

OXIDATION MECHANISMS OF LEAD SULPHATE IN SULPHURIC ACID — OVERVIEW*

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Introduction

Understanding the oxidation mechanisms of lead sulphate to lead dioxide in sulphuric acid solution is very important for the improvement of the positive plate of a lead/acid battery. It has been shown that the development of a new phase of lead dioxide by the electrooxidation of lead sulphate requires centres of PbO_2 [1 - 3].

The mechanism of the oxidation of lead sulphate to lead dioxide was first studied by Fleischmann and Thirsk [1]. The oxidation of lead sulphate appears to be controlled by nucleation and three-dimensional crystal growth with an overlapping effect. Hampson *et al.* [2] found that the oxidation mechanisms for cycled lead electrodes are a two-dimensional, instantaneous nucleation process with subsequent overlap of growing centres. Casson [3] showed that the current-time transient under potentiostatic control after the first cycle involves two processes. The first is an instantaneous nucleation and the single layer growth of lead dioxide, while the second process is the conversion of the remaining lead sulphate in more extensive layers.

The morphological transformation during the discharge/charge cycle is related to the growth of lead sulphate and lead dioxide crystals. The sulphuric acid concentration in a practical lead/acid battery changes with the discharge/charge cycle. Hence, the dependence of the charge reaction rate and the growth of lead dioxide on the sulphuric acid concentration is important in the improvement of the charge characteristics of a lead/acid battery.

It is difficult to charge a positive plate that has been immersed in sulphuric acid solution for some period of time after overdischarge. Such a phenomenon is probably caused by the formation of a film of lead sulphate or lead monoxide at the interface between the grid alloy and the active material of the failed battery. It is most important to understand the oxidation behaviour of lead sulphate near the grid/active-material interface because it influences the cycle life and capacity of the lead/acid battery.

In this study, the potentiostatic oxidation of lead sulphate to lead dioxide has been investigated by the use of a scanning electron microscope. The electrode was made by the cathodic reduction of $\beta\text{-PbO}_2$ electrodeposited onto

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a gold planar plate in order to avoid complications caused by the composition of the anodic film on lead. Fundamental investigations of the oxidation of lead sulphate in various concentrations of sulphuric acid were made in order to determine the factor(s) that control the charge reaction rate.

At first, a lead dioxide film with a thickness of about $7\ \mu\text{m}$ was used. Later, a film with a thickness of about $30\ \mu\text{m}$ was employed in order to avoid oxidation of the grid material.

In a practical lead/acid battery, the lead alloy serves as a substrate for the active material which is very porous. Therefore, it is essential to investigate the state of the interface between the porous lead dioxide and the lead substrate after battery discharge. Thus, in the final experiment, pasted porous lead dioxide on a lead substrate was used as a test electrode in order to observe the interface between the porous lead dioxide and the lead substrate after overdischarge.

Experimental

A β - PbO_2 electrode was prepared by electrodeposition onto a gold plate from $2.5\ \text{M}\ \text{HNO}_3$ containing $0.03\ \text{M}\ \text{Pb}(\text{NO}_3)_2$ for 30 min at $3\ \text{mA}\ \text{cm}^{-2}$. The thickness of lead dioxide on the gold plate was about $7\ \mu\text{m}$ and the apparent surface area was $0.785\ \text{cm}^2$. The lead dioxide electrode was discharged in $0.5\ \text{M}\ \text{H}_2\text{SO}_4$ at $0.1\ \text{mA}\ \text{cm}^{-2}$ until the electrode potential reached $0.8\ \text{V}$ versus $\text{Hg}/\text{Hg}_2\text{SO}_4/0.5\ \text{M}\ \text{H}_2\text{SO}_4$.

A thick lead dioxide electrode was prepared by electrodeposition onto the gold plate from $2.0\ \text{M}\ \text{HNO}_3$ containing $0.3\ \text{M}\ \text{Pb}(\text{NO}_3)_2$ for 240 min at $2\ \text{mA}\ \text{cm}^{-2}$. A dense lead dioxide film was obtained with a thickness of about $30 - 40\ \mu\text{m}$ and an apparent surface area of $0.785\ \text{cm}^2$. The X-ray diffraction (XRD) pattern of the film showed that it consisted of α - and β -lead dioxides. The electrode was discharged at $50\ \mu\text{A}\ \text{cm}^{-2}$ in $5.0\ \text{M}\ \text{H}_2\text{SO}_4$ under various conditions.

The porous lead dioxide electrode was prepared as follows. Lead monoxide ($2.5\ \text{g}$), $5.0\ \text{M}\ \text{H}_2\text{SO}_4$ ($0.2\ \text{ml}$), and distilled water ($0.4\ \text{ml}$) were mixed for about 5 min to make a paste of active material. The lead plate was immersed in dilute nitric acid in order to remove lead oxides and other impurities from the surface. The apparent surface area of the lead plate was $3.14\ \text{cm}^2$. The paste was put on the clean lead plate and pressed. The resulting electrode was washed in distilled water, and then dried for 15 h. It was then oxidized to lead dioxide over 24 h at $16\ \text{mA}\ \text{cm}^{-2}$ in $1.0\ \text{M}\ \text{H}_2\text{SO}_4$. The electricity passed in the process corresponded to 200% of the theoretical amount required to oxidize lead monoxide completely to lead dioxide. The electrode was discharged in $2.5\ \text{M}\ \text{H}_2\text{SO}_4$ at $30\ ^\circ\text{C}$ under various conditions, and was then immersed in $2.5\ \text{M}\ \text{H}_2\text{SO}_4$ until the change in the open-circuit potential was less than $1\ \text{mV}\ \text{h}^{-1}$. The lead sulphate electrodes prepared by these procedures were oxidized potentiostatically in a sulphuric acid solution; the current-time transients were recorded.

The lead dioxide film was removed from the gold or lead plate after discharge or charge. Both the interface between the gold-plate/film and the surface of the lead dioxide film were examined with a scanning electron microscope and analyzed by using X-ray diffraction spectroscopy.

Potentiostatic oxidation of thin lead sulphate films in sulphuric acid

Lead sulphate formed on the electrode was oxidized by using a potential step method, stepped from the equilibrium potential to 1.01, 1.11 and 1.31 V *versus* Hg/Hg₂SO₄ in 0.5 M H₂SO₄ [4]. The current-time transients during the potentiostatic oxidation at various potentials were recorded. A dimensionless current was obtained by dividing the anodic current by the maximum current and a dimensionless time was obtained by dividing the time by the time at the maximum current. Dimensionless current-time transients are plotted in Fig. 1.

The transients consist initially of a rapidly falling current that then rises and passes through a maximum. During the initial falling period, double-layer charging is expected to control the anodic current. The subsequent rising and falling transient probably corresponds to the oxidation of lead sulphate with two- or three-dimensional crystal growth of lead dioxide. Hence, it appears that the charge-transfer reaction controls the growth of lead dioxide. The charge contained in the rising and falling current-time transient is a few tenths of a percent of the amount of electricity passed during the discharge. This implies that the oxidation of lead sulphate to lead dioxide proceeds with increase and decrease in the reaction interface area until the charge ratio reaches at least 30 - 40%.

