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The perchlorate-assisted formation of lead dioxide on lead

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Perchloric acid affects the phase formation process during the oxidation of lead to PbO_2 in dilute sulphuric acid. In sulphuric acid, the reaction involves a two-dimensional instantaneous nucleation process for the production of PbO_2. In the mixed acid, the growth of PbO_2 in low concentrations (20 mM) of added perchlorate ion remains two-dimensional but the nucleation becomes progressive and at higher perchlorate concentrations phase formation occurs by three-dimensional growth. A range of perchlorate concentration (30–40 mM) exists where the attack is on an 'advancing front' (analogous to the electrodeposition of a metal from solution), in which the PbO_2 steadily advances into the metal. A mechanism is proposed for the Planté reaction process.

1. Introduction

There have been a few investigations of the effect of aggressive ions (perchlorate ion is the best example) in promoting the oxidation of lead to lead dioxide in sulphuric acid [1–8]. It has been shown that the effect of the aggressive ion on the oxidation process occurs at potentials where the electrode is covered with a layer of lead sulphate. This layer, when formed in sulphuric acid alone, efficiently covers the lead surface and passivates the electrode. When the lead electrode is in the lead dioxide region at potentials more positive than ~ 1.1 V against an Hg_2SO_4/Hg electrode in the same solution[†] the $PbSO_4$ layer is transformed to PbO_2. In the small potential range lying negative of the solid-phase lead sulphate region in which Archdale and Harrison [9] demonstrated that lead dissolves as a solution-soluble species, we have shown that additions of even considerable amounts of perchlorate ion to the bulk sulphuric acid solution do not alter the process or the kinetics [8]. The first sign of the influence of the perchlorate ion is seen in sweeping experiments as an enhancement of anodic current on the positive-facing slope of the active/passive transition, indicating that as soon as the electrode contains surface lead sulphate some degree of depassivation is effected by the perchlorate ion [7]. It has been our intention to investigate the electrochemical effects of the perchlorate ion in assisting the oxidation of lead to lead oxide. This paper contains the results of our experiments in that region of potential where the formation of lead dioxide from lead sulphate occurs.

2. Experimental

Experiments were carried out on pure lead electrodes (Koch-Light, 99.999%, area 0.071 cm^2) mounted in Teflon. The preparation and shrouding of the electrode and the electrolytic cells used have been described previously [7].

The instrumentation consisted of a Kemitron potentiostat (LCV-2) and pulse generator (PM3); the output was recorded using a Bryans X–Y recorder (series 26 000). The electrode was polished on roughened glass lubricated with tri-distilled water, etched for 60 s in 1.6 M HNO_3 and thoroughly washed prior to immersion in the cell electrolyte solution. AnalaR H_2SO_4 and $HClO_4$ were used for solution preparation. One-half molar H_2SO_4 was used throughout (this

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[†] All potentials in this paper are referred to this reference electrode system.

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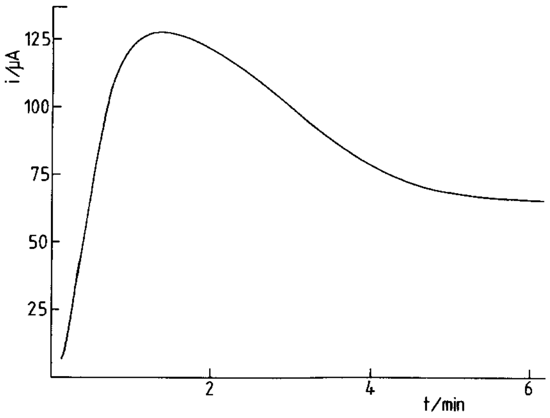

Fig. 1. Current–time transient obtained by stepping the electrodes from 700 mV to 1400 mV in 0.5 M H_2SO_4 at 23° C.

concentration was chosen since it conforms to current industrial practice) with varying concentrations of $HClO_4$ added to the solution.

The electrode was introduced to the cell at 700 mV and was maintained at this potential for 1 hour, during which time the current passing through the electrode fell to between 1 to 3 μA. At this point we considered that the electrode was completely blocked by lead sulphate and that the underlying lead was satisfactorily protected from further oxidative attack. The lead sulphate layer produced at 700 mV was therefore sufficiently coherent to ensure that a satisfactory surface for the study of its further oxidation was available [2].

