

The effect of expanders on lead-sulphate formation and reduction

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Abstract

The influence of some organic expanders on the formation of lead-sulphate has been studied by means of potentiostatic transients. The experimental data have been discussed according to the theories which have been proposed in the literature for the electro-crystallisation of lead-sulphate and lead. The discussion of the data obtained confirms the inhibiting effect of the expanders on lead sulphation. In fact, the tests showed that, when the expanders are added to the electrolyte, a longer time is required to reach the current maximum of the $i(t)$ curve and a reduction of its intensity. According to the theoretical interpretation, this finding indicates a decreasing of the kinetic constant of the solid state process. The analysis of the $i(t)$ transients obtained during the sulphate reduction revealed an influence of expanders only when the sulphate layers has been formed in their presence. Thus, it seems that the adsorption of the organic expanders on lead is of primary importance for their action while adsorption on lead-sulphate appears to be negligible. © 2000 Elsevier Science S.A. All rights reserved.

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1. Introduction

It is known [1,2] that lead passivation in sulphuric acid occurs through two parallel processes, lead dissolution followed by lead-sulphate precipitation and a solid state mechanism. It has also been reported [3] that some organic substances used as expanders in the manufacturing of negative plates inhibit this last process.

The solid state processes for a sulphate layer formation have been extensively studied [4], the literature reports various calculations on different mechanism for layers formation, by instantaneous or progressive nucleation followed by a two or three-dimensional growth of the crystals. As far as lead-sulphate is concerned, recently a more complex interpretation has been proposed [5,6] which takes into account also the process of lead dissolution and precipitation.

Conversely, the reduction of the lead-sulphate layers has been discussed according to a mechanism of dissolution and electro-crystallisation under diffusional control [7–9].

In the present work, the results of tests carried out with pure electrolyte and with the addition of some expanders used in battery plates manufacturing, have been reported.

1.1. Lead-sulphate formation

The trend of the potentiostatic transients $i(t)$ can be described by kinetic laws [4] which depend on the modalities of crystals nucleation and growth. This can be illustrated in the case of instantaneous nucleation followed by a bi-dimensional growth of a lead-sulphate layer of thickness h , being M the molar weight of lead-sulphate (303 g), ρ its density (6.2 g cm⁻³), N° the number of initial nuclei and K the rate constant for crystallisation, in this case the following expression of the current/time curve is obtained:

$$i = at \exp(-bt^2) \quad (1)$$

the parameters a and b being defined by:

$$a = 2zF\pi hK^2N^\circ(M/\rho) \quad b = \pi K^2N^\circ(M/\rho)^2.$$

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The $i(t)$ curve presents a maximum value i_{\max} for the time t_{\max} which depends on the parameters a and b according to the following expressions:

$$t_{\max}^2 = \frac{1}{2b} i_{\max} = at_{\max} e^{-1/2}.$$

The mathematical expression of the transient can be normalised by computing the dimensionless expression:

$$\frac{i}{i_{\max}} = \frac{t}{t_{\max}} \left[\frac{1}{2} - \frac{1}{2} \left(\frac{t}{t_{\max}} \right)^2 \right]. \quad (2)$$

Ref. [4] reports similar relationships for the cases of progressive nucleation and for three-dimensional crystal growth. For all the proposed mechanisms [4], the $i(t)$ expression can be normalised and, consequently, the expression $K\sqrt{N^\circ}$ can be related to the time t_{\max} . The normalised function can be compared to the experimental curve in order to determine the crystallisation mechanism which better adheres to the experimental reality. Thus, some relevant parameters of the kinetic expression can be obtained.