XRD patterns and scanning electron micrographs were obtained for the electrode surface after oxidation to 1.11 V and after various amounts of electricity had passed during discharge. The results of the XRD analysis were inconsistent with those obtained with scanning electron microscopy. At 20% capacity, XRD analysis indicated the formation of lead

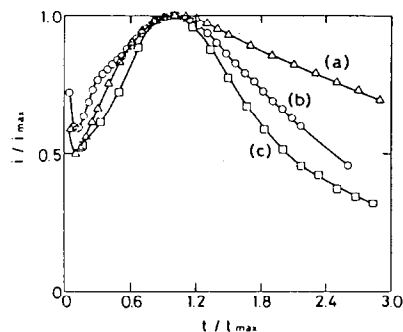


Fig. 1. Dimensionless current-time transients calculated from current-time transients during potentiostatic oxidation of lead sulphate at: (a) 1.01 V, (b) 1.11 V, (c) 1.31 V, in 0.5 M H₂SO₄ [4].

dioxide in the lead sulphate film, but lead dioxide crystals could not be observed with a scanning electron microscope. This suggests that the lead dioxide layer grows within the interior of the lead sulphate film and that the surface of the latter is not oxidized at 20% capacity. The charge in the rising and falling transient accounted for about 30% of the electricity passed during the discharge, so that the rising and falling current-time transient seems to correspond to the growth of the lead dioxide layer within the interior of the lead sulphate film.

Figure 2 shows the cross section of the electrode oxidized at 1.11 V to 20, 50, 70 and 100% of the discharge capacity. The lead dioxide layer is observed in the cross section of the electrode oxidized to 20% capacity and lead sulphate is present on the lead dioxide layer. The lead dioxide formed beneath lead sulphate has uniform thickness. It is considered that the lead dioxide first grows perpendicularly to a gold substrate and then grows parallel to the substrate. At 70% capacity, the lead sulphate near the electrode surface is oxidized to lead dioxide. Thus, the oxidation of the lead sulphate film to lead dioxide starts at the deepest part of the film and the lead dioxide layer grows extensively with two-dimensional crystal growth beneath the film. Finally, lead sulphate near the electrode surface converts to lead dioxide.

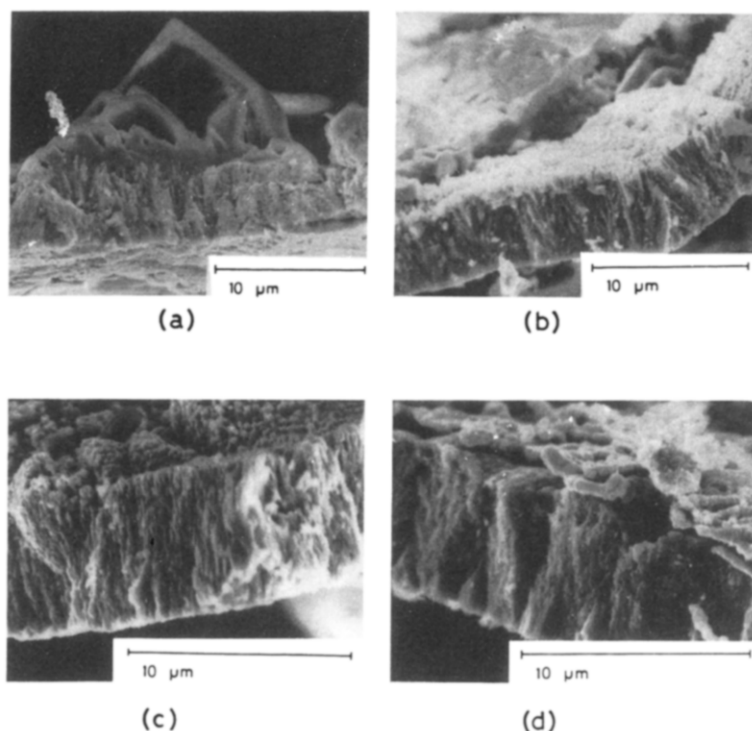


Fig. 2. Electron micrographs of electrode cross section oxidized at 1.11 V to: (a) 20%; (b) 50%; (c) 70%; and (d) 100% of discharge capacity [4].

A study was made of the interface between a gold plate and a lead sulphate film oxidized at 1.11 V to various charge ratios. The lead sulphate crystals were very large and inter-connected. The lead dioxide layer was porous and was different from the lead sulphate crystals. The latter were observed at 30% capacity, but not beyond 50% capacity. The lead dioxide region increased and the lead sulphate region decreased during oxidation of the film. It is considered that the oxidation of lead sulphate within the film was completed at 30 - 50% capacity. Therefore, the current peak results from the crystal growth of lead dioxide beneath the film. The oxidation starts at the grain boundaries and then proceeds at the interface between lead dioxide and lead sulphate. Initially, the area of this interface appeared to increase during the oxidation of the film, then decrease beyond 13.6% capacity. The lead sulphate had a cubic crystalline form prior to oxidation, and then changed to cylindrical crystals during the oxidation. Examination by scanning electron microscopy showed that the growth of the lead dioxide layer was not cylindrical, thus the conversion process of lead sulphate to lead dioxide cannot be explained by a simple two-dimensional crystal-growth mechanism that involves the cylindrical growth of lead dioxide. The lead sulphate film is very thick and has neither an ionic nor an electronic conductivity. Hence, it is proposed that the dissociation of lead sulphate to Pb^{2+} ions and SO_4^{2-} ions precedes the electrodeposition of lead dioxide. At the interface between lead sulphate and lead dioxide, the mass transport process of Pb^{2+} ions from lead sulphate to lead dioxide does not limit the reaction rate, because the diffusion path is very short. The oxidation is controlled by the charge-transfer reaction at the reaction interface. Therefore, the change in the reaction interface area controls the anodic current transient during the potentiostatic oxidation of lead sulphate.

