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Fundamentals of lead-acid cells. X. The formation of PbO_2 on lead and antimonial lead

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The electrochemical oxidation of films of lead sulphate formed by the cyclic sweep method has been examined using the potential step technique. Gross differences in behaviour are observed between the lead and antimonial lead alloy, the most important being the appearance of an additional peak in the transient response of the antimony alloy. An interpretation is given in terms of the structure of the grown lead sulphate film. The oxidation behaviour of the lead sulphate deposits depends on the length of time the electrode is held potentiostatically controlled in the lead sulphate region before being stepped to the PbO_2 region. The results can be readily interpreted in terms of the density of nucleation sites and the formation of the PbO_2 phase by the two-dimensional growth of instantaneously nucleated layers.

1. Introduction

In a previous paper [1] we reported on the cyclic potentiodynamic behaviour of lead and antimonial lead and showed that the extent of oxidative attack as a consequence of cyclic sweeping between the lead sulphate and lead dioxide potential regions was very much enhanced by the addition of antimony to lead. This was a useful result for it provided a background to both the behaviour of the float/cycle performance of stand-by batteries and also active material/grid interactions in automotive batteries.

There were some questions, however, which were not completely settled by the potentiodynamic experiments. Specifically lacking was detail in the comparison between the lead dioxide formation reactions from lead sulphate deposits formed from antimonial and antimony free substrates. This area is particularly interesting in view of the need to maximize rates of battery charging (lead sulphate → lead dioxide) in the face of the electrochemical limitations. A second point of interest arises from the fact that a time delay element between the completion of battery discharge and commencement of charge is often quite important to charge acceptance behaviour reflecting some ageing process of newly grown, oxidizable lead sulphate which is little understood.

It was considered that the technique most likely to provide the additional sought-for data was potential step experiments from a controlled potential level. In order to provide a substrate of sufficient electrochemical capacity for study, electrodes which had been potentiodynamically cycled to constant response were employed. This paper records the experimental results and conclusions.

2. Experimental

The preparation and shrouding of pure lead and lead–antimony (5.15%) rotating disc electrodes, the electrolytic cells and apparatus by which the electrochemistry is carried out have been previously described [1, 2].

It was our intention to follow industrial practice so that cast and aged lead and alloy metal were used. In earlier experiments [2, 3] lead was electrodeposited on lead to attain a consistent response from a carefully controlled surface. In our experiments we mechanically polished on roughened glass and lightly etched in aqueous nitric acid (10 vol%).

In order to achieve the conditions encountered in the lead–acid cell, electrodes were cycled to a constant response. The most convenient way was to cycle potentiodynamically between the lead

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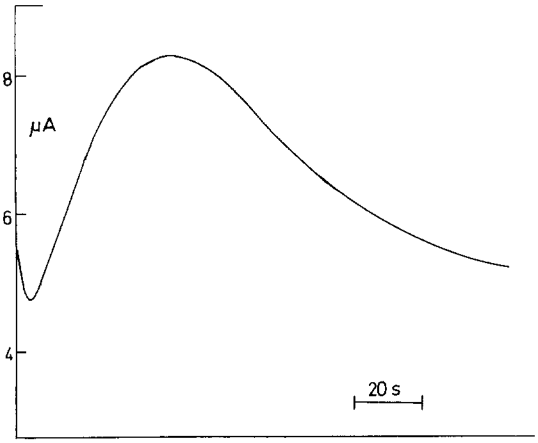

Fig. 1. Current–time response to a potential step experiment (400 mV to 1275 mV) for a lead sulphate electrode formed on pure lead by cycling (400 mV to 1520 mV) in 5 M H_2SO_4. Hold time 15 min at 400 mV. Electrode area, 0.071 cm^2; 23° C.

sulphate region and the lead dioxide region (400 mV–1520 mV at 50 mV s^{-1}). All potentials are referred to the Hg_2SO_4/Hg electrode in the same electrolyte.

Potential step experiments were made from 400 mV after completion of the cyclic preparation of the lead sulphate and a stabilizing period ('hold') at 400 mV. The current in this 'hold' period was quite small ($\sim 1\ \mu A$) and was generally less than observed in earlier experiments on electrodeposited lead [2, 3]. There was no apparent reduction of the current with time during the hold period.