In the case of instantaneous nucleation followed by a bi-dimensional crystal growth, after substitution of numerical values, the following expressions are obtained:

$$K\sqrt{N^\circ} = \frac{8.16 \times 10^{-3}}{t_{\max}}$$

$$h = 4.17 \times 10^{-7} i_{\max} t_{\max}.$$

With respect to the previous approach, the process of lead-sulphate formation is complicated by the need of taking into account the low, but non-zero, solubility of lead ions, the characteristics of the membrane sulphate layer and the porosity of lead. Hampson and Lakeman [10] discussed the trend of potentiostatic transients in terms of three different behaviours according to the value of the potential applied for PbSO_4 formation. For low potential values ($V < -920$ mV/vs. $\text{Hg}/\text{Hg}_2\text{SO}_4$ electrode) the $i(t)$ curve presents at the beginning a parabolic trend, for intermediate potentials ($-920 \div -880$ mV/vs. $\text{Hg}/\text{Hg}_2\text{SO}_4$ electrode) the initial part of curve is linear, while for higher potentials ($V > -880$ mV/vs. $\text{Hg}/\text{Hg}_2\text{SO}_4$ electrode) the transient appears to be distorted. All three trends of the transient curve have been analysed by considering different crystallisation laws: the parabolic trend is compatible with instantaneous nucleation followed by three-dimensional growth; the linear behaviour can be interpreted by a change from three to two-dimensional crystal growth; the distortion at high potential values has been attributed to the adsorption of chemical species onto the centres under growth [11].

An improvement in the interpretation of the formation of lead-sulphate layers on lead, was proposed by Varela et al. [5,6], by considering lead ions dissolution together with sulphate formation by a dissolution/precipitation mechanism. Thus, the trend of potentiostatic transients can be mathematically described by considering that the current

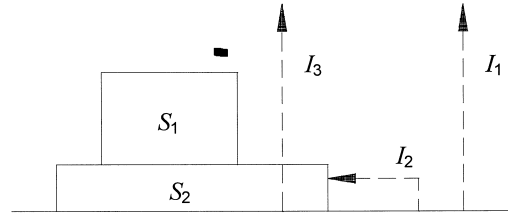


Fig. 1. Schematic representation of the lead-sulphate layers under growth during anodic oxidation of lead in sulphuric acid.

required for lead-sulphate formation, following the anodic potential step, is the sum of three terms.

The first one (I_1) is due to the dissolution of lead into the electrolyte, the second one (I_2) corresponds to the formation of a semipermeable membrane layer of lead-sulphate (by bi-dimensional instantaneous nucleation for example), and the third one (I_3) is due to a process of migration of lead through the semipermeable layer, followed by its precipitation as lead-sulphate crystals.

With reference to Fig. 1, where a schematic representation of the growing lead-sulphate layer is given, if S_1 is the surface area covered with lead-sulphate crystals, and S_2 the area covered by the semipermeable membrane of lead-sulphate, the three terms of the current, corresponding to the rates of the above described processes, can be expressed according to the following relationships:

$$I_1 = I^\circ(1 - S_2) \quad (3)$$

$$I_2 = at \exp(-bt^2) = Q_g \frac{dS_2}{dt} \quad (4)$$

$$\frac{dS_1}{dt} = K_p(S_2 - S_1) \quad (5)$$

$$I_3 = 2FK_f(S_2 - S_1) \quad (6)$$

where:

$$a = 2zF\pi hK^2(M/\rho)N^\circ, \quad b = \pi N^\circ K^2(M/\rho)^2,$$

$$Q_g = \frac{a}{2b}$$

I° is the rate of lead dissolution from an active surface; K_p is the rate constant of surface blockage due to the passive film; K_f is the rate constant for the dissolution of the conducting film; K is the rate constant for crystals growth; M is the molar mass of lead-sulphate; ρ is the density of lead-sulphate; h is the film thickness; N° is the number of nucleation centres; z is the number of electrons involved in the electrochemical reaction; F the Faraday constant.

By solving the set of differential equations, the surface areas S_1 and S_2 can be obtained as a function of time and then the three terms I_1 , I_2 and I_3 of the current can be derived, whose sum is the total current I .

