THE MECHANISM OF THE FORMATION OF POSITIVE BATTERY PLATES FROM PURE LEAD
1. CYCLIC VOLTAMMETRY

C LAZARIDES and N A HAMPSON

Chemistry Department, Loughborough University, Leicestershire, LE11 3TU (Gt Britain)

G M BULMAN

Tungstone Batteries Ltd , Lathkill Street, Market Harborough, Leicestershire, LE16 9EZ (Gt Britain)

Summary

The electrochemical behaviour of a pure lead electrode in sulphuric acid—perchloric acid electrolyte mixtures has been examined by cyclic voltammetry. The characteristics in the lead/lead sulphate potential range, and in the lead sulphate/lead dioxide region, have been observed for concentrations of perchloric acid from 1 to 200mM in 0.5M sulphuric acid.

In the lead/lead sulphate region, the perchlorate ion promotes surface attack on the lead by displacing the passivating sulphate ion. The effect increases with perchlorate concentration, reaching a maximum at about 50mM concentration, followed by a 'self-stifling' effect at higher perchlorate levels.

The mechanism in the lead sulphate/lead dioxide region possibly involves a reduction in the thickness of the passivating layer by the perchlorate anion.

Introduction

The method of producing lead dioxide electrodes by a process in which the surface of the lead is corroded (Planté process), is relatively crude. However, the majority of the standby batteries used in the U.K are produced with the aid of such a process. We have discussed the use of different formation agents [1] and although the nitrate ion in certain concentrations may offer an advantage [2], the perchlorate ion is undoubtedly unrivalled as the preferred aggressive ion.

The chemistry of the Planté formation process, although occupying an important place in classical battery technology, has not received a great deal of attention in the scientific press. Indeed, information on the mechanism of the formation is generally inadequate.

Recently however, Azim and co-workers [3 - 5] have reported galvano-static and potentiostatic measurements on lead systems in which the per-chlorate-assisted oxidation was studied. These workers have identified the pitting corrosion process as the mechanism of the aggressive ion attack and have described the general features of the process in terms of the possible displacement of sulphate by perchlorate. This explanation is along the general lines for the theory of pit growth [6].

An interesting and important aspect of the electrochemistry of the lead sulphate/perchlorate system is the behaviour on cycling, since one cycle of charge and discharge takes place during Planté plate production [7]. Additionally, the examination of the cyclic behaviour can give a greater insight into the mechanism of the Planté process The cyclic voltammetry of lead in sulphuric/perchloric acid has therefore been examined, and this paper records the results.

Experimental

Electrodes

The working electrode was a disc made from pure lead rods (99.999%) supplied by Koch-Light. The lead was cut and machined to a surface area of 0 071 cm^2 and set in a hollow Teflon holder. A spring soldered at the back of the disc ensured good contact with the stainless steel rod to which the holder was fitted A wire, dipped into a well filled with mercury at the top end of the stainless steel rod, formed the terminal for the working electrode. This arrangement also allowed the system to be used as a rotating disc electrode.

The electrodes were pretreated by polishing on roughened glass, using tri-distilled water as a lubricant. Immediately prior to an experiment, the electrode was etched (60 s; HNO_3 1.58M) and thoroughly washed with tri-distilled water before immersing it, still wet, in the electrolyte solution. The working electrode occupied the centre compartment of a 3-limb cell.

The reference electrode used was Hg/Hg_2SO_4, connected to the working electrode *via* a Luggin capillary and ground-glass joint. Potentials are referred to the $Hg-Hg_2SO_4$ reference electrode in H_2SO_4 of the same molarity as the working solution ($E_h^{\theta} = 0.668$ V).

The counter electrode was a lead coil of large surface area occupying the third compartment of the cell.

Electrolytes

The working electrolyte solution was 0.5M H_2SO_4, prepared from AnalaR grade reagents. The solutions containing perchlorate ions were prepared using AnalaR grade perchloric acid in 0.5M sulphuric acid. Tri-distilled water was used throughout and the concentrations examined were. 1mM, 10mM, 54mM, 100mM, 200mM. All experiments were carried out at room temperature (22 - 23 °C), in the presence of the atmosphere.