The electrode was finally stepped to a more positive potential and the current–time transient was recorded. Replicate experiments were made, each time using a freshly polished, etched and passivated electrode.

3. Results and discussion

Fig. 1 shows the current–time transient obtained by stepping the electrode from 700 mV in the $PbSO_4$ region to 1400 mV in the PbO_2 region. It is similar to other curves observed for the oxidation of $PbSO_4$ on lead [10]. It consists of a rising part, in which the current is proportional to the time, goes through a maximum and then begins to fall again. However, the current does not fall to zero, but to a steady-state value. We consider that this steady-state current is due to the evolution of oxygen from the product PbO_2. Evidence for the onset of this is obtained during the course of the experiment, as the development of a 'noisy' signal indicates the presence of gaseous oxygen on the porous PbO_2. These results are similar to those reported by us [11] for the oxidation of massive lead and indicate that the process is a two-dimensional growth of PbO_2 on lead sulphate which follows the equation:

$$i = (zF\pi M/\rho)N_0k^2t \exp[(-\pi M^2N_0k^2t^2)/\rho^2]. \tag{1}$$

This was tested by comparing the equation with the experimental data in the form of the dimensional plot of i/i_m versus t/t_m (Fig. 2), showing that the results fit the theoretical curve. Further proof can be obtained by analysing the falling part of the current–time transient. It is necessary to first subtract the current going into the oxygen evolution reaction (i_∞): this was done with the assumption that this reaction was fully developed throughout the 'long-time' part of Equation 1. Plotting $\log_{10}[(i-i_\infty)/t]$ versus t^2 indicates that this assumption is justified, as shown in Fig. 3.

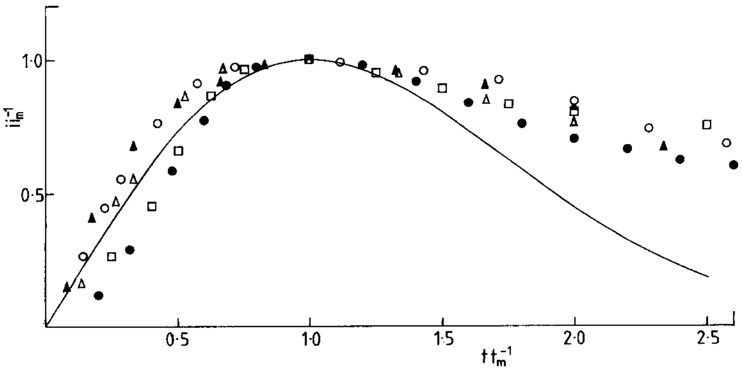

Fig. 2. i/i_m versus t/t_m for potential step experiments on electrodes stepped from 700 mV to: ○, 1300 mV, ▲, 1325 mV; □, 1350 mV; ●, 1375 mV; △, 1400 mV, in 0.5 M H_2SO_4 at 23° C. Full line indicates the theoretical instantaneous nucleation process.

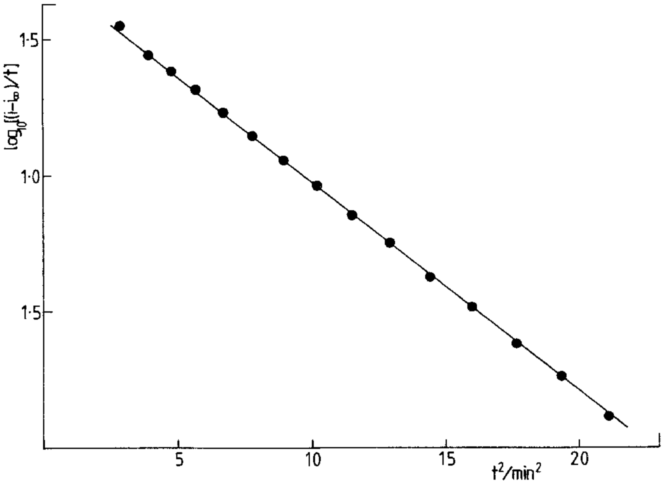

Fig. 3. $\log_{10}[(i-i_\infty)/t]$ versus t^2 for the falling part of the transient shown in Fig. 1.