The interface between a gold plate and the lead sulphate film oxidized to about 25% capacity at 1.01, 1.11 and 1.3 V *versus* $\text{Hg}/\text{Hg}_2\text{SO}_4$ was investigated. Cylindrical lead sulphate crystals were observed at 1.01 - 1.31 V, but their sizes were different. For oxidation at 1.01 V, large cylindrical lead sulphate crystals predominated, while at 1.31 V, both large and small crystals remained at the interface between the gold plate and the lead sulphate film. For oxidation at 1.11 V, cylindrical crystals were observed with a size that was larger than that of crystals formed at 1.31 V. The reaction interface area at 1.31 V is the largest of the three. As mentioned before, only large lead sulphate crystals were observed and small crystals had disappeared at 1.01 V. The reaction interface area at this stage is therefore very small, and the oxidation of lead sulphate to thick lead dioxide proceeds more extensively. The dimensionless current at 1.01 V exhibited the least change for the three oxidation potentials, as shown in Fig. 1. The oxidation at 1.01 V appears to proceed with the smallest change in the reaction interface area. On the other hand, the oxidation at higher potentials proceeds with a greater change in the reaction interface area. It is considered that the difference between the three transients is caused by a difference in the extent of the change in the reaction interface area. Figure 3 is a schematic illustration of the

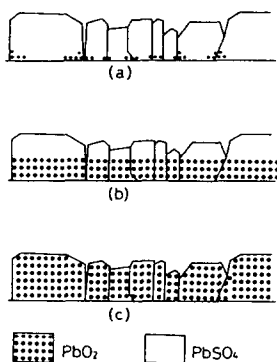


Fig. 3. Schematic illustration of a model for the oxidation of a lead sulphate film to lead dioxide in three stages [4].

oxidation of the lead sulphate film to lead dioxide in three separate steps, namely: (a) oxidation takes place in the deepest parts of the lead sulphate film and the lead dioxide layer at the interface between the gold plate and the lead sulphate film is formed; (b) oxidation proceeds within the interior of the film where a two-dimensional change in the reaction interface area occurs and a thick lead dioxide layer grows; (c) lead sulphate remaining near the interface between the electrolyte and the electrode is oxidized without an increase in the reaction interface area.

Effect of sulphuric acid concentration on oxidation of lead sulphate

Figure 4 displays the current-time transients in 0.1, 0.5, 1.0, 2.5 and 5.0 M H₂SO₄ during potentiostatic oxidation at ($E_0 + 0.2$) V versus Hg/Hg₂SO₄,

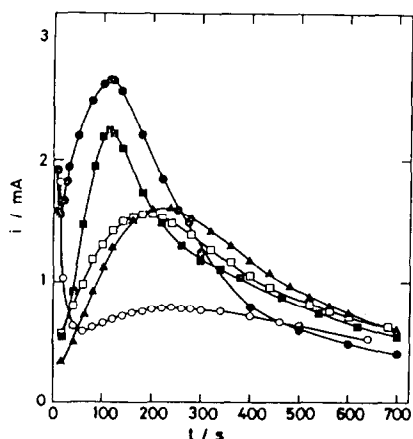


Fig. 4. Current-time transients of oxidation of lead sulphate to lead dioxide at ($E_0 + 0.2$) V in various H₂SO₄ concentrations: ▲, 0.1 M; ●, 0.5 M; ■, 1.0 M; □, 2.5 M; ○, 5.0 M [5].

where E_e is the equilibrium potential of the lead dioxide electrode in sulphuric acid solution [5]. All transients displayed rising and falling currents. The anodic current was the largest in 0.5 M H_2SO_4 . The oxidation of the lead sulphate film to lead dioxide depends on the concentration of sulphuric acid solution. From this result, it can be seen that the oxidation of the lead sulphate film proceeds via a dissolution-precipitation mechanism in the interior of the film. The electrolyte solution seems to penetrate the film via the grain boundaries. The oxidation rate is considered to depend on the effective reaction area and the charge-transfer reaction rate. The oxidation of the lead sulphate can be expressed by:



The anodic current can be written as [2]:

$$i = nFAkC_{Pb^{2+}}^x C_{H^+}^y \quad (3)$$

where: A is the reaction interface area (which changes with the extent of the oxidation); $C_{Pb^{2+}}$ and C_{H^+} are the concentrations of the Pb^{2+} ions and the H^+ ions in the sulphuric acid solution (these depend on the concentration of sulphuric acid solution); x and y are the reaction orders of Pb^{2+} ions and H^+ ions, respectively, for the anodic reaction; k is the potential dependence constant.

As expected from eqn. (3), the anodic current changes with the concentrations of the Pb^{2+} and H^+ ions and the reaction interface area. These concentrations are related to the charge-transfer reaction rate at the reaction interface. Figure 5 shows the cross-sections of an electrode oxidized to 50% of the discharge capacity. The lead dioxide layer consists of small inter-connected crystals. The crystal size decreases with increase in the concentration of sulphuric acid solution. The electrode surface is covered with the lead sulphate crystals in 5.0 M H_2SO_4 . The thickness of the lead dioxide layer is almost the same in 0.1, 0.5, 2.5 and 5.0 M H_2SO_4 .

Scanning electron microscopy showed that the oxidation of lead sulphate to lead dioxide occurred beneath the lead sulphate film for 30 - 40% of the discharge capacity in all sulphuric acid solutions. The lead dioxide layer was formed with increasing and decreasing reaction interface areas. It was expected that the electron micrograph of the electrode surface in 5.0 M H_2SO_4 would be similar to those in other sulphuric acid solutions. This proved, however, not to be the case.

The electrode potential of lead dioxide is higher than the oxygen evolution potential. Oxygen evolution can occur at the oxidation potential of the lead sulphate film. The oxygen overpotential on lead dioxide is very large, but it decreases with increase in the concentration of sulphuric acid solution [6]. The oxygen overpotential on lead dioxide in 5.0 M H_2SO_4 is smaller than in the other sulphuric acids, so that oxygen evolution also takes place during the course of the oxidation of the lead sulphate film to lead

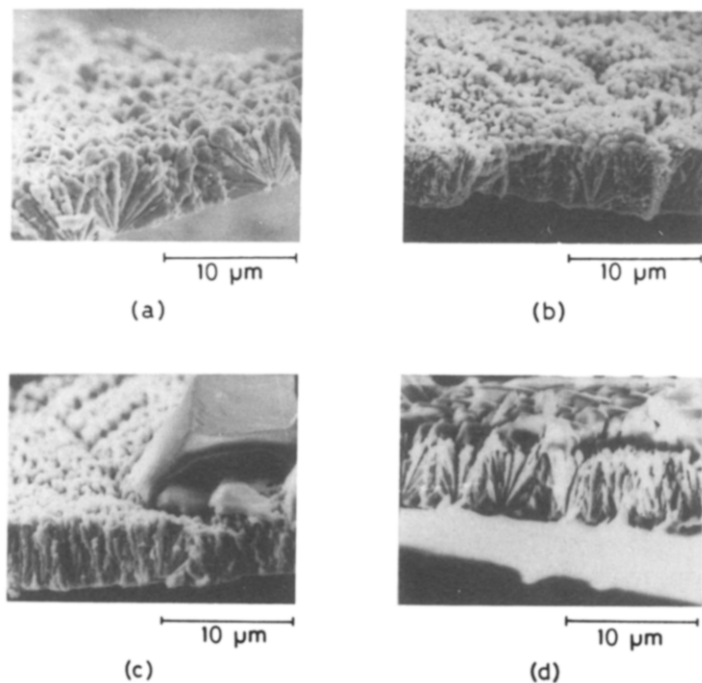


Fig. 5. Electron micrographs of cross section of electrode oxidized to 50% discharge capacity at ($E_e + 0.2$) V in (a) 0.1 M, (b) 1.0 M, (c) 2.5 M, (d) 5.0 M H_2SO_4 [5].

dioxide. Therefore, the anodic current results from both the oxidation of the lead sulphate film and the evolution of oxygen. The electricity for the oxidation of the lead sulphate film to lead dioxide is smaller than that obtained from the integration of the current-time transient (50% of the discharge capacity). The oxidation of the lead sulphate in 5.0 M H_2SO_4 has still to reach 50% and the electrode surface is normally covered with lead sulphate crystals.

