

A Model Describing the Electroreduction of Basic Pb(II) Compounds Formed on Pb in H₂SO₄ Solutions

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O estudo cinético da eletrorredução de compostos superficiais básicos que contêm Pb(II) formados sobre eletrodos de Pb de alta pureza em soluções de H₂SO₄ tem sido realizado utilizando pulsos potencioestáticos de corrente complementados com técnicas voltamétricas combinadas pelo ajuste adequado das condições de formação de camada e eletrorredução anódica.

Os processos de eletrorredução podem ser interpretados em termos de um mecanismo complexo de nucleação e crescimento. Conseqüentemente, uma nucleação progressiva tridimensional com crescimento controlado por transferência de carga é considerada como a principal etapa determinante da velocidade, onde o controle provém do crescimento da fração superficial de Pb metálico livre, não coberto por espécies PbO. Uma simulação computacional do voltamograma correspondente à eletrorredução de compostos superficiais básicos que contêm Pb(II) é apresentada, baseada na dependência dos parâmetros cinéticos com o potencial obtida pelo método de ajuste não-linear dos transientes potencioestáticos. Encontrou-se boa concordância entre a teoria e os resultados experimentais.

The kinetic study of the electroreduction of basic Pb(II)-containing surface compounds formed on highly pure Pb electrodes in H₂SO₄ solutions was carried out using potentiostatic current pulses complemented with combined voltammetry techniques by properly adjusting both the anodic layer formation and the electroreduction conditions.

The electroreduction processes can be interpreted in terms of a complex nucleation and growth mechanism. Accordingly, a progressive three-dimensional nucleation with charge transfer controlled growth is discussed as the main rate-determining step, where the control results from the growth of the surface fraction of free Pb metal not covered by the PbO species. A computer simulation of the voltammogram corresponding to the electroreduction of the basic Pb(II) compounds is presented, based on the potential dependence of kinetic parameters obtained by non-linear fit procedures from potentiostatic transient data. Good agreement was found between the theory and the experimental results.

Keywords: *lead/sulphuric acid system, electroreduction of lead monoxide layers, computer simulation of voltammograms*

Introduction

The electrochemistry of lead in sulphuric acid is of practical interest because of its relevance to the lead-acid battery. This device is one of the most important electrochemical energy storage systems in use today, but despite the large number of investigations lead electrode reactions are still not completely understood. At anodic potentials lead electrodes in sulphuric acid electrolytes exhibit a wide variety of phenomena which occur both interfacially and in the solid state, and their explanation requires proper use of

modern theories of surface electrochemistry as well as those of nucleation and growth process models¹⁻³.

According to Pavlov and co-workers^{4,5}, the characteristics of passive films formed on lead electrodes in H₂SO₄ solution can be separated into three distinct potential regions: (i) at potentials from - 0.95 V to - 0.30 V (vs. Hg/Hg₂SO₄) the passive layer consists of PbSO₄ crystals; (ii) the layer produced from - 0.30 V to 0.95 V is composed of PbSO₄ and an inner layer including several basic lead compounds; and (iii) above 0.95 V the α -PbO₂ and β -PbO₂ species become the predominant anodic surface products.

The inner layer formed in the intermediate potential range assigned to basic Pb(II)-containing compounds, like basic lead sulphates, lead hydroxide and lead monoxide, builds up progressively beneath the initially grown PbSO₄ as a result of the increasing pH gradient within its porous layered structure.

In a previous work⁶, it was postulated that the potentiostatic electroreduction of the basic Pb(II)-containing surface compounds (which were considered, in principle, to be a PbO layer) formed on lead in sulphuric acid solutions can be mainly interpreted according to a progressive nucleation and 3D growth model under charge transfer control, including a death correction term for right circular cone phase centers⁷, and a second current contribution which prevails only at very short times, and follows an instantaneous nucleation and 2D growth model under diffusion control.

The aim of the present paper is to demonstrate the validity of the proposed model to explain the kinetics and mechanism of the electroreduction of anodic surface products formed under different Pb oxidation conditions, by using both potentiostatic steps and linear potential sweeps to study the complex cathodic reactions of basic Pb(II) compounds. Voltammetric results were simulated from the potentiostatic experiments by assuming that a single linear potential scan is the sum of an effectively infinite number of potential increments, and that between successive increments the surface coverage of the electrode remains constant⁸.

