Kinetics of electrocrystallization of PbO₂ on glassy carbon electrodes: Partial inhibition of the progressive three-dimensional nucleation and growth

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SUMMARY

Electrocrystallization of PbO₂ on glassy carbon electrodes was studied in 1 M HNO₃ + 0.1 M Pb(NO₃)₂ using cyclic voltammetry, rotating disk electrode, chronoamperometry and scanning electron microscopy. In order to explain the experimental curves a new theory of three-dimensional nucleation and progressive growth was developed and applied to analyse the experimental chronoamperometric curves. Numerical approximations led to the determination of kinetic parameters.

Keywords: electrodeposition, nucleation, charge transfer, lead dioxide

INTRODUCTION

Studies on the lead dioxide electrodeposition process have been and still are of the

continuous interest because of the wide diversity of applications of this material as electrode in batteries [1,2], waste water treatment by electrooxidation of organics [3, 4], ozone generation [5], electrosynthesis [6-9], and electrowinning of metals [10]. These studies deal with numerous subjects such as performance characteristics as an anode material [11], physicochemical properties [12], electrocatalytic behaviour [13, 14] and structural changes [15]. Some problems related to the stability of the lead dioxide coating have been reported [16, 17]. Improvements of the performance of this anode depend on the structure and properties of the lead dioxide film [18, 19]. Fundamental and applied investigations were carried out to explain: (a) effect of the operational variables such as deposition current density [20], presence of additives [21], temperature and agitation [22], in the massive lead dioxide electrodeposition process and (b) the lead dioxide electrocrystallization, using voltammetric and potential step experiments [23- 26], to determine the role played by the nucleation process in the anodic electrodeposition.

The electrodeposition of lead dioxide was one of the first processes subjected to investigate the thermodynamics and kinetics of electrocrystallization. Fleischmann et al. [27-30] carried out extensive studies of the deposition of α and β -lead dioxide on platinum electrodes from perchloric, and nitric acids and from acetate solutions by potential step techniques. They suggested a mechanism for the electrodeposition of lead dioxide from aqueous solutions of Pb(II) postulating the existence of insoluble intermediates adsorbed on the electrode. This investigation, together with other contributions, led to the classical electrocrystallization theories [31, 32].

For the lead dioxide electrocrystallization peak-shaped [24, 33- 35] and S-shaped [36 -41]

transients have been observed. Potential step and voltammetric experiments with ring-disk electrodes were carried out. The analysis of the transient current-time curves was always limited to the early stages of the process (i. e. initial current transient at short times) in terms of a progressive nucleation and three-dimensional growth kinetics. This simple analysis looks for an I vs t^n relationship before overlap of the centres begins and can determine, with the help of optical and electron microscopy, the kinetics of electrocrystallization as a function of the parameter n . Nevertheless, this analysis of the transients is hampered: only $\approx 20\%$ of the rising transient is completely free of overlap effects and the presence of special characteristics (induction time) in the curve complicates its application [42].

However, several studies have focused their attention on the nature of the intermediates. Laitinen and Watkins [34] detected soluble Pb(IV) species during deposition and stripping of lead dioxide and Campbell and Peter [38] have reported similar results from ethanoate solutions. Chang and Johnson [39] have also found soluble species and have pointed out the complexity of the mechanism for electrodeposition of lead dioxide from aqueous solutions of Pb(II). These findings have motivated Chang and Johnson [39, 40] and Velichenko et al. [41, 43, 44] to propose some modifications to the mechanism of Fleischmann et al. [27-30] for lead dioxide electrodeposition. For example, Velichenko et al., suggests that the soluble intermediate product seems to be Pb(III), probably complexed with hydroxide, i. e. Pb(OH)^{2+} :

On the other hand Chang and Johnson [39, 40] proposed a similar mechanism where the soluble intermediate product was Pb(IV) in the form of Pb(OH)_2^{2+} .

Analyses of prolonged current transient for lead dioxide electrodeposition are not found in the literature. Classical three-dimensional (3D) nucleation and crystal growth leads to the S-shaped chronoamperometric transients [31, 45] for models based on activation-controlled growth and nucleation. However, transients with a maximum are sometimes found experimentally, for example for hard gold [46] or PbO_2 electrodeposition [47]. The cases when the current reaches zero at longer times may be explained assuming two-dimensional growth [31, 45] or inhibition [46, 48]. Curves with a maximum are observed for hemispherical [49-52] or hemispheroidal [53, 54] growth, however, the ratio of the maximum current to the steady-state value is 1.285 for instantaneous and 1.332 for progressive nucleation. Larger ratios may be explained assuming partial inhibition of the vertical growth process [46]. Inhibition process may be described assuming time dependent rate constant of the vertical growth process. Such processes were assumed earlier by Armstrong et al. [55] for 3D growth process leading to passivation with the vertical rate constant described as: $k \sim \exp(-a t^3)$ and by Bosco and Rangarajan [48] (who corrected earlier errors). A two-rate model, in which the rates in horizontal and vertical directions were different, was first introduced by Armstrong et al. [55] for a conical growth,

