FILM FORMATION IN THE Pb(II) REGION OF THE Pb/H$_2$SO$_4$ SYSTEM

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Introduction

A detailed knowledge of the initial stages of formation and reduction of the different films on lead is essential for the complete understanding of the complex processes involved in a working cycle of a lead/acid battery. In particular, the rationalization of the processes occurring after the PbSO$_4$ formation, but before PbO$_2$ generation, requires a clear description of the sulphate layer formation/reduction mechanism under the same experimental conditions. This may help to clarify some of the controversies existing in the literature with regard to the models used for the description of the Pb(II) region [1 - 3].

This work explores, in detail, the voltammetric characteristics of lead in 5 M H$_2$SO$_4$ solutions. Special attention is given to the charges involved in each process, in order to make better use of the electrochemical technique. On this basis, the analysis is focussed on the anodic extreme of the Pb(II) potential region where different films co-exist during the voltammetric experiments.

Experimental

Working electrodes comprised lead rod (Aldrich Gold Label 99.9995%) with a diameter of 0.4 cm that was glued inside a pyrex glass tube with epoxy resin (slow cure). The resulting exposed area was 0.13 cm^2. The surface was mechanically polished with 600 grade emery paper using water as both a lubricant and a cooling agent. The electrode was then treated with a saturated solution of ammonium acetate, washed, and immediately introduced into the cell. The electrode was polarized at -1.2 V *versus* an Hg/Hg$_2$SO$_4$/5 M H$_2$SO$_4$ reference electrode, to which all potentials in this work are referred. Unless otherwise stated, each voltammogram was conducted on

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a freshly prepared surface. Each experiment was repeated several times in order to ensure a reproducibility better than 5% in peak currents and/or 10% in peak charges. All experiments were carried out at room temperature in 5 M H_2SO_4 (Merck p.a.) solutions using triply-distilled water.

Results and discussion

The initial stages of the formation of $PbSO_4$ can be studied by careful selection of the scan region in the voltammogram, see Fig. 1. The shape of curves A ($E_\lambda = -0.907$ V) and B reveals the existence of a nucleation and growth mechanism, as shown theoretically by Fletcher et al. [4]. This can only be observed over a very narrow range of switching potentials, as revealed by comparison of curves A ($E_\lambda = -0.912$ V) and C. Separate chrono-amperometric studies [5] carried out by stepping the electrode potential from -1.2 to -0.95 V and analysing the i versus t transient, together with comparison with theoretical plots [6], confirmed that the formation of $PbSO_4$ proceeds initially through instantaneous nucleation with two-dimensional
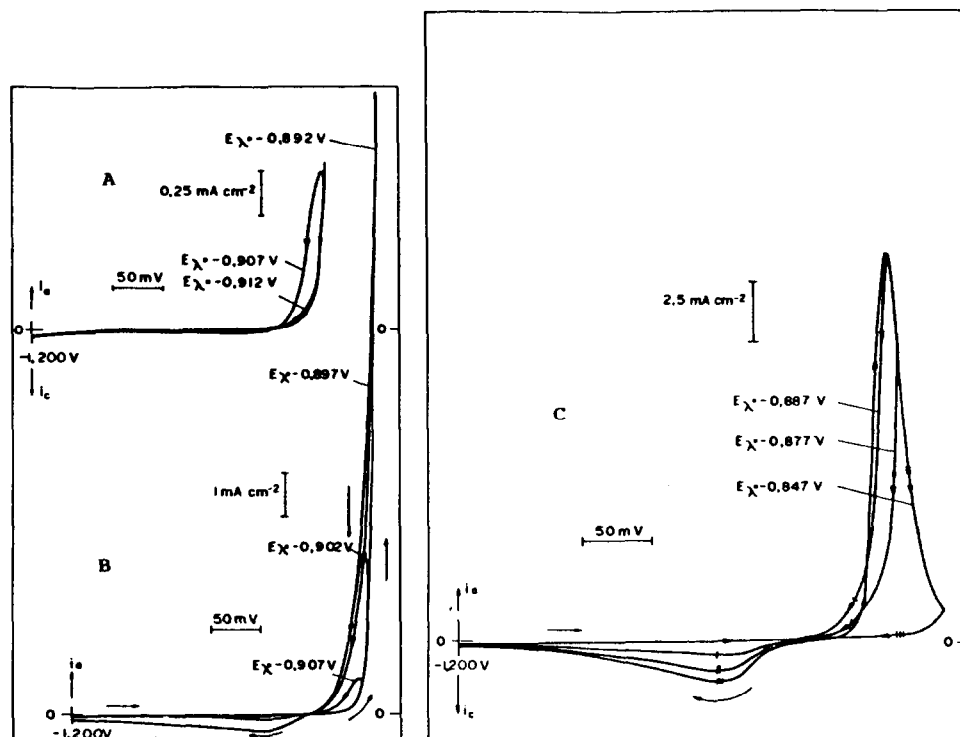