The dependence of the peak current on the concentration of sulphuric acid solution is presented in Fig. 6. The peak current corresponds to the rate of the charge transfer reaction, and is greatest in 0.5 M H_2SO_4 . The rate depends on the Pb^{2+} ion and H^+ ion concentrations, as expected from eqn. (3). The concentration of H^+ ions increases with increasing sulphuric acid concentration, while the concentration of Pb^{2+} ions exhibits a maximum at 1.0 M H_2SO_4 , Table 1 [7]. It is considered that the charge-transfer rate becomes higher in sulphuric acid solution containing higher concentrations of Pb^{2+} ions and lower concentrations of H^+ ions. The dependence of the peak current on the concentration of sulphuric acid solution is more similar to the change in the concentration of Pb^{2+} ions than that of H^+ ions. Hence, it would appear that the reaction rate is determined mainly by the concentration of Pb^{2+} ions. The peak current in 0.5 M H_2SO_4 is, however, larger than that in 1.0 M H_2SO_4 . This fact cannot be explained

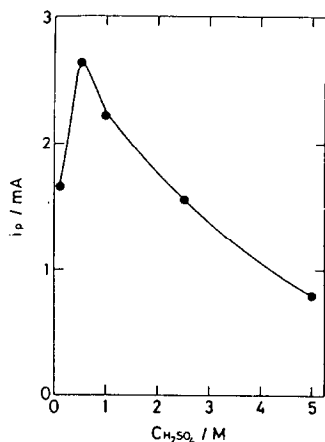


Fig. 6. Dependence of oxidation current peak on sulphuric acid concentration [5].

TABLE 1

Concentrations of Pb^{2+} and H^+ ions in various concentrations of sulphuric acid [5]

$C_{H_2SO_4}$ (M)	$C_{Pb^{2+}}$ ($10^{-5} M$)	C_{H^+} (M)
0.1	1.58	0.0293
0.5	1.88	0.0793
1.0	2.40	0.1335
2.5	1.60	0.3667
5.0	0.56	1.6540

solely by the effect of the concentration of Pb^{2+} ions since the latter is smaller in 0.5 M H_2SO_4 than in 1.0 M H_2SO_4 . Therefore, the effect of H^+ ion concentration must also be considered in order to explain the dependence of the peak current on the concentration of sulphuric acid.

Oxidation of lead sulphate at a gold/active-material interface

A dense lead dioxide film prepared by electrodeposition onto a gold plate (thickness 30 - 40 μm) was used as the electrode system [8]. The electrode was discharged at $50 \mu A cm^{-2}$ in 5.0 M H_2SO_4 , under conditions summarized in Table 2, until the potential had fallen to 700 mV *versus* Hg/Hg_2SO_4 . The electrode was then potentiostatically discharged at 700 mV *versus* Hg/Hg_2SO_4 .

All electrodes discharged under the various conditions were oxidized potentiostatically at 1.320 V *versus* Hg/Hg_2SO_4 in 5.0 M H_2SO_4 until the

TABLE 2

Discharge conditions of the electrodes

Discharge procedure	Temperature (°C)	Discharge period (day)	$Q_{\text{discharge}}^a$ ($10^{-3} \times C$)
(A)	30	3	560
(B)	30	6	678
(C)	50	2	1047

*Electricity passed during discharge.

amount of electricity passed during the oxidation reached 100% of that passed during the discharge. The given potential is about 200 mV more positive than the equilibrium potential of $\text{PbO}_2/\text{PbSO}_4$ in 5.0 M H_2SO_4 . The solid curves in Fig. 7 show the current-time transients during the potentiostatic oxidation of the electrodes discharged under the various conditions. It can be seen that the oxidation currents increase sharply during the initial period of potentiostatic oxidation, and then decrease gradually with time. The oxidation current curves do not decrease monotonically but contain a small shoulder. These transients are very different from those given in Fig. 4. The dashed curve shows the current-time transient for the potentiostatic oxidation of lead sulphate formed during the discharge of a thin lead dioxide film, as presented in Fig. 4. In this case, the thickness of the lead dioxide film is about $7 \mu\text{m}$, and the film is converted totally to lead sulphate during the course of the galvanostatic discharge. The current for the oxidation of lead sulphate increases sharply and then decreases for a short time. In the case of a thin lead dioxide electrode, however, the oxidation current increases again and then decreases during the potentiostatic oxidation. The current-time transient is explained by an increase and then a decrease in the reaction site area, *i.e.*, the interface between lead sulphate and lead dioxide. Comparison of the oxidation currents in Fig. 7 reveals that the reaction site does not alternate as

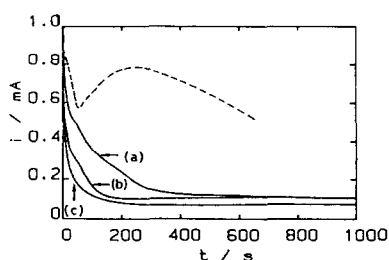


Fig. 7. Current-time transients during potentiostatic oxidation of an electrode discharged under various conditions: (a) discharged 3 days at 30 °C; (b) discharged 6 days at 30 °C; (c) discharged 2 days at 50 °C. Dashed curve taken from Fig. 4 [8].

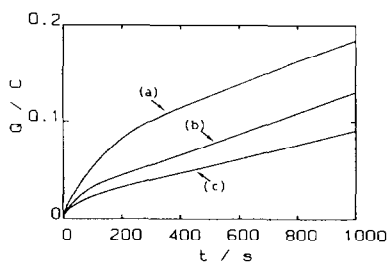


Fig. 8. Amount of electricity passed during potentiostatic oxidation: (a) discharged 3 days at 30 °C; (b) discharged 6 days at 30 °C; (c) discharged 2 days at 50 °C [8].

much during the potentiostatic oxidation of a thick lead dioxide in 5.0 M H_2SO_4 .

The oxidation currents at 1000 s are probably totally due to oxygen evolution. This is because the oxidation current of the electrode (Fig. 3(a) and (b)) at 1000 s becomes constant at the same time in both sets of conditions. In fact, both the temperature and the discharge period strongly influence the charge characteristics of the positive electrode.

The amount of electricity passed during potentiostatic oxidation of the electrode is plotted against time in Fig. 8. The total charge passed through the electrode during both the galvanostatic and potentiostatic discharge is different for each discharge condition, as shown in Table 2. The electrode discharged under condition (C) gave the largest amount of electricity while that discharged under condition (A) gave the smallest amount of electricity. Thus, the amount of lead sulphate formed in the electrode increased with increase in either the temperature or the discharge period. It is to be expected that the amount of electricity passed through the electrode during potentiostatic oxidation increases with increase in the amount of lead sulphate. Nevertheless, the reverse was found to be the case, see Fig. 8.

