In our recent paper [1] we have studied PbO_2 deposition on glassy carbon (Le Carbone Lorraine) without forced mass transport and found a mechanism of partial inhibition of the progressive three dimensional nucleation and growth.

This paper studies the nucleation mechanism of lead dioxide both with and without mechanical agitation (rotating electrode) on a glassy carbon (Radiometer) electrode in order to quantitatively analyze the effects of pure convection-diffusion in the nucleation process and in the growth of the lead dioxide. Therefore, the classical models [28-30] will be applied, both at initial transient (initial 20% of current at steady state) as it is found in the literature in static conditions, and at prolonged transients, analyzing the complete curve. The validity of the model is verified and kinetic studies are carried out both in the presence of and in the absence of convection-diffusion in the process.

EXPERIMENTAL SECTION

A standard two-compartment electrochemical cell with a volume of 50 mL was used for the experiments. The chemicals were Analar quality and were used as received. The cell was filled with an aqueous solution of 0.1 M lead(II) nitrate + 1M nitric acid, prepared using ultrapure water (Millipore Milli-Q system). A platinum wire acted as the counter electrode. A SCE served as the reference electrode.

The working electrode was a glassy carbon disc mounted in Teflon (EDI10000 Rotating Disc Electrode, Radiometer Copenhagen, diam. 3 mm). Before each experiment, it was polished first with fine emery paper, followed by decreasing size alumina particles in suspension on a polishing cloth until a mirror finish was obtained. After that, electrode was thoroughly rinsed with water.

Solutions were thoroughly purged of oxygen prior to running the experiment by bubbling with nitrogen N50 (Air Liquide) for 20 minutes. During measurements a flow of gas was maintained over the solution surface. Lead dioxide deposits were removed with 1:1 H₂O₂/Acetic acid followed by rinsing it thoroughly with water.

All experiments were carried out using a Voltalab Electrochemical system consisting of a DEA 332 potentiostat and an IMT 102 Electrochemical Interface. The system was connected to a personal computer for recording and treatment of curves. Temperature was kept at 25 °C.

RESULTS

Theoretical models

Lead dioxide electrodeposition on glassy carbon is characterized by a marked crystallization overpotential (cop) [35]. In such a case theories of nucleation and kinetic growth [32-34] are particularly valid. These theories provide mathematical expressions for j-t transients obtained by means of chronoamperometry for the different cases of nucleation (instantaneous and progressive) and growth (two- or three-dimensional). Table 1 presents a summary of such equations j-t, found in the literature for a process of nucleation and growth under kinetic control (no mass transport effects), both for the initial transient, where the nuclei grow independently from each other, and for the longer times when the overlapping between the nuclei takes place. Presented equations do not include possible induction time. The predicted transients depend on the geometry of the nuclei. For a progressive three-dimensional growth of right circular cones, the j-t transient increases to a plateau. In the case of growth of hemispheres, the curve presents a maximum followed by a plateau and the ratio of the peak current to the plateau is 1.33. If the geometric form considered is

cylindrical it presents a maximum followed by a plateau but the ratio of the peak to plateau current densities, for progressive nucleation, is 1.79.

Influence of the forced convection

As previously mentioned, different authors have studied the process of the electrodeposition of lead dioxide in convection-diffusion conditions. The work of Chang and Johnson [21, 22] has furnished important conclusions regarding the qualitative effects involved in the mass transport by convection-diffusion on the j - t response. Under certain experimental conditions, the steady-state current decreases with increase in the rotation velocity. This fact has been explained by Chang and Johnson [21] and other authors [18-20] assuming that the process is under kinetic control and that there are soluble intermediates that are removed from the electrode surface by convection. Nevertheless, even in detailed studies such as that presented by Chang and Johnson [21], no mathematical treatment has been carried out, applying the classical theories of nucleation and growth, to characterize the nucleation and growth under these conditions.

Figure 1 show the j - t curves obtained on a glassy carbon disk at 0 and 2500 rev min^{-1} for different final step potentials into the region of kinetic control [1], in a solution 0.1 M lead (II) nitrate + 1 M nitric acid. As the step potential increases, the chronoamperometric responses obtained with the glassy carbon disk in static conditions present S-shaped curves similar to those predicted for some classical models of nucleation and growth, leaving a perfectly defined plateau at high potentials. This shape differs from those presented in previous works [1, 23], obtained with other different vitreous carbons [40]. Similar curves registered in the rotating disk electrode conditions display much lower currents and a small drop in a steady-state current with time. This effect is more pronounced as the final step potential increases. It is interesting to note that, for all

the potentials studied, in the presence of rotation, the slope of the current-time curves (at shorter times) as well as their steady state values are lower in comparison with the curves recorded in static conditions at the same rotating disk electrode.