The addition of perchlorate ions to the system had a fundamental effect. The results of the stepping experiments with 5 mM ClO_4^- were very interesting for they indicated that this concentration marked the threshold of the gross perchlorate ion attack (Fig. 4). The peak currents (i_m) increase with potential until the 700 to 1350 mV step, thereafter a decrease is observed. This increase and decrease in i_m can be interpreted if the extent of the PbO_2 film increased at high potential and at the same time becomes tighter and thus more passivating. The increased secondary rise at high overpotential indicates that ClO_4^- ions (probably adsorbed) are able to penetrate the passive layer under the influence of the potential to promote further corrosion.

Figs. 5, 6 and 7 show a series of transients corresponding to stepping from 700 mV to 1400 mV for a number of solutions containing perchlorate. The results show that the currents in the transients increase even with small ClO_4^- additions, but above 20 mM ClO_4^- the shape of the transients alter significantly. This is particularly true of the 'falling' part which exhibits a progressively greater 'steady state' value. The falling part is completely absent between 30 and 40 mM. Thereafter, although the current maximum continues to increase somewhat with added ClO_4^-, a well-defined trailing part is apparent once more. The well-defined tail is apparent up to 200 mM ClO_4^- concentration.

The initial part of the perchlorate system transients also progressively changes with concentration. Although below 20 mM the transients resemble Fig. 1, a concavity develops at this ClO_4^- concentration when the results are plotted in the reduced

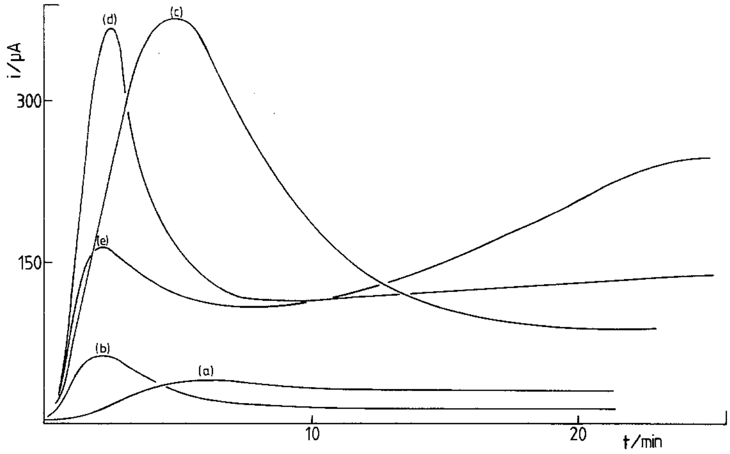

Fig. 4. Current–time transients obtained by stepping the electrode from 700 mV to: (a) 1259 mV, (b) 1300 mV, (c) 1350 mV, (d) 1375 mV, (e) 1400 mV, in 0.5 M H_2SO_4 containing 5 mM $HClO_4$ at 23° C.

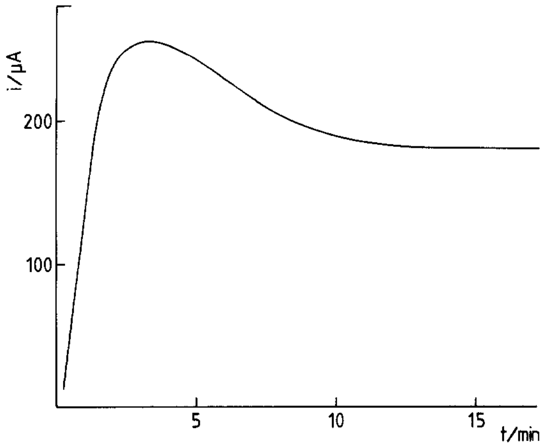

Fig. 5. Current–time transient observed by stepping the electrode from 700 mV to 1400 mV in 0.5 M H_2SO_4 containing 20 mM $HClO_4$ at 23° C.

form. This indicates a change to a progressive process and Fig. 8 shows how the reduced plots compare with the theoretical instantaneous nucleation process and the progressive two-dimensional process. For the latter the current–time equation is

$$i = \frac{zF\pi M}{\rho} hA\, k^2 t^2 \exp\left(-\frac{\pi M^2 A k^2 t^3}{3\rho^2}\right). \qquad (2)$$

The growth law for the PbO_2 development throughout the range of potentials is not very consistent; at low potentials the progressive process gives the better fit, at higher potentials the process reverts to the instantaneous two-dimensional law. This indicates that at low potentials insufficient nucleation centres are available for growth corresponding to the available rising potential and as the