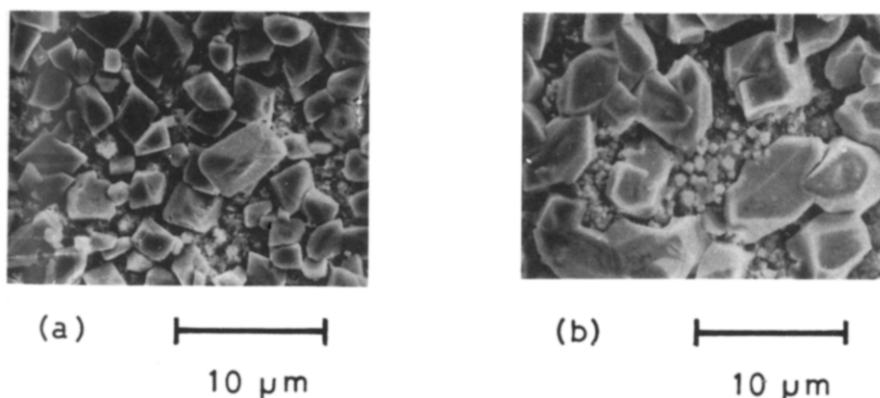


Fig. 9. Scanning electron micrographs of electrode surface: (a) discharged 3 days at 30 °C; (b) discharged 6 days at 30 °C [8].

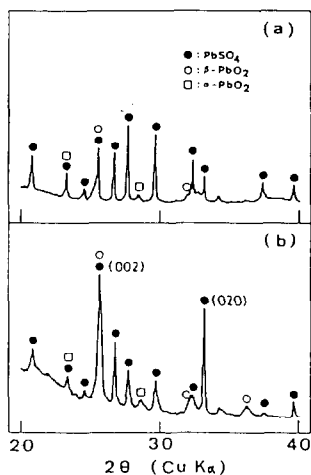


Fig. 10. X-ray diffraction patterns of electrode discharged for 2 days at 50 °C: (a) electrode surface; (b) interface between lead dioxide film and gold plate [8].

Figure 9 shows electron micrographs of the surfaces of the electrodes discharged for either 3 or 6 days at 30 °C. The lead sulphate crystal size was larger for the longer discharge period. Lead sulphate crystals, which formed on the electrode surface during the initial period of discharge grew into large crystals during later stages through ageing.

Lead sulphate crystals grow via a dissolution-precipitation process in sulphuric acid [9, 10]. Large lead sulphate crystals are formed on the electrode surface during the final stages of potentiostatic discharge because the discharge current at this time is very small [11, 12]. These crystals exhibit a sharply defined cubic form. It is difficult to oxidize such lead sulphate as the oxidation rate depends on crystal size [12].

XRD phase analysis detected α -PbO₂, β -PbO₂, and PbSO₄ on the surface of the electrodes discharged at 30 °C. Both α -PbO₂ and β -PbO₂, but not PbSO₄ or PbO, were detected at the interface between the gold plate and the film. The XRD patterns of an electrode discharged at 50 °C are given in Fig. 10. Both the diffraction pattern of the electrode surface and that of the interface show numerous peaks that correspond to lead sulphate crystals. This result suggests that lead sulphate crystals are formed both on the electrode surface and at the interface when discharge is carried out at 50 °C. Furthermore, the relative intensities of diffraction peaks corresponding to the (002) plane ($2\theta = 25.6^\circ$) and the (020) plane ($2\theta = 33.2^\circ$) of lead sulphate deposited at the interface are both stronger than those for lead sulphate deposited on the electrode surface. Thus, lead sulphate formed at the interface is oriented in the (002) and (020) planes. Lead sulphate growth at the interface may be limited in a direction parallel to the substrate and appears to be difficult to oxidize.

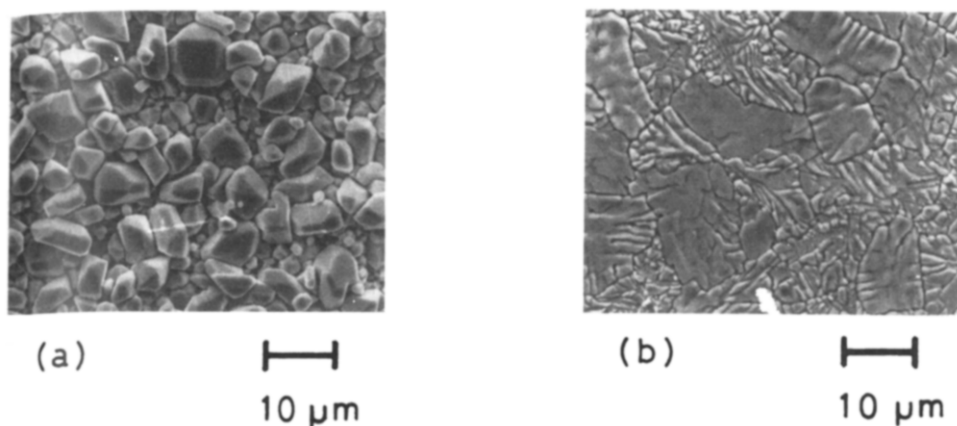


Fig. 11. Electron micrographs of electrode discharged for 2 days at 50 °C: (a) electrode surface; (b) interface between lead dioxide film and gold plate [8].

Electron micrographs of the electrode discharged for 2 days at 50 °C are given in Fig. 11. The electrode surface is totally covered with lead sulphate crystals. From Figs. 9 and 11, it can be seen that crystals formed on the surface of the electrode discharged for 2 days at 50 °C are of similar size to those on an electrode discharged for 6 days at 30 °C. In the case of the former electrode, the lead sulphate crystals are also present at the interface between the lead dioxide film and the gold plate. The latter crystals are large and plate-like. The change of PbO_2 to PbSO_4 at those sites where the discharge extends deeply into the active mass produces stress in the film due to the difference in the molar volumes of PbO_2 and PbSO_4 . Therefore, the lead dioxide film cracks during the course of discharge at 50 °C. Sulphuric acid solution penetrates through such cracks and, as a result, lead sulphate crystals are formed at the interface between the gold plate and the film.