1.2. Lead-sulphate reduction

Scharifker and Mostany [7] and Scharifker and Hills [8] have investigated the reduction of lead ions, which should

occur according to a mechanism of three-dimensional instantaneous nucleation and growth of crystals under diffusional control. The following relationship, which fairly well fits the experimental values, has been proposed:

$$i(t) = \frac{P_1}{\sqrt{t}} [1 - \exp(-P_2 t)] \quad (7)$$

where:

$$P_1 = zFc_j \frac{\sqrt{D_j}}{\pi} \quad P_2 = N^\circ \pi D_j \sqrt{8\pi c_j M \rho^{-1}}.$$

Scharifker applied this equation to lead nucleation from a lead nitrate solution, thus, D_j and c_j refer to the diffusivity and concentration of lead ions in the electrolyte. Varela et al. [9] used a similar approach for lead-sulphate reduction in sulphuric acid, by considering for D_j and c_j the diffusivity and concentration of lead ions in the sulphate layer and introducing in Eq. (7) an additional term $P_3 t^{-1/2}$ accounting for the reduction of Pb^{2+} contained in the electrolyte within the pores of the layer, where $P_3 = zFD_i^{1/2} \Delta c_i / \pi^{1/2}$, D_i and Δc_i being the diffusion coefficient and concentration gradient of the diffusing ions in the limiting layer.

Also in the case of reduction, as in the previous case of lead-sulphate formation, the transient curve presents a maximum of the absolute value of the current, i_{peak} , whose value can be obtained by derivation of Eq. (7), allowing the expression of such equation in a dimensionless form:

$$\left(\frac{i}{i_{\text{peak}}} \right)^2 = 1.9542 \frac{t_{\text{peak}}}{t} \left\{ 1 - \exp \left[-1.2564 \left(\frac{t}{t_{\text{peak}}} \right) \right] \right\}^2. \quad (8)$$

For lead-sulphate, setting $k = \sqrt{8\pi c_j M \rho^{-1}}$, the following values of i_{peak} and t_{peak} can be derived:

$$i_{\text{peak}} = 0.6382 zFD_j c_j \sqrt{N^\circ k} \quad (9)$$

$$t_{\text{peak}} = \frac{1.2564}{N^\circ \pi k D_j}. \quad (10)$$

From the experimental values of the product $i_{\text{peak}}^2 t_{\text{peak}}$, the expression $c_j \sqrt{D_j}$ can be computed and assuming a reasonable value for the diffusivity D_j in the sulphate layer, the values of c_j and N° can be obtained.

2. Experimental

The processes of lead-sulphate formation and reduction has been studied by means of potentiostatic transients, i.e., by applying a potential step in the anodic or cathodic direction starting, respectively, from a potential value corresponding to a completely reduced lead-surface (e.g., -1.2 V/vs. Hg/Hg₂SO₄ electrode) or from a potential at

which the lead is covered only by a sulphate layer (e.g., -0.8 V/vs. Hg/Hg₂SO₄ electrode).

The electrodes, obtained by cutting a pure lead rod (purity 99.9985%), have been embedded in a resin in order to have a flat circular exposed area of about 1 cm². To investigate the formation of lead-sulphate by means of potentiostatic transients the lead electrode has been initially maintained at a potential of -1.2 V/vs. Hg/Hg₂SO₄ electrode for 30 min to obtain a complete reduction of its surface, then the potential has been stepped to -0.89 V/vs. Hg/Hg₂SO₄ electrode. The duration of this final step, during which recording of the current intensity took place, varied from 10 to 100 s. This procedure was repeated three times, then 20 ppm of the expander were added to the electrolyte and three other similar oxidation/reduction cycles were carried out.

The transient test corresponding to lead-sulphate reduction was carried out on sulphate formed at -0.8 V/vs. Hg/Hg₂SO₄ electrode. To this purpose, the lead was oxidised by means a potential ramp (20 mV/s) starting from -1.2 V/vs. Hg/Hg₂SO₄ electrode and terminating at the chosen oxidation potential. Then the electrode was maintained at the upper potential for 180 s before the reduction step. The reduction was obtained by a potentiostatic pulse from the passivation potential to a potential ranging between -1.07 V/vs. Hg/Hg₂SO₄ electrode and -1.1 V/vs. Hg/Hg₂SO₄ electrode.