Experimental

The experimental setup was the same as that described elsewhere^{6,9,10}. *Specpure* lead discs (Johnson Matthey Chemicals Ltd., 0.30 cm² apparent area) embedded in PTFE holders were used as working electrodes. These electrodes were mechanically polished with 600 and 1200 grade emery papers and afterwards thoroughly rinsed in triply-distilled water. Electrochemical runs were performed in aqueous 5 M H₂SO₄ at 25 °C, under purified nitrogen gas saturation. The solution was prepared from analytical grade (p.a. Merck) reagent and Milli-Q* water. Potentials were measured and referred to in the text against a Hg/Hg₂SO₄/K₂SO₄(sat.) electrode, $E_{\text{Hg}/\text{Hg}_2\text{SO}_4} = 0.68 \text{ V}$ (vs. SHE).

Prior to each run the working electrode was cathodically polarized at -1.30 V for $\tau_0 = 5 \text{ min}$, *i.e.* in the hydrogen evolution reaction (HER) potential range, to achieve a reproducible electroreduced Pb surface. Subsequently, the electrode was subjected to a linear positive-going potential sweep at $v_a = 0.02 \text{ V s}^{-1}$ up to $E_{s,a} = 0.40 \text{ V}$, and then the potential was held at $E_{s,a}$ for different times τ in the range $0 \leq \tau \leq 30 \text{ min}$, to modify the total amount of the surface products. Finally, two types of experiments were carried out. In the first type the electrode was subjected to a single negative-going potential sweep between the anodic $E_{s,a}$ and the cathodic $E_{s,c}$ switching potentials at a scan rate $v_c = 0.02 \text{ V s}^{-1}$. The second type of experiment consisted of

potential steps covering the entire PbO electroreduction potential range, $-0.80 \text{ V} \leq E_f \leq -1.02 \text{ V}$.

Computer program in QUICK-BASIC 4.5 were run on an IBM PS/2 50 computer.

Results and Discussion

Voltammetric data

The voltammograms of lead in 5 M H₂SO₄ at $v = 0.02 \text{ V s}^{-1}$ run between $E_{s,c} = -1.30 \text{ V}$ and $E_{s,a} = 0.40 \text{ V}$ for different anodization times τ at $E_{s,a}$ are shown in Fig. 1. The positive-going potential sweep exhibits a well defined anodic current peak (A1) at *ca.* -0.96 V corresponding to the electrooxidation of Pb to Pb(II), followed by a wide passive current region. The cathodic processes occurring in the potential ranges of peaks C2 and C1 can be associated with the electroreduction of basic Pb(II) compounds (mainly PbO) and PbSO₄ layers, respectively^{6,9,11}. Although both the current and charge of cathodic peak C1 increase only slightly with the increase of τ , the location and magnitude of peak C2 depend strongly on τ . Thus, for higher τ the peak potential $E_{p,C2}$ shifts to more negative values and the $\log Q_{C2}$ (the cathodic charge corresponding to peak C2) increases linearly with $\log \tau$ (Fig. 2), according to the following relationship:

$$\log Q_{C2} = -0.50 + 0.51 \log \tau \quad (1)$$

Electroreduction current transients

The potentiostatic cathodic current transients obtained for the PbO electroreduction process at $E_f = -0.90 \text{ V}$ after

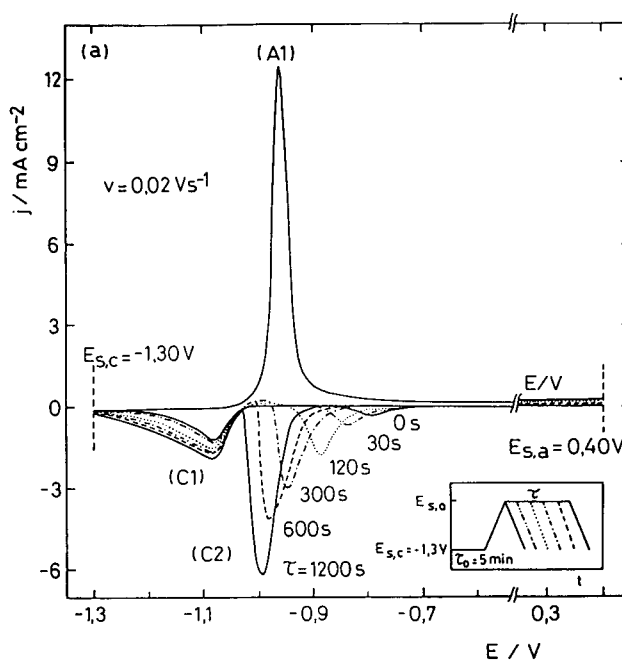


Figure 1. Voltammograms of Pb in 5 M H₂SO₄ run at $v = 0.02 \text{ V s}^{-1}$ between $E_{s,c} = -1.30 \text{ V}$ and $E_{s,a} = 0.40 \text{ V}$, and a potential holding at $E_{s,a}$ for a time τ within the $0 \leq \tau \leq 20 \text{ min}$ range.