Instrumentation

All experiments were carried out using a potentiostat (Kemitron type P50). Linear sweep voltammetry experiments were monitored on an X–Y recorder (Bryans Series 26000) Potentiostatic experiments were monitored on a Y–t recorder (Bryans Series 27000).

Linear sweep voltammetry

Linear sweep voltammetry (L.S.V.) experiments in the lead sulphate and lead dioxide region were carried out using various concentrations of perchloric acid.

Lead–lead sulphate region

For the experiments in the electrode potential region of lead sulphate formation, the electrode was held at a cathodic potential close to the potential required for the onset of hydrogen evolution for one hour to minimise the chances of the development of any sulphate film. Cycling was then carried out at various sweep rates between the limits of −1250 mV and −450 mV.

Lead sulphate–lead dioxide region

The experiments in the lead dioxide region consisted of cycling to a constant response (approx. 1 h), by sweeping between 400 and 1500 mV. The electrode was momentarily brought up to 2000 mV at the start of the experiment to "initiate" the reaction in order to produce the lead dioxide [8, 9]

Sweep rates used for both types of experiments were usually in the range 200 - 3 mV/s, starting with high sweep rates and cycling to a constant response before moving to a lower sweep rate.

Steady state experiments

Steady state polarisation experiments were also carried out at 100 mV intervals from the hydrogen region to the oxygen region in order to obtain the potentials at which the principal electrochemical reaction occurs. This was done for the series of concentrations mentioned above.

Results and discussion

Polarisation of lead in sulphuric acid over a very extensive range of potentials, from that of hydrogen evolution to the potential of oxygen evolution, shows two regions connected with the electrochemistry of lead. The first represents the $Pb \rightarrow PbSO_4$ reaction and occurs at about −900 mV, while the second occurs at a much more positive potential and represents the oxidation of $PbSO_4 \rightarrow PbO_2$. This is shown clearly in Fig. 1 which is the first sweep in a slow L.S.V. experiment on lead in 0.5M H_2SO_4.

Figure 2 shows the results for a sweep in 0.5M H_2SO_4 containing 100mM ClO_4^-. We can see that the potentiodynamic curve is significantly
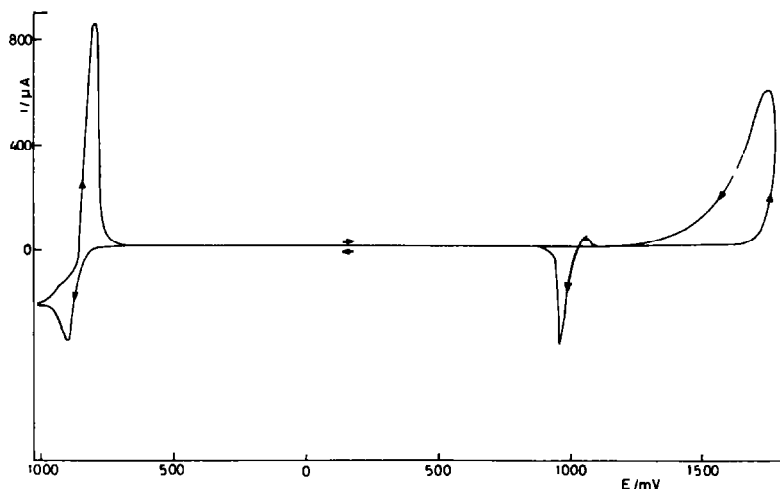
Fig 1 L S V curve, lead in pure sulphuric acid, sweep rate 50 mV s^{-1}, 23 °C