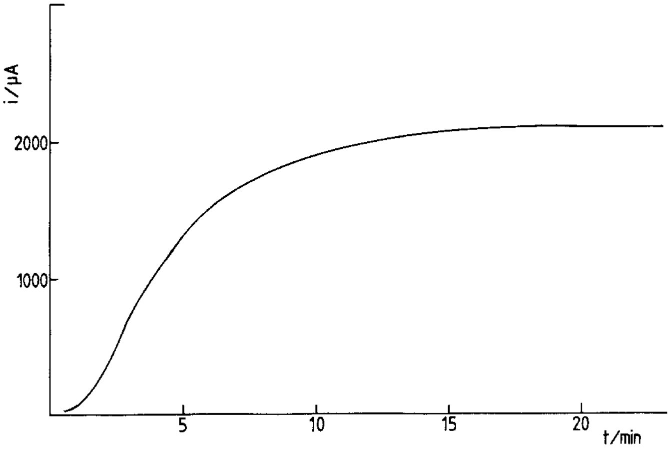

Fig. 6. Current–time transient obtained by stepping the electrode from 700 mV to 1400 mV in 0.5 M H_2SO_4 containing 30 mM $HClO_4$ at 23° C.

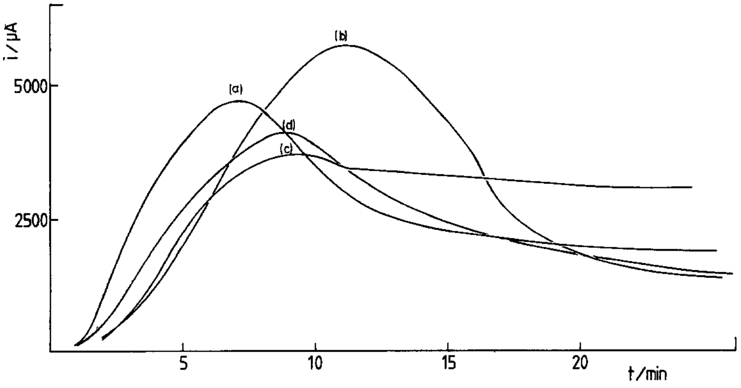

Fig. 7. Current–time transients obtained by stepping the electrode from 700 mV to 1400 mV in 0.5 M H_2SO_4 containing: (a) 54 mM $HClO_4$, (b) 75 mM $HClO_4$, (c) 100 mM $HClO_4$, (d) 200 mM $HClO_4$ at 23° C.

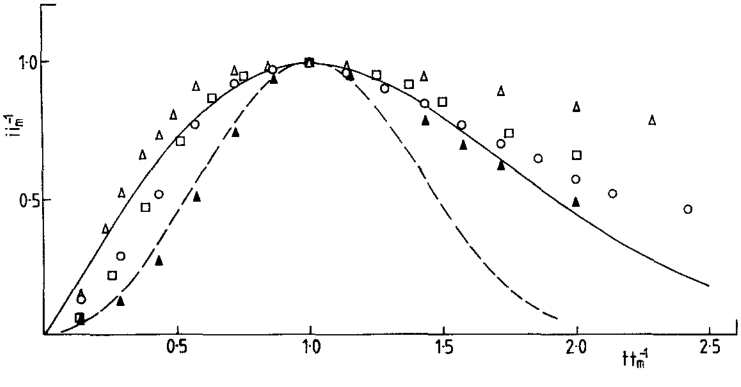

Fig. 8. i/i_m versus t/t_m for potential step experiments on electrodes stepped from 700 mV to: ○, 1300 mV; ▲, 1325 mV; □, 1350 mV; △, 1400 mV, in 0.5 M H_2SO_4 containing 20 mM $HClO_4$ at 23° C. The full line represents the theoretical instantaneous nucleation, the broken line represents the progressive two-dimensional process.