The experimental apparatus was the AMEL mod. 5000 Electrochemical System, controlled by a PC. A computer program was purposely developed for managing the recording of fast transients. The sampling time used to record the current values during the transient can be set in the range from 100 μs to 1 s.

All the tests were carried out at a temperature of 25°C in 0.5 M sulphuric acid. The organic additives were previously dissolved in the acid and then tested in the cell. In order to help the dissolution process, the lignosulphonate-type substances were first dissolved in a small amount of NaOH 0.1 M, and then added to the sulphuric acid solution, whose concentration was properly adjusted.

3. Results and discussion

In order to interpret the experimental transients for lead-sulphate formation, the Varela et al. [5,6] approach was used, by preliminarily considering the influence on the computed curves of the parameters I° , zFK_f and K_p appearing in the set of Eqs. (3)–(6).

This computation has been carried out with the base values of $a = 2$, $b = 0.025$, $I^\circ = 0.1$, $zFK_f = 2$ and $K_p = 0.1$. By varying one single parameter, keeping the other constant, the results reported in Figs. 2–4 were obtained, which refer to the influence of parameters I° , zFK_f and K_p , respectively. It can be observed that I° greatly affects

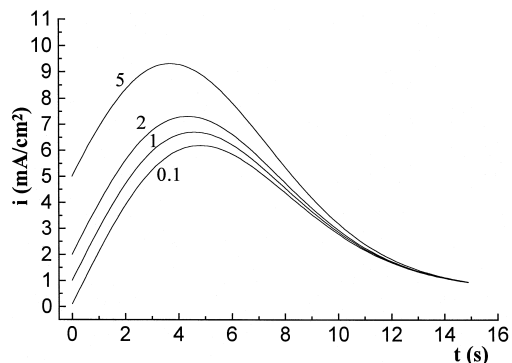


Fig. 2. Influence of parameter I^o on the transient profiles computed according to Eqs. (3)–(6).

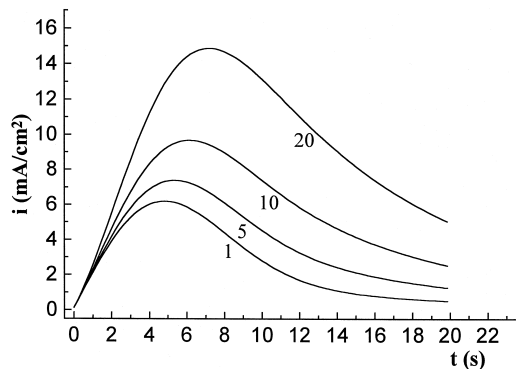


Fig. 3. Influence of parameter K_f on the transient profiles computed according to Eqs. (3)–(6). The numerical values shown on the curves refer to the expression zFK_f .

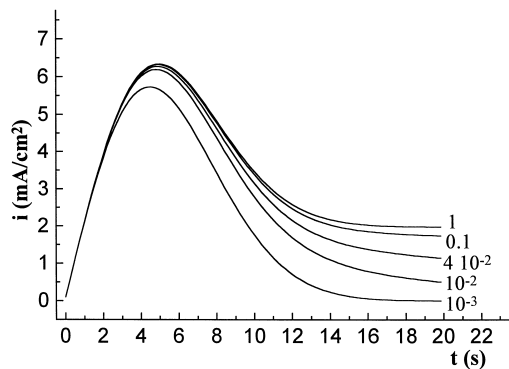


Fig. 4. Influence of parameter K_p on the transient profiles computed according to Eqs. (3)–(6).

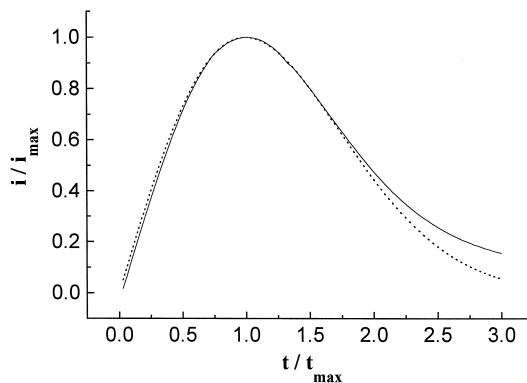


Fig. 5. Normalised curves i/i_{max} vs. t/t_{max} . The solid curve was computed by means of Eqs. (3)–(6) with $I^o = 0.1$, $a = 2$, $b = 0.025$, $zFK_f = 2$ and $K_p = 0.1$; the dashed curve was computed according to Eq. (2).

the initial part of the transient, K_f influences the position and height of the current peak, while K_p exhibits its influence on the final part of the curve.