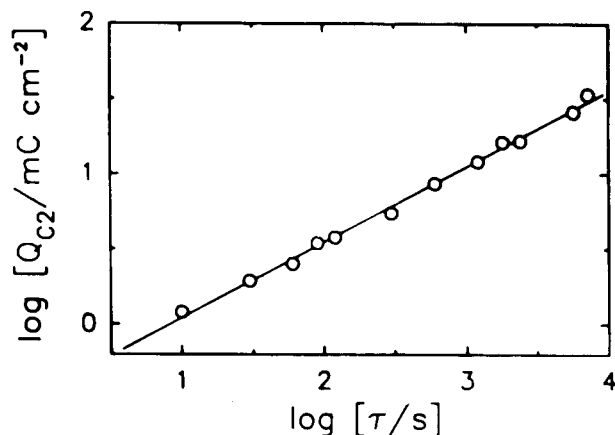


Figure 2. Dependence of Q_{C2} on τ from voltammetric data recorded under the conditions shown in Fig. 1.

a potential step at $E_{s,a} = E_i = 0.40$ V for τ in the range $1 \leq \tau \leq 30$ min can be appropriately described by the expression:

$$j(t) = P_1 [1 - \exp(-P_2 t^3)] \exp(-P_2 t^3) + P_3 \exp(-P_4 t) \quad (2)$$

which mainly corresponds to a progressive nucleation and 3D growth under charge transfer control⁷, whereas the second term, which predominates only at very short times, can be related to an instantaneous nucleation and 2D growth under diffusion control. In Eq. 2 growing nuclei are considered to be right circular cones distributed at random on a planar electrode surface, and the parameters corresponding to the main current contribution are given by:

$$P_1 = z F k_1 \quad (3)$$

$$P_2 = \frac{\pi M^2 k_2^2 A}{3 \rho^2} \quad (4)$$

where k_1 and k_2 denote the rate constants describing crystal growth perpendicular and parallel to the electrode plane surface, respectively, and where A is the nucleation rate constant, ρ the density of the surface layer, and M the molecular weight of PbO. Figure 3 illustrates the good agreement between the experimental and calculated data. The potential E_f was chosen to allow the separation of the electroreduction processes of the inner PbO layer from those corresponding to the PbSO₄ species, which take place when $E_f \leq -1.05$ V. It is important to mention that the electroreduction charge of the current transients increases with τ according to Eq. 1, but for each τ it remains unaltered for E_f varying in the whole potential range of the voltammetric peak C2, *i.e.* -0.82 V $\leq E_f \leq -1.02$ V.

In previous research it was found that the electroreduction mechanism of PbO layers formed at $E_i = 0.40$ V during $\tau = 30$ s, and electroreduced at different E_f follows Eq. 2⁶. The potential dependence of model parameters approached $\log P_h$ ($h = 1, 2$) vs. E_f plots with slopes close to -0.120 V

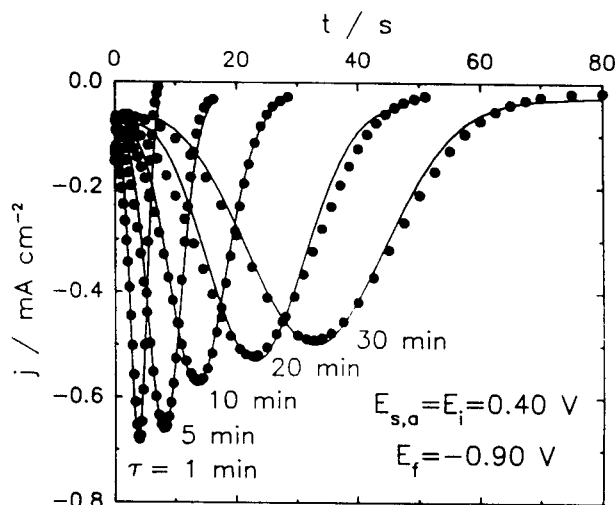


Figure 3. Fitting of current transient data recorded at $E_f = -0.90$ V after a potential holding at $E_i = 0.40$ V during different τ in the $1 \leq \tau \leq 30$ min range, according to Eq. 2 (full traces).