3. Results and discussion

3.1. *Pure lead*

Fig. 1 shows the results of a potential step on a film of $PbSO_4$ formed on pure lead. The behaviour is quite typical of all our results on pure lead and indicates a nucleation and growth process.

In all the potential step experiments, at the front of every rising transient a current 'spike' was observed which is mainly due to double layer charging. Although the lack of any rotation speed dependence of the spike (or the subsequent current) indicates that lead ions do not leave the electrode during the reaction, it was difficult to obtain any quantitatively useful information regarding the electrode/electrolyte interphase. The complication was the very high initial current in the transient itself. It was interesting to note, however, that in experiments with hold periods in excess of 15 min the spike was relatively small and constant. A further point of interest is that a larger spike was observed with the alloy than with pure lead.

Although the current after the spike did not rise from zero it was possible to identify the form of the current increase. It was in our case, however, different from the previously reported data obtained by Fleischmann and Thirsk [3] and us [2] using potentiostatically formed $PbSO_4$ from freshly electrodeposited lead. In those cases the i–t^3 relationship observed at the beginning of the current increase was indicative of a three-dimensional growth and a progressive nucleation process with ultimate current limitation due to overlap of growing centres. It was crucial for this experimental process that the excursion into the PbO_2 region be the first otherwise there is a great deal of evidence to show that the electrocrystallization process responsible for the first current rise is a two-dimensional instantaneous nucleation and growth [2, 4].

In the present experiments the part of the initial rising currents which can be analysed conforms to a linear I versus t relationship characteristic of a two-dimensional growth process. This is shown clearly in Fig. 2.

A further difference is the attainment of the current maximum at a time very much less than that observed under corresponding conditions in the earlier experiments on uncycled electrodes [2, 3]. For example, times of $\sim$10 min were quite typical of the Casson work which is about ten times that of similar experiments here. We can conclude from these results that the cycled electrode contains sufficient nuclei for the electrocrystallization to proceed at a speed sufficient to change the process from the relatively slow three-dimensional one observed with uncycled electrodes to the faster two-dimensional process.

The equation for the two-dimensional process previously found for the conversion of lead sulphate to lead dioxide [3] is

$$i = (zF\pi M/\rho)N_0k^2t\exp(-\pi M^2N_0k^2t^2/\rho^2). \qquad (1)$$

where M is the molar mass, ρ the density of the phase, N_0 the density of nucleation sites on pure Pb and k the nucleation constant. A further proof

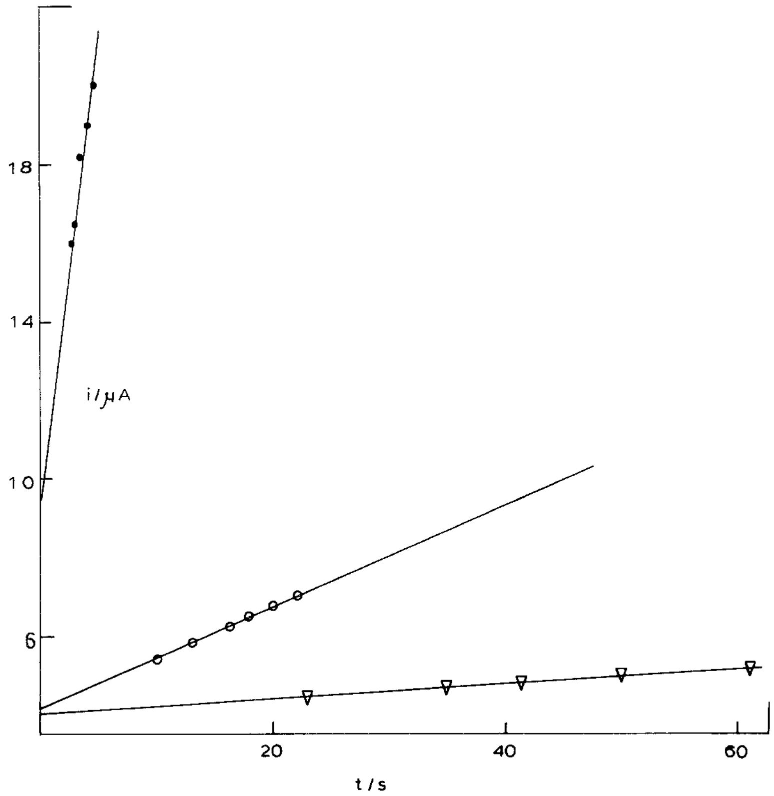

Fig. 2. Current rise in transient responses for a series of hold times at 400 mV. Details as Fig. 1. ● 6 min hold; ○ 15 min hold; △ 30 min hold.

that Equation 1 applies in this case is clear from Fig. 3 where we plot ln $[(i - i_r)/t]$ versus t^2 where i_r is the residual current, and obtain a linear relationship; here the current is corrected for the oxygen evolution process.

