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CYCLIC VOLTAMMETRY ON LEAD ELECTRODES IN SULPHURIC ACID SOLUTION

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Summary

The oxidation of lead in 5 M H₂SO₄ was studied by cyclic voltammetry. When a potential scan is applied from −1.0 V to 2.6 V vs. R.H.E. the PbSO₄/PbO₂ oxidation peak can be observed in the anodic voltammogram provided the scan rate is 0.16 mV/s or lower. When the potential scan is restricted to the potential range +0.6 V to +2.6 V the anodic voltammogram shows two peaks which were assigned to the formation of α-PbO₂ and β-PbO₂ respectively. This α-PbO₂ is formed underneath the PbSO₄ film. During the reverse sweep the main reduction peak at 1.65 V corresponds with the reduction of β-PbO₂ to PbSO₄. α-PbO₂ is not reduced at a definite potential but it is reduced to n-PbO·PbSO₄ with n increasing from the oxide-electrolyte interface towards the interior of the electrode and with more cathodic potential. At potentials below 0 V, the basic lead sulphates are reduced.

The effect of the addition of small amounts of H₃PO₄ to the H₂SO₄ electrolyte during the potential scanning results in an increase of the α-PbO₂ peak and a disappearance of the β-PbO₂ peak.

Introduction

The oxidation of Pb in H₂SO₄ to PbSO₄ and PbO₂ and the corresponding reduction reactions have been extensively studied both at Pb metal electrodes and at battery plates [1, 2]. Insight into the role of the PbSO₄ film during the anodic oxidation process was given by Ruetschi [3, 4]. Using PbSO₄ membranes Ruetschi [3] showed that the PbSO₄ film is impermeable for SO₄²⁻ and HSO₄⁻ ions but permeable for H⁺ ions. This accounts for the setting up of a potential difference across the PbSO₄ layer in such a way that during anodic oxidation a region of high pH is created underneath the PbSO₄ film. In this region lead oxide and basic lead sulphates can be formed. This explains why several basic lead sulphates are observed in battery plates.

Linear sweep voltammetry has been applied by Panesar [5], Carr et al. [6], Brennan et al. [7] and Sharpe [8] to investigate the oxidation-reduc-
tion behaviour of Pb, antimonial Pb and also of pure α-PbO₂ and β-PbO₂ electrodes. The studies show that only one peak (Pb/PbSO₄) is observed when the potential is swept from -0.7 V to +2.4 V vs. R.H.E. at scan rates of 0.5 mV/s and 58 mV/s. Evidence of the subsequent formation of PbO₂ and/or PbO₂⁺ could only indirectly be found from the cathodic voltammogram. At low speed rates (10 mV/s) Carr et al. [6] observed a current arrest corresponding to PbO₂ formation. When the potential sweep is restricted to the potential region 1.5 to 2.4 V Panesar obtained the PbSO₄/PbO₂ oxidation peak in the anodic voltammogram.

This paper reports results obtained by linear sweep voltammetry on Pb electrodes in 5 M H₂SO₄ and the effect of the addition of small amounts of H₃PO₄ to this electrolyte.

Experimental

A pure lead rod (99.999%) was embedded in a Perspex holder such that an area of 0.64 cm² was exposed. The electrode was placed in the usual electrochemical cell with a Pt counter electrode and a Pt hydrogen electrode as reference electrode. The electrolyte was 5 M H₂SO₄ (prepared from p.a. H₂SO₄) and flushed with N₂. All experiments were carried out at room temperature.

The potential scan could be programmed with a potentiostat (Wenking) and voltage scan generator (Wenking SMP 69 or VSG 72). The potential–current response was recorded on a XY recorder (Philips PM 8120). Before the experiments the electrode was polished and then cathodically polarized in the same cell and electrolyte with 350 mA/cm²

Results and Discussion

*Potential range* -1.0 V to +2.6 V

When a cyclic sweep is performed from -1.0 V to 2.6 V at sweep rates of 50 mV/s, the voltammogram (Fig. 1) shows one pronounced anodic peak (A) at -0.28 V and three cathodic peaks: at +1.65 V (peak d), at -0.32 V (peak b), and at -0.44 V (peak a). The small anodic peak c is observed during the cathodic sweep at 1.6 V. In the high anodic potential region the current increases steeply owing to the O₂ evolution reaction. During the reverse sweep this current is higher than during the preceding anodic sweep, due to an apparently higher catalytically active surface. This change of the surface properties is also indicated by the occurrence of peak d: peak d is due to the reduction of PbO₂ to PbSO₄*, thus during the anodic sweep PbO₂ formation takes place simultaneously with O₂ evolution. The

*A list of relevant electrode reactions is given in the Appendix.*
voltamogram is strongly dependent upon sweep rate and potential range (lower limit and upper limit) e.g. application of a potential scan, at the same scan rate, from $-1.0 \, \text{V}$ to $+2.2 \, \text{V}$ does not show the reduction peak d; however, when the potential is held at $2.2 \, \text{V}$ for a few minutes, peak d is observed.

