THE PLANTÉ FORMATION PROCESS FOR LEAD–ACID POSITIVE ELECTRODES

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Summary

The perchlorate assisted oxidation of lead to lead dioxide in dilute sulphuric acid containing perchlorate ion has been investigated under conditions similar to those used for Planté electrode production. The optimum concentration of perchlorate ion has been estimated.

It is shown that if the electrode is not fully passivated by lead sulphate before the potential is increased to form PbO_2, the process of PbO_2 formation proceeds progressively.

Introduction

Planté's original process for lead–acid cells simply involves multiple charging and reversals of lead sheets in dilute sulphuric acid. It was very quickly realised that the process could be both speeded-up and improved by the use of a developed lamellar cast electrode and the addition of a forming agent to the electrolyte. The direct Planté process by which lead metal is transformed to satisfactory lead dioxide (positive) battery plates has been through a number of developments since its inception, and it is rather surprising that the method is still used today to produce stationary lead–acid cells which are required for service demands of absolute reliability, minimal open-circuit loss, and a very long service life. Battery positives for these standby duties are produced extensively in England and the Planté process carried out consists of the perchlorate ion-promoted oxidation of lamellar lead electrodes in dilute (0.5 - 1M) sulphuric acid. A developed surface of about 6:1 nominal superficial area is cast from very pure lead and this forms the basic plate. After oxidation the plate is reduced to lead sulphate and cleansed by washing completely free from the perchlorate ion. A final oxidation in sulphuric acid completes the formation process.

We have been interested in the electrochemistry of the Planté process for some time and accounts of our research have been presented from time to time [1 - 5].

In these accounts the primary objective was to find conditions where the component aspects of the process could be studied, uncomplicated by other processes. Thus the investigation of the specific effect of the formation of the lead dioxide layer [5] was achieved by first carefully growing a well-defined lead sulphate layer on the lead, whereby a well-defined pre-electrode state was established, and then stepping the potential to the region where lead dioxide could be formed.

The industrial process by which the Planté formation is carried out is not well-controlled in the above sense. The current is galvanostatically controlled and the electrode potential takes care of itself. From our investigation of the industrial process it appears that the effect of the current is immediately to passivate the surface for lead dissolution and solid phase lead sulphate formation, for the potential immediately rises to that for the development of PbO_2. This process can best be studied in the laboratory by immediately potentiostatting at the lead dioxide potential without prior formation of a lead sulphate phase. This paper describes the results of the investigation.

Experimental

Experiments were undertaken with pure lead electrodes (Koch-Light, 99.999%) shrouded in Teflon [3]. The electrode was polished on roughened glass lubricated with tri-distilled water, etched for 1 min in 1.6M HNO_3, and thoroughly washed again in tri-distilled water. The electrode was then immediately introduced into a conventional three-compartment cell in which the potential difference between the reference electrode* and the working electrode was measured *via* a Luggin probe terminating at a position 0.05 cm from the working electrode. The counter electrode was lead sheet (Koch-Light, 99.999%) and the base electrolyte solution was sulphuric acid (AnalaR, 0.5M). Added perchloric acid (AnalaR) concentrations in the range up to 200 mM were used to study the effect of the perchlorate ion as an aggressive agent.

Currents were measured using a chart recorder (Bryans, Y/t series, 2700).

Results and discussion

Perchlorate-free electrolyte solutions
Figure 1 shows a typical current–time curve for lead in sulphuric acid. At all potentials in the experimental range 1100 - 1300 mV the forms of the current–time curves were similar. After a sharp rise and fall, due to double
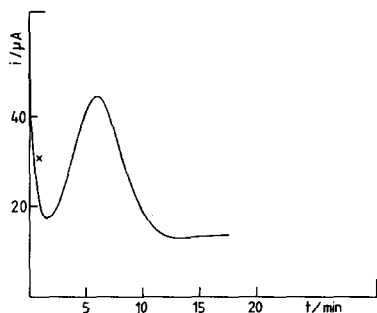
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*The reference electrode was Hg/Hg_2SO_4, H_2SO_4 (0.5M).

