A ROTATING RING–DISC ELECTRODE STUDY OF IMPURITY EFFECTS ON LEAD CORROSION IN SULPHURIC ACID

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Summary

The technique of rotating-ring–disc voltammetry was employed here to investigate the effects of electrolyte contamination on the reactions of lead in sulphuric acid. A number of anions and cations were investigated, together with acid samples from local battery manufacturers and leach solutions from PVC separators The influence of contaminants on the soluble Pb(IV) intermediate generated during PbO_2 formation and reduction, as well as on the oxidation of underlying lead, are described

Introduction

The characteristics of lead–acid batteries (grid corrosion, cycle life, charge capacity, oxygen and hydrogen overvoltages) are known to be seriously affected by traces of impurities, both organic and inorganic Some additives are detrimental while others are known to have beneficial effects The source of contamination of lead–acid battery electrolytes can range from grid alloying elements to impurities leaching out of battery separators

Thus, a number of workers have reported that the presence of small amounts of Cl^- [1 - 3] and NO_3^- [1] severely affects the corrosion rate of lead anodes in sulphuric acid

A number of metallic impurities (Cu^{2+}, Al^{3+}, Mg^{2+}, Ca^{2+}, Na^+) have been reported to have no effect on the corrosion rate of lead, while others such as Fe, Ni, and Co appear to have an inhibiting effect [1] The presence of up to 3 mg l^{-1} of Ag^+ has also been shown to slow down corrosion of the lead anode [4]

Conflicting results have been published on the effect of Mn^{2+}. Some workers report that Mn shows no effect [5, 6], while others report a decrease in Pb corrosion rate in the presence of Mn [7, 8]. Small amounts of H_3PO_4 in sulphuric acid result in many effects on the battery reactions [9 - 12], for example, prolonged cycle life, transformation of β-PbO_2 to α-PbO_2, corrosion inhibition of pure lead, retardation of hard sulphates

formation which leads to deactivation of active material, and variation of $PbSO_4$ crystal morphology. Most of these effects were considered to result from chemisorption of phosphoric acid on $PbSO_4$ formed during discharge.

There is no doubt that many organic compounds, when present in the electrolyte, exert a deleterious effect on lead anodes For example, Dashiani [13] reported the behaviour of various alloys in sulphuric and tartaric acids, while Gratsianskii [14] studied Pb–In alloys in sulphuric and citric acids Surfactants have also been reported to increase the corrosion rate of Pb and various alloys

In the present study, the electrochemical technique of Rotating Ring–Disc (RRD) voltammetry was employed to investigate the effect of impurities on the electrochemical behaviour of lead in sulphuric acid Samples of acid used by local battery manufacturers, and leach solutions from PVC battery separators were investigated for possible contamination A number of anionic and cationic species were also tested for any interference effects on the lead reactions.

Experimental

Ring–disc measurements were performed on a rotating Au ring–Pb disc electrode which used lead of 99 999% purity The counter electrode consisted of a 99 999% pure lead rod, and a two compartment Pyrex electrolytic cell with a stopcock at the base for solution drainage was used in all experiments All potentials were measured *vs* an Hg/Hg_2SO_4 reference electrode

The Au ring–Pb disc electrode was rotated at 2500 rpm in all experiments using a Pine Instrument ASR Rotator A Pine AFRDE3 bipotentiostat was employed to scan the disc potential between 0 7 and 1.6 V *vs* Hg/Hg_2SO_4 at a scan rate of 10 mV per second, while a Riken-Denshi $X-Y_1$, Y_2, 2-pen recorder was used to simultaneously record the disc and ring current traces.

The electrolyte consisted of 29 wt.% H_2SO_4 which was prepared from analytical grade sulphuric acid and triply-distilled water Before use this was pre-electrolyzed for 48 h using two Pb electrodes and a cell voltage of 2.8. Nitrogen gas was bubbled through the electrolyte before and during all experiments.