affected; specifically, the peak for the oxidation of Pb to PbSO$_4$ is enhanced around the trailing edge and, indeed, a subsidiary peak is observed at approx. −700 mV. This peak indicates further oxidative attack of the lead surface at potentials more positive than the PbSO$_4$/Pb equilibrium potential under the influence of the perchlorate ion. It seems likely that the electrode initially passivates (at ~ −900 mV) at the lead sulphate potential, and at a somewhat more positive potential the sulphate film is penetrated aggressively by the ClO$_4$$^-$ ion and a further quasi active region is observed. Alternatively, the current falls, but relatively slowly over a large potential range, indicating a pitting attack (pitting corrosion). No discrete peak for PbO$_2$ formation appears due to the oxygen evolution reaction intruding into the PbO$_2$ formation reaction
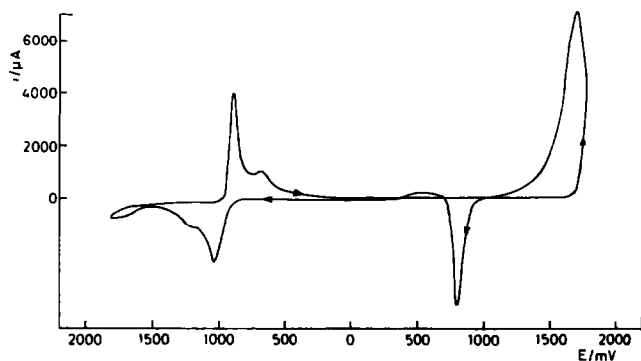

Fig 2 L S V curve for lead, 100mM HClO$_4$ in 0 5M H$_2$SO$_4$, −1800 mV to +1800 mV, sweep rate 50 mV s^{-1}, 23 °C

On increasing the positive limit of the sweep, PbO_2 is produced, as shown by the occurrence of a reduction peak in the reverse sweep from the positive limit. This peak is at $\sim$ 900 mV However, as soon as the discharge is completed, there is evidence for the active dissolution of the underlying base Pb, as shown by the anodic current at $\sim$ 600 mV. The explanation for this is that the discharge of PbO_2 produces a $PbSO_4$ layer which is not perfect enough to render the surface completely immune from the aggressive attack, and so the lead surface is attacked This anodic current was quite large in early experiments (e g , the first cycle) but was reduced in subsequent cycling. The peak for the reduction of $PbSO_4$ to Pb appears to be normal. It is to be concluded that the perchlorate ion has affected both the Pb to $PbSO_4$ reaction and also the $PbSO_4$ to PbO_2 oxidation, the significant effect is, however, the penetration of the $PbSO_4$ layer by the perchlorate ion

Lead–lead sulphate, $\sim -900\,mV$

This potential region was investigated under the conditions which might be expected for Planté formation Electrodes were subjected to cyclic voltammetry at a series of sweep rates.

Figure 3 shows stabilised cyclic voltammograms for a system free from perchlorate ions. The trace is similar to many which appear in the literature and consists of a peak in the positive-going direction representing the oxidation of Pb to $PbSO_4$, followed by a cathodic peak in the reverse sweep.

The effect of increase in the sweep speed is to amplify the current However, there was a simple correlation between peak height and rate of potential change in the oxidation peak.

It is clear from Fig. 4 that i_p, the current maximum in the anodic going sweep, is proportional to $\nu^{1/2}$, where ν is the sweep rate. However,
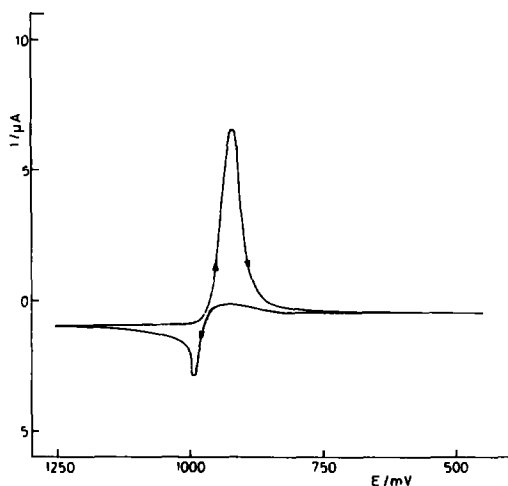