Fig. 1. Typical current–time transient for the oxidation of Pb in H_2SO_4 (0.5M) at 1150 mV, 23 °C. ×, initial spike due to double layer charging.

layer effects, a slow increase in current was followed by a decrease, indicating the growth of solid phase PbO_2. Thereafter an increase in current was observed over the remainder of the time of the experiment. This increase was due almost exclusively to an increase in the oxygen evolution reaction from the lead dioxide surface. The form and magnitude of the current–time curves were independent of the speed at which the electrode was rotated. This fact indicated the lack of participation of a current controlling reaction *via* the agency of the solution. Had such processes been present, then the currents would have increased with the speed of rotation. This is because the diffusional processes occur more rapidly at high rotation speed when the hydrodynamic diffusion layer is thin.

This conclusion is confirmed by the rising and falling transient attained as the formation reaction proceeds, which indicates the presence of a solid state crystallisation process. Initially, the current is low (ideally it starts from zero), as the requirement that the rate of crystallisation is proportional to the area of growing phase present, controls the current. The current increases as the growth of the new phase occurs. However, the current goes through a maximum as the growing centres overlap. The birth of the PbO_2 centres can be instantaneous or progressive as the reaction proceeds. Well-defined relationships have been established for such processes. The equations have been reviewed by Thirsk and Harrison [6].

Plots of log i against log t for the first rising transient throughout the experimental range (Fig. 2) indicated that the current increases initially in an ill-defined way, plots curving upwards especially at the less positive potentials. However, the slope of the lines was generally near to unity. This suggests an instantaneous two-dimensional nucleation process [6]. Another way to test the dimensionality of the process is by examining the falling part of the transient. For the two dimensional instantaneous process the expected plot of $\log_{10}(i/t)$ *vs.* t^2 was not a straight line. However, that corresponding to the two dimensional progressive behaviour $\log_{10}(i/t^2)$ *vs.* t^3 (Fig. 3) gave a straight line corresponding to the equation*

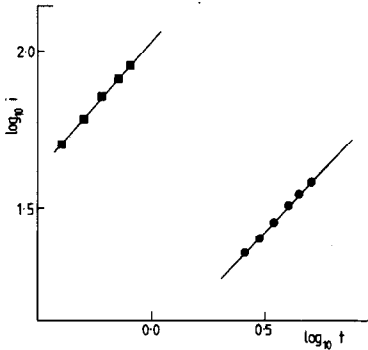*These equations are fully explained in ref. 6.

Fig. 2 (left). $\log_{10} i$ vs. $\log_{10} t$ for the initial parts of the transients of the type corresponding to Fig. 1. ●, 1150 mV; ■, 1300 mV, in 0.5M H_2SO_4.
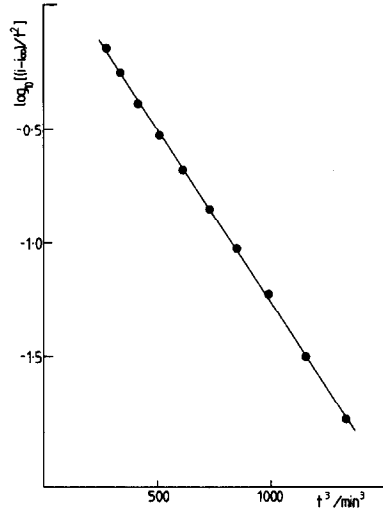
Fig. 3 (right). $\log_{10}(i/t^2)$ vs. t^3 for the falling parts of the transients of the type corresponding to Fig. 1 (i corrected for the oxygen reaction). ●, 1150 mV.

$$i = \frac{nF\pi MhAk^2 t^2}{\rho} \exp\left[-\frac{\pi M^2 Ak^2 \cdot t^3}{3\rho^2}\right] \tag{1}$$

in the form

$$\ln i/t^2 = [\ln nF\pi MhAk^2/\rho] - \frac{\pi M^2 Ak^2 \cdot t^3}{3\rho^2}. \tag{2}$$

