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Cycling of electrodeposited beta lead dioxide

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The electrochemical behaviour of lead dioxide cycled in sulphuric acid under galvanostatic (discharge) and potentiostatic (charge) conditions has been investigated. The results illustrate the effect of the sulphate barrier layer forming on PbO_2. This layer shifts the equilibrium potential of the electrodes without influence on the kinetics of the reduction, which seems to be dependent on a diffusive step associated with the onset of an O^{2-} gradient in the dioxide. As for the sulphate oxidation, it has been found that this process is mainly affected by the end potential reached during the previous galvanostatic reduction.

1. Introduction

The literature reports a great number of investigations on the properties of the alpha and beta allotropic forms of lead dioxide, electrodeposited on various substrates, or formed on lead, or present in positive lead–acid battery plates.

With regard to dioxide reduction, Mark [1] showed the different behaviour of the two allotropes and the findings can be related to the results of Angstadt *et al.* [2] who studied electrodes made from a mixture of the two forms. Canagaratna *et al.* [3, 4] found a single current peak corresponding to $PbSO_4$ formation in voltammetric curves of beta PbO_2; the reduction process seems to be controlled by a charge transfer step on a surface undergoing a decrease in area with time. Another peak, appearing at higher potential, has been attributed to absorbed oxygen reduction.

Nguyen Cong *et al.* [5, 6] attributed the different behaviour of the allotropes to the characteristics of the $PbSO_4$ obtained during reduction and found that alpha PbO_2 forms when pure beta PbO_2 is cycled [6]. Recent investigations [7] show that a colloidal sulphate film forms on the PbO_2 surface as a consequence of a large supersaturation of lead ions occurring at the beginning of the reduction.

A different approach to this topic has been followed by Pohl and Rickert [8] who considered the change of PbO_2 stoichiometry and recognized two processes in the reduction, the first involving lead, hydrogen and oxygen partial reactions, associated with changing stoichiometry, and a subsequent dissolution of the dioxide with $PbSO_4$ formation.

Concerning the sulphate oxidation, Fleischmann [9] and Hampson and coworkers [3–4, 10–11] have shown that, in potentiostatic conditions, the process is controlled by nucleation and three-dimensional growth of the PbO_2 crystals. No nucleation process should occur in the case of $Pb/PbO_2/PbSO_4$ and $Pt/PbO_2/PbSO_4$ electrodes. Dawson *et al.* [12], in partial contrast with the above conclusions, postulated an initial oxidation of the basic lead sulphate formed during the PbO_2 discharge underneath the sulphate layer, followed by the oxidation of $PbSO_4$.

Nguyen Cong *et al.* [5, 6] attributed the shape of the potentiostatic charge curves to a change with time of the number of the reactive centres present in the lead sulphate. More recently Takehara and Kanamura [7, 13, 14] explained the trend of the $I(t)$ curves with a change of the reaction area, as the electrochemical process appears to be controlled by charge transfer.

In the present paper we have pursued the study of the electrochemical behaviour of PbO_2 [15–17] limiting our investigations to the beta form and paying particular attention to the relation between the electrode behaviour and the morphology of its surface and to the eventual alpha allotrope formation.

2. Experimental details

Beta PbO_2 was anodically electrodeposited on Pt foils of 1 cm^2 of useful area, according to a procedure reported elsewhere [15]. The mean thickness of the PbO_2 layers (from 3 to 10 μm) was determined analytically. The electrode potential was referred to a standard Hg/Hg_2SO_4 half cell. All experiments were run at a temperature of 23° C.

The electrodes, just after dioxide electrodeposition, were immersed in 8 N H_2SO_4 saturated with lead sulphate and anodically polarized at a constant current of 10 μA for 15 min. The system was then left at open circuit for 1 h and at the end of this period the rest potential was measured and the reduction of lead dioxide at constant current, I_r, (from 0.5 to 1 mA) was started. The end of discharge potential, V_r, was chosen between 950 and -300 mV.