Figure 12 provides a schematic illustration of the electrode discharged under the various conditions given in Table 2. In the case of discharge for 3 days at 30 °C, lead sulphate crystals are observed only on the electrode surface. The size of these crystals increases with the discharge time. The difference between the oxidation currents (as shown in Fig. 7(a) and (b)) is due to the difference in the crystal size of the lead sulphate formed on the electrode surface. On the other hand, for discharge at 50 °C, lead sulphate crystals are formed both on the electrode surface and at the interface between the lead dioxide film and the gold plate. The crystals are first formed on the electrode surface during the initial period of discharge, and then at the interface. The size of crystals formed on the electrode surface at 50 °C for 2 days is nearly the same as that at 30 °C for 6 days. Therefore, the different oxidation currents in Fig. 7(b) and (c) are caused by the formation of lead sulphate crystals at the interface. In 5.0 M H_2SO_4 , the current–time transient during the potentiostatic oxidation is complicated by oxygen evolution, because the oxygen overvoltage of lead dioxide decreases with increasing

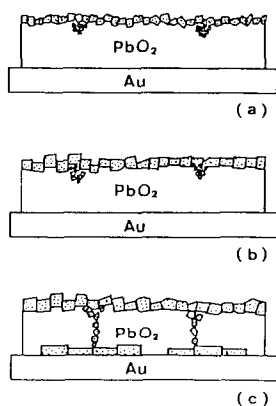


Fig. 12. Schematic illustration of an electrode discharged under various conditions: (a) 3 days at 30 °C; (b) 6 days at 30 °C; (c) 2 days at 50 °C [8].

sulphuric acid concentration [7]. Therefore, the electrode discharged for 2 days at 50 °C in 5.0 M H_2SO_4 was potentiostatically oxidized at 1.150 V *versus* $\text{Hg}/\text{Hg}_2\text{SO}_4$ in 0.5 M H_2SO_4 . In 0.5 M H_2SO_4 , the oxidation reaction of lead sulphate is predominant and oxygen evolution is negligible. (Note, a potential of 1.150 V *versus* $\text{Hg}/\text{Hg}_2\text{SO}_4$ is about 200 mV more positive than the equilibrium potential of lead dioxide in 0.5 M H_2SO_4 .)

The transient in Fig. 13 consists of a sharp peak followed by a broad peak. These two peaks correspond to the oxidation of lead sulphate formed both on the electrode surface and at the interface between the lead dioxide film and the gold plate. In order to determine which peak corresponds to which process, the oxidation of the discharged electrode was terminated at the end of the first sharp peak in Fig. 13 ($t = 250$ s) and the electrode examined by scanning electron microscopy. The electricity passed during the oxidation was about 50% of the discharged electricity. It was found that the lead sulphate on the electrode surface was virtually oxidized to lead dioxide (only a few crystals were observed on the electrode surface). By contrast, most of the lead sulphate crystals at the interface were unchanged. Thus, the

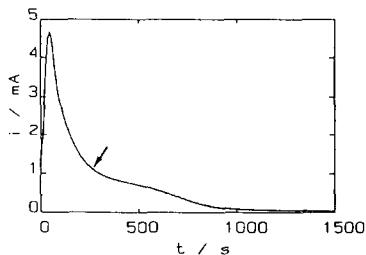


Fig. 13. Current-time transient during potentiostatic oxidation of electrode (discharge conditions: 2 days, 50 °C, 5.0 M H_2SO_4) at 1.150 V *vs.* $\text{Hg}/\text{Hg}_2\text{SO}_4$ in 0.5 M H_2SO_4 at 30 °C [8].

initial sharp current peak in Fig. 13 corresponds to the oxidation of lead sulphate at the electrode surface, and the subsequent broad peak corresponds to the oxidation of lead sulphate at the interface. The oxidation rate at the interface was slower than that at the electrode surface. The lead sulphate at the interface could be totally oxidized in 0.5 M H_2SO_4 . In 5.0 M H_2SO_4 , however, the oxidation continued until the electricity passed was twice the theoretical discharged electricity required to convert the lead sulphate crystals. This is due to a loss of electricity through oxygen evolution. At this stage, the electrode surface was totally oxidized and only lead dioxide was observed. On the other hand, large amounts of lead sulphate remained at the interface between the lead dioxide film and the gold plate. The slow oxidation of the lead sulphate formed at the interface may result from the size and shape of the lead sulphate crystals formed there (*i.e.*, large, plate-like, oriented). Moreover, the slow diffusion of sulphuric acid formed at the interface by the oxidation of lead sulphate results in the corresponding slow oxidation of lead sulphate. The slow diffusion rate is due to the low porosity of the active material. The oxidation of lead sulphate includes the dissolution of lead sulphate and the charge transfer of Pb^{2+} to Pb^{4+} . Large, plate-like and oriented crystals have less defects in the crystal lattice and therefore may be more difficult to dissolve. The small reaction site area of large crystals results in a decrease in the apparent charge-transfer rate.

When lead sulphate is formed at the interface between the active material and the grid alloy, it cannot be totally oxidized to lead dioxide in 5.0 M H_2SO_4 . Therefore, if the electrode is cycled in 5.0 M H_2SO_4 , lead sulphate crystals gradually accumulate at the interface so that the whole of the interface will eventually become covered with such crystals. Since the electronic and ionic conductivities of lead sulphate are both low, the electrode cannot be oxidized. Therefore, failure of the charge characteristics may be caused by the lead sulphate crystals formed at the interface. In other words, lead sulphate formed at the interface between the active material and the grid alloy is an important possible cause of battery failure. Thus, modifying the shape and size of lead sulphate crystals formed at the interface between the grid alloy and the active material is a vital factor in attempts to improve the cycle life and the discharge capacity of lead/acid batteries.

Oxidation of lead sulphate formed at the interface between a lead plate and porous active material

A paste of active material on a lead plate (thickness about 2 mm) was used as the test electrode [13]. The porous lead dioxide (prepared by the electrochemical oxidation of the electrode) was discharged galvanostatically at 8 mA cm^{-2} and then potentiostatically at -450 mV versus $\text{PbO}_2/\text{PbSO}_4$ in 2.5 M H_2SO_4 at 30°C under the various conditions summarized in Table 3.

Figure 14 shows electron micrographs of the electrode surface before, and after, discharge. No lead sulphate crystals were observed on the surface

TABLE 3

Discharge conditions of the electrodes

Discharge conditions				
Electrode	Galvanostatic		Potentiostatic	
	Discharge current (mA cm ⁻²)	Cut-off potential* (mV)	Discharge potential* (mV)	Discharge period (days)
(A)	-8	-250	—	—
(B)	-8	-150	-150	2
(C)	-8	-150	-150	5

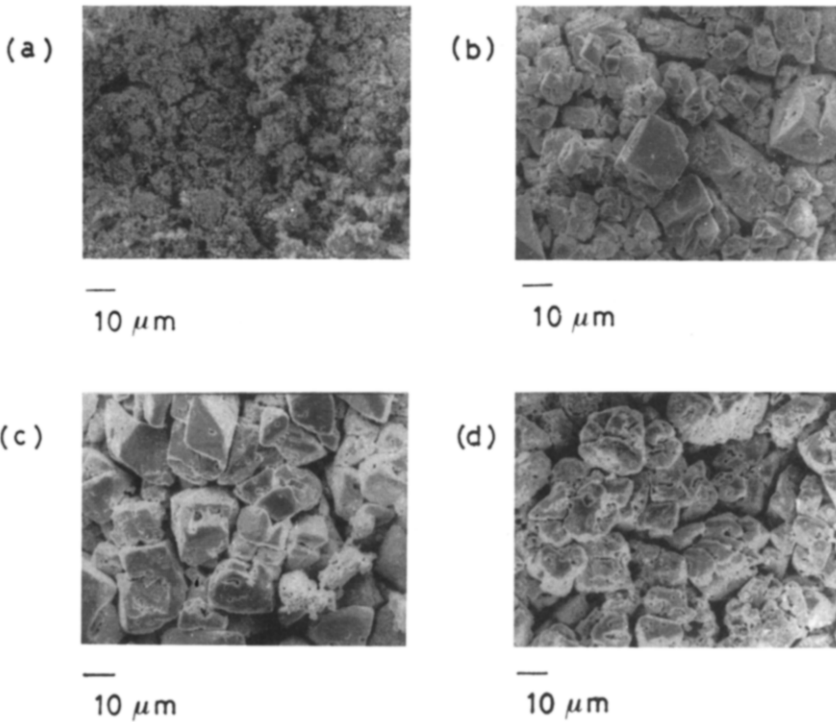
*From equilibrium potential of PbO₂/PbSO₄.