With the lowest and highest value of the above parameters, the normalised curves i/i_{max} vs. t/t_{max} have been traced and compared to the curves obtained by assuming a bi-dimensional crystals growth with instantaneous nucleation according to Eq. (2). An example of this calculation is reported in Figs. 5 and 6, where the dashed curves refer to the computation by means of Eq. (2), while the solid curves are obtained by solving Eqs. (3)–(6) with $I^o = 0.1$, Fig. 5 and $I^o = 5$, Fig. 6, all other parameters were set, for both diagrams, to the arbitrary base value previously reported.

The possibility of varying five parameters renders rather easy the fitting of the experimental transient by the computed curve. In fact, the comparison between the theoretical current transients and the experimental ones is pretty good. Fig. 7 shows the three components I_1 , I_2 , I_3 of the total current I computed by fitting the experimental curve

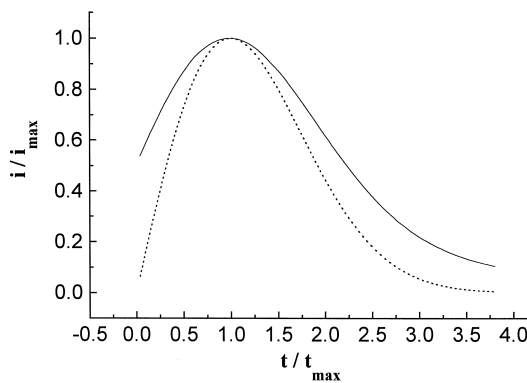


Fig. 6. Normalised curves i/i_{max} vs. t/t_{max} . The solid curve was computed by means of Eqs. (3)–(6) with $I^o = 5$, $a = 2$, $b = 0.025$, $zFK_f = 2$ and $K_p = 0.1$; the dashed curve was computed according to Eq. (2).

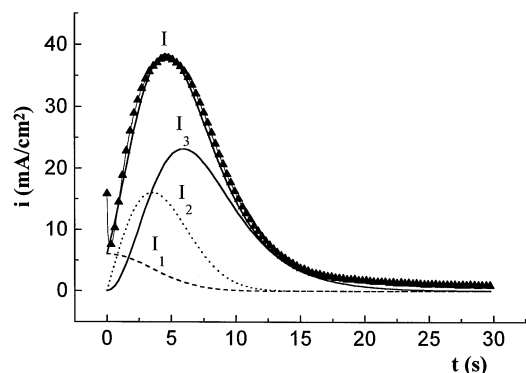


Fig. 7. Components I_1 , I_2 , I_3 of the total current I , computed by fitting the experimental curve obtained at 25°C for pure lead in 0.5 M sulphuric acid. Curve fitting was achieved with the following values of the parameters: $a = 7.5$, $b = 0.04$, $I^\circ = 6$, $zFK_f = 60$ and $K_p = 0.3$. Triangles refer to the experimental curve.

obtained at 25°C for pure lead in 0.5 M sulphuric acid. Curve fitting in Fig. 7 was obtained with the following values of the parameters: $a = 7.5$, $b = 0.04$, $I^\circ = 6$, $zFK_f = 60$ and $K_p = 0.3$.