After discharge, the electrodes were oxidized at a constant potential of 1300 mV. The oxidation was stopped for values of the ratio R between the anodic and cathodic electric charge ranging between 1 and 3. The reduction–oxidation cycles were repeated at least 10 times. Some electrodes, at different state of charge, were examined by means of scanning electron micro-

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scopy (SEM) and the deposit was analysed using the X-ray diffraction technique.

3. Results and discussion

3.1. *Galvanostatic reduction*

Freshly electrodeposited PbO_2 attains, in 8 N H_2SO_4 solution, a rest potential of about 1050 mV. During the first galvanostatic discharge (Fig. 1), the electrode potential arrests at a value ranging from 920 to 980 mV. After the first reduction and oxidation cycle the dioxide potential shifts to more positive values becoming, at rest, greater than 1100 mV. An additional plateau, at a potential above 1000 mV, appears in the $V(t)$ discharge curves (Fig. 1).

These potential arrests, as is well known [1–2, 18, 19], correspond to lead sulphate formation. Our previous investigations [16, 17] have shown that at the end of PbO_2 discharge most of the lead sulphate exhibits an evident crystalline structure while the remaining part appears as a very thin film covering lead dioxide crystals which are still clearly visible with SEM.

During the reduction the electrode potential decreases very slowly to a value V_0, equal to about 900 mV, at which the sulphate layers must be considered complete. On continuing the discharge the potential drops to a lower value, V_1, approximately equal to -300 mV and from this moment, basic lead sulphate is obtained, followed by metallic lead formation and by hydrogen evolution [5, 6, 18, 20, 21].

Owing to the high overvoltage of oxygen on PbO_2 the potentials measured at open circuit can be considered as near-equilibrium potentials. Thus, their shift towards positive values after the first $PbSO_4$ oxidation can be attributed to a change of the chemical potential of compounds or ions determining the free energy of the electrochemical reaction. It seems likely that an increase in the local concentration of the ions (H^+ and SO_4^{2-}) takes place on the electrode after oxidation.

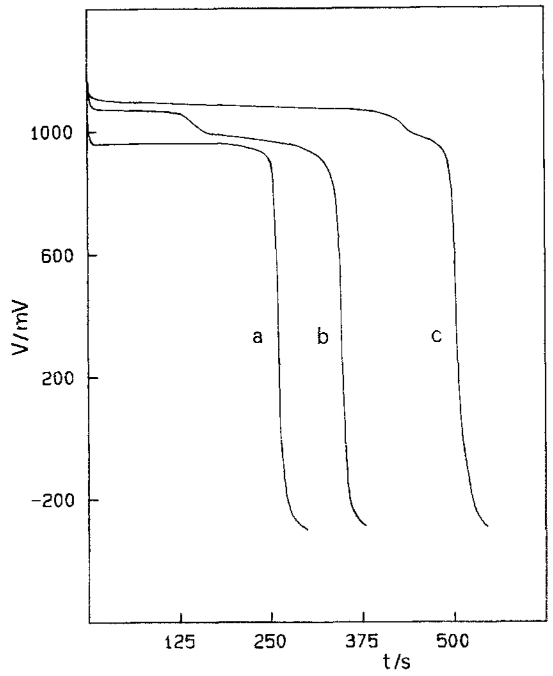

Fig. 1. $V(t)$ curves for PbO_2 reduction at the first (curve a), second (curve b) and sixth cycle (curve c), I_r = 0.5 mA, V_r = -300 mV, R = 2.