This shows the slow formation of PbO₂. Evidence of formation of PbO₂ in the anodic voltammogram can only be observed at very slow scan rates; at $0.16 \, \text{mV/s}$ an anodic peak C is seen at $2.05 \, \text{V}$ (Fig. 1).

Peak A corresponds with the oxidation of Pb to PbSO₄ (reaction 1). The peak b in the reduction sweep is present only if the upper limit of the potential has been more anodic than $1.0 \, \text{V}$. For potential sweeps to values between $0.1$ and $1 \, \text{V}$ and at sweep rates from $0.5$ to $50 \, \text{mV/s}$ only reduction peak a is observed but not peak b (Fig. 2).

**Potential range $+0.6$ to $+2.6 \, \text{V}$**

When the cyclic sweep is performed from $0.6$ to $2.6 \, \text{V}$ (after a preceding cycle $-1.0$ to $2.6 \, \text{V}$ to $0.6 \, \text{V}$), the peak corresponding with PbSO₄ oxidation is gradually built up with repeated cycling. The anodic diagram (Fig. 3) shows 2 anodic peaks B and C. Depending upon the sweep rate, peak B and
C are found at 1.67 and 1.94 V for \( v = 0.5 \) mV/s and at 1.96 and 2.20 V for \( v = 50 \) mV/s. Reduction peak d is much less dependent upon the sweep velocity: 1.68 V at \( v = 0.5 \) mV/s and 1.60 V at \( v = 50 \) mV/s.

During the reverse sweep a small anodic peak \( \overline{c} \) occurs at 1.58 V during the reduction cycle. After a few cycles this peak decreases and finally disappears. With prolonged cycling peak B decreases while peak C increases. If the lower limit of the potential scan is set at 1.22 V instead of 0.6 V the same results are obtained. In our opinion both peaks B and C must correspond with \( \text{PbO}_2 \) formation. This is concluded from the fact that it has been well established [1, 2] that formation of \( \alpha\text{-PbO}_2 \) or \( \beta\text{-PbO}_2 \) depends on the pH of the electrolyte. Even in strong acid solution \( \alpha\text{-PbO}_2 \) can be formed because underneath the \( \text{PbSO}_4 \) film on \( \text{Pb} \) a film of different pH can exist [4]. This leads to formation of lead oxide [9 - 11]. Therefore, the oxidation of lead oxide to \( \alpha\text{-PbO}_2 \) (under the \( \text{PbSO}_4 \) film) must be indicated by peak B. Peak B occurs only if during the potential scan the electrode is not reduced to potentials at which also \( \text{PbSO}_4 \) can be reduced, hence peak B is manifest only in the scan range 0.6 to 2.6 V. At peak C \( \text{PbSO}_4 \) is oxidized to \( \beta\text{-PbO}_2 \). If the oxidation cycle is started at \(-1.0 \) V, peak C is the only peak present as shown by the broken line of Fig. 1. So, it must be concluded that under these circumstances alkaline conditions cannot be built up sufficiently under the \( \text{PbSO}_4 \) film, since this latter is too thin and no \( \alpha\text{-PbO}_2 \) can be formed underneath.

On pure \( \beta\text{-PbO}_2 \) electrodes Panesar [5] observed in the anodic sweep (scan range 1.50 to 2.40 V; 0.5 mV/s) one anodic peak at 2.1 V, corresponding
Fig. 3. Voltammogram of a Pb electrode in 5 M H$_2$SO$_4$, potential range +0.6 V to 2.6 V.  
1. First cycle recorded after applying the potential program −1.0 V to 2.6 V to 0.6 V; sweep rate 50 mV/s. With repeated cycling between 0.6 and 2.6 V the peaks B and C are built up; 2, recorded after 8 cycles; sweep rate 5 mV/s.