Fig. 2 contains data corresponding to three experiments in which, after cycling, the electrode was held for different times potentiostatted in the lead sulphate region. It can be seen that the rising slopes di/dt are quite sensitive to the hold period which from Equation 1 indicates that the effect of the prolonged time in the PbO_2 reduction region

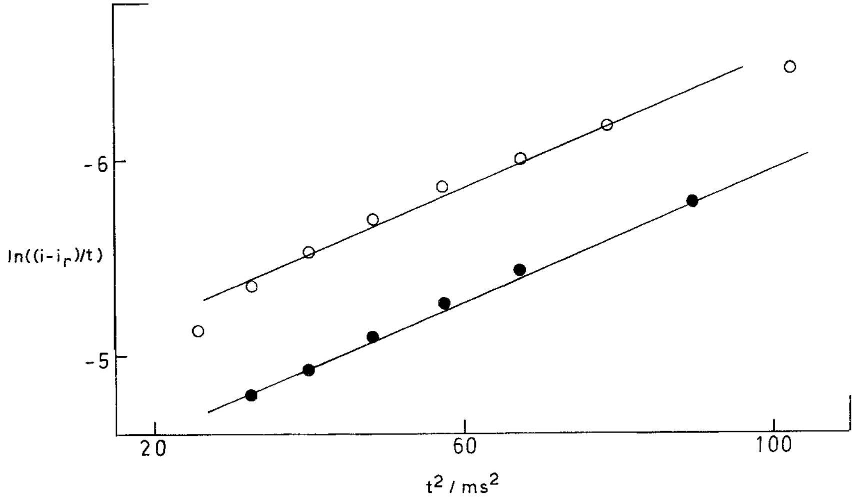

Fig. 3. ln $[(i - i_r)/t]$ versus t^2 for the falling parts of transients for a series of hold times at 400 mV. ○ 30 min hold time; ● 46 min hold time. Details as Fig. 1.

Table 1. The charge contained under the transient curve (corrected for oxygen evolution) and the residual oxygen current (pure Pb)

'Hold' time (min)	i_r (μA)	*Charge contained in peak* (mC cm^{-2})
6	6.0	17.3
14	4.4	11.6
15	4.5	8.3
25	4.0	3.1
30	4.2	5.0
46	6.5	6.2

is to remove nucleation centres. The same conclusion is obtained by considering the position in time of the current maximum which is displaced to longer times by prolonging the pre-oxidation hold period. From Equation 1 by differentiation and setting $di/dt = 0$ we find that t_m, the time of current maximum, is related to N_0 and k by

$$t_m^2 = \rho^2/2\pi M^2 N_0 k^2. \qquad (2)$$

The increase in t_m with hold time confirms that nucleation centres have been removed by the prolonged hold period. It should be noted that it is unlikely that the hold has any effect upon k since this is generally only dependent on potential; it is possible, however, that a small amount of recrystallization of the $PbSO_4$ layer occurs during the potential hold; this is likely to be small. We can therefore ascribe the effect of hold time to the nucleation site density.

At long times the oxidation process is complicated by the intruding oxygen evolution reaction. This is well known [2], although it is nevertheless surprising that the intrusion of the oxygen evolution reaction could be detected so early on in the oxidation. In earlier experiments oxygen intrusion was observed only after 15 min at 1350 mV, while here at 1275 mV clear evidence for oxygen was obtained after a few minutes. The effect of the intrusion of the gaseous evolution can be observed by considering the charge (corrected for the apparent steady state oxygen current) in the rising and falling transient before an experimental steady state current is observed. This is shown in Table 1. The charge under the peak decreases with hold time to a fairly steady value.