Abyaneh [53, 54] for hemospheroidal growth (the growth cross-section is an ellipse) and discussed in detail by Bosco and Rangarajan [48]. Li and Lasia [46] used a partial inhibition model to explain hard gold electrocrystallization with instantaneous three-dimensional (3D) nucleation and growth, in which the vertical growth is described by two rate constants, one time independent and other time dependent, decreasing exponentially:

$$k' = k_1 \exp(-\lambda t) + k_2 \quad (4)$$

where the total rate constant changes from $k_1 + k_2$ at short times to k_2 at longer times and the parameter λ characterises the rate of this change. This model was applied to explain gold electrocrystallization with instantaneous three-dimensional (3D) nucleation [46].

In the present paper a theory of 3D progressive nucleation and crystal growth assuming different growth rates in vertical and horizontal directions is presented and applied to explain transients for electrocrystallization of PbO_2 . Voltammetry was used to determine general behaviour of the electrocrystallization process, RDE experiments to check the kinetic control conditions and potential steps were applied to choose the growth model and to determine the growth kinetics. The morphology of the particles was investigated using scanning electron microscopy.

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 solutions of 0.1M lead(II) nitrate + 1 M nitric acid, prepared using

ultrapure water obtained from a Millipore Milli-Q system. A platinum wire acted as the counter electrode and a SCE served as the reference electrode.

The working electrode was a glassy carbon rod CV25 (Le Carbone Lorraine) 3 mm in diameter and a glassy carbon disc (EDI10000 Rotating Disc Electrode, Radiometer Copenhagen, diameter: 3 mm) for the rotating disc experiments. Before each experiment, glassy carbon electrodes were polished first with a fine emery paper, followed by polishing with decreasing size alumina particles in suspension on a polishing cloth until a mirror finish was obtained. In both cases, electrodes were thoroughly rinsed with water.

Oxygen was removed by bubbling nitrogen (N50 Air Liquide) for 20 min. During measurements a flow of gas was kept over the solution surface. Lead dioxide deposits were removed from the surface with 1:1 H₂O₂/Acetic acid mixture followed by thorough rinsing with water.

All experiments were carried out using a Voltalab Electrochemical system consisting of a DEA 332 potentiostat and a IMT 102 Electrochemical Interface. The system was connected to a personal computer for data recording and processing.

A JSM-840 JEOL Scanning electron microscope was employed to obtain topographical views of the electrodes surfaces.

RESULTS AND DISCUSSION

Theory. Bosco and Rangarajan [48] presented a general equation describing 3D

nucleation and growth of right circular cones. In order to explain our experimental results a model of partial inhibition of the vertical growth was assumed, Eqn. (4). Therefore, the rates of vertical and horizontal growth (in cm/s) are $q(t) = v_1 e^{-\lambda t} + v_2 = M/\rho(k_1 e^{-\lambda t} + k_2)$ and $p(t) = v = Mk/\rho$, respectively, where k_i are the rate constants (in mol/cm² s) of the vertical (k_1 , k_2) and horizontal (k) growth, ρ is the deposit density, M is its the atomic (molecular) weight. If the growth rates are time independent the growth geometry may be represented by right circular cones [48]. The growth profile can be determined assuming that the horizontal growth is observed during time $t-t_1$ and the vertical growth during time t_1 . Then the extent of the horizontal growth is $x = v(t-t_1)$ and that of the vertical growth [48]:

$$y = \int_0^{t_1} (v_1 e^{-\lambda t} + v_2) dt = \frac{v_1}{\lambda} (1 - e^{-\lambda t_1}) + v_2 t_1 \quad (5)$$

Elimination of t_1 leads to:

$$y = \frac{v_1}{\lambda} \left[1 - \exp\left(-\lambda t + \frac{\lambda}{v} x\right) \right] + v_2 t - \frac{v_2}{v} x \quad (6)$$

which represents a sum of the linear and exponential profiles, i.e. feature between the right circular cone and an exponential growth form (Fig. 2a, Ref.48).