Peak d corresponds to the reduction of PbO$_2$. The reversible potentials of α-PbO$_2$/PbSO$_4$ and β-PbO$_2$/PbSO$_4$ in H$_2$SO$_4$ differ only by 8 mV, (see eqns. 10 and 11), therefore distinct reduction peaks can only be expected if the rate processes of the reduction differ considerably and/or if the local pH is different. With freshly prepared α-PbO$_2$ electrodes we observed a reduction peak at 1.7 V. Panesar [5] found a broad reduction peak with a preceding plateau. After a few cycles this plateau has developed into the main reduction peak. Carr et al. [6] observed for α-PbO$_2$ a shoulder following the reduction peak, using a higher scan rate (58.3 mV/s). With repeated cycling, the main peak decreased and the shoulder increased, which they attributed to a decrease in the α peak and an increase in β-PbO$_2$. For pure β-PbO$_2$ a reduction peak at about the same potential was observed. The height of peak d depends on the upper limit of the anodic sweep. With increasing potential limit peak d increases.
If the anodic sweep is reversed at potential limits situated between peak B and C then peak d becomes very small (Fig. 4). This clearly indicates that peak C and peak d correspond to the same reaction, i.e. the $\beta$-PbO$_2$/PbSO$_4$ reaction. The reduction process of $\beta$-PbO$_2$ begins at the $\beta$-PbO$_2$/H$_2$SO$_4$ electrolyte interface and gradually moves inwards towards the Pb electrode. Part of the underlying $\alpha$-PbO$_2$ is reduced together with $\beta$-PbO$_2$ to PbSO$_4$. The PbSO$_4$ layer impedes the diffusion of H$_2$SO$_4$ to the inner part of the electrode, so, depending on the availability of H$_2$SO$_4$ and the pH, $\alpha$-PbO$_2$ is reduced to $n$-PbO$\cdot$PbSO$_4$ with $n$ increasing towards the electrode and with more cathodic potential. During potential scanning this conversion process takes place gradually until finally the potential is reached at which basic lead sulphate can be reduced.

The potential at which $\alpha$-PbO$_2$ is reduced to $n$-PbO$\cdot$PbSO$_4$ varies from 1.468 V for $n = 1$ to lower values (see eqns. 12 - 15). In the voltammogram no reduction peak is observed which could be attributed to $\alpha$-PbO$_2$ reduction. The reason for this must be that the amount of the basic lead sulphates is small and strongly dependent upon pH.
During the first cathodic sweep the reduction peak d is followed by an anodic peak c (Fig. 3). This peak should be assigned to the oxidation of newly exposed Pb to PbO and basic sulphates, as well as to the oxidation of these latter products to α-PbO₂. With repeated cycling c disappears.

At peak b, PbO is reduced to Pb, while at peak a PbSO₄ is reduced to Pb. Panesar argues that at b, α-PbO₂ is reduced, because a close correspondence was observed between the peaks d and b. However, his results show that peak d is also found when the electrode is held for 16 h at 450 mV. At this potential α-PbO₂ cannot be formed [cf. eqns. (8), (11) - (14)]. Likewise Ruetschi [3] disputes Panesar's conclusion regarding peak b. On the basis of his film theory, Ruetschi calculates that at pH 9.34 PbO is reduced to Pb at −0.15 V.
Because it is well known that small amounts of phosphoric acid, improve the cycle life of battery plates [2, 12, 13], the effect of the addition of H$_3$PO$_4$ was studied.

Small quantities of H$_3$PO$_4$ were added to the sulphuric acid electrolyte after the Pb electrode had been subjected to several sweeps in the potential region 0.6 to 2.6 V ($v = 50$ mV/s). Addition of 0.01 $M$ H$_3$PO$_4$ to 100 ml of electrolyte at first slightly increases peak B (Fig. 5), while peak C disappears in the anodic sweep; in the cathodic sweep peak d is reduced. With repeated cycling peak B shifts in the anodic direction (after many cycles peak $B' = 1.95$ V), and peak d is reduced further.

The effect depends upon the amount of the H$_3$PO$_4$ addition. Under the experimental conditions used here, C had completely disappeared after the addition of 0.007 $M$ H$_3$PO$_4$, peak d is then reduced to 50% of the value before the H$_3$PO$_4$ addition. Prolonged cycling without H$_3$PO$_4$ addition does not effect peak d while B decreases and C increases somewhat.

For comparison a voltammogram on Pb was run in 1 $M$ H$_3$PO$_4$ in the potential range 0.6 to +2.6 V ($v = 50$ mV/s) and this shows (Fig. 6) a broad maximum at 1.8 V and two reduction maxima at 1.5 and 0.85 V.

