

The behaviour of PbO_2 in concentrated sulphuric acid

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Linear sweep experiments on Pb in H_2SO_4 at concentrations in excess of 5 mol dm^{-3} have been conducted using computer controlled techniques. Measurements have indicated that the maximum charge in the PbO_2 reduction peak occurs at 5 mol dm^{-3} , the available capacity decreasing with the concentration of H_2SO_4 .

1. Introduction

Traditionally the concentration of sulphuric acid in lead acid cells is about 5 mol dm^{-3} in the fully-charged condition. Automotive batteries with the requirement of generating high engine cranking capability are furnished with electrolyte solution at a somewhat higher final concentration ($sg = 1.280$) and standby batteries with the requirement of low loss due to local action at the negative plate contain a rather lower concentration (maybe as low as $sg = 1.210$). With the introduction of fully-sealed lead cells containing a static phase on which the electrolyte is absorbed the concentrations within the cell may exceed 5 mol dm^{-3} . There is surprisingly little in the literature regarding the behaviour of the two lead cell electrodes in sulphuric acid concentrations greater than 5 mol dm^{-3} . Consequently it was considered timely to examine the behaviour of PbO_2 at these higher concentrations.

2. Experimental procedure

The electrometric experiments were made using a micro-computer as described by Mitchell *et al.* [1]. In the present case, the computer used was a Z-80 microprocessor-based 64K system (Kemitron 3000) commanding a potentiostat (Hi-Tek, Type DT 2101) and the output was monitored on a dual channel oscilloscope (Hameg HM 512).

Electrodes were prepared with lead (99.999%,

Koch-Light) as the control working surface (0.071 cm^2) of a rotating disc electrode. The reference electrode was $Hg|Hg_2SO_4$ in the same H_2SO_4 electrolyte solution as the working electrode. All measurements were made at a room temperature of $22 \pm 0.5^\circ \text{ C}$.

3. Results and discussion

At each sulphuric acid concentration the lead electrode was cycled between the limits 550 and 1550 mV at the appropriate rate of potential sweep to a constant response. This was found to require about 1.5 h potential cycling.

Figure 1 shows a typical current response corresponding to a cyclic linear sweep between the limits 600-1450 mV. For the cases with no interference from gaseous evolution, e.g. as in Fig. 3, the anodic and cathodic charges balanced to within experimental limits. A well-defined oxidation and rather shallow reduction peak is obvious. These are similar to previously reported data [2] and the effects of potential sweep rate on the peak oxidation currents (i_p) are shown in Fig. 2 for the various acid concentrations investigated. It is clear that the expected $i_p - \nu^{1/2}$ ($\nu =$ potential scan rate) relationship is observed, although, at the low concentrations the lines do not extrapolate back through the origin in agreement with the work of Hampson *et al.* [2]. The peak currents found for the oxidation of the lead used in that work [2] were

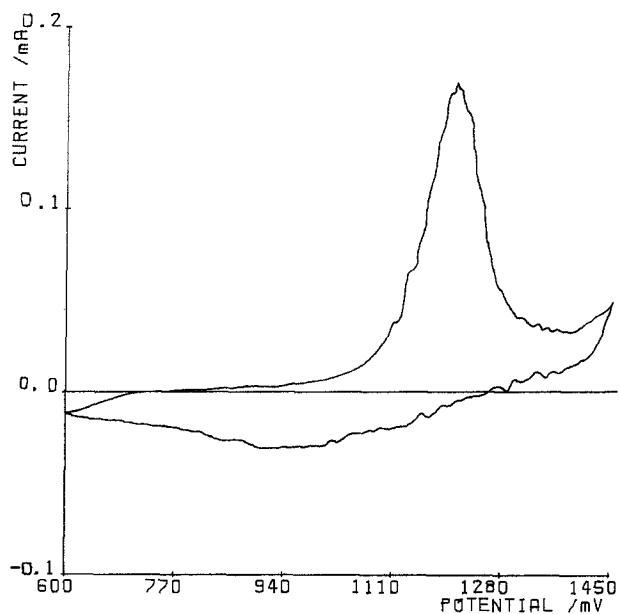


Fig. 1. Constant response curve for pure Pb for the range 600 → 1450 mV after cycling for 1.5 h. Sweep rate, 100 mV s⁻¹.

significantly smaller than those observed in the present study. This is apparently the influence of the low level impurities in the lead on the earlier work. This is confirmed by work [3] with similar antimony/lead binary alloys when results agreed to within 5%. The lead in the earlier work [2] contained Ag(0.0025 wt%), Cu(0.0026 wt%), Ti(0.0025 wt%), Bi(0.010 wt%) and further work will clearly be needed in order to decide which of

these materials is exerting the protective effect or whether there is any synergism.