Fig. 14. Electron micrographs of electrode surface before, and after, discharge under conditions of Table 3: (a) before discharge; (b) discharged electrode (A); (c) discharged electrode (B); (d) discharged electrode (C) [13].

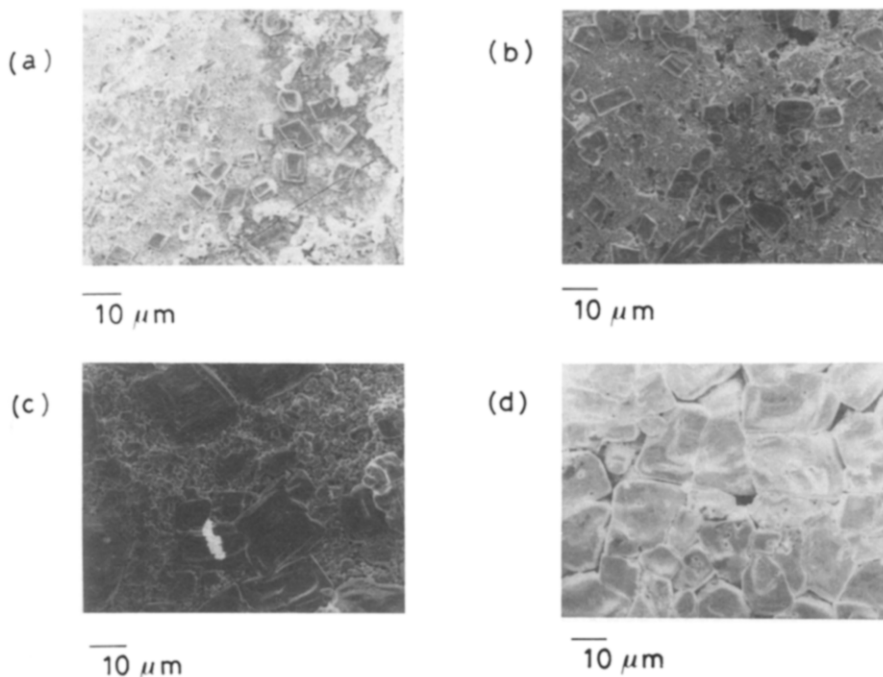


Fig. 15. Electron micrographs of interface between porous electrode and lead plate before, and after, discharge under conditions in Table 3. (a) Before the discharge; (b) discharged electrode (A); (c) discharged electrode (B); (d) discharged electrode (C) [13].

before discharge. After discharge, however, the surface was covered with lead sulphate crystals of size about $20 - 30 \mu\text{m}$. The size and number of the lead sulphate crystals formed during the galvanostatic discharge remained virtually unchanged during a following potentiostatic discharge for 2 and 5 days. Most of the lead sulphate crystals on the electrode surface were formed during the galvanostatic discharge, while further crystals were formed within the inner part of the electrode during the following potentiostatic discharge (-450 mV from the equilibrium potential of $\text{PbO}_2/\text{PbSO}_4$).

Electron micrographs of the interface between the active material and the lead plate, both before, and after, discharge, are given in Fig. 15. A few small lead sulphate crystals are observed at the interface before the discharge. From a comparison of the interface before, and after, galvanostatic discharge, it can be seen that the state of the interface barely changed during the discharge. Therefore, very little discharge reaction occurred at the interface during the galvanostatic discharge. The large and plate-like lead sulphate crystals were deposited and grew at the interface during the course of the following potentiostatic discharge.

For a dense lead dioxide film deposited on a gold plate, no lead sulphate crystals were formed at the interface between the film and the plate during overdischarge at 30°C . When the electrode was discharged at 50°C , however,

sulphate crystals were indeed formed at the interface. On the other hand, lead sulphate crystals were formed at the interface between the porous active material and a lead plate during discharge at 30 °C, as shown in Fig. 15. Since gold is inert, the formation of lead sulphate crystals at the interface between the dense lead dioxide film and the gold substrate results from the discharge reaction of the lead dioxide film. Lead sulphate crystals between the lead plate and the porous lead dioxide film were very similar to those at the interface between the gold plate and the dense lead dioxide film. The more dense lead dioxide electrode may, however, prevent the formation of lead sulphate crystals at the interface between a current collector and an active material.

The XRD patterns of the discharged electrode showed that the discharge reaction of the porous lead dioxide electrode is terminated during the 2-day potentiostatic discharge, and that lead sulphate crystals are formed only at the interface between the active material and the lead plate during the following 3-day potentiostatic discharge.

Figure 16 shows a schematic representation of the interface between porous lead dioxide and a lead plate of the electrodes discharged under various conditions. A few small lead sulphate crystals remain at the interface before the discharge, Fig. 16(a). Lead sulphate crystals do not grow at the interface during the galvanostatic discharge, Fig. 16(b). Lead sulphate crystals develop at the interface during the following potentiostatic discharge, Fig. 16(c). The whole of the interface is covered with large and plate-like sulphate crystals during the course of the following 5-day potentiostatic discharge, Fig. 16(d).