Analysis of prolonged transients (with overlap)

The chronoamperometric curves of the electrodeposition of lead dioxide, obtained at 0 rpm, display clearly formed plateaux at longer times, suggesting an application of the model of growth of the straight circular cones, equations (18) and (19) in Table 1. Figure 1 shows the comparison of the experimental curves and the fit to the progressive nucleation and growth model of three-dimensional cones (equation 19 of Table 1) with the outward growth on a substrate base plane surface not covered by growing nuclei [41]:

$$j = j_0 \exp \left[-\frac{\pi M^2 k^2 N_0 A}{3 \rho^2} (t - t_0)^3 \right] + z F k \left[1 - \exp \left[-\frac{\pi M^2 k^2 N_0 A}{3 \rho^2} (t - t_0)^3 \right] \right] \quad (4)$$

Other models including generalized electrocrystallization model [42] were also tested but no better approximation was found.

This equation contains four parameters: t_0 (s) is the induction time, j_0 (mA cm⁻²) is the current density, k (mol cm⁻² s⁻¹) constant of the growth rate, N_0 number of nuclei. They are displayed, together with their standard deviations, in Table 2. It should be added that j_0 is not very important in the whole approximation and the rate constant k is clearly determined when a well-defined current density plateau is observed. The values present the trend normally found in the literature: as the step potential increases, a decrease in induction time and an increase in the growth and nucleation constants is observed.

The curves registered at 2500 rpm (rev min^{-1}) fit much better at all the potentials than those reordered in static conditions (0 rpm), although the curve registered at $E_f = 1520$ mV is not completely depeoled (time of experiment insufficient). Therefore, although a good fit of the values was obtained, precautions must be taken.

It is important to emphasize that the plateau on the curves registered in static conditions at lower potentials ($E_f = 1520$ mV and 1540 mV vs. SCE) is not well developed and the fit cannot be complete. For higher potentials ($E_f = 1560$ mV and 1580 mV vs. SCE) the fit is better and it could provide representative values of k .

From the superposition of the theoretical and experimental curves it is clear that fit is worse at the foot of the curve and close to the plateau. This effect is more noticeable in static conditions where in addition, full overlapping of centers is delayed.

Analysis of initial transient (without overlap)

In order to obtain further information regarding the process, traditional analyses found in the literature has been carried out, studying only the initial part of nucleation and growth curves, before overlapping, (20% of the current of the plateau or steady state current density) following the induction time. In this case, the modeling has been carried out with only three parameters, as the values of k obtained in the complete analysis have been introduced as a constant. Figure 2 shows the superposition of the theoretical and experimental curves and Table 3 presents the obtained parameters. The approximations, both for the static and the RDE conditions are much better, providing values of the parameter (χ) an order of magnitude lower.

DISCUSSION

In the literature, the analysis of the j - t responses for the electrodeposition of lead dioxide has been concentrated on the initial instants of the nucleation process and growth [12, 16, 30, 40], by means of the different mathematical equations, displayed in Table 1. The conclusions presented indicate that the process takes place via a progressive nucleation and three-dimensional growth of the nuclei. The latter part of the curve has never been analyzed earlier. In the present study, we have carried out analyses using the same equation (19) for the whole curve and for the initial growth part. It is interesting to compare the information obtained at high step potentials ($E_f = 1560$ and 1580 mV vs. SCE) with that obtained at low step potentials ($E_f = 1520$ and 1540 mV vs. SCE). At low potentials, during the time in which the experiment was carried out, the value of the plateau current density was not reached which reveals the difficulty of the process of nucleation and growth and the fact that complete overlap of the nuclei was not reached. As the step potential increases, the nucleation and growth become faster and the fit between the theoretically predicted and the experimental curves improves. Figures 3A and 3B show the values of t_0 , k and N_0A as functions of the step potential for analysis at long and short time intervals, respectively. From these results, important conclusions can be drawn. The presence of agitation mainly affects the constant of growth k , decreasing it, independently of the step potential. The values of the three-dimensional constant of nucleation, N_0A , are not particularly affected by the agitation, although they are slightly greater in the absence of agitation. The values of the induction times in the presence of and in the absence of agitation are similar, however, discrepancies exist when our data are compared with those of other authors [21, 22] at short time intervals and at low step potentials.

Certain critical concentration of lead species is necessary to start grows of nuclei. With increase in agitation rate (rotation rate) soluble lead III or IV species are removed more quickly from the electrode surface and the crystal growth is slowed down. At more positive potentials their concentration is larger and the crystallization rate increases. The induction time may be related to the formation of adsorbed OH species and depends on the electrode potential but it is practically independent of the rotation rate indicating that it is determined by a surface process.

CONCLUSIONS

The introduction of convection as a dominating contribution to the transport leads to unexpected changes in the lead dioxide electrodeposition under these experimental conditions. Therefore, increase of convection does not enhance deposition of lead dioxide on the electrode surface, as it is expected in CSV experiments with forced convection in the preconcentration step.