It is clear from Fig. 2 that there is a large decrease in the peak currents in passing from 5 mol dm⁻³ to 10 mol dm⁻³ H₂SO₄ the greatest relative change occurring in the region around 5 mol dm⁻³. At concentrations around 7 mol dm⁻³ the recoverable charge was ~ 25% of that obtainable at 5 mol dm⁻³ as shown by Table 1 which

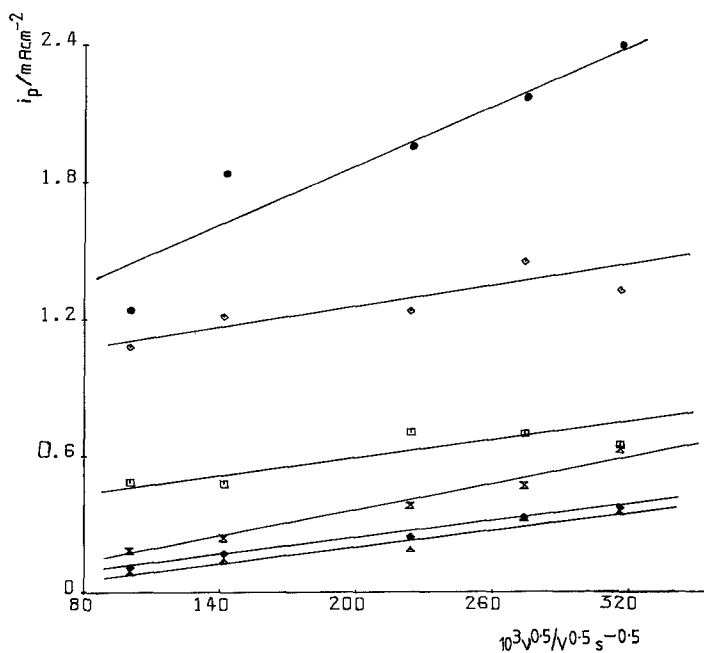


Fig. 2. Plot of i_p versus $v^{1/2}$ in the range 10–100 mV s⁻¹ for various concentrations of H₂SO₄: ●, 5.0 mol dm⁻³ H₂SO₄; ◇, 5.5 mol dm⁻³ H₂SO₄; □, 6.0 mol dm⁻³ H₂SO₄; △, 6.5 mol dm⁻³ H₂SO₄; ×, 7.0 mol dm⁻³ H₂SO₄; ◆, 10.0 mol dm⁻³ H₂SO₄.

Table 1. Charge ($mC\ cm^{-2}$) contained in the positive-going sweep in various concentrations of H_2SO_4 .

Concentration of H_2SO_4 ($mol\ dm^{-3}$)	Sweep rate ν ($mV\ s^{-1}$)		
	100	75	50
5.0	3.333	4.532	8.490
5.5	2.238	2.965	5.010
6.0	1.355	1.942	2.546
6.5	0.976	1.191	1.226
7.0	1.402	1.543	1.926
10.0	0.950	0.970	1.137

contains data obtained by direct integration of the anodic current in the stabilized voltammogram. This was done by utilizing the on-line computer using the 'extended Simpson's rule technique' [4]. Table 1 shows a maximum at $7.0\ mol\ dm^{-3}$. This local maximum is maintained at all rates of potential sweeping in replicate experiments. It can be concluded that as the concentration of sulphuric acid is increased, the form of the lead sulphate film becomes passivating at a smaller deposit thickness. If the reaction is controlled by a film as is clear from earlier work that if the film is more mechanically sound at high concentrations the $i_p - \nu^{1/2}$ relationship will clearly be justified. Hence it seems that a mechanically sounder film is being produced at the higher concentrations. An alternative explanation is possible in terms of

the change in peak potentials producing a $PbSO_4$ film which is tighter on the electrode. However, at the formation potentials corresponding to the higher concentrations, this explanation does not seem to be tenable in view of the local charge maximum at $\sim 7\ mol\ dm^{-3}$.