It should be noted that in the present analysis of the results a correction was made to the current magnitude, due to the presence of a pseudosteady-state current at long times. This current is due to the oxygen evolution reaction occurring from product PbO_2 when it is formed. The validity of eqn. (2) for the oxidation process under investigation was tested by plotting the transient data in terms of units corresponding to the maximum, i.e., i/i_m was plotted against t/t_m (here again, i was corrected for the oxygen evolution). The results of this are shown in Fig. 4 and the reduced plot [6] is compared with theoretical equations for both the instantaneous and progressive two-dimensional processes. It is clear that the progressive process fits the experimental facts most satisfactorily. This behaviour [6] differs from that observed with well-formed lead sulphate surfaces where the instantaneous two-dimensional process represented by the equation
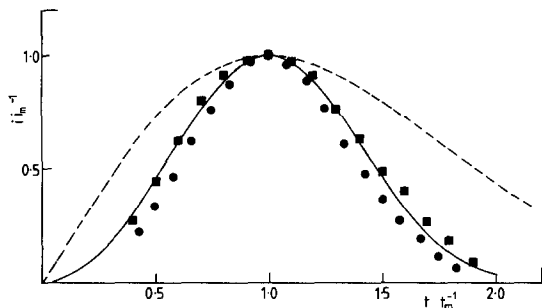
Fig. 4. Reduced plot i/i_m *vs.* t/t_m for experiments corresponding to Fig. 1. (Current at long times corrected for the oxygen reaction.) — – – —, theoretical curve for a two-dimensional instantaneous process ($i = (nF\pi M/\rho)No\,k^2t\,\exp\,[(-\pi M^2Nok^2t^2)/\rho^2\,]$); ———, theoretical curve for a two dimensional progressive process ($i = (nF\pi M/\rho)h\,Ak^2t^2\,\exp\,-[(-\pi M^2Ak^2t^3)/3\rho^2\,]$).

$$i = \frac{nF\pi MNok^2t}{\rho}\,\exp\left[-\frac{\pi M^2Nok^2t^2}{\rho}\right] \qquad (3)$$

related the current and time [5].

We can interpret this difference in terms of the electrochemical reactions:

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

$$PbSO_4 + 2H_2O \longrightarrow PbO_2 + HSO_4{}^- + 3H^+ + 2e \qquad (5)$$

occurring simultaneously rather than eqn. (5) taking place on a fully passivated lead sulphate surface.

At the oxidation potentials used, reaction (4) would be very rapid initially. However, as soon as a significant layer of $PbSO_4$ is formed some reduction in the rate of reaction (4) would occur. On oxidation and transformation of $PbSO_4$, as reaction (5) proceeds, the layer of $PbSO_4$ becomes incomplete and we can obtain the chemical redox process

$$PbO_2 + Pb + 2H_2SO_4 \longrightarrow 2PbSO_4 + 2H_2O \qquad (6)$$

whereby the corrosion reaction can penetrate further into the metal surface. The initial response of the electrode will be an instantly nucleated two-dimensional process on a $PbSO_4$ layer which has not been fully developed. The formation of $PbSO_4$ by the redox reaction (6) requires the nucleation of new PbO_2 centres for the reaction to proceed. The electrocrystallisation reaction therefore, becomes progressively nucleated. The transition between an equation of form (3) to form (1) is to be expected and the progressive process will then dominate in the long term. This explanation is consistent with the induction periods present in this series of experiments which were absent from experiments on well-developed $PbSO_4$ surfaces. The time taken

before the current started to rise was long in the case of stepping to potentials just inside the lead dioxide region (~ 1100 mV) and decreased as the potential was stepped to more positive values. This is in accord with the need to form a film of $PbSO_4$ on the lead suitable for oxidation to PbO_2. At more positive potentials this took much less time so that the induction period was short.