Fig 3 L S V curve, lead–lead sulphate region Lead in pure sulphuric acid, sweep rate 50 mV s^{-1} , 23 °C
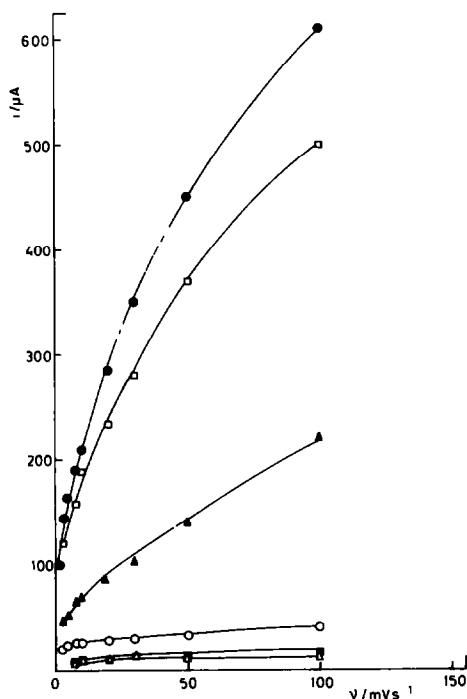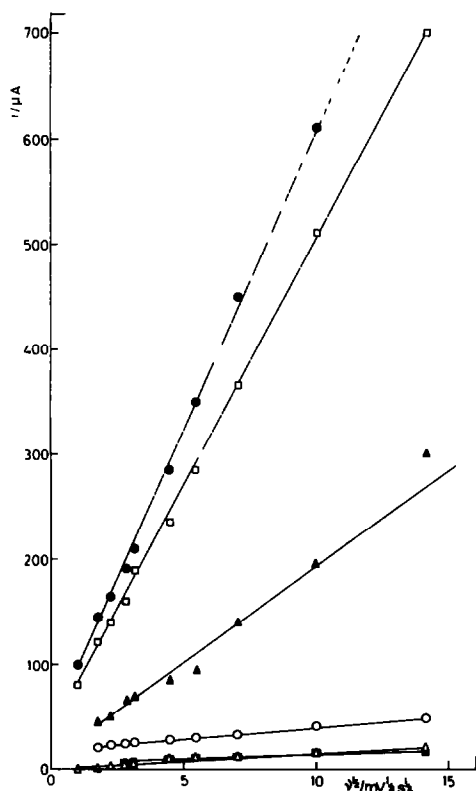
Fig 4 (left) Lead/lead sulphate region i_p vs sweep rate $\nu^{1/2}$ for L S V curves of different ClO_4^- ion concentration △, 0mM $HClO_4$, ■, 1mM $HClO_4$, ▲, 10mM $HClO_4$, ●, 54mM $HClO_4$, □, 100mM $HClO_4$, ○, 200mM $HClO_4$

Fig 5 (right) i_p vs sweep rate, ν, for L S V curves of different ClO_4^- ion concentration (Code as for Fig 4)

aside from the perchlorate-free system, all the lines had a positive intercept on the current axis. The currents in these sweeping experiments were found to be independent of electrode rotation speed and confirm that the reaction is independent of diffusion of Pb(II) products in solution. We are therefore forced to conclude that the reaction must be a solid state one. The square root sweep rate–peak current relation could represent a controlling diffusion process in the solid state, possibly diffusion through a porous $PbSO_4$ layer.

If the products of the reaction remain at the electrode as a film of $PbSO_4$ of constant thickness, then it might be expected that the peak current would be a linear function of the sweep rate. Figure 5 shows that this is not so, and the passivating $PbSO_4$ film contains a variable amount of charge, depending on the sweep rate. Moreover, the curvature of this plot (away from the axis) indicates thinner films at higher sweep speed. This might well be expected, for, at high sweep rates (higher currents — higher reaction rates), the crystals produced will be smaller as they would not have time to grow.

Consequently, complete blocking of the lead surface would be achieved more efficiently than at lower speeds

The addition of $HClO_4$ amplified the current up to a maximum at 54 mM, which thereafter decreased. Once more, the current is sweep rate dependent in exactly the same way as in the absence of perchlorate ions This is shown by the cyclic voltammogram in Fig 6.