decade⁻¹ and -0.040 V decade⁻¹, respectively⁶. For electroreduction current transients obtained at different E_f values after a potential holding at $E_i = E_{s,a}$ for different τ within the above mentioned range, those slopes are maintained and the values of $\log P_h$ ($h = 1, 2$) can be appropriately represented by the following relationships:

$$\log P_1 = -6.90 - 8.34 E_f - 0.101 \log \tau \quad (5)$$

$$\log P_2 = -21.22 - 25.10 E_f - 1.82 \log \tau \quad (6)$$

On the other hand, the charge density comprised in the case of an instantaneous nucleation and 2D growth under diffusion control is given by the P_3/P_4 ratio⁶. This charge density, which is associated with the small current contribution described for the second term in Eq. 2, seems to be practically constant in the whole E_f range covered in this work, and it involves less than 10% of the whole electroreduction charge. During the anodic polarization, due to the decrease of the concentration of SO₄²⁻ and the increase of the concentration of Pb²⁺ in the inner zone of the passive film, the pH increases⁶. When polarization turns into cathodic values, the Pb²⁺ concentration decreases abruptly and, in order to maintain the electroneutrality of the solution in the pores, H⁺ ions migrate from the solution into the pore, and combine with the OH⁻ liberated from the PbO electroreduction. Thus, the initial electroreduction current decay can be associated with the electroreduction of Pb(II) ions controlled by the diffusion of OH⁻ to the solution or H⁺ to the inner layer of the passive film.

Simulation of single cathodic potential sweeps

In order to achieve the simulation it is initially necessary to describe both the current density j and the surface coverage θ in terms of the dependent variables E and t for any given transient. As the second term of the current

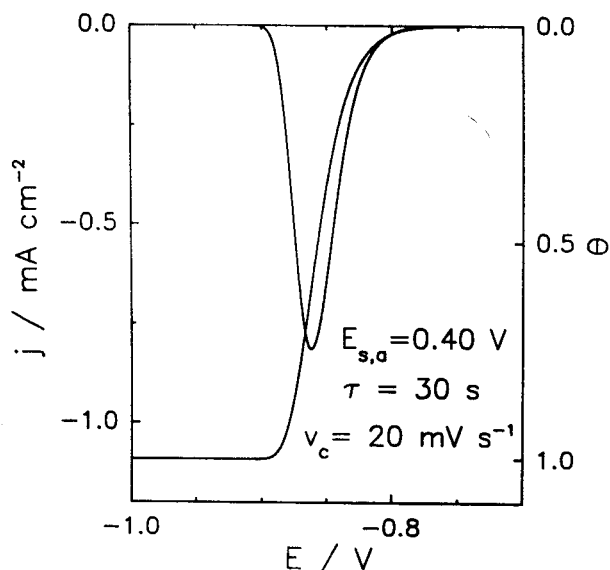


Figure 4. Typical simulated voltammogram and surface coverage for $v_c = 20 \text{ mV s}^{-1}$. Initial surface coverage $\theta_0 = 0.05\%$, $\Delta E = 0.01 \text{ mV}$; $\tau = 30 \text{ s}$.

density in Eq. 2 makes only a small contribution to the whole faradaic charge, for the sake of simplicity it was neglected in the voltammetric simulations. Therefore, the coverage θ_i by the PbO species at the inner surface layer can be expressed for a 3D progressive nucleation and growth process under charge transfer control by⁷:

$$1 - \theta_i = \theta = 1 - \exp(-P_2 t^3) \quad (7)$$

where $\theta = (1 - \theta_i)$ represents the coverage by the growth phase, that in this case is related to the Pb resulting from the PbO electroreduction. This means that θ corresponds to the surface fraction due to free Pb metal not covered by the PbO species. Therefore, at the end of the electroreduction process for E_f values set in the $-0.80 > E_f > -1.04 \text{ V}$ range, θ tends to 1, although the outer PbSO₄ layer, which can be electroreduced only in the case where $E_f < -1.05 \text{ V}$ ⁶, remains on the metal surface. Calculations based on the use of the PbO coverage, which tends to 0 when $t \rightarrow \infty$, give similar results.