Perchlorate-containing electrolyte solutions

Figure 5 shows the effect of adding 10 mM of perchlorate ion in the form of $HClO_4$ to the dilute sulphuric acid. This has the effect of shortening the induction periods and increasing the height of the electrocrystallisation peaks. We have noticed in previous work that perchlorate ion tends to displace sulphate ion from the surface of the lead [3, 5] and this is possibly the cause of the shorter induction time, a passive layer resulting more readily in the presence of the mixed ion environment. At higher final potentials the induction period was very short indeed and the electrocrystallisation peak became quite sharp. However, large and rising currents were observed at long times. Figure 6(a), (b) and (c) shows the kinetic plots for the analysis of Fig. 5 type transients. The process is clearly a two-dimensional, progressively nucleated process under all conditions. This is similar to the behaviour of well-developed layers of $PbSO_4$ on lead. However, the difference in the lengths of the induction periods marks the distinction between the two systems, which can be identified with the incomplete $PbSO_4$ layer on which PbO_2 must eventually grow.

We showed [5] that on a completely passive lead sulphate surface the presence of an ~30 mM concentration of perchlorate gave a current response which consisted of a rising transient followed by a steady current. In the present experiments it was found that at the oxidation potential of ≈1200 mV a rising response was obtained which peaked and then gave a steady state current at a value somewhat lower than the peak, Fig. 7. The response and the correlations, which show the process to be three-dimensional with progressive nucleation conforming to an equation of the type
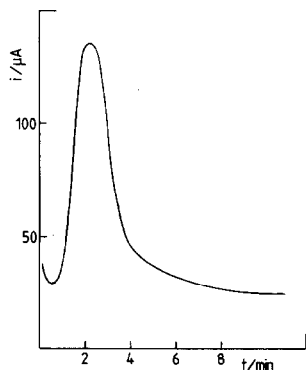

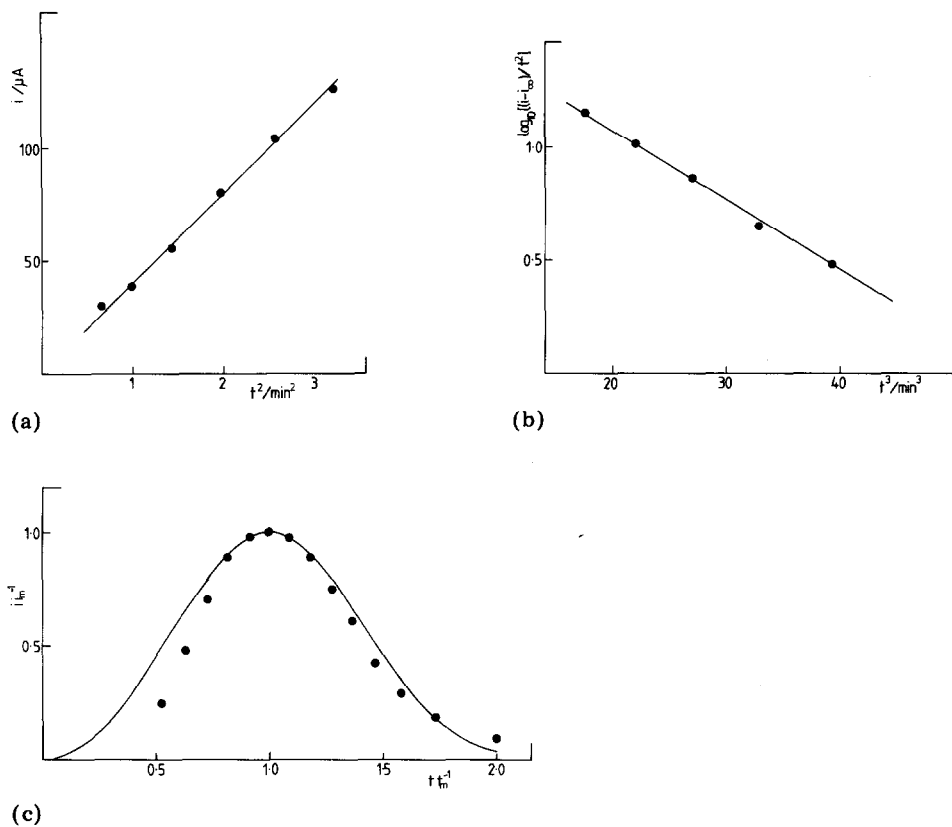Fig. 5. As Fig. 1 but with added $HClO_4$ (10 mM) at 1275 mV.