When organic expanders are added to the sulphuric acid solution the current transient is modified and, consequently, the parameters for curve fitting are markedly affected. Two examples are reported in Figs. 8 and 9 where the plotted curves have similar definition as in Fig. 7, i.e., the three computed components plus the total current, compared to the experimental curve obtained in the presence of 20 ppm of the expander. The organic expander used for the experimental data of Fig. 8 is S004, which is a sodium lignosulphonate, while the expander of Fig. 9 is DD5, a blend of kraft lignosulphonate with condensed naphthalenesulphonate. Curve fitting for Fig. 8 resulted from the following values of the parameters: $a = 1.2$, $b = 0.003$, $I^\circ = 3$, $zFK_f = 13$ and $K_p = 0.025$; those of Fig. 9 were: $a = 1.6$, $b = 0.006$, $I^\circ = 6$, $zFK_f = 14$ and $K_p = 0.03$.

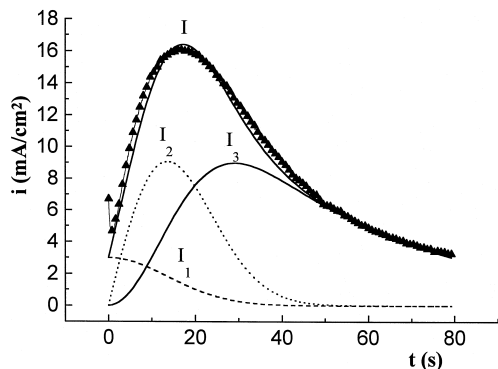


Fig. 8. Components I_1 , I_2 , I_3 of the total current I , computed by fitting the experimental curve obtained at 25°C for pure lead in 0.5 M sulphuric acid containing 20 ppm of expander S004. Curve fitting was achieved with the following values of the parameters: $a = 1.2$, $b = 0.003$, $I^\circ = 3$, $zFK_f = 13$ and $K_p = 0.025$. Triangles refer to the experimental curve.

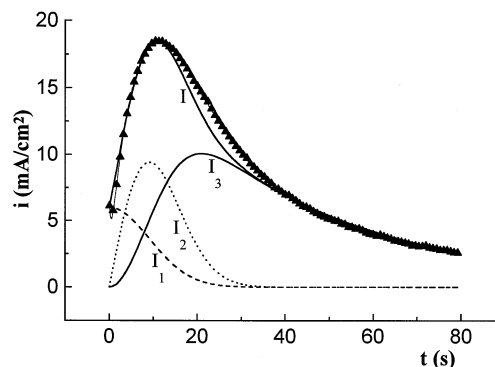


Fig. 9. Components I_1 , I_2 , I_3 of the total current I , computed by fitting the experimental curve obtained at 25°C for pure lead in 0.5 M sulphuric acid containing 20 ppm of expander DD5. Curve fitting was achieved with the following values of the parameters: $a = 1.6$, $b = 0.006$, $I^\circ = 6$, $zFK_f = 14$ and $K_p = 0.03$. Triangles refer to the experimental curve.

The fitting of experimental data in the presence of expanders appears to be sufficiently good. It is interesting to note that such fitting was obtained by markedly decreasing, with respect to the expander free sulphuric acid solution, the parameters b , K_f and K_p .

As far as the tests on lead-sulphate reduction are concerned, the experiments carried out without expanders are in good agreement with those found by Varela et al. [9]. We confirmed that the computation according to the model proposed by such authors, assuming for the diffusivity D_j the value of $3 \times 10^{-11} \text{ cm}^2 \text{ s}^{-1}$, provided a value of the concentration c_j close to $0.5 \rho/M$, and a value of the number of nuclei N° of $8 \times 10^{-10} \text{ cm}^{-2}$. An example of such computation is shown in Fig. 10, where the normalised curves $i/|i_{\text{peak}}|$ vs. t/t_{peak} both for the experimen-