The PVC separators which were examined in this study were cut into strips, packed into a 250 ml beaker and immersed in pre-electrolyzed 29 wt % H_2SO_4. After a period of three weeks, the leach solution was decanted and tested in the electrolysis cell using the following procedure

The Au ring–Pb disc electrode was first pre-cycled in the pure H_2SO_4 between 0 8 and 1.6 V Hg/Hg_2SO_4 until reproducible behaviour was obtained The reference and ring–disc electrodes were then lowered into the bottom section of the electrolysis vessel and the pure acid was drained off to a point just above the electrode tips, taking care not to lose acid continuity between the three electrodes in the cell or to disturb the disc surface. The

electrolysis vessel was then refilled to the original level with the acid leach solution, the electrodes were raised to their original positions, and the voltage scan continued, to obtain one or more cycles in the leach solution. The ring–disc electrode was then removed from the cell, resurfaced, and returned to the cell for further potential cycling Similar tests were performed with several samples of 29 wt.% sulphuric acid supplied by local battery manufacturers from their acid storage vessels

In the experiments with the anionic and cationic species the ring–disc electrode was again precycled in pure 29 wt % H_2SO_4 until constant behaviour was established A volume of H_2SO_4 containing the compound to be studied was then added to the cell electrolyte and the cycling continued All cations were added as either sulphates or oxides, while the anions were introduced as acids or sodium salts

Results and discussion

The typical behaviour of a Pb disc electrode, when the potential is scanned between 0 8 and 1 6 V *vs* an Hg/Hg_2SO_4 reference electrode, is shown in Fig 1. The increase in current observed in this initial scan at potentials greater than 1.5 V corresponds to the co-formation of O_2 and PbO_2. Reversal of the potential scan gives rise to an anodic peak, as well as to small, superimposed cathodic peaks corresponding to the reduction of PbO_2 and $PbSO_4$. This anodic peak, which appears on the reverse scan, has been attributed to oxidation of underlying Pb just before PbO_2 reduction [15]
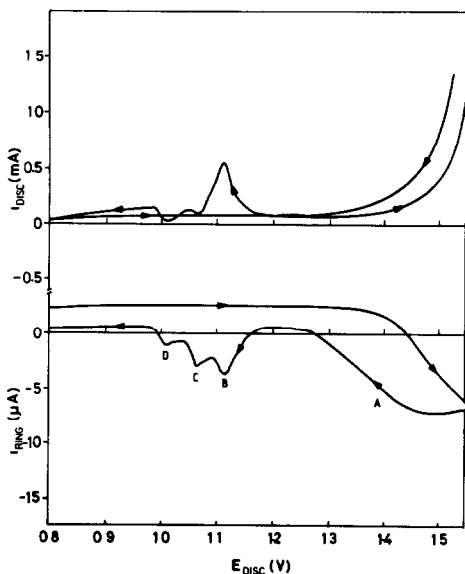

Fig 1 Disc and ring currents in pre-electrolyzed 29 wt % H_2SO_4, cycle 1 E_R = 0 2 V *vs* Hg/Hg_2SO_4

By potentiostatting the ring electrode at 0 2 V *vs* Hg/Hg$_2$SO$_4$ while scanning the disc between 0 8 and 1.6 V, a number of ring peaks (A, B, C, and D in Fig. 1) can initially be observed during PbO$_2$ formation and reduction, these ring peaks corresponding to the reduction of Pb^{4+} ions discharged at the disc electrode during cycling [16] The large ring peak (A) which is observed during the forward sweep is related to soluble Pb(IV) discharged during PbO$_2$ formation, followed by oxygen reduction

On reversal of the potential scan, three current peaks appear at the ring electrode Ring peak B corresponds to the anodic disc current which appears on the reverse cycle, and is attributable to oxidation of the underlying lead, while peaks C and D are associated with the intermediate Pb(IV) species released into the solution during the discharge cycle
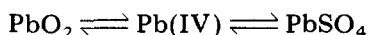
$$PbO_2 \rightleftharpoons Pb(IV) \rightleftharpoons PbSO_4$$