The centre contributes to the growth at the height h only if it was nucleated before a time

$s(h, t)$, determined as $h = \int_s^t q(u) du$. A centre nucleated at time τ ($0 < \tau < s$) will be contributing at

time t and height h a circular cross-section radius of $\int_w^t p(u) du$, where w is given by

$h = \int_\tau^w q(u) du$. The extended area of the growing centers at time t and height h is given as [48]:

$$S_{X,h} = \int_0^{s(h,t)} d\tau \left(\frac{dN}{dt} \right) \tau \left\{ \int_{w(h,\tau)}^t p(u) du \right\}^2 \quad (7)$$

where dN/dt is the nucleation rate at time τ and $s(h,t)$ is the time at which this height is reached (nucleation may start later than at $t = 0$). For the progressive nucleation $dN/dt = N_0 A$, where N_0 is the number of sites per surface unit area (nuclei cm^{-2}) and A is the nucleation rate constant (s^{-1}).

Applying the Avrami's overlap theorem one gets the overall macrogrowth S (in cm):

$$S = \int_0^{h_m} [1 - \exp(-S_{X,h})] dh \quad (8)$$

where h_m is the maximal height of the deposit:

$$h_m = \int_0^t q(u) du \quad (9)$$

The chronoamperometric current transient is given as:

$$i = \frac{zF\rho}{M} \frac{dS}{dt} \quad (10)$$

where z is the number of electrons (per atom or molecule) exchanged during deposition.

Integration by parts in Eqn. (7) leads to [56]:

$$S_{X,s} = 2\pi N_0 A \int_{W(s,t)}^t \tau(w;s,t) P_t(w) p(w) dw \quad (11)$$

and

$$S = \int_0^t [1 - \exp(S_{X,s})] q(s) ds \quad (12)$$

where:

$$P_t(w) = \int_w^t p(u) du \quad (13)$$

parameter $\tau(w;s,t)$ is a function of variable w and parameters s and t , and it may be obtained from:

$$Q(\tau) = Q(w) - Q(t) + Q(s)$$

or in another form

$$\begin{aligned} & \frac{v_1}{\lambda}(1 - e^{-\lambda\tau}) + v_2\tau \\ &= \frac{v_1}{\lambda}(1 - e^{-\lambda w}) + v_2w - \frac{v_1}{\lambda}(1 - e^{-\lambda t}) + v_2t + \frac{v_1}{\lambda}(1 - e^{-\lambda s}) + v_2s \end{aligned} \quad (14)$$

and $W(t,s)$ from:

$$Q(W) = Q(t) - Q(s) \quad (15)$$

where

$$Q(z) = \int_0^z q(u) du \quad (16)$$

In order to solve the integral in Eqn. (12) the parameter τ must be calculated by solving numerically non-linear Eqn. (14), and, similarly, parameter W from Eqn. (15).

The calculations were carried out using non-linear least-squares program in Fortran (Microsoft Fortran Power Station 4.0 with IMSL). It was assumed that the observed current consists of two parts [46, 57]: current due to three-dimensional crystal growth, i_{3D} , and the current due to outward growth at a free surface uncovered by growing nuclei, i_f [46]. The total current is given as:

$$i = i_f + i_{3D} = j_0 e^{-S_{X,s}} + P_0 \frac{d}{dt} \left\{ \int_0^t \left(1 - e^{-S_{X,s}} \right) \left(1 + P_1 e^{-\lambda s} \right) ds \right\} \quad (17)$$

$$S_{X,s} = 2P_2 \int_W^t \tau(w; s, t) (t - w) dw$$

where

$$\begin{aligned} j_0 &= zFk_0 \\ P_0 &= zFk_2 \\ P_1 &= k_1 / k_2 \\ P_2 &= \frac{\pi N_0 A M^2 k^2}{\rho^2} \end{aligned} \quad (18)$$

k_0 is the growth rate constant on the base plane of the substrate and the induction time, t_0 , was also introduced in equations: $t = t_{\text{total}} - t_0$, and t_{total} is the time measured from the application of potentiostatic pulse. Transient charging current occurring immediately after application of the pulse was eliminated in order to decrease number of adjustable parameters in the model.