Fig. 1. Cyclic voltammograms with different switching potentials (E_λ) for formation of $PbSO_4$ on freshly prepared lead in 5 M H_2SO_4. Scan rate = 20 mV s^{-1}.

growth. This initial nucleation of $PbSO_4$ was also evident in multicycle experiments where the second and subsequent voltammograms showed a cathodic shift of around 30 mV for the whole anodic peak when compared with the first cycle. Therefore, the overall picture for this initial region is still in agreement with the model proposed by Archdale and Harrison [7]. In addition, the set of curves in Fig. 1 shows the presence of an isopotential point at around -0.965 V which almost coincides with the reversible potential (-0.973 V) for the system $Pb/PbSO_4$, 5 M H_2SO_4, as predicted by Fletcher [8]. On the other hand, it is clear from curve C in Fig. 1 that the nucleation phenomenon gives rise to a continuous film before the peak potential. This is in agreement with previous studies on the kinetics of the film formation [9].

A quantitative analysis of the charges involved in the different stages of $PbSO_4$ formation is presented in Table 1. The reversibility (q_t^c/q_t^a) increases with the switching potential (E_λ), but it remains lower than 50% for E_λ well beyond the peak. In addition, the difference ($q_t^a - q_t^c$) has large values and this suggests the existence of a complex phenomenon associated with the irreversibility of the process.

Figure 2 presents voltammograms corresponding to the complete lead sulphate region. A comparison with the normal response (curve a) reveals
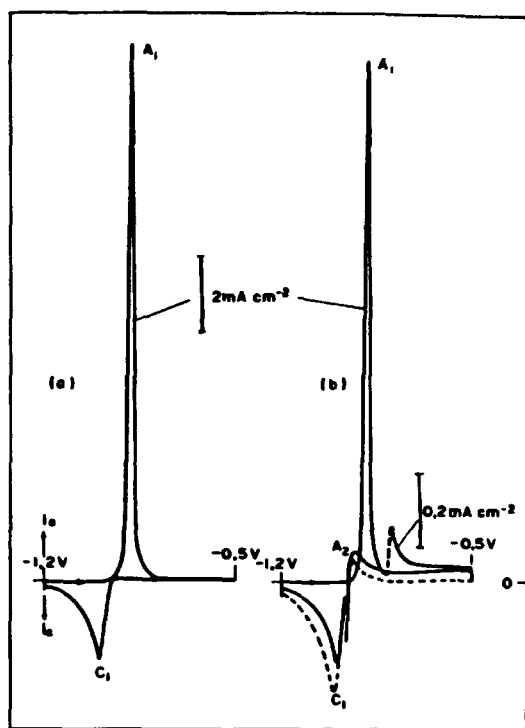

Fig. 2. Cyclic voltammograms in $PbSO_4$ region showing effect of increasing current sensitivity (curve b, (——)) and of holding potential at -0.5 V for 20 min (curve b, (———)). Scan rate = 10 mV s^{-1}.