We can conclude that considerably more oxidation (of $PbSO_4$ to PbO_2) occurs with parallel oxygen evolution if the number of nucleation centres in the lead sulphate is reduced by holding in the PbO_2 reduction region. This parallel oxidation must be small for the level of current in the quasi-steady-state response at long times was found to be independent of the hold time (Table 1) even though considerable amounts of $PbSO_4$ must be still available for reduction after the termination of the peak. The $PbSO_4$ oxidation process is rendered relatively inefficient by the removal of PbO_2 nucleation centres since the vast majority of the current passing after the peak is going into the oxygen reaction.

A further confirmation of the slow annihilation of nucleation centres with hold time arises from the intercepts at $t = 0$ in Fig. 2. The longer the hold the less the initial current which indicates that the extent of the growth points as well as the number are modified by the reduction.

A final interesting point requiring comment is that our previous work on cycled electrodeposited lead [2] showed that a very shallow secondary peak was present. We have been unable to discover such a response in these experiments even though the current responses were monitored for considerable times. It may be that in our system this peak was obscured by oxygen evolution rather than being absent; in any case it seems that this difference is an electrometallurgical effect.

3.2. *Antimonial lead*

Fig. 4. shows the current response transient of the antimonial lead alloy. It is seen that it differs considerably from that of pure lead. The most significant difference is the appearance of a second peak. This feature was observed in every experiment with the alloy. In Fig. 5 we show the first available slopes of the rising portions of the transients. These compare in both magnitude and dependence on the hold time with the single peak observed with the pure lead. Table 2 contains the charge in the first peak of the alloy response as a function of hold time and these data are within 20% of corresponding ones for the pure lead. The effect of the hold time on t_m for the first peak is in agreement with the single peak on pure lead. We can conclude from this that the electrocrystallization reaction in the first peak for the alloy is identical with the single electrocrystallization process on pure lead.

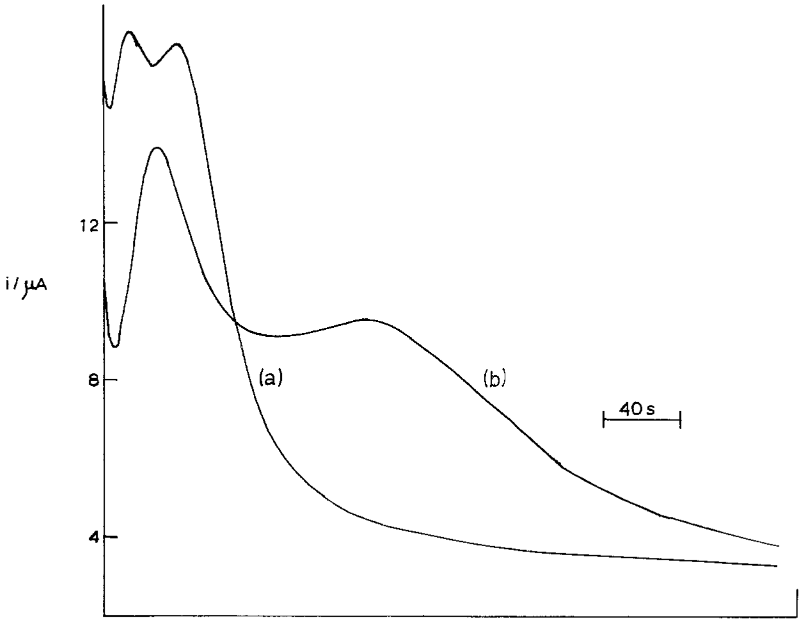

Fig. 4. As Fig. 1 but for lead/antimony alloy. (a) 11 min hold at 400 mV, (b) 35 min hold at 400 mV.