Thus, the appearance of the ring peak B indicates that as the Pb beneath the PbO$_2$/PbSO$_4$ layer is oxidised, Pb(IV) ions which are formed diffuse through the surface layer and are reduced to Pb(II) at the gold ring

As the PbO$_2$/PbSO$_4$ layer builds up with continued cycling, however, the peaks associated with the corrosion of underlying Pb can no longer be observed at the Pb disc nor at the gold ring (Fig 2). Thus, a definite disc peak corresponding to PbO$_2$ formation can be distinguished as shown in Fig 2 Reversal of the potential scan, however, gives rise to a single cathodic disc peak for the reduction of PbO$_2$ to PbSO$_4$, while the ring trace also exhibits two current peaks only
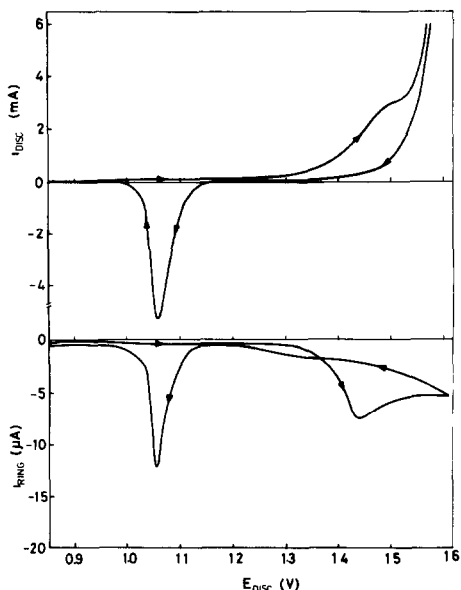

Fig 2 Disc and ring currents in pre-electrolyzed 29 wt % H$_2$SO$_4$, cycle 10

The previous Figures thus illustrate the typical cyclic behaviour of a lead electrode in pure sulphuric acid When impurities are present in the electrolyte, however, deviations from the above behaviour could result, depending on the nature of these impurities.

A number of samples of acid obtained from local battery manufacturers were tested and Fig. 3 shows the behaviour typically displayed by the lead electrode when cycled between 0.7 and 1.6 V *vs* Hg/Hg$_2$SO$_4$ In these experiments the Pb disc electrode was first cycled in pure H$_2$SO$_4$ until constant behaviour was established (Fig. 3, curve 1). The pure acid was then drained from the cell and replaced with manufacturers' acid by the procedure previously described. Curves 2 of Fig. 3, thus obtained, show a shift in the potential of the PbO$_2$ disc peak as well as a slight reduction in the PbO$_2$ → PbSO$_4$ discharge peak in these acid samples A dramatic increase in the soluble Pb(IV) ring peak can also be observed, indicating that more of the soluble Pb(IV) species is being generated at the disc electrode during PbO$_2$ formation and reduction.
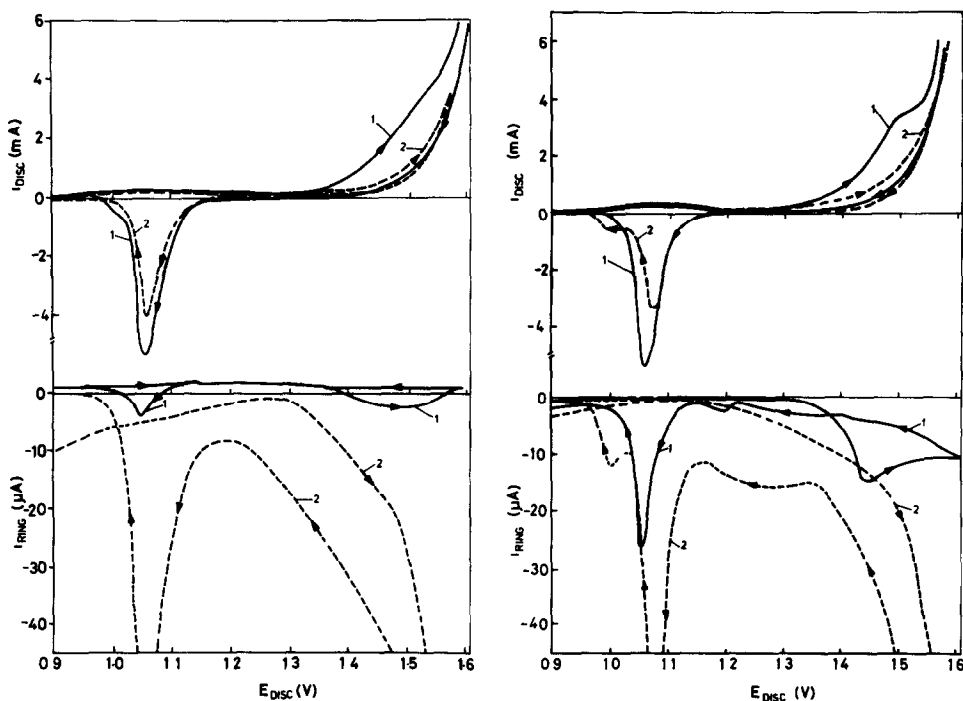