Fig. 6. (a) i vs. t^2 for the initial part of the transient corresponding to Fig. 5; (b) $\log_{10}[(i - i_\infty)/t^2]$ vs. t^3 for the falling part of Fig. 5; (c) reduced plot i/i_m vs. t/t_m corresponding to Fig. 5 (current at long times corrected for the oxygen reaction). Curve drawn indicates the theoretical two dimensional progressive nucleation process.
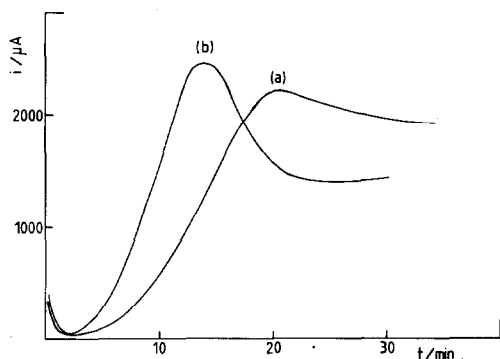

Fig. 7. Current–time transients for the oxidation of Pb in H_2SO_4 (0.5M) containing 54 mM $HClO_4$. (a) at 1225 mV; (b) at 1250 mV.

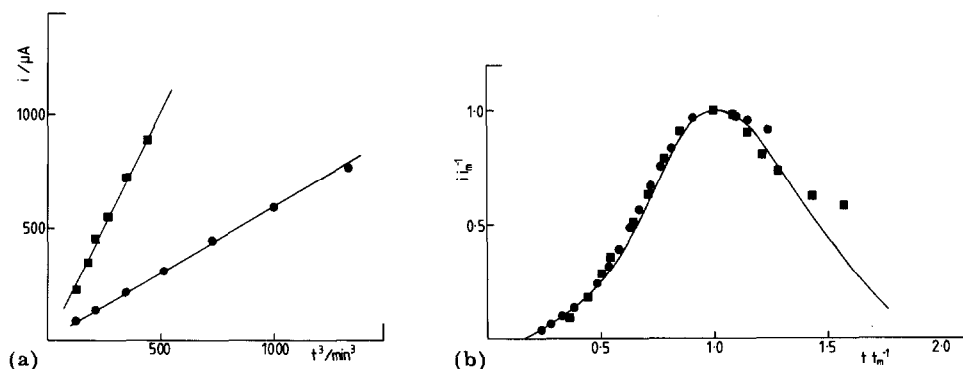$$i = A(1 - \exp \beta t^3) \exp (-\beta t^3), \tag{7}$$
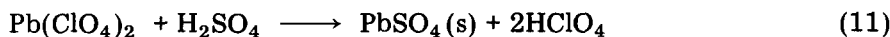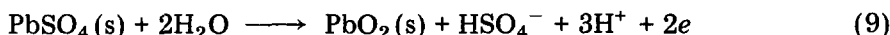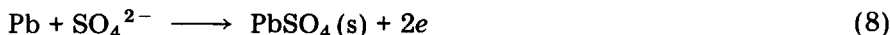
are shown in Fig. 8(a) and (b).

Fig. 8. (a) i vs. t^3 for transients corresponding to Fig. 7. ●, 1225 mV; ■, 1250 mV. (b) reduced plot i/i_m vs. t/t_m corresponding to Fig. 7. Curve drawn indicates the theoretical three dimensional progressive nucleation process ($i = nFk_2[1 - \exp(-\pi M^2 k_1^2 A t^3)/3\rho^2] \exp[(-\pi M^2 k_1^2 A t^3)/(3\rho^2)])$. Key as for Fig. 8(a).