The concept that the presence of aggressive anions in solution is the cause of the breakdown of passive films is well known. According to Russian workers, the adsorptive displacement of passivating species from the surface occurs when the anion concentration has attained a critical value. The anions cause intense destruction of the underlying metal by the formation of complexes with the metal surface species passing into solution. The localised nature of the process depends on non-uniform current distribution and also on structural non-uniformity

In the general picture, an important step is the transport and interconversion of ions within the pit formed in the localised attack, forming what might be thought of as a feed-back process. The principle is that, at the surface, sulphate ions are displaced by ClO_4^- so that $PbClO_4^-$ complexes can move off into the double layer. However, once outside the double layer region precipitation occurs. Lead sulphate is formed and perchlorate ion is regenerated to displace further sulphate ions at the lead surface. As perchlorate is introduced into the system, the process of displacement and precipitation is increased. This is shown by the curves of Fig 5, where currents are amplified at the higher concentrations.

As the perchlorate ion concentration is still further increased, the amount of current in the stabilised potentiodynamic curve goes through a maximum, somewhere in the region of 54mM in 0.5M H_2SO_4 Further addition caused reduced currents at all the sweep rates and potentials. This is an interesting observation for it suggests that at bulk concentrations in excess of ~54mM, there is insufficient sulphate ion in the advancing pits to precipitate

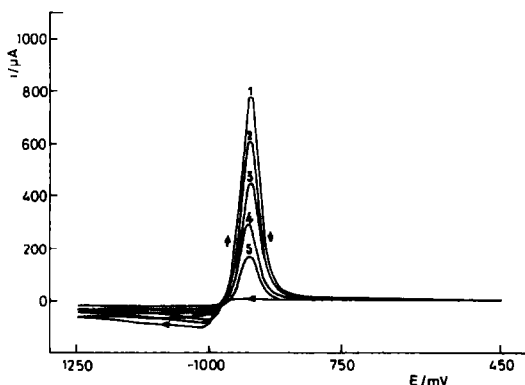Fig 6 L S V stabilised curves for lead in 0 5M H_2SO_4 containing 54mM $HClO_4$ Sweep rates, 1, 200, 2, 100, 3, 50, 4, 20 and 5, 5 mV s^{-1}, 23 °C
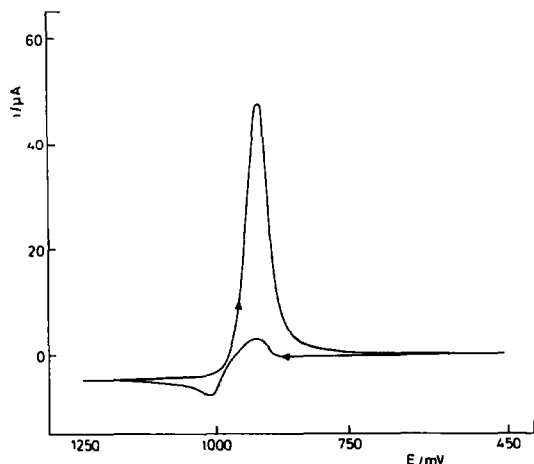
Fig 7 Stabilised cyclic voltammogram (200 mV s^{-1}) for lead, 200mM HClO$_4$ in 0 5M H$_2$SO$_4$, 23 °C

completely all the lead perchlorate, and lead sulphate is formed nearer the pore entry, causing early passivation by plugging up the pore. This effect is enhanced at higher perchlorate ion concentration and the current in the oxidation peak decreases. It should be emphasised, however, that we are only observing the electrochemistry of the "available" electroactive material. Further PbSO$_4$ may be present on the electrode, but isolated from the electric current Figure 7 shows the stabilised cyclic voltammogram for a 200mM HClO$_4$ solution. An interesting feature of this Figure is that on the reverse sweep, the potentiodynamic curve shows an active anodic region in the cathodic direction. This indicates that the film undergoes aggressive attack by the perchlorate ion and the normally passive sulphate film is broken down.

It should be noted that the simple theory that PbSO$_4$ films are permeable to ClO$_4^-$ ions [10] and that lead dissolves anodically in the form of Pb(ClO$_4$)$_2$ cannot be correct in view of the appearance of the maximum at 54mM