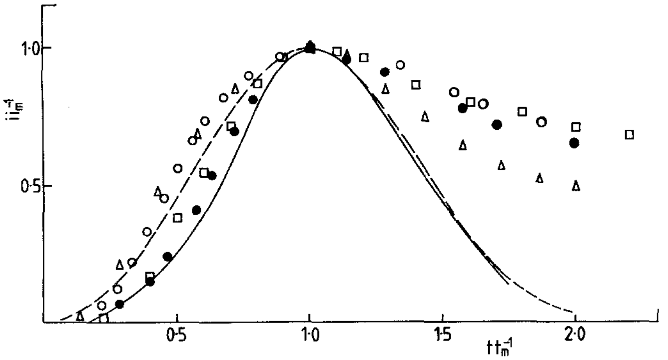

Fig. 9. i/i_m versus t/t_m for potential step experiments on electrodes stepped from 700 mV to: ●, 1250 mV; ○, 1300 mV; □, 1350 mV; △, 1400 mV, in 0.5 M H_2SO_4 containing 54 mM $HClO_4$ at 23° C. The broken line represents the theoretical two-dimensional process, the full line represents the three-dimensional process.

reaction proceeds, further additional growth points become activated. At high potentials the large overvoltage activates every possible growth point.

As the concentration of ClO_4^- is increased the nucleation becomes progressive, all instantaneously nucleated two-dimensional character being lost. In addition the current in the 'nucleation part' of the transients is everywhere increased by the ClO_4^- (Table 1). This indicates that the ClO_4^- ion produces a thicker layer of PbO_2 of which the late developing regions grow with nucleation which occurs after the initial nucleation of the PbO_2 film has started.

The results for the 54 mM ClO_4^- concentration, given in the reduced form in Fig. 9, show considerable three-dimensional nucleation character. This is clearly a change from a layer growth of a passivating phase to the indepth growth of a non-

Table 1. Variation of i_m with concentration of perchlorate ion for several values of potential step from 700 mV.

	i_m (μA)				
$HClO_4$ (mM) in 0.5 M H_2SO_4	700–1250 (mV)	700–1300 (mV)	700–1325 (mV)	700–1350 (mV)	700–1400 (mV)
0	25	38	53	60	128
5	40	62	50	375	165
20		54	80	105	255
30	500†	1100†	2000†	1400†	2000†
40	450†	2200†	2500†	2550†	
54	1150	2400		4700	4750
75	600	800		2850	5750
100	1400	1800		3550	3700
200	1920	2400		2800	4100

† Current levels off, no falling part to the transient.

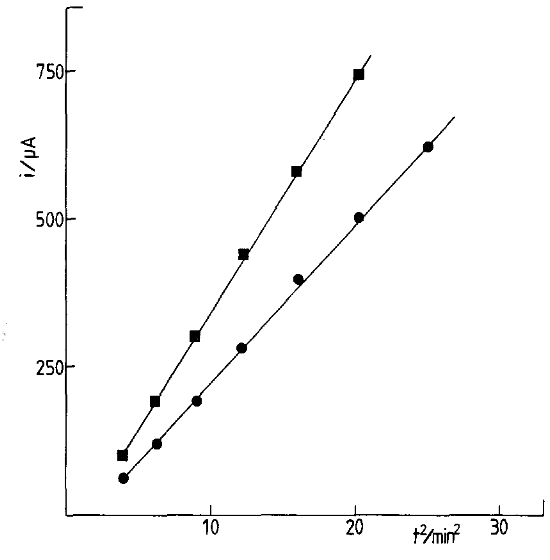

Fig. 10. i versus t^2 for rising transient for electrodes stepped from 700 mV to 1350 mV: ●, 30 mM $HClO_4$ in 0.5 M H_2SO_4 ; ■, 40 mM $HClO_4$ in 0.5 M H_2SO_4.

passive layer. The initial currents begin to be rectilinear with t^2 (Fig. 10) and ultimately t^3 (Fig. 11) and the final (corrected) falling parts of the higher ClO_4^- concentrations also conform to a linear relationship between $\log_{10} i/t^3$ versus t^3, verifying the change to three-dimensional nucleation (Fig. 12). This is a difficult model mathematically; however, Armstrong and Thirsk [12] give for the case of the growth of right circular cones (which seems to be the most suitable for PbO_2):

$$i = zFk_2\ [1 - \exp(-\pi M^2 k_1^2 A t_3)/3\rho^2]$$
$$\times \exp[(-\pi M^2 k_1^2 A t^3)/3\rho^2]. \qquad (3)$$

Figs. 11 and 12 show that in the region 54 mM to 75 mM data fit this three-dimensional process quite satisfactorily.