This equation can be discussed in terms of previous results [5]. Under these conditions, the reactions proceeding form a front which progressively advances, similar to electrodeposition of a metal from solution, so that a layer by layer growth occurs. We are dealing under these circumstances therefore with a system which can sustain a self-regenerating reaction. This is

$$Pb + SO_4^{2-} \longrightarrow PbSO_4(s) + 2e \tag{8}$$

$$PbSO_4(s) + 2H_2O \longrightarrow PbO_2(s) + HSO_4^- + 3H^+ + 2e \tag{9}$$

$$PbO_2(s) + Pb(s) + HClO_4 \longrightarrow 2Pb(ClO_4)_2 + 2H_2O \tag{10}$$

$$Pb(ClO_4)_2 + H_2SO_4 \longrightarrow PbSO_4(s) + 2HClO_4 \tag{11}$$

with the propagating sequence given by eqns. (9) - (11). Reaction (8) is fast at the oxidation potential (~ 1200 mV), while reaction (9) is slow and crystallization-controlled. Reaction (10) is a fast reaction and reaction (11) constitutes the regeneration of reactants. Provided that the layers can be penetrated by the ionic species of $HClO_4$ in the optimum concentration, the reactions are self-perpetuating. If insufficient $HClO_4$ is present then the reaction tends towards the simple reaction in H_2SO_4 described above. If the optimum concentration of ClO_4^- is exceeded then eqn. (11) 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 the electrodeposition reaction (7). It is the generation of electrodeposited PbO_2 which presumably accounts for the ultimate three-dimensional current limitation.

This type of behaviour fits well with our current observations. Under the present conditions the addition of perchlorate ion has caused a change from a two-dimensional, progressively nucleated process to a three-dimensional process which is advancing uniformly into the metal lattice.

When the concentration of added perchlorate ion was increased to the region of 100 mM/l, current responses of similar shape to those obtained at ~50 mM/l were observed. The current maxima, however, were lower than those for the 54 mM/l concentrations. This is an interesting observation for it confirms that there is an optimum perchlorate ion addition for the most efficient "attack" on the lead substrate.

It was observed that the current responses to the changes in potential were smooth provided that the concentrations of added perchlorate remained below 100 mM. Above this limit the currents were rather erratic, changing abruptly about a mean value. We interpreted this as oxygen evolution which from time to time altered the effective electrode area, as bubbles grew and then suddenly detached. The increased oxygen evolution reaction was presumably caused by the change in the electrolyte medium. Progressive additions of perchlorate produced more erratic currents, in line with continued lowering of the oxygen evolution potential. Table 1 shows the results obtained.

TABLE 1

$HClO_4$ conc. (mM)	Potential (mV)											
	1100			1150			1200			1300		
	S	i_m	t_m	S	i_m	t_m	S	i_m	t_m	S	i_m	t_m
0	0.75	18	17	1.0	44	6.0	0.8	65	4.9	1.0	140	1.0
10	1.2	34	10	1:3	45	9.0	1.6	57	3.6	1.9	165	2.8
54	—	70	100	—	240	100	3.3	1750	33	2.8	3500	13
100				—	150	180	2.2	825	34	2.85	3000	8
200				—	200	180	—	175	40	—	1500	10

S = slope of log i vs. log t of rising part of transient.
i_m = current maximum (μA).
t_m = time (min) at maximum current.

Conclusions

(1) For the oxidation of Pb to PbO_2 in sulphuric acid (0.5M), the two-dimensional formation process changes from instantaneous to progressive nucleation, if the electrode surface is not passive.

(2) The PbO_2 formation reaction is a solid state one.

(3) The presence of an optimum perchlorate concentration for Planté formation is confirmed (30 - 50 mM/l ClO_4^- in 0.5M H_2SO_4).

(4) Increasing concentrations of perchlorate do not produce ever increasing rates of attack on lead. This is possibly due to the fact that the perchlorate, in displacing the sulphate ion from the lead surface, inhibits the regeneration reaction (11).

Acknowledgements

List of symbols

i	Current
n	Number of electrons transferred
F	Faraday
M	Molecular weight
h	Height of a nucleus
A	Rate of nucleation
k	Chemical rate constant
t	Time
No	Initial number of nuclei
ρ	Density
A,C	Constants in eqn. (6)

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