The lead sulphate–lead dioxide region

In this region, which is near the oxygen evolution potential, the presence of oxygen gas in the solution was of no consequence and unavoidable in any case. Figure 8 shows a typical cycle-stabilised potentiodynamic curve for lead sulphate/lead dioxide in 0.5M H$_2$SO$_4$. A small, well-defined peak at ~ 1000 mV observed in early experiments, developed to a maximum after about 2 h cycling at 50 mV s^{-1} and then reduced to a virtual plateau. This is interesting and different from the observations [8] in 5M H$_2$SO$_4$ and is possibly the development of significant amounts of α-PbO$_2$ under the higher pH conditions formed in the more dilute solution With prolonged cycling of a stabilising structure this α-component is evidently transformed to β
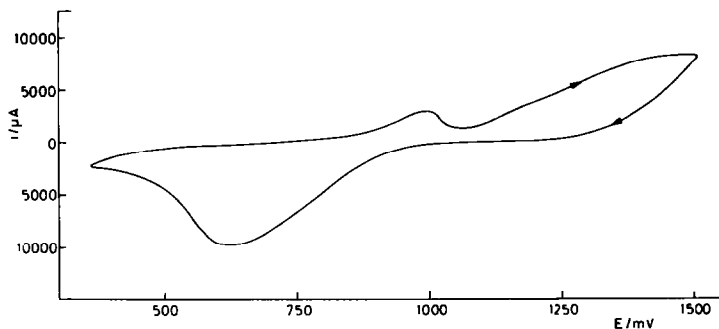
Fig 8 Stabilised cyclic voltammogram of the lead sulphate/lead dioxide region for pure lead in 0 5M H_2SO_4, sweep rate 50 mV s^{-1}, 23 °C

Figure 9 shows a typical cycle-stabilised L.S.V curve for 0 5M H_2SO_4 containing 54mM ClO_4^-. Comparison with Fig. 8 shows important differences. Surprisingly, the current in the reduction "loop" of the curve is less than the corresponding one in the perchlorate free system. There is no sign whatever of the small peak at ~1000 mV The rise of oxygen evolution and PbO_2 formation is enhanced. The peak potential of the reduction process is shifted to more negative potentials by the perchlorate ions However, the redox reactions commence at about the same potentials

Above ~54mM ClO_4^- it was not possible to get a steady response at potentials greater than 400 mV The unsteadiness was apparently due to the evolution of oxygen from a surface which was not completely passive. Thus, a rise in current was followed by a rapid fall in current, presumably as the "quasi passive" film was broken down by the aggressive attack of the perchlorate and then was healed by sulphate formation at higher potential. This
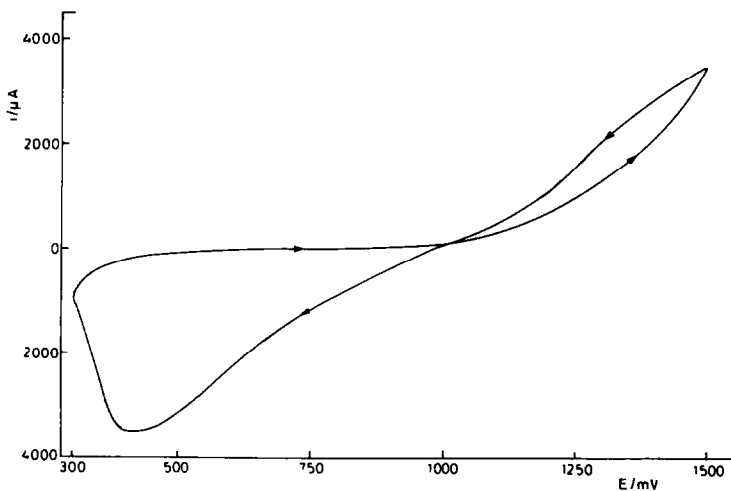

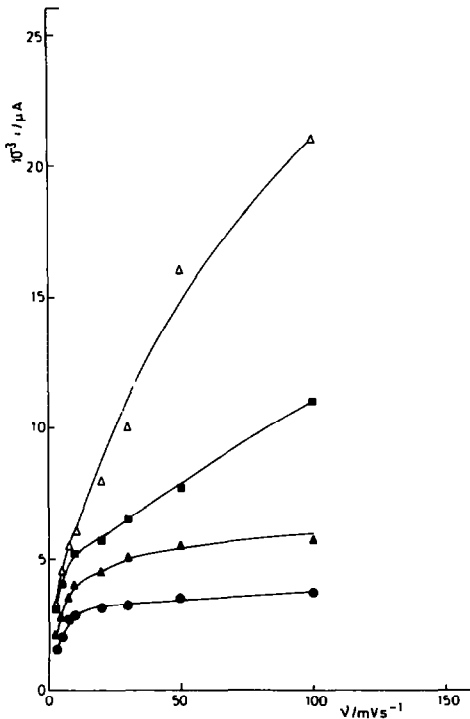Fig 9 Stabilised L S V curve for lead in 0 5M H_2SO_4 containing 54mM ClO_4^-, sweep rate 50 mV s^{-1}, 23 °C