TABLE 1

Charges involved in $PbSO_4$ formation

$-E_\lambda$ (V)	q_t^a (mC cm^{-2})	q_t^c (mC cm^{-2})	q_t^c/q_t^a
0.907	1.1	0.1	0.09
0.892	11.6	1.9	0.16
0.887[a]	14.4	2.4	0.17
0.877	16.2	4.5	0.28
0.847	21.5	7.7	0.36
0.600	27.0	13.3	0.49

[a]Peak potential; scan rate = 20 mV s^{-1}; initial potential = -1.2 V.

that with 10-fold increase in the sensitivity after peak A_1, peak A_2 can be detected in the cathodic sweep (curve b). This last peak possibly corresponds to a reactivation of the lead surface due to film-breaking. This behaviour has been attributed previously to the reduction of PbO lying underneath the $PbSO_4$ layer [10, 11]. The present work proves (see below), however, that the anodic polarization in these experiments is insufficient to form any PbO. Thus, the reactivation is solely due to the breaking of the film of $PbSO_4$ caused, perhaps, by a decrease in the electrostriction pressure upon reversing the potential sweep [5]. The reactivation is also evident for partially aged films, as illustrated by the dotted curve in Fig. 2(b), but it becomes less important for slowly grown films where the number of defects should be considerably less. This is illustrated by the results presented in Table 2 for experiments similar to those of Fig. 2, carried out at different scan rates.

It can be seen that, for the slower sweeps, the voltammetric reversibility (q_t^c/q_t^a) is almost complete, while the extent of film breakage, as indicated by $(q_t^a - q_t^c)$, is negligible or non-existent if 1.6 mC cm^{-2} is considered to be the charge associated with the unreducible film. As the sweep rate increases, the anodic peak current also increases but the charge under the peak (q_t^a)

TABLE 2

Analysis of voltammetric behaviour in $PbSO_4$ region

Scan rate (mV s^{-1})	i_p^a (mA cm^{-2})	q_t^a (mC cm^{-2})	q_t^c (mC cm^{-2})	q_t^c/q_t^a	$(q_t^a - q_t^c)$ (mC cm^{-2})
1	2.83	54.6	53.0	0.97	1.6
5	6.76	33.3	26.0	0.78	7.3
10	12.04	28.4	16.9	0.60	11.5
20	18.84	27.0	13.3	0.49	13.7
50	29.13	24.0	10.4	0.44	13.6
100	48.59	20.2	8.0	0.40	12.2

diminishes drastically. Simultaneously, the reversibility of the process decreases, giving rise to a situation where only 40% of the anodic charge is recovered in the cathodic sweep. All these facts, observed for a smooth lead surface, should be taken into consideration when analysing the operational behaviour of a lead/acid battery.