The 'plateau region' around 30–40 mM ClO_4^- ion concentration is interesting. Apparently, at these conditions, the proceeding reaction forms a front which progressively advances in the same manner as for the electrodeposition of a metal from solution, in which a layer by layer growth occurs. It seems likely that we are dealing under these circumstances with a system which can sustain a self-regenerating reaction. This is probably:

$$Pb + SO_4^{2-} \rightarrow PbSO_4(s) + 2e \qquad (4)$$

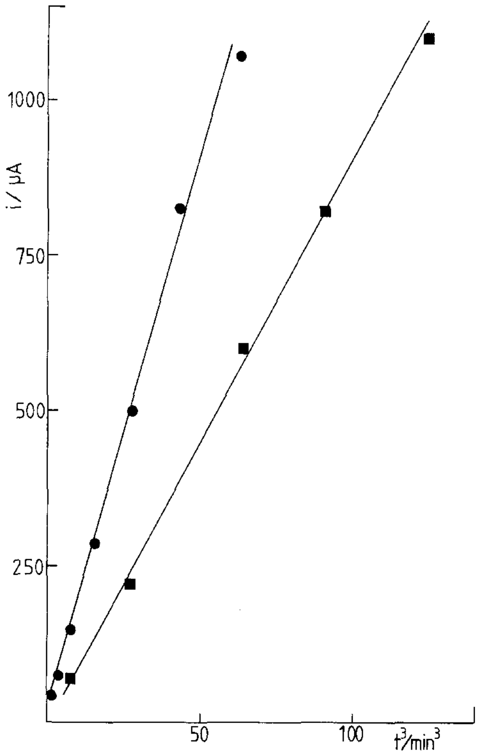

Fig. 11. i versus t^3 for rising transient for electrodes stepped from 700 mV to 1350 mV: ●, 54 mM $HClO_4$ in 0.5 M H_2SO_4. ■, 75 mM $HClO_4$ in 0.5 M H_2SO_4.

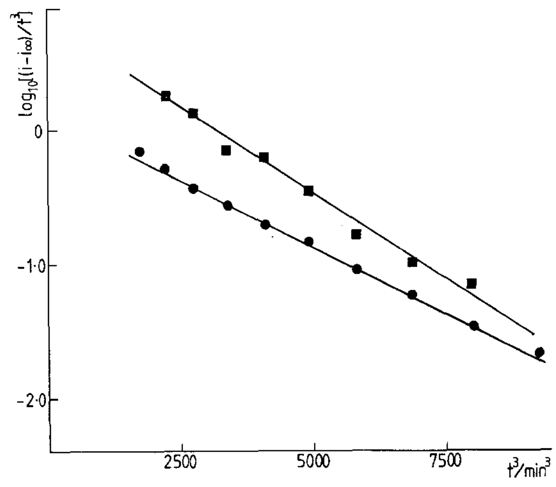

Fig. 12. log $[(i - i_\infty)/t^3]$ versus t^3 for the falling parts of transients for step experiments from 700 mV to: ●, 1300 mV; 54 mM $HClO_4$ in 0.5 M H_2SO_4 ; ■, 1400 mV; 75 mM $HClO_4$ in 0.5 M H_2SO_4.

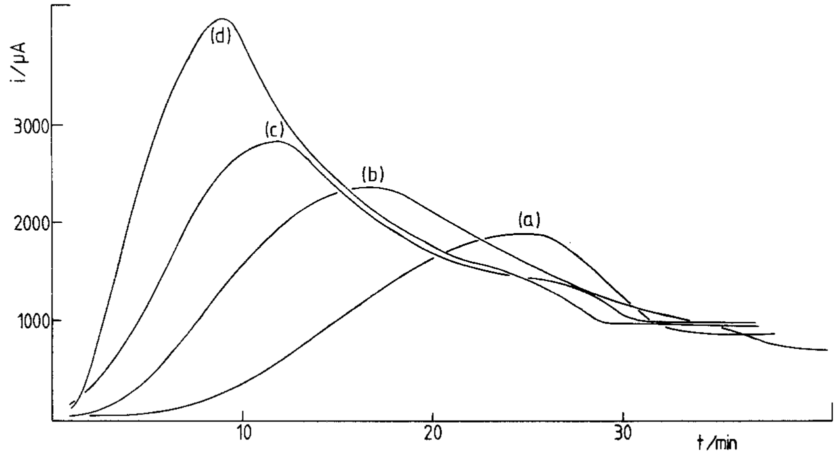

Fig. 13. Current–time transients obtained by stepping the electrode from 700 mV to: (a) 1250 mV, (b) 1300 mV, (c) 1350 mV, (d) 1400 mV, in 0.5 M H_2SO_4 containing 200 mM $HClO_4$ at 23° C.