Fig 3 Curves 1 Disc and ring currents in pre-electrolyzed 29 wt % H$_2$SO$_4$, cycle 10 Curves 2 Disc and ring currents obtained immediately after pre-electrolyzed acid substituted with typical sample of manufacturers' acid

Fig 4 Curves 1 Disc and ring currents in pre-electrolyzed 29 wt % H$_2$SO$_4$, cycle 10 Curves 2. Disc and ring currents obtained immediately after pre-electrolyzed acid substituted with sample "X" from battery manufacturers' acids.
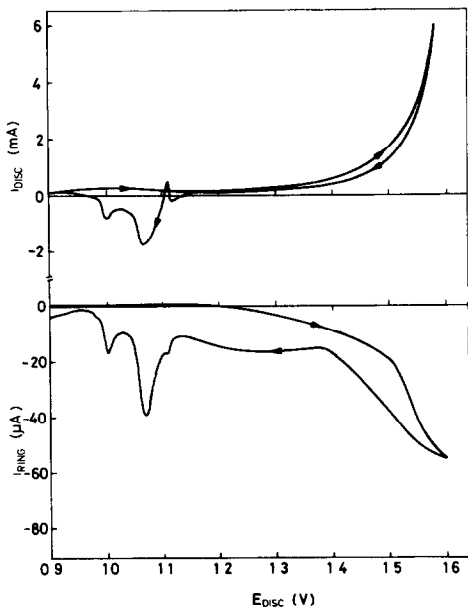
Fig 5 Disc and ring currents obtained after continuous cycling of Pb disc of Fig 4 in acid sample "X"
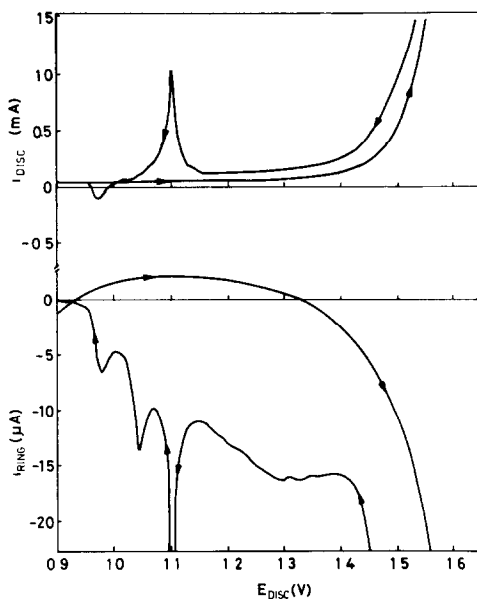
Fig 6 Disc and ring currents for freshly polished Pb disc—Au ring electrode in acid sample "X", cycle 1