The potential region in which basic lead sulphates ($PbSO_4 \cdot xPbO$, $1 < x < 4$) and PbO are formed covers the range -0.3 to 1.3 V. This region can be conveniently analysed by cyclic voltammetry by sweeping a fresh electrode from -1.2 V to potentials progressively anodic into region a_2, as shown in Fig. 3. As the switching potential (E_λ) increases anodically, peaks C_2 and C_3 develop. It appears from the data in Fig. 3, that peak C_3 appears before C_2 and, therefore, should be attributed to the reduction of basic lead sulphate, since this compound must be formed before lead oxide in an environment where H_2SO_4 begins to be depleted. If, in addition, the potential is held at E_λ for some time, the size of the peaks C_2 and C_3 increases accordingly, provided that $E_\lambda > 0.1$ V (region a_2). On the other hand, a separate experiment showed that holding E_λ at -0.3 V (end of region a_1) for 20 min resulted in a very small cathodic charge in the potential region
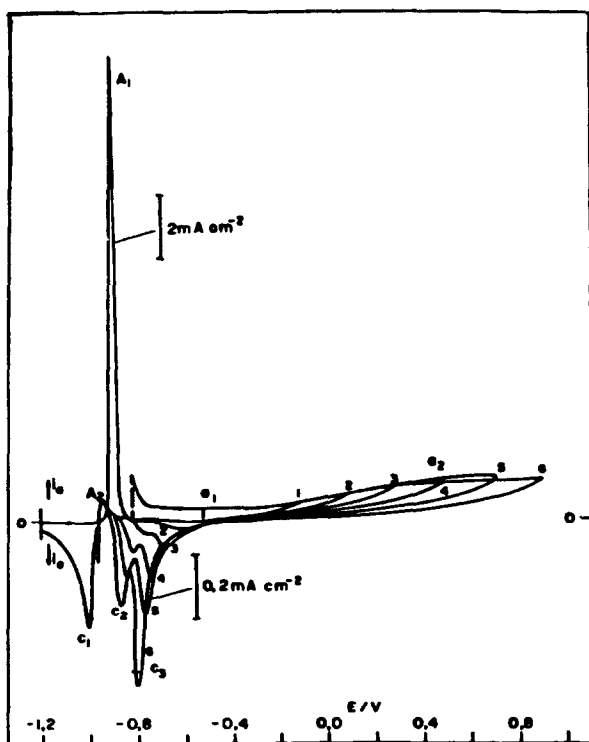

Fig. 3. Progressive voltammetric excursions into Pb(II) region on a freshly prepared lead surface in 5 M H_2SO_4. Scan rate = 10 mV s^{-1}.

TABLE 3

Analysis of voltammetric behaviour in $PbSO_4$ region

Scan rate (mV s^{-1})	q_t^a (mC cm^{-2})	q_t^c (mC cm^{-2})	q_{a1}^a (mC cm^{-2})	q_{a2}^c (mC cm^{-2})	q_{a2}^a (mC cm^{-2})	q_{a2}^c (mC cm^{-2})
1	93.6	92.8	51.9	51.8	41.7	41.0
5	54.0	47.2	33.3	25.9	20.7	21.3
10	47.9	37.2	28.4	16.9	19.5	20.3
50	32.0	18.3	24.0	10.4	8.0	7.9
100	27.5	14.9	20.2	7.9	7.3	7.0

of peaks C_2 and C_3, while for $E_\lambda = -0.1$ V the resulting cathodic peaks were approximately equivalent to those of curve 5 in Fig. 3. These results confirm, therefore, that the reactivation process (peak A_2) described in the previous section (Fig. 2) is due exclusively to cracking of the $PbSO_4$ film.

A charge analysis for a set of experiments where E_λ was varied from -0.3 to 1.0 V, with a holding time of 20 min at the given E_λ, showed that the (anodic) charges associated with region a_2 were related to those corresponding to peaks C_2 plus C_3, suggesting a reversible behaviour that will be further discussed below. Table 3 shows the result of the analysis of the total charges involved in voltammograms of the type presented in Fig. 3 at different sweep rates with no holding time.

Starting from -1.2 V, q_t^a and q_t^c are the charges for $E_\lambda = 0.9$ V, while q_{a1}^a and q_{a1}^c correspond to $E_\lambda = -0.4$ V. The charges corresponding to the process in region a_2 of Fig. 3 are, then, $q_{a2}^a = q_t^a - q_{a1}^a$ and $q_{a2}^c = q_t^c - q_{a1}^c$, respectively. It can be observed that for every sweep rate $q_{a2}^a \cong q_{a2}^c$, indicating that the internal films in region a_2 are completely reduced under the present conditions. This is in disagreement with previous reports [11, 12] where PbO formation is considered to be a highly irreversible process. From this analysis, it must be concluded that the nature of the inner film formed in region a_2 is highly complex and comprises reversibly formed PbO and $PbSO_4 \cdot x$ PbO, as well as some extra $PbSO_4$ that is also completely reduced in the cathodic sweep.

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