The use of Eqs. 5 to 7 combined with the first term of Eq. 2 allows the complete description of the voltammograms. The method has been described in detail elsewhere^{8,11,12}. Because of the exponential dependence of the model parameters P_1 and P_2 with the electroreduction potential given in Eqs. 5 and 6, it is necessary to define the initial surface coverage θ_0 . The linear potential sweep simulation initiates at a certain arbitrary potential, but no matter which potential is chosen there will always be a corresponding finite value of θ . Throughout the present work the initial surface coverage was taken as 0.05% at $E_{s,a}$. Furthermore, as a potential sweep will be approximated with the sum of a number of finite potential increments (ΔE), it is clearly important to test whether the simulated data

converges as ΔE diminishes under a standard set of conditions. Accordingly the simulation procedure can be demonstrated to be self-contained. For the following constants: $\tau = 30 \text{ s}$, $v_c = 0.02 \text{ V s}^{-1}$, $E_{s,a} = 0.40 \text{ V}$, $\theta_0 = 0.05\%$, $R_{ohmic} = 0 \Omega$, ΔE was varied between 10 and 0.01 mV, and it was found that the simulation does indeed converge for $\Delta E \leq 0.1 \text{ mV}$.

A typical voltammogram is given in Fig. 4 for $v_c = 0.02 \text{ V s}^{-1}$, $\theta_0 = 0.05\%$ and $\Delta E = 0.01 \text{ mV}$. The E/j shape corresponds to expectations: a slowly rising current followed by a rapid passivation. Such an asymmetric shape is to be expected in view of the high slopes found for the potential model parameter dependence, as can be seen in Eqs. 5 and 6. Owing to the exponential dependence the electroreduction process begins slowly, but its rate increases with the potential, so that after the maximum ($j_{p,C2}$) the current falls abruptly. The dependence of the surface coverage on potential is also shown in Fig. 4. It is interesting to note that at the peak of the voltammogram the electrode surface coverage reaches *ca.* 60%.

This value can be attributed to the fact that j_p is a function of the growth model parameters, the potential dependence of these kinetic parameters, and the nature of the overlap of the expanding nuclei⁸.

The influence of the anodization time τ

The influence of τ on the simulation was investigated for $\theta_0 = 0.05\%$. At constant τ , as ΔE was diminished the convergence was as expected, and ΔE was fixed for convenience at $\Delta E = 0.01 \text{ mV}$. The resulting voltammograms shown in Fig. 5 exhibit trends identical to the experimental ones. The apparent cathodic charge density of the simulated voltammograms increases according to τ , following Eq. 1. As the first term in Eq. 2 comprises the main current contribution, the cathodic charge involved in the electroreduction of PbO layers can be approximated by⁶:

$$Q \approx 0.18 P_1 P_2^{-1/3} \quad (8)$$

and, hence:

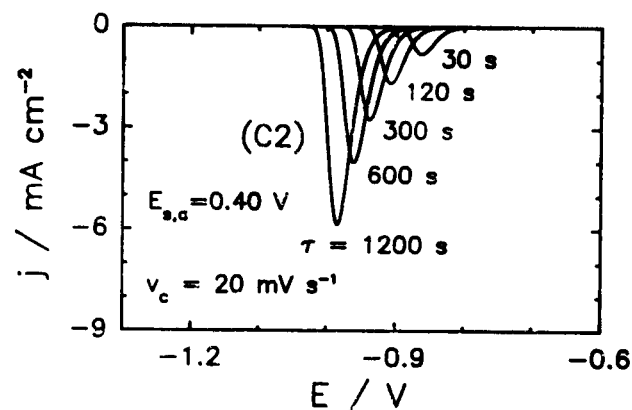


Figure 5. Influence of τ on the simulated voltammetric data.

$$\log Q \approx \log 0.18 + \log P_1 - (1/3) \log P_2 \quad (9)$$

Thus, the parametric functionalities of data given by Eqs. 5 and 6 approach the values predicted by the well-established reaction model, according to Eqs. 1 and 9.

Conclusions

The electroreduction of basic Pb(II)-containing surface compounds was investigated by linear sweep voltammetry and potentiostatic step techniques.

Through the potentiostatic current transient data, the electroreduction of the PbO layer can be explained in terms of a process limited by a progressive nucleation and 3D growth under charge transfer control including a death correction term for right circular cone phase centers.

The kinetic data obtained from the potentiostatic current transient analysis permitted a computer simulation of the cathodic linear potential sweep of voltammograms corresponding to the electroreduction of the PbO. The good agreement between simulated and experimental voltammograms found at $v_c = 0.02 \text{ V s}^{-1}$ and anodization times in the $1 \leq \tau \leq 30$ min range confirms the validity of the proposed model.

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