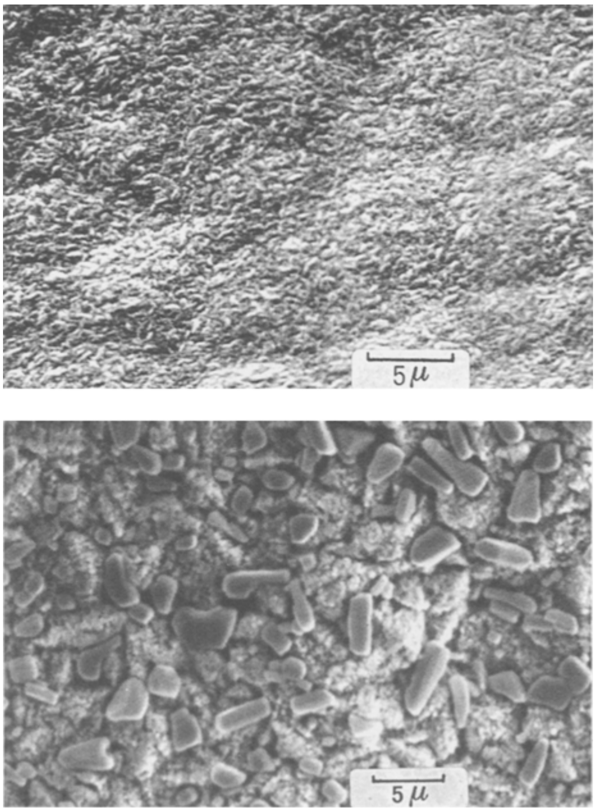

Fig. 2. SEM micrographs of the electrode surface: (a) just after electrodeposition; (b) after the first cycle; I_r = 0.8 mA, V_r = 600 mV, R = 2.

Indeed, this could happen if a sulphate layer, with membrane properties, covered the surface of lead dioxide freshly electrodeposited but not the surface of the dioxide obtained from lead sulphate. On the other hand SEM observations show that the dioxide obtained from sulphate is morphologically quite different from the electrodeposited one (Figs 2a and b). When the electrode is recharged a porous structure, on which the sulphate layer is likely to achieve membrane properties more slowly, is produced, which becomes more extended throughout the cycles. The barrier layer, changing the local ionic concentration on some reactive areas, may explain the double plateau observed in the $V(t)$ discharge curves.

The behaviour of zones of the electrode surface having different potential has been investigated by studying two coupled electrodes, one just electrodeposited and one cycled. The rest potential of the system differs only slightly (approx. 1%) from the value of the cycled electrode suggesting that the anodic reaction at the electrodeposited PbO_2 is markedly hindered.

This hypothesis is consistent with the results of additional tests. The rest potential shift and the high potential plateau are visible (Fig. 3, curve a) even

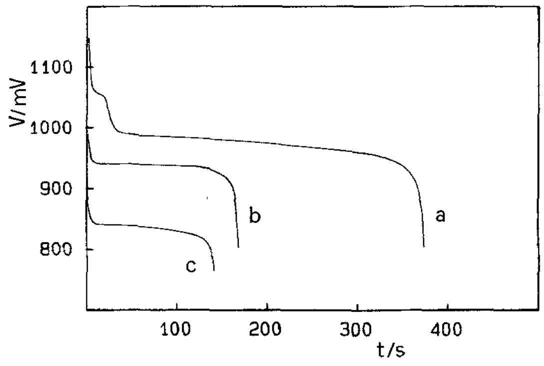

Fig. 3. Curve a: second cycle discharge for an electrode partially discharged at the first cycle (5% of Q_r), $I_r = 0.5\,\mathrm{mA}$, $R = 2$. Curve b: first discharge in pure H_2SO_4 for an electrode previously dipped in $H_2SO_4 + 100\,\mathrm{mg\,l^{-1}}$ Sb^{3+} ions, $I_r = 0.5\,\mathrm{mA}$. Curve c: first discharge in H_2SO_4 added with $100\,\mathrm{mg\,l^{-1}}$ of Sb ions, $I_r = 0.5\,\mathrm{mA}$.