The second peak observed with the alloy is difficult to analyse due to the convolution with the first process and the evolution of oxygen. The most convenient way to proceed is to investigate the falling part of the second transient. A correction was made for the oxygen current and the falling parts of the second peak are represented in Fig. 6 by plotting ln $[(i - i_r)/t]$ versus t^2. Satisfactory straight lines confirm that the process follows Equation 1. Moreover we can conclude from this that since no correction in t is required the process starts at time $t = 0$. The position in time of the

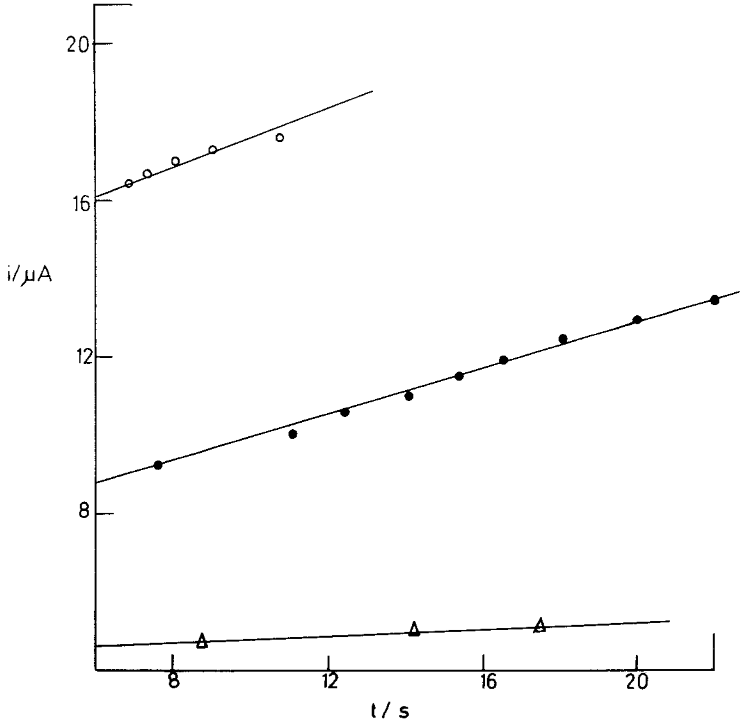

Fig. 5. As Fig. 2 but for lead/antimony alloy. ○ 11 min hold; ● 35 min hold; △ 60 min hold.

Table 2. As in Table 1 but for antimonial Pb

'Hold' time (min)	i_r (μA)	*Charge contained in 1st peak* (mC cm^{-2})
11	3.5	12.2
35	2.5	12.2
46	4.0	11.9
60	3.6	9.2
103	3.0	5.5

maximum for the second process is dependent upon the hold and the dependency is linear as shown in Fig. 7.

Equation 2 can be rewritten with this in mind to predict the effect of holding as

$$t^2_{\mathbf{hold}} \propto \rho^2/2\pi M^2 N'_{\mathrm{o}} k_2^2 \qquad (3)$$

where N'_{o} is the density of nucleation sites on Pb–Sb alloy, i.e. when no holding time is allowed the second peak is observed at a very short time and the current falls from an initially high value. This trend is clearly discernable from the transients of Fig. 4.

The observed differences in behaviour of the alloy and pure lead are important for they are of immediate application to lead cell technology. The development of the extra two-dimensional oxidation peak in the case of the alloy reinforces the view [1] that the film on antimonial lead in sulphuric acid is not completely passivating and that a thickening occurs. The results here indicate that a further layer is produced in addition to that on pure lead. Moreover this secondary layer contains at least as much charge as the primary layer. Holding the electrode in the reduction region annihilates the nucleation centres in both of the layers, this observation has implications in the charging behaviour of the lead–acid cell where it is clearly disadvantageous to delay recharge. With the antimonial alloy the extent of the removal of the nucleation centres in the secondary layer appears less than that in the primary layer and answers the perplexing question of why antimony is beneficial in the grid for the recharge characteristics. The presence of nucleation sites in the secondary layer is an additional threshold pathway to faster rates of recharging.

It is interesting that the only two electrocrystallization processes observed with the more corrodible antimonial lead are similar to the first two processes observed in the commercial ('porous') electrode [4]. It should be noted in this connection