In this context, we think that the study of the influence of the forced convection on the lead dioxide crystallization using RDE can provide useful information in order to compare with other mass transport enhancement methods, such as ultrasounds.

Analysis (of the initial or prolonged transients) have led to the following conclusions:

- The analysis of the whole transients reveals that the process of nucleation and growth of lead dioxide on the glassy carbon substrate, in the presence of forced convection on a RDE, cannot be fully explained by the known models, a discrepancy is observed at short and long times. However, a reliable value of the rate constant k is obtained from the plateau current.

- The parameters obtained are consistent with the new reaction mechanism [18-22] involving the existence of a soluble intermediate species. The values of k , clearly depends on agitation conditions but the dependence of t_0 and N_0A is not important, supporting the hypothesis that during the induction period, the limiting step is associated with the first stage of nucleation (adsorption of OH on the substrate). Therefore, the stability of the incipient nuclei is not influenced by the agitation. The growth of a stable nucleus, via the incorporation of material on the surface of the lead dioxide, may be limited by the presence of this soluble intermediate on the surface of the nucleus and therefore affected by the agitation.
- The process of electrocrystallization of lead dioxide is dependent on the nature of the substrate [1, 23, 40], especially, in the case of the different types of glassy carbon. In our earlier study on another type of glassy carbon curves with well developed maximum were obtained. In this latter case, the influence of the variable agitation may only be studied maintaining the nature of the substrate identical [42].

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Captions

Figure 1.- Theoretical fit (••) of experimental curves (—) for lead dioxide electrodeposition on a vitreous carbon RDE. Analysis of prolonged transient obtained at different step potentials. A) rotation rate 0 rev min⁻¹. B) rotation rate 2500 rev min⁻¹.

Figure 2.- Theoretical fit (●●) of experimental curves (–) for lead dioxide electrodeposition on a vitreous carbon RDE. Analysis of initial transient obtained at different step potentials. A) rotation rate 0 rev min^{-1} . B) rotation rate 2500 rev min^{-1} .

Figure 3.- Dependence of t_0 , $\log N_0A$ and $\log k$ on applied potential for lead dioxide electrodeposition on vitreous carbon RDE. (A) Analysis of prolonged transient (B) Analysis of initial transient.

Growth	Geometry	Nucleation	Without overlap	With overlap
2D	Disk	instantaneous	(4) $j = \frac{2\pi zFMhk^2N_0}{\rho} t$ [36]	(14) $j = \frac{2\pi zFMhk^2N_0}{\rho} t \exp\left(\frac{-\pi M^2k^2N_0}{\rho^2} t^2\right)$ [36]
		progressive	(5) $j = \frac{\pi zFMhk^2N_0A}{\rho} t^2$ [36]	(15) $j = \frac{\pi zFMhk^2N_0A}{\rho} t^2 \exp\left(\frac{-\pi M^2k^2N_0A}{3\rho^2} t^3\right)$ [36]
	Cone	instantaneous	(6) $j = \frac{3\pi zFMhk^2N_0}{2\rho} t$	(16) $j = \frac{3\pi zFMhk^2N_0}{2\rho} t \exp\left(\frac{-3\pi M^2k^2N_0}{4\rho^2} t^2\right)$
		progressive	(7) $j = \frac{3\pi zFMhk^2N_0A}{2\rho} t^2$	(17) $j = \frac{3\pi zFMhk^2N_0A}{2\rho} t^2 \exp\left(\frac{-\pi M^2k^2N_0A}{2\rho^2} t^3\right)$
3D	Cone	instantaneous	(8) $j = \frac{\pi zFM^2k^2N_0}{\rho^2} t^2$ [36]	(18) $j = zFk' \left[1 - \exp\left(\frac{-\pi M^2k^2N_0}{\rho^2} t^2\right) \right]$ [36]
		progressive	(9) $j = \frac{\pi zFM^2k^2N_0A}{3\rho^2} t^3$ [36]	(19) $j = zFk' \left[1 - \exp\left(\frac{-\pi M^2k^2N_0A}{3\rho^2} t^3\right) \right]$ [36]
	Hemisphere	instantaneous	(10) $j = \frac{2\pi zFM^2k^2N_0}{\rho^2} t^2$ [37]	(20) $j = 2zFk' p t e^{-p^2 t} \int_0^t e^{pu^2} du$ $p = \frac{\pi M^2k^2N_0}{\rho^2} j_{\max}/j_{ss} = 1.285$ [38]
		progressive	(11) $j = \frac{2\pi zFM^2k^2N_0A}{3\rho^2} t^3$ [37]	(21) $j = 3zFk' p_1 t e^{-p_1 t} \int_0^t (t^2 - u^2) e^{-p_1(2u^2 - 3u^2)} du$ $p_1 = \frac{\pi M^2k^2AN_0}{3\rho^2} j_{\max}/j_{ss} = 1.33$ [38]
	Cylinder	instantaneous	(12) $j = \frac{3\pi zFM^2k^2N_0}{\rho^2} t^2$	(22) $j = \frac{2\pi zFM^2k^2N_0}{\rho^2} t^2 \exp\left(\frac{-\pi M^2k^2N_0}{\rho^2} t^2\right) + zFk' \left[1 - \exp\left(\frac{-\pi M^2k^2N_0}{\rho^2} t^2\right) \right]$ [39]
		progressive	(13) $j = \frac{4\pi zFM^2k^2N_0A}{3\rho^2} t^3$	(23) $j = \frac{\pi zFM^2k^2N_0A}{\rho^2} t^3 \exp\left(\frac{-\pi M^2k^2AN_0}{3\rho^2} t^3\right) + zFk' \left[1 - \exp\left(\frac{-\pi M^2k^2AN_0}{3\rho^2} t^3\right) \right]$ [39]