$$PbSO_4(s) + 2H_2O \rightarrow PbO_2 + HSO_4^- + 3H^+ + 2e \tag{5}$$

$$PbO_2(s) + Pb + 4HClO_4 \rightarrow 2Pb(ClO_4)_2 + 2H_2O \tag{6}$$

$$Pb(ClO_4)_2 + H_2SO_4 \rightarrow 2HClO_4 + PbSO_4(s) \tag{7}$$

with the propagating sequence given by Equations 5–7. Reaction 4 is very fast at this potential, while Reaction 5 is a slow, crystallization-controlled reaction; Reaction 6 is a fast chemical reaction and Reaction 7 is the regeneration of reactants. Provided that the layers can be penetrated by the ionic species of H_2SO_4 and $HClO_4$ in the optimum concentrations, then the reaction is self-perpetuating. If insufficient $HClO_4$ is present then the reaction tends towards the simple reaction in H_2SO_4, as observed. If the optimum concentration of ClO_4^- is exceeded then Equation 7 does not produce sufficient lead sulphate for continuation of the chain and a passivating layer of PbO_2 is formed from solution-soluble Pb^{2+} species by electrodeposition [13]. It is the generation of this quality of electrodeposited PbO_2 which presumably accounts for the ultimate three-dimensional current limitation.

Above 75 mM, although the shapes of the curves remain the same (Fig. 13), the currents are slightly decreased at high potentials. This effect is rather obscure; however, we can attempt an explanation if the higher solution concentration of Pb^{2+} in the higher ClO_4^--containing solutions produces a more efficient passivation and the maximum current becomes less. This gross solution process is to be distinguished from that at low ClO_4^- concentration when the reaction takes place in the adsorbed state. The undulating character of the currents at long times must be evidence for the growth of different layers of PbO_2.

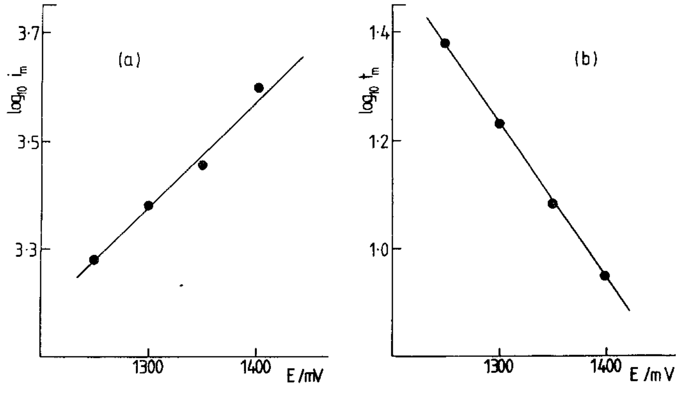

Fig. 14. Potential dependencies of i_m and t_m for curves shown in Fig. 13 (200 mM $HClO_4$). (a) log i_m versus E; (b) log t_m versus E.

The position of the transients depends upon the potential to which the electrode is stepped. Differentation of Equation 3 and the isolation of the turning point yields

$$i_m = zFk_2/4$$

and

$$t_m = (3\rho^2 \ln 2/\pi M^2 k_1^2 A)^{1/3}. \qquad (8)$$

The potential dependencies of i_m and t_m can be obtained by plotting $\log_{10} i_m$ against E (Fig. 14a) and $\log_{10} t_m$ against E (Fig. 14b). These give slopes of 514 mV/decade and − 350 mV/decade respectively. Thus for k_1, the parallel growth rate constant, the potential dependence of t_m is − 350 mV/decade, which implies a potential dependence of 525 mV/decade; and for k_2, the orthogonal rate constant, a potential dependence of 514 mV/decade.

These potential dependencies of growth rate constants are much less than the values of those corresponding to systems free of perchlorate ions [10]. Bearing in mind that the current densities in the perchlorate systems are considerably greater than for the perchlorate-free systems, that is, the reactions are occurring in considerably greater depth, this decrease reflects the increased extent of the field over which the reaction is driven.

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