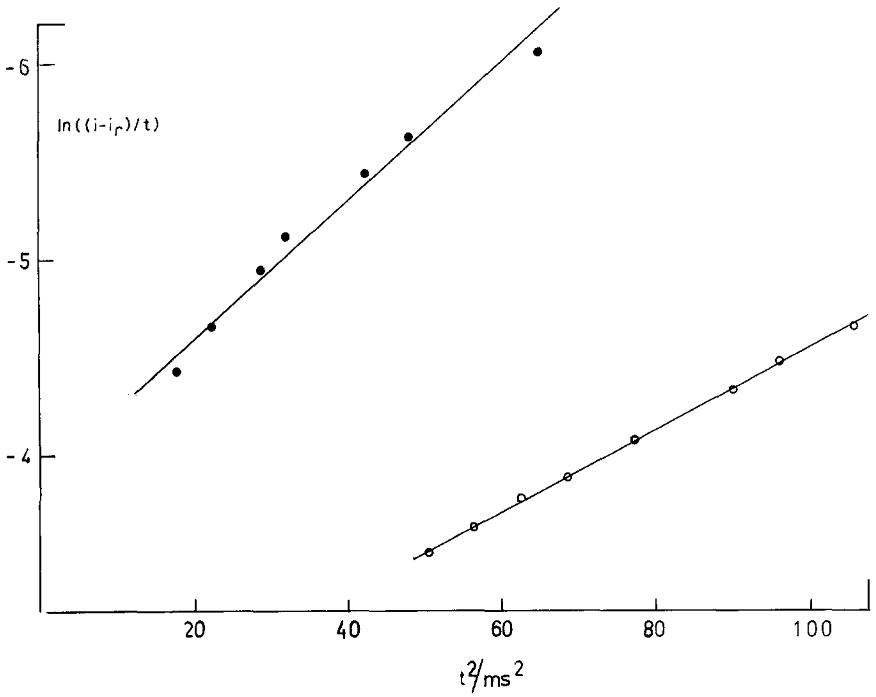

Fig. 6. ln $[(i - i_r)/t]$ versus t^2 for the falling parts of the second peaks of the transient corresponding to the lead/antimony alloy. ● 11 min hold time; ○ 46 min hold time. Other details as Fig. 1.

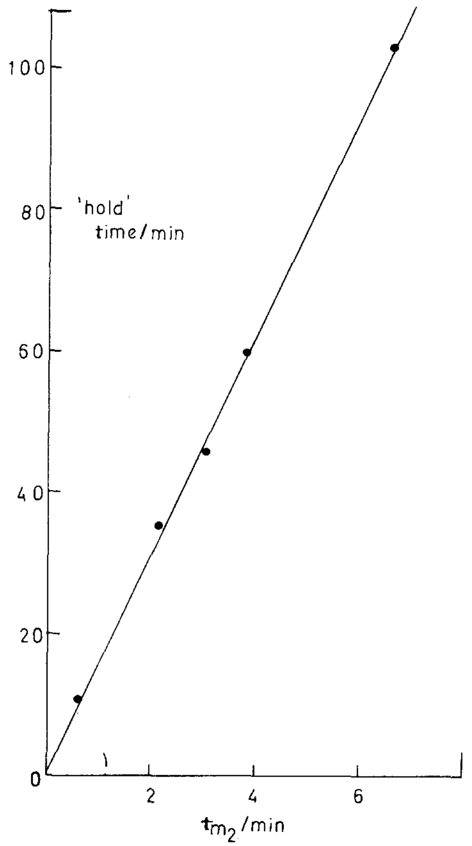

Fig. 7. The effect of hold time on second peak corresponding to the lead/antimony alloy. Details as Fig. 1.

that the currents involved here are only a fraction of that observed in the earlier work, nevertheless, a similar layered growth is indicated.

The identity of the nucleation sites is being investigated, however, it seems likely that they are related to lead dioxide.

4. Conclusions

The following conclusions were reached:

(a) On lead cycled between the $PbSO_4$ and the PbO_2 regions and then stepped from $PbSO_4$ the oxidation transient indicates the conversion to PbO_2 as a two-dimensional instantaneous nucleation process with subsequent overlap of growing centres.

(b) 'Holding' the $PbSO_4$ filmed electrode in the $PbSO_4$ potential region removes nucleation centres.

(c) Removal of nucleation centres renders low the ultimate efficiency of the oxidation process, considerable oxygen being evolved before the oxidation is complete.

(d) On antimonial lead the oxidation of (cyclically) grown lead sulphate is complicated and two current peaks in the transient reveal two two-dimensional instantaneous nucleation and growth processes.

(e) The analysis of the charge in the transients and the shape indicates that the single layer of lead sulphate on lead is probably identical with the primary layer on antimonial lead.

(f) The presence of the secondary layer on antimonial lead assists the efficiency of oxidation of the $PbSO_4$ deposit.

Acknowledgement

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