Table 1.- Initial and prolonged current density transient for electrocrystallization under kinetics controlled growth process.

0 rpm					2500 rpm				
$E_f(mV)$	$t_0(s)$	$j_0(mA cm^{-2})$	N_0A (nuclei $cm^{-2} s^{-1}$)	k (mol $s^{-1} cm^{-2}$)	$t_0(s)$	$j_0(mA cm^{-2})$	N_0A (nuclei $cm^{-2} s^{-1}$)	k (mol $s^{-1} cm^{-2}$)	
1520	420 ± 2	0.039 ± 0.001	(3.02 ± 0.07) 10 ⁵	(1.200 ± 0.002) 10 ⁻⁸	442 ± 2	0.045 ± 0.001	(1.54 ± 0.03) 10 ⁶	(1.76 ± 0.02) 10 ⁻⁹	
1540	209 ± 2	0.054 ± 0.001	(3.11 ± 0.08) 10 ⁵	(1.351 ± 0.002) 10 ⁻⁸	204 ± 1	0.054 ± 0.001	(2.48 ± 0.01) 10 ⁵	(5.840 ± 0.004) 10 ⁻⁹	
1560	138.1 ± 0.8	0.077 ± 0.001	(9.7 ± 0.2) 10 ⁵	(2.282 ± 0.001) 10 ⁻⁸	140.7 ± 0.7	0.089 ± 0.001	(1.239 ± 0.009) 10 ⁶	(5.998 ± 0.004) 10 ⁻⁹	
1580	71.9 ± 0.9	0.123 ± 0.001	(1.56 ± 0.03) 10 ⁶	(2.362 ± 0.002) 10 ⁻⁸	82.1 ± 0.7	0.106 ± 0.001	(1.033 ± 0.007) 10 ⁶	(8.312 ± 0.005) 10 ⁻⁹	

Table 2.- Kinetics parameters of lead dioxide electrodeposition derived from analysis of prolonged transients.

0 rpm					2500 rpm			
$E_f(mV)$	$t_0(s)$	j_0 (mA cm ⁻²)	N_0A (nuclei cm ⁻² s ⁻¹)	k (mol s ⁻¹ cm ⁻²)	$t_0(s)$	j_0 (mA cm ⁻²)	N_0A (nuclei cm ⁻² s ⁻¹)	k (mol s ⁻¹ cm ⁻²)
1520	524.4 ± 0.7	0.039 ± 0.001	(2.21 ± 0.04) 10 ⁵	(1.200 ± 0.002) 10 ⁻⁸	442 ± 2	0.050 ± 0.001	(1.54 ± 0.03) 10 ⁶	(1.76 ± 0.02) 10 ⁻⁹
1540	329.8 ± 0.5	0.054 ± 0.001	(5.4 ± 0.1) 10 ⁶	(1.351 ± 0.002) 10 ⁻⁸	207.1 ± 0.5	0.069 ± 0.004	(2.23 ± 0.01) 10 ⁵	(5.840 ± 0.004) 10 ⁻⁹
1560	171.4 ± 0.5	0.077 ± 0.001	(2.59 ± 0.08) 10 ⁶	(2.282 ± 0.001) 10 ⁻⁸	139.7 ± 0.3	0.094 ± 0.003	(9.59 ± 0.05) 10 ⁵	(5.998 ± 0.004) 10 ⁻⁹
1580	128.4 ± 0.2	0.138 ± 0.002	(6.1 ± 0.2) 10 ⁷	(2.362 ± 0.002) 10 ⁻⁸	132.9 ± 0.5	0.131 ± 0.004	(2.92 ± 0.05) 10 ⁶	(8.312 ± 0.005) 10 ⁻⁹

Table 3.- Kinetics parameters of lead dioxide electrodeposition derived from analysis of initial transients.