Fig 10 Lead sulphate/lead dioxide region i_p vs ν for L S V curves of different ClO_4^- ion concentration $\triangle$, 0mM $HClO_4$, $\blacksquare$, 1mM $HClO_4$, $\blacktriangle$, 10mM $HClO_4$, $\bullet$, 54mM $HClO_4$

behaviour has been observed by others [5] who described potential oscillations occurring in galvanostatic charging experiments carried out in $H_2SO_4/$-$HClO_4$ mixtures. Another feature of the curves was that the small polarisable region between PbO_2/O_2 formation and PbO_2 discharge (reduction) was eliminated by the ClO_4^- ion.

For the reduction curve (negative going sweep) there was no satisfactory relationship between peak current and sweep speed (Fig. 10). Addition of ClO_4^- decreases the peak current for the reduction of PbO_2. This reduction is progressive in the available experimental range. It is clear from the curves that the formation of PbO_2 is complicated by the oxygen evolution reaction

The reduction of the formed PbO_2 is clearly highly irreversible, as shown by the shifts in peak potential to lower values at the higher sweep rates. The fall in reduction current caused by ClO_4^- ions is clearly proportional to the quantity of PbO_2 which is available for electrochemical reduction, rather than revealing the total oxidation which has occurred. We are forced to conclude that the effect is therefore to cause a thinning of the formed and available PbO_2 layer. It must be recognised, however, that the total quantity of oxidised product increases with ClO_4^- concentration as recorded in this laboratory [8] and by Azim and co-workers [5]. Since this reducible material must be in contact with the electrode, we are observing

the lead sulphate passive layer which has been oxidised to PbO_2. This available layer is apparently thinner, the more ClO_4^- there is in the bulk, possibly through a poorer contact with the substrate.

The present L.S.V. experiments have yielded only a limited amount of information regarding the behaviour of the ClO_4^- ion on the cycled electrode. It will be necessary to study reactions in the two potential regions of interest in order to describe the electrochemical reaction completely

Conclusions

(1) The ClO_4^- ion acts by displacing passivating SO_4^{2-} ion from the electrode.

(2) The ClO_4^- effect increases with concentration and may produce a 'self-stifling' behaviour if the ClO_4^- ion excludes sufficient SO_4^{2-} to interfere with the 'feed-back' reaction.

(3) In the PbO_2 region, the ClO_4^- ion reduces the thickness of the passivating layer If ClO_4^- exceeds a limit, the system cannot be rendered completely passive

(4) Cyclic experiments are only of limited use in investigating the processes involved and further pulse experiments are in hand.

Acknowledgements

References

1 S E Afifi, W H Edwards and N A Hampson, *Surf Technol*, *4* (1976) 173
2 W H Edwards and N A Hampson, *J Appl Electrochem* , *9* (1979) 381
3 A A Abdul Azim, *Corros Sci* , *10* (1970) 421
4 A A Abdul Azim and M M Anwar, *Corros Sci* , *9* (1969) 245
5 A A Abdul Azim and S E Afifi, *Corros Sci* , *12* (1972) 603
6 Yu A Popov, Yu V Alekseev and Ya M Kolotyrkin, *Electrokhimiya*, *14* (1977) 1447
7 H Bode, *Lead–Acid Batteries*, Wiley-Interscience, New York, 1977
8 N A Hampson, S Kelly and K Peters, *J Appl Electrochem* , *10* (1980) 91
9 M Fleischmann and H R Thirsk, *Trans Faraday Soc* , *51* (1955) 71
10 P Ruetschi, *Electrochem Soc* , *120* (1974) 331