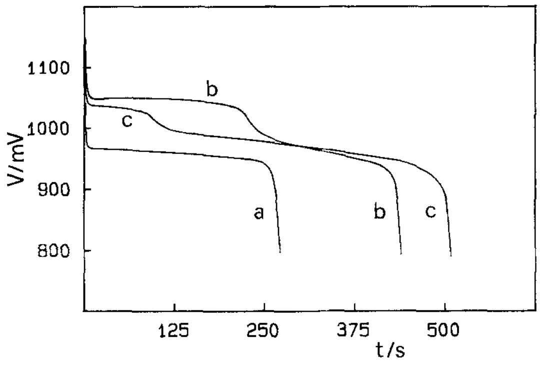

Fig. 4. Galvanostatic reduction curves at the first (curve a), second (curve b) and third cycle (curve c) for a sample left at open-circuit for 16 h between the second oxidation and the third reduction, $I = 0.5\,\mathrm{mA}$, $V_r = 800\,\mathrm{mV}$, $R = 2$.

when the sample has been submitted to a slight initial reduction corresponding to a quantity of charge less than 5% of the total reduction charge. Moreover, the potential plateau relative to the first reduction occurs at a lower potential, with a lower quantity of charge involved in the presence of Sb trivalent ions (Fig. 3, curves b and c), which exert [16, 17] a marked passivating action on PbO_2. Finally, the plateau at high potential tends to disappear when the electrode just reoxidized is left at rest for many hours ($t > 10\,\mathrm{h}$) (Fig. 4). This is a consequence of: (i) the reaction between zones of the surface at different potential; (ii) the passivation of the electrode induced by H_2O decomposition.

Obviously, the assumption made does not exclude the possibility that a change of the dioxide chemical potential, due to a variation of stoichiometry, occurs because the O/Pb ratio in the PbO_2 depends on the electrolyte composition [8]. In fact, after anodic polarization of a freshly prepared electrode for some hours, at a potential higher than 1200 mV, the rest potential decreases slowly with time, remaining greater than the usual values for many hours. The same response is obtained from a cycled electrode left at open circuit just after oxidation. Such behaviour is certainly due to a slow process of stoichiometric change occurring during the sulphate layer formation.

The experiments showed that, during reduction: (i) the potential change from the first to the second plateau is rapid, (ii) the electric charge associated with the first plateau is increasing with the number of cycles while the opposite happens for the second plateau, (iii) the high potential step almost disappears if the dioxide is left at rest for some hours. Moreover, X-ray analysis of the electrode in no case revealed the presence of the alpha form of PbO_2. All these findings support the idea that the observed behaviour of PbO_2 at discharge, during cycling, is due to the influence exerted by the sulphate layer on the electrolyte composition at the electrochemical active areas.

The $V(t)$ curves show that, in agreement with our previous findings [17], the presence of the sulphate layer does not influence the cathodic overpotential. The ions crossing the sulphate layer are therefore not controlling the process and, as the stationary conditions of galvanostatic reduction are reached in a time greater than 2–3 s, the process seems controlled by a diffusion step [17].

Some information about this step can be drawn from the analysis of the potential transient due to the instantaneous depolarization of an electrode under discharge. The corresponding experimental data fit both of these expressions well: $\eta = K + K \ln(t)$ and $d\eta/dt = K + K \exp(-b\eta)$, the first being related to a diffusive step [22], the second to an electron charge transfer process.

The coefficient b has a value without physical meaning (1.8 mV) while the K value, near to $RT/4F$ (Fig. 5), supports the idea of a diffusion step controlling lead dioxide reduction. As the sulphate layer does not influence the overpotential during the transient, the diffusion must be related to the onset of an O^{2-} gradient in the dioxide.

The tests performed also provided information on the charge, Q_r, associated with the reduction. At the first reduction Q_r is independent of the PbO_2 layer thickness and its value, ranging from 120 to $140\,\mathrm{mC\,cm^{-2}}$ (corresponding to a layer of lead sulphate about $0.3\,\mu\mathrm{m}$ thick on a layer of lead dioxide about $5\,\mu\mathrm{m}$ thick) was, in the present work, currently used to check the quality of the electrode preparation.