Though the large and plate-like lead sulphate crystals are formed at the interface between the porous lead dioxide film and the lead plate, their size

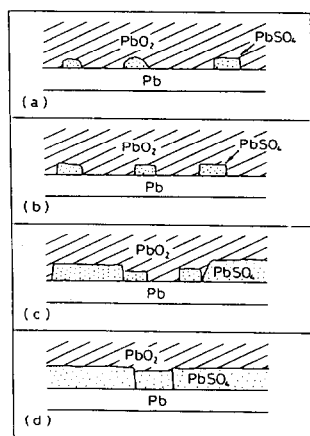


Fig. 16. Schematic representation of the interface between a lead plate and porous lead dioxide discharged under the various conditions of Table 3: (a) Before discharge; (b) discharged electrode (A); (c) discharged electrode (B); (d) discharged electrode (C) [13].

and shape are very different from those of lead sulphate crystals formed on the electrode surface. The discharge reaction rate at the interface region is slow because of the slow mass transport. Such a slow reaction rate is expected from the discharge current during the course of the potentiostatic oxidation. During this period, the discharge reaction mainly proceeds in the interface region. The crystal size of lead sulphate increases with decrease in the discharge current [12]. Thus, the formation of large lead sulphate crystals may be due to the slow growth rate during the potentiostatic discharge. Moreover, the concentration of sulphuric acid solution at the interface region decreases with the extent of the discharge reaction, because the sulphuric acid is consumed, and the diffusion rate through the lead dioxide film is not sufficient to maintain a constant concentration. The solubility of lead sulphate in sulphuric acid increases with decreasing sulphuric acid concentration from 5.0 to 1.0 M [7]. The discharge was conducted in 2.5 M H_2SO_4 . The sulphuric acid concentration at the interface decreases to less than 2.5 M during the discharge. The recrystallization process rate increases with increasing solubility of lead sulphate. The formation of large lead sulphate crystals is therefore due to the decrease in the sulphuric acid concentration at the interface during potentiostatic discharge.

The lead sulphate crystal growth in the interface region was controlled by a special situation. The growth rate in a direction parallel to the substrate may be larger than that in the perpendicular direction because it is limited by the substrate. Therefore, plate-like crystals will be formed at the interface between the active material and the lead plate. The oxidation of such an electrode was carried out at 200 mV from the equilibrium potential of $\text{PbO}_2/\text{PbSO}_4$ in 2.5 H_2SO_4 at room temperature. Figure 17 shows the current-time transients during the potentiostatic oxidation of the electrodes discharged under different conditions. The oxidation current of the electrode discharged galvanostatically exhibits a sharp increase at the beginning of the potentiostatic oxidation, and then decreases continuously with time. This result

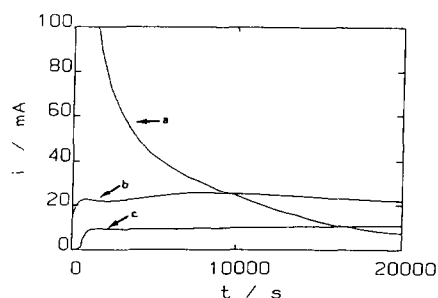


Fig. 17. Current-time transients during potentiostatic oxidation of electrodes under various conditions given in Table 3. (a) Discharged electrode (A); (b) discharged electrode (B); (c) discharged electrode (C) [13].

shows that the charge acceptance of an electrode discharged under galvanostatic conditions is very good. In the case of electrodes (B) and (C), which were discharged galvanostatically and then potentiostatically for 2 or 5 days, respectively, the very small oxidation currents were observed at the beginning of the potentiostatic oxidation, and then small, constant oxidation currents passed through the electrodes. This constant current decreased with increase in the potentiostatic discharge period. Such behaviour suggests that the polarization is caused by the resistance layer formed in the electrode during discharge. The surface of the electrode only discharged galvanostatically was oxidized to lead dioxide during potentiostatic oxidation for 10 h; no lead sulphate crystals were observed. However, in the case of an electrode discharged galvanostatically and then potentiostatically discharged for 2 or 5 days, lead sulphate crystals were observed on the electrode surface after potentiostatic oxidation for 10 h. The electrode active materials after the 10 h potentiostatic oxidation were examined by XRD. For an electrode only discharged galvanostatically, lead sulphate crystals formed on the electrode were totally oxidized and the diffraction peaks corresponded to lead dioxide, as expected from the current-time transient. In the case of electrodes discharged galvanostatically and then potentiostatically for 2 or 5 days, the

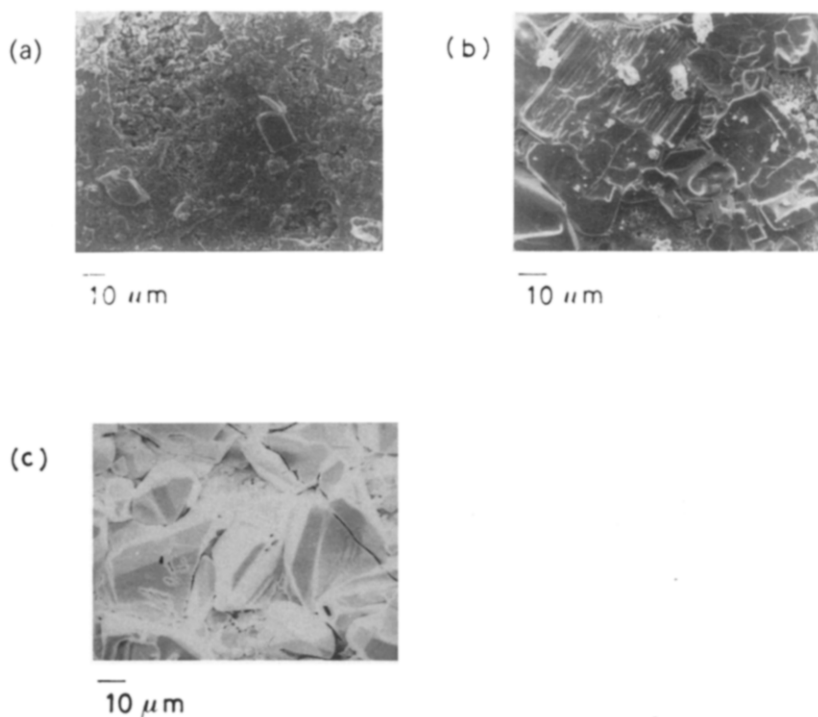


Fig. 18. Electron micrographs of interface between porous lead dioxide and lead plate after potentiostatic oxidation for 10 h. Electrode discharged under conditions given in Table 3. (a) Discharged electrode (A); (b) discharged electrode (B); (c) discharged electrode (C) [13].

relative intensities of the XRD peaks of lead dioxide increased with increase in the period of potentiostatic oxidation. Diffraction peaks for lead sulphate were observed, however, even though an extensive potentiostatic oxidation was undertaken. The electrodes discharged galvanostatically and then potentiostatically could not be oxidized completely. Figure 18 shows electron micrographs of the interfaces between the active material and the lead plate after potentiostatic oxidation for 10 h. After 10 h potentiostatic oxidation, a few small lead sulphate crystals were observed at the interface between the lead plate and the porous lead dioxide electrode discharged only galvanostatically. By contrast, the large plate-like lead sulphate crystals formed at the interface in electrodes discharged galvanostatically and then potentiostatically for 2 or 5 days were virtually unaffected during the potentiostatic oxidation.

The reaction site of the oxidation of lead sulphate crystals is the interface between lead sulphate and lead dioxide. The reaction site area of large lead sulphate crystals is smaller than that of small crystals. It may be impossible to oxidize large lead sulphate crystals because of this small reaction site area. In the case of a dense lead dioxide film, however, lead sulphate crystals formed at the interface region can be oxidized over a longer period. These findings can be attributed to a difference in either the crystal size of the lead sulphate or the thickness of the lead sulphate layer at the interface region.

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