Figure 4 shows the results obtained with one particular acid sample, "X", tested In this case a dramatic change in both the Pb disc and Au ring traces was immediately observed, the PbO_2 reduction peak decreasing, while a considerable enhancement of the Pb(IV) ring current occurred Continuation of the potential cycling, however, gave rise to further distortions in the ring–disc voltammograms, as shown in Fig 5 Most noticeable is the reappearance in both the disc and ring current traces of the peaks associated with oxidation of underlying Pb, suggesting the presence of impurities in this acid sample which increase the corrosion rate of Pb in sulphuric acid

The Pb disc–Au ring electrode was then removed from the acid, resurfaced, and returned for further cycling Figure 6 shows the first voltammogram which was obtained, again with evidence of an increase in the oxidation of underlying Pb on the reverse scan Continued cycling yielded the voltammogram of Fig. 7 Thus, the characteristic behaviour of the Pb electrode could not be established in this sample, even after 14 cycles, and more It should be emphasized again, however, that sample "X" was an exceptional case, the more typical behaviour being shown in Fig 3

In the next series of experiments, the acid solutions used to leach two different lots of PVC separators were tested to determine whether any
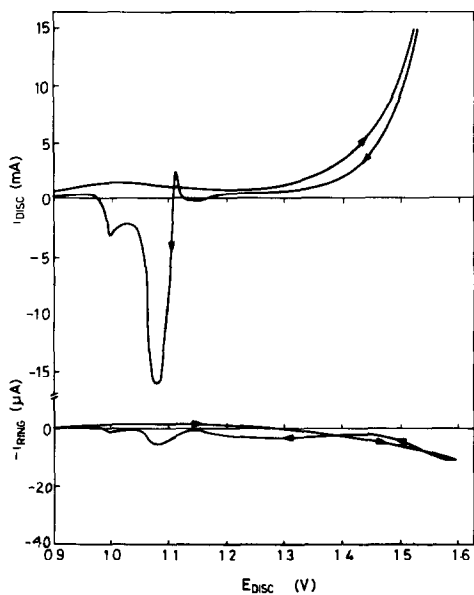
Fig 7 Disc and ring currents obtained after continued cycling of Pb disc of Fig 6 in acid sample "X" (cycle 14)
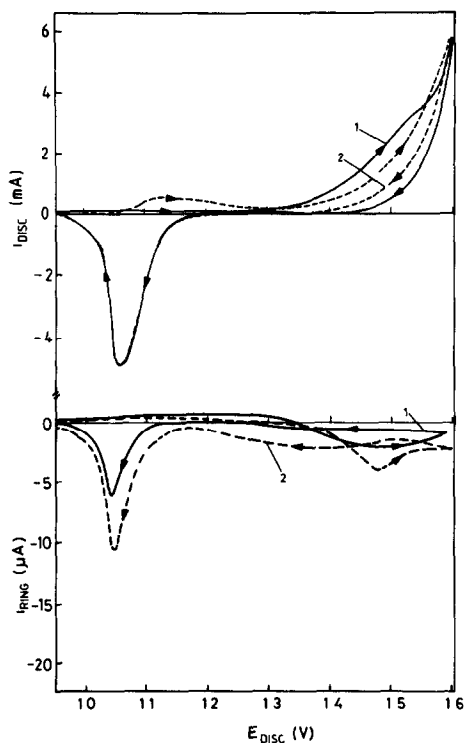
Fig 8 Curves 1 Disc and ring currents in pre-electrolyzed 29 wt % H_2SO_4, cycle 10 Curves 2 Disc and ring currents obtained immediately after pre-electrolyzed acid substituted with leach solution for separator "A"

impurities were likely to be leaching out of the separators and affecting the Pb reactions The results obtained for separator A are shown in Fig 8 Replacement of the pure acid with the leach acid resulted in a shift in the PbO_2 peak potential, and a slight increase in the amount of soluble Pb(IV) intermediate was detected at the ring No change in the oxidation of the underlying Pb is evident however