Figure 6 shows the influence of the number of cycles on Q_r, under various conditions. For an applied oxidation potential of 1300 mV, Q_r decreases with cycling when the ratio R between the anodic and the cathodic electric charge is lower than 1.8 (Fig. 6, curves b and d) due to the decreased conversion efficiency. Only for $R > 1.8$ does Q_r increase if $V_r < V_0$, curve a; Q_r remains constant if $V_r > V_0$, curve c. In all cases the contribution to Q_r of the second reduction plateau decreases with the cycle number.

3.2. *Potentiostatic oxidation*

The charge potentiostatic curves $I(t)$ (Fig. 7) show that the sulphate oxidation process depends on the end potential of reduction, V_r. If this value is greater than V_0 the current intensity during charge diminishes

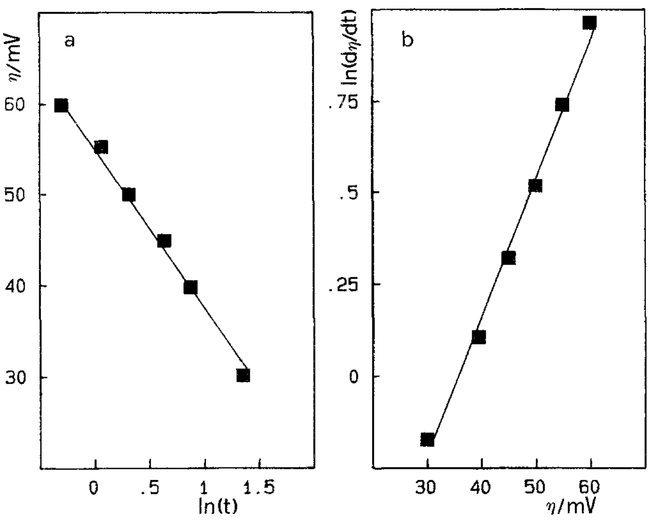

Fig. 5. (a) Plot of the overpotential η vs ln (t) and (b) plot of ln ($d\eta/dt$) vs η for the depolarization transient of an electrode at 50% of first reduction, I_r = 0.6 mA.

monotonically with time while for V_r ranging between V_0 and V_1 the charging curves present a current peak. If the discharge is prolonged after V_r has become equal to V_1, basic lead sulphate can form and eventually a shoulder can be observed before the peak.

The peak appears 100–150 s after the beginning of the reoxidation when a charge approximately equal to 30% of Q_r has passed. The intensity of the current peaks and the amplitude of the shoulder, eventually present, also depend on the ratio R. For $R < 1.8$, that is for Q_r decreasing, the shoulder rapidly vanishes with cycle number and the intensity of the current peak remains constant. On the contrary, for $R > 1.8$ the peak and the shoulder become more and more evident with increasing cycle number.

Let us consider two PbO_2 electrodes in the same state of charge, one obtained by stopping the first discharge at $V_r > V_0$ and the other by reducing PbO_2 up to $V_r < V_0$ and then oxidizing the sulphate up to a minimum of the $I(t)$ curves. These electrodes behave differently with respect to the oxidation process (Fig. 7) and that must be associated with a difference between the reaction zones.

This consideration agrees well with the conclusions of Takehara and Kanamura [13, 14] who showed that: (i) the oxidation of lead sulphate starts at the deepest part of the $PbSO_4$ layer, (ii) the rising and the falling portions of the $I(t)$ curves are due to a change of the area on which the reaction, controlled by charge transfer, takes place.

X-ray analysis performed after electrode cycling never revealed alpha PbO_2 formation and this agrees with literature data according to which the ratio between the mass of alpha and beta allotropes decreases with cycling.