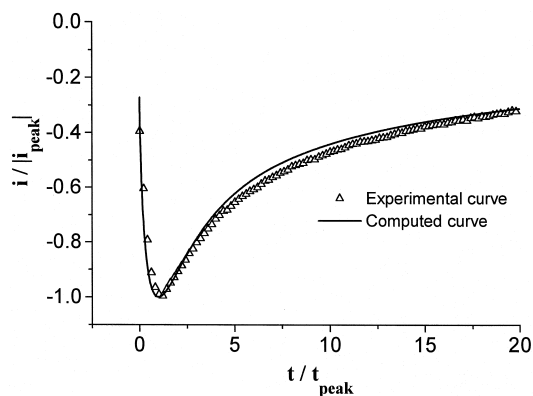


Fig. 10. Comparison of normalised curves $i/|i_{\text{peak}}|$ vs. t/t_{peak} referring to an experimental reduction transient (triangles) and a computed curve (solid line) according to Eq. (8). The experimental conditions correspond to the reduction at $-1 \text{ V/vs. Hg/Hg}_2\text{SO}_4$ electrode of a lead-sulphate layer previously formed at $-0.8 \text{ V/vs. Hg/Hg}_2\text{SO}_4$ electrode in a 0.5-M sulphuric acid solution free of expander.

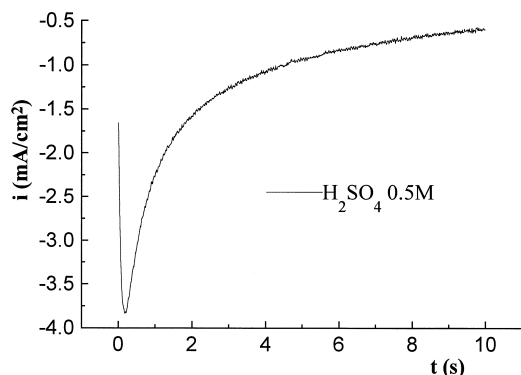


Fig. 11. Experimental reduction transient obtained at -1 V/vs. Hg/Hg₂SO₄ electrode in expander free 0.5 M sulphuric acid.

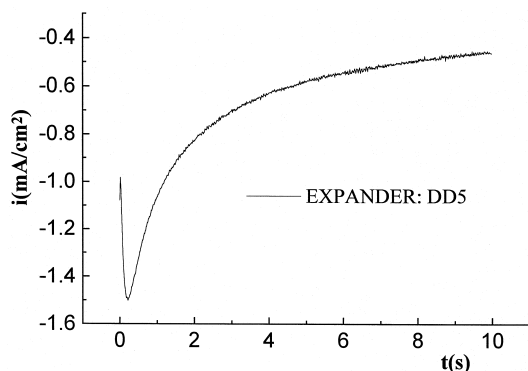


Fig. 12. Experimental reduction transient obtained at -1 V/vs. Hg/Hg₂SO₄ electrode in 0.5 M sulphuric acid containing 20 ppm of expander DD5.

tal reduction transient and that computed according to Eq. (8) are plotted. The experimental data in Fig. 10 refer to the reduction at -1 V/vs. Hg/Hg₂SO₄ electrode of a lead-sulphate layer previously formed at -0.8 V/vs. Hg/Hg₂SO₄ electrode in a 0.5-M sulphuric acid solution free of expander.

When an expander is added to the sulphuric acid solution, a change is observed in the transient response, as indicated in the example reported in Figs. 11 and 12, where a marked decreasing of the current peak is observed in the presence of the expander. The computation carried

Table 1

Values of parameters obtained for the experimental data of Figs. 11 and 12

	Expander free 0.5 M H ₂ SO ₄	0.5 M H ₂ SO ₄ with 20 ppm of expander
t_{peak} (s)	0.21	0.11
i_{peak} (mA)	3.82	1.49
c_j (mol cm ⁻³)	0.014	0.006
k	4.14	2.76
N°	2×10^{10}	4×10^{10}

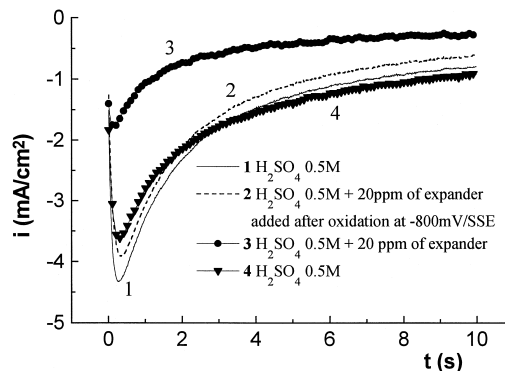


Fig. 13. Experimental reduction transients obtained at -1 V/vs. Hg/Hg₂SO₄ electrode in 0.5 M sulphuric acid under different conditions: curve 1, without expander; curve 2, by adding 20 ppm of expander Diwatex-XP9 after the formation of the PbSO₄ layer at -0.8 V/vs. Hg/Hg₂SO₄ electrode, before the reduction step; curve 3, by adding 20 ppm of expander Diwatex-XP9 before PbSO₄ formation and reduction; curve 4, by substituting, after step 3, the electrolyte solution containing the expander with a fresh one without expander.