The results for separator B are shown in Fig 9 Again a shift in the potential of the PbO_2 can be observed In this case, however, there is a large increase in the amount of soluble Pb(IV) generated during charge and discharge, but again there is no evidence of enhanced Pb oxidation below the oxide layer

The results obtained from rotating-ring–disc experiments on the introduction of various cationic and anionic species to the pure H_2SO_4 electrolyte are summarised in Table 1
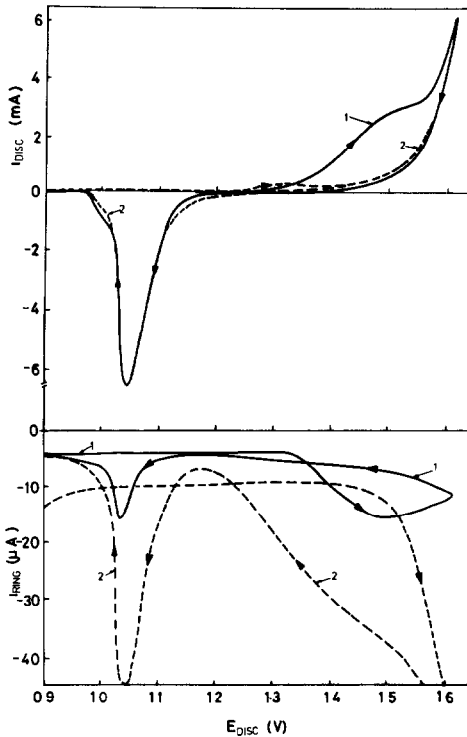
Fig 9 Curves 1 Disc and ring currents in pre-electrolyzed 29 wt % H_2SO_4, cycle 10 Curves 2 Disc and ring currents obtained immediately after pre-electrolyzed acid substituted with leach solution for separator "B"

TABLE 1

Effects of additives on $PbSO_4/PbO_2$ electrode in H_2SO_4

Species	Concentration (wt %)	Effect on Pb disc voltammogram	Effect on soluble Pb(IV)
Na(I)	0 5	Nil	Nil
Mg(I)	0 5	Nil	Nil
Al(III)	0 5	Nil	Nil
Ca(III)	0 1	Nil	Nil
V(IV)	0 5	Large reduction in charge and discharge peaks	Reduction in ring peaks
Ca(II)	0 5	Negligible	Increase in Pb(IV) ring peak
Fe(III)	0 1	Negligible	Increase in Pb(IV) ring peak
Acetate	1 0	Negligible	Negligible
Nitrate	$\geqq 5\ 0$	Increase in discharge peak	Increase in Pb(IV) ring peak

Conclusion

The electrochemical technique of Rotating-Ring–Disc voltammetry has been shown here to be of great value in the study of the effect of impurities on the reactions of lead in sulphuric acid Impurities leaching out of one batch of PVC separators have been shown to increase the amount of the Pb(IV) intermediate generated during the charge and discharge cycles of the $PbSO_4/PbO_2$ electrode, while unidentified contaminants in one sample of acid from a local battery manufacturer exhibited increased corrosion rates of underlying Pb

Although the present study has been concerned with the effects of contaminants on the reactions of lead in sulphuric acid, and the likely effects on actual battery performance have not been established, the results presented do suggest that electrolyte purity, as well as electrochemical compatibility of materials used in the manufacture of lead–acid batteries should be of great importance Extensive work has already gone into the study of numerous additives and their effect on battery performance The literature contains a great deal of contradictory information, however It is usually impossible to rely on cross-correlation of data due to the difference in test conditions (acid strength, temperature, current densities, and impurity levels)

A small number of anions and cations have been tested here, but a systematic investigation of a wider range of species is required Such an extensive investigation is at present under way, initially to screen the impurities which adversely influence the lead reactions, but once these are identified, more detailed studies will be required to understand the mechanisms of these interactions and their implications for battery performance and characteristics

Acknowledgements

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