2.1. Note on the stability of PbO_2 in H_2SO_4

In the course of this investigation an attempt was made to use PbO_2 as a reference electrode. This was done by forming a thick deposit of PbO_2 on a lead rod (99.999%, Koch-Light) by employing the Planté formation process [5] using perchlorate ion as the aggressive ion. The conventional thickness of PbO_2 was generated on the lead base according to practice established over many years in the lead-acid industry.

It was found that the electrode could be used satisfactorily up to a concentration of $6\ mol\ dm^{-3}$ with the well-defined peaks occurring at the expected overpotentials. A typical voltammogram is shown in Fig. 3 for $5\ mol\ dm^{-3}\ H_2SO_4$ solution.

For concentrations in excess of $6\ mol\ dm^{-3}$ the form of the voltammogram was a gradually rising line in the anodic direction. The only feature occurred at $-1000\ mV$. (working electrode vs 'PbO₂ reference') where on the cathodic sweep the current rose abruptly and fell progressively to $-1400\ mV$. An examination of the reference

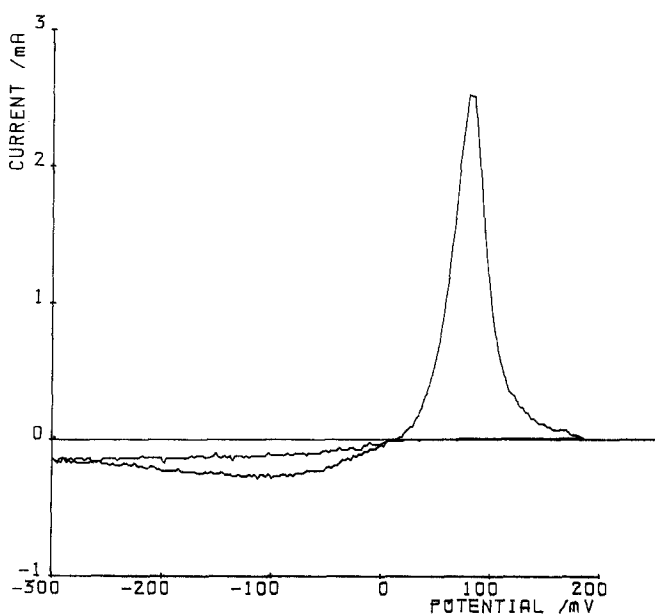
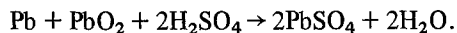
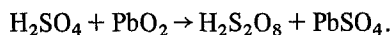


Fig. 3. Constant response curve for pure Pb for the range $-300 \rightarrow 200\ mV$ after cycling for 1.5 h. Sweep rate, $100\ mV\ s^{-1}$.

electrode indicated that it had been transformed to PbSO_4 presumably by the reaction between the PbO_2 on the surface and the underlying Pb



The implication is that the strong H_2SO_4 solution is able to penetrate the barrier between the PbO_2 and the Pb whereas the more dilute (5 mol dm^{-3}) solution could not. It would appear that the PbO_2 produced on Pb in concentrated (7 mol dm^{-3}) H_2SO_4 forms a barrier layer sufficiently passivating for penetration by the electrolyte solution. The barrier layer between Pb and PbO_2 for the case of PbO_2 produced on Pb in dilute electrolyte is not so effective in excluding the molecules of H_2SO_4 from concentrated electrolyte solution and the self-discharge reaction occurs. No chemical evidence was found for the development of peroxodisulphuric acid via a reaction of the type:



This is an important technological point for it

implies that in certain cell situations recharging in dilute electrolyte which ultimately increased in concentration considerably above 5 mol dm^{-3} (possibly in the contemporary static electrolyte phase battery) could give rise to undue positive cell self-discharge and enhanced positive plate corrosion.

Acknowledgements

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