out according to Eqs. (8)–(10) provides the values reported in Table 1.

For this test the expander used was Diwatex-XP9, which is a sodium salt of sulphonated kraft lignin derived from softwood. The test was carried out by adding the expander to the sulphuric acid solution before the formation of the lead-sulphate layer. If a different experimental procedure is adopted, i.e., after two subsequent oxidations and reductions of the lead electrode without expander, the organic substance is added to the solution after formation of the lead-sulphate layer, the reduction transient is practically identical to the one obtained without the expander, Fig. 13. On the contrary, if the expander is added to the solution before lead-sulphate formation, the transient curve is markedly changed, curve 3 in Fig. 13; see also Fig. 12.

This effect was confirmed by substituting the electrolyte solution with a new one free of expander, after performing oxidations and reductions in the presence of the expander. It can be observed that, after substituting the electrolyte solution, gradually the reduction transient (curve 4 in Fig. 13) tends to the one obtained in sulphuric acid free of expander.

4. Conclusions

As far as the formation of lead-sulphate is concerned, the results presented in this work, based on the potentiostatic transient technique, indicate that the expanders exert a marked influence on the kinetics of the formation of the sulphate layer. Namely, all the tested organic substances cause a decreasing in the rate of formation of the semipermeable PbSO₄ layer. This conclusion comes from the experimental observation that the time corresponding to

the current peak in the transient curve is increased in the presence of expanders and can be justified both by interpreting the transients on the basis of instantaneous nucleation followed by two-dimensional crystal growth and by interpreting the curves by the model proposed by Varela et al. [5,6].

In the case of lead-sulphate reduction to metallic lead, it has been observed that the expanders lower the concentration of mobile ions in the sulphate layer, as a result of the different structure of the passivating film formed in the presence of the organic substance.

A more careful examination of the overall results obtained with different expanders, points out some aspects of the kinetic mechanism for lead-sulphate formation, which indicate the need for further investigation, both experimental and theoretical, in order to verify the capability of the proposed models to describe the real behaviour of the lead/lead-sulphate system.

Particularly, while on one hand it appears clear that potentiostatic transients $i(t)$ cannot be completely interpreted by a simple model based on instantaneous nucleation and two-dimensional crystal growth, on the other hand, the possibility of changing five parameters in the more complex model proposed by Varela et al., achieves a good fitting of the experimental curves well beyond the current peak. It has also been observed that the presence of organic expanders causes a marked decreasing of the rate of formation of the semipermeable lead-sulphate layer, together with the decreasing of the rate constant K_p of surface blockage due to PbSO_4 crystals and the constant K_f related to migration of Pb^{2+} in the lead-sulphate film.

These findings could be explained by assuming a relatively important adsorption of the expanders not only on metallic lead, but also on lead-sulphate. Moreover, the expander should also influence migration of lead ions in the thin PbSO_4 membrane layer. Though this last assumption could be confirmed by the decrease, in the presence of expanders, of the concentration of mobile ions in the film as derived by the elaboration of the experimental data, the

hypothesis on the adsorption of the expanders onto lead-sulphate does not find, at present, any experimental confirmation.

In conclusion, the potentiostatic transient technique, both for lead-sulphate formation and reduction, appears to be a very important tool for understanding the involved kinetic mechanism also in the presence of organic expanders. The application of theoretical models proposed in the literature ends to a fairly good formal description of the transient curves, but further investigation is needed in order to physically describe all the aspects related to structural changes caused by the expanders.

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