Kinetics control conditions. Figure 1 shows the cyclic voltammograms on a glassy carbon disc in 0.1 M lead(II) nitrate + 1M nitric acid solution recorded at 0 (solid line) and 2500 rpm (dashed line). During the scan in the anodic direction a significant crystalization overpotential can be noticed before lead dioxide electrodeposition occurs: The anodic current density suddenly increases at potential higher than 1600 mV. The backward cathodic scan shows initially a steep decrease of the current density in the potential range negative of the lead dioxide deposition (above the forward current density, seen following the arrow). The cross-over on the potential axis provides an approximation of the equilibrium potential and the difference in

potential between this point and the potential at which deposition commences on the forward sweep corresponds to the crystallization overpotential. The cathodic peak at a more negative potential corresponds to the lead dioxide reduction. Current density and peak area increase with rotation rate in the potential range of mass transport control (potentials higher than 1600 mV vs. SCE). Similar responses have been obtained by other authors [24, 35, 38, 39, 41, 58]

Figure 2 shows the $j-t$ profiles for lead dioxide deposition on a glassy carbon disc at 0 and 2500 rpm following a potential step to 1520 mV vs. SCE. For a mass-transport-limited process, values of current density are expected to increase proportional to square root of the rotation rate. In our case, the current densities in the presence of rotation are lower and this effect has been highlighted as significant indicator of the mechanistic complexity of this deposition reaction by other authors [39]. In their paper, Chang and Johnson postulated kinetic control conditions for lead dioxide electrodeposition at high concentration of Pb(II) and low values of pH and potentials lower than 1600 mV. We have found a similar behaviour under our experimental conditions. To explain this fact Chang and Johnson proposed generation of a soluble intermediate species, which is transported away from the electrode, by the convective-diffusion mechanism, causing inhibition of the nucleation and growth of existing nuclei. In a later paper [40], the same authors, using a rotated ring-disk electrode, proposed the existence of Pb(IV) species, probably associated with oxygen hydroxy group (PbO^{2+} or $\text{Pb}(\text{OH})_2^{2+}$), as the soluble intermediates. Other authors have found similar results [38, 41, 43], as was indicated in the introduction section, but proposing Pb(III) as a intermediate. Our results permit us conclude that the electrocrystallization, in these experimental conditions, is controlled by kinetics of the process.

Potential step experiments. Figure 3 shows the j - t transients for lead dioxide electrodeposition at a static glassy carbon rod electrode. Each curve shows an induction time, t_0 , and depends strongly on the step potential, E_f , (i. e. final deposition potential). At lower potentials, after a long induction time, the current density increases to reach a steady-state value. As the step potential increases, the induction time decreases and a sharp peak appears. After the peak, the current density decreases to a steady-state value.

Figure 4 shows the SEMs of the lead dioxide electrodeposition on a static glassy carbon rod electrode. A nearly hemispherical granular crystalline growth can be noticed. Different sizes of the nuclei are in agreement with the progressive nucleation mechanism. The shape observed is in agreement with the exponential growth, Eqn. (6), this paper, and Fig. 2a, Ref. 48.

Application of the theory. To explain the crystal growth of PbO_2 a model described by Eqn. (4) was used. Such a behaviour may arise from the fact that, for example, some centres are inhibited (e.g. by adsorption of a poison) or may be connected with the presence of a soluble lead species around the electrode. Nevertheless, this is the simplest semiempirical model which can explain the observed i - t behaviour under the kinetic control conditions. The results of the approximations are presented in Figure 5 and in Table 1. At lower potentials, where the data acquisition was stopped before reaching the plateau, a simple progressive 3D nucleation and crystal growth model was sufficient to explain the experimental data:[57, 59]

$$j = j_0 \exp(-P_2 t^3 / 3) + P_0 [1 - \exp(-P_2 t^3 / 3)] \quad (19)$$

In this case the rate constant k_1 is assumed to be zero and the growth rate equals k_2 . The obtained results indicate that the inhibition rate increases with overpotential from 3.3×10^{-3} to $8.6 \times 10^{-3} \text{ s}^{-1}$. Assuming that the horizontal growth is not inhibited and it is equal to the initial vertical growth rate: $k = k_1 + k_2$, the nucleation rate may be estimated. It can be noticed that the rate constant k_2 is practically constant (except the extreme potential values) and k_1 increases with the deposition potential. Moreover, the induction time decreases with electrode potential. The inhibition parameter, λ , is relatively constant except the most negative potential. Finally, the nucleation rate $N_0 A$ increases with the applied potential. This behaviour is in agreement with the theory and crystal growth and other experimental results [57].

It is worth to compare our results with those reported by Li et al.[24]. These authors studied electrocrystallization of lead dioxide at different conditions, using carbon fibre microelectrodes and obtaining a single centre of lead dioxide. This method simplifies the analysis data avoiding the overlapping and the problems arising from the surface roughness. Nevertheless, as it can be seen in Figure 6, growth rate constants are closed to the values reported by us in the present paper (with vitreous carbon macroelectrodes and a theoretical model very different). According to Li et al [24], their results are also similar to those reported by Fleischmann and Liler [27] for the growth of lead dioxide on platinum macroelectrodes and analysis of the initial rising current transient.