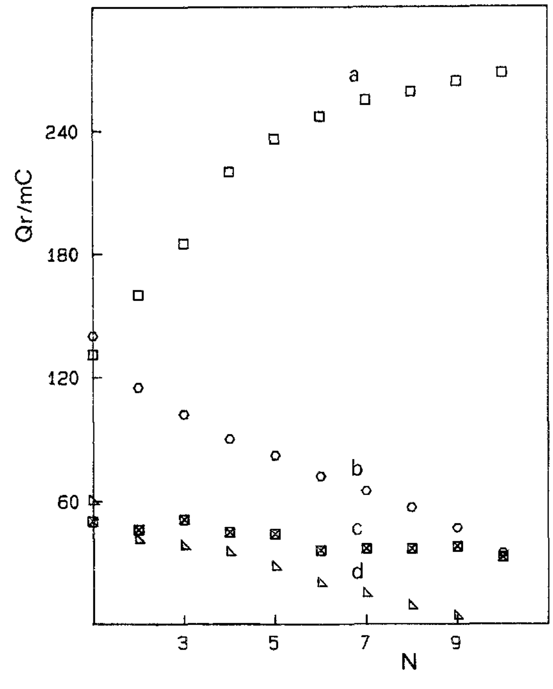

Fig. 6. Reduction quantity of charge Q_r vs number of cycles N for PbO_2 electrodes, I_r = 0.5 mA, V oxidation = 1300 mV: (a) R = 2, V_r = −300 mV; (b) R = 1.2, V_r = 600 mV; (c) R = 2, V_r = 950 mV; (d) R = 1.2, V_r = 950 mV.

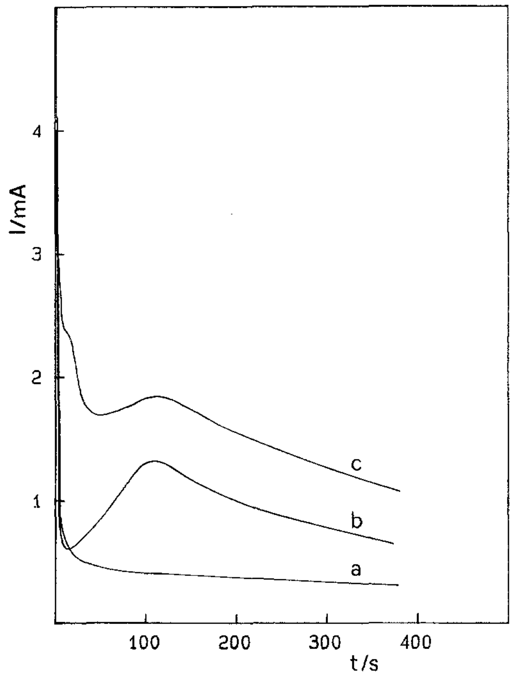

Fig. 7. $I(t)$ curves for PbO_2 oxidation at the fifth cycle, I_r = 0.7 mA, V oxidation = 1300 mV, R = 2: (a) V_r = 960 mV; (b) V_r = 900 mV; (c) V_r = −320 mV.

Comparison of the charge curves for electrodes practically free from basic lead sulphate (curve b in Fig. 7) and containing a certain quantity of this compound (curve c in Fig. 7), suggests that the first transient cannot be ascribed to $PbO–PbSO_4$ solely. Its presence may be associated with the shoulder appearing in curve c but the effect on the oxidation process appears to be of limited importance.

4. Conclusions

It has been shown that the behaviour of PbO_2 electrodes is influenced by the sulphate barrier layer which forms on their surface. The effect has been attributed to a change in the concentration of the ions determining the equilibrium potential. The kinetics of the reduction do not seem to be influenced by the sulphate layer and appear to be due to an O^{2-} gradient occurring in the dioxide.

The experimental results obtained on potentiostatic sulphate oxidation agree with the literature and show that the trend of the $I(t)$ curves markedly depends on the end discharge potential.

X-ray analysis of the samples at various cycling stages in the experimental conditions chosen has not revealed the formation of the alpha PbO_2 allotrope.

Acknowledgements

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