It should be added that our approximations use 6 adjustable parameters: j_0 , P_0 , P_1 , P_2 , t_0 and λ , that is two more than a simple 3D nucleation and crystal growth model. However, the two additional parameters are P_1 and λ are well determined by the peak height and the peak shape.

The parameter j_0 is small and not very important in the whole approximation. The quality of fit may well be seen from Table 1, where the standard deviations of the parameters are quite small.

CONCLUSIONS

Electrochemical and SEM studies of PbO_2 electrocrystallization on glassy carbon electrodes indicate that this process proceeds via three-dimensional nucleation and crystal growth with a partial inhibition of vertical growth. However, at low overpotentials, the process proceeds without apparent inhibition. At lower potentials the process is characterised by a long induction time which decreases with overpotential. A theory of this process was developed and successfully applied and the kinetic parameters obtained.

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Figure captions

Fig 1. Cyclic voltammogram in 0.1M lead(II) nitrate + 1M nitric acid at a glassy carbon electrode, sweep rate 5 mV s^{-1} . rotation speed 0 rpm. rotation speed 2500 rpm.

Fig 2. Chronoamperometric curves for PbO_2 deposition in 0.1M lead(II) nitrate + 1M nitric acid

at a glassy carbon electrode (potential step 1520 mV vs. SCE). rotation speed 0 rpm.

..... rotation speed 2500 rpm.

Fig 3. Chronoamperometric curves for PbO_2 deposition in 0.1M lead(II) nitrate + 1M nitric acid at a glassy carbon electrode (rotation speed 0 rpm)._____ Potential step 1500 mV.

..... Potential step 1520 mV. Potential step 1540 mV. _____ Potential step 1560 mV.

..... Potential step 1580 mV. _____ Potential step 1600 mV. All potential referred to SCE.

Fig 4. Scanning electron micrographs of a glassy carbon surface at the initial time during a lead dioxide electrodeposition chronoamperometric experiment.

Fig. 5. Comparison of the experimental (solid line) and approximated (dotted line) current transients for PbO_2 electrocrystallisation on a glassy carbon electrodes. Conditions as in Fig. 3. $a=1500$ mV, $b=1520$ mV, $c=1540$ mV, $d=1560$ mV, $e=1580$ mV, $f=1600$ mV

Fig. 6. Potential dependence of the rate constants for the growth of PbO_2 . Details in figure.

Table I. Kinetic parameters of electronucleation and growth of PbO_2 .

E_r mV	j_0 mA cm^{-2}	$P_0 = 2Fj_0$ mA cm^{-2}	$P_1 = k_1/k_2$	P_2 s^{-3}	$\lambda \times 10^3$ s^{-1}	t_0 s	k_1 $\text{mol cm}^{-2} \text{s}^{-1}$	k_2 $\text{mol cm}^{-2} \text{s}^{-1}$	$N_0 A^a$ $\text{nucl. cm}^{-2} \text{s}^{-1}$
1500	0.3167 ± 0.0007	3.78 ± 0.16		$(1.30 \pm 0.08) \times 10^{-9}$		313 ± 3	0	2.0×10^{-8}	1.6×10^3
1520	0.31 ± 0.01	2.071 ± 0.003		$(4.4 \pm 0.2) \times 10^{-8}$		259 ± 5	0	1.1×10^{-8}	1.8×10^5
1540	0.505 ± 0.006	1.15 ± 0.01	1.88 ± 0.01	$(4.089 \pm 0.09) \times 10^{-7}$	3.31 ± 0.06	106 ± 1	1.1×10^{-8}	6.0×10^{-9}	6.9×10^5
1560	0.431 ± 0.008	1.37 ± 0.01	2.43 ± 0.02	$(1.11 \pm 0.03) \times 10^{-6}$	6.0 ± 0.1	70 ± 1	1.7×10^{-8}	7.1×10^{-9}	9.4×10^5
1580	0.81 ± 0.04	1.35 ± 0.04	3.32 ± 0.09	$(7.6 \pm 0.5) \times 10^{-6}$	5.12 ± 0.07	16 ± 2	2.3×10^{-8}	7.1×10^{-9}	4.1×10^6
1600	0.52 ± 0.10	1.5 ± 0.1	4.9 ± 0.4	$(1.08 \pm 0.05) \times 10^{-5}$	8.6 ± 0.3	0	3.8×10^{-8}	7.8×10^{-9}	2.5×10^6

^a Calculated assuming $k = k_1 + k_2$