The results of Fig. 5 suggest that in the presence of small amounts of H$_3$PO$_4$ the formation of $\beta$-PbO$_2$ on a Pb electrode is inhibited. This could
then imply increased $\alpha$-$\text{PbO}_2$ formation which is in agreement with the observed fact [5] that increase in $\alpha$-$\text{PbO}_2$ favours cycle life. Some workers [2] suggest that in the presence of $\text{H}_3\text{PO}_4$ plumbous phosphate is formed at the electrode which is then oxidized to plumbic phosphate. In excess sulphuric acid hydrolysis leads to the separation of the two lead dioxide modifications.

References


Appendix

\[
\begin{align*}
(1) \ \text{Pb} + \text{H}_2\text{SO}_4 & \rightarrow \text{PbSO}_4 + \text{H}^+ + 2e \\
\epsilon &= 0.302 - 0.0295 \ \text{pH} - 0.0295 \ \log a_{\text{H}_2\text{SO}_4} \\
(2) \ \text{Pb} + \text{SO}_4^{2-} & \rightarrow \text{PbSO}_4 + 2e \\
\epsilon &= -0.356 - 0.0295 \ \log a_{\text{SO}_4^{2-}} \\
(3) \ 2 \ \text{Pb} + \text{SO}_4^{2-} + \text{H}_2\text{O} & \rightarrow \text{PbO} \cdot \text{PbSO}_4 + 2 \ \text{H}^+ + 4e \\
\epsilon &= -0.099 - 0.0295 \ \text{pH} - 0.0148 \ \log a_{\text{SO}_4^{2-}} \\
& \quad - 0.113 - 0.0295 \ \text{pH} - 0.0148 \ \log a_{\text{SO}_4^{2-}} \\
(4) \ 4 \ \text{Pb} + 2 \text{SO}_4^{2-} + 4 \ \text{H}_2\text{O} & \rightarrow 3 \ \text{PbO} \cdot \text{PbSO}_4 \cdot \text{H}_2\text{O} + 6 \ \text{H}^+ + 8e \\
\epsilon &= +0.037 - 0.0443 \ \text{pH} - 0.0074 \ \log a_{\text{SO}_4^{2-}} + \\
& \quad + 0.030 - 0.044 \ \text{pH} - 0.0074 \ \log a_{\text{SO}_4^{2-}} \\
(5) \ 5 \ \text{Pb} + 7 \ \text{H}_2\text{O} & \rightarrow 5 \ \text{PbO} \cdot \text{H}_2\text{O} + 10 \ \text{H}^+ + 10e \\
\epsilon &= +0.260 - 0.0591 \ \text{pH} \\
(6) \ \text{Pb} + 2 \ \text{H}_2\text{O} & \rightarrow \text{PbO} + 2 \ \text{H}^+ + 2e \\
\epsilon &= 0.248 - 0.0591 \ \text{pH} \\
\epsilon &= 0.242 - 0.0591 \ \text{pH}
\end{align*}
\]
(7) \( 5 \text{Pb} + \text{SO}_4^{2-} + 4 \text{H}_2\text{O} \rightarrow 4 \text{PbO} \cdot \text{PbSO}_4 + 8 \text{H}^+ + 10e \)
\[ e = 0.115 - 0.047 \text{pH} - 0.006 \log a_{\text{SO}_4^{2-}} \] [10]

(8) \( \text{Pb} + 2 \text{H}_2\text{O} \rightarrow \alpha \cdot \text{PbO}_2 + 4 \text{H}^+ + 4e \)
\[ e = 0.665 - 0.059 \text{pH} \] [9]

(9) \( \text{Pb} + 2 \text{H}_2\text{O} \rightarrow \beta \cdot \text{PbO}_2 + 4\text{H}^+ + 4e \)
\[ e = 0.677 - 0.059 \text{pH} \] [1]

(10) \( \text{PbSO}_4 + 2 \text{H}_2\text{O} \rightarrow \beta \cdot \text{PbO}_2 + 4\text{H}^+ + \text{SO}_4^{2-} + 2e \)
\[ e = 1.687 - 0.1182 \text{pH} + 0.0295 \log a_{\text{SO}_4^{2-}} \]
\[ 1.690 - 0.113 \text{pH} + 0.0295 \log a_{\text{SO}_4^{2-}} \] [14]

(11) \( \text{PbSO}_4 + \text{H}_2\text{O} \rightarrow \alpha \cdot \text{PbO}_2 + \text{SO}_4^{2-} + 4\text{H}^+ + 2e \)
\[ e = 1.698 - 0.113 \text{pH} + 0.029 \log a_{\text{SO}_4^{2-}} \]
\[ 1.697 - 0.1182 \text{pH} + 0.029 \log a_{\text{SO}_4^{2-}} \] [14]

(12) \( \text{PbO} \cdot \text{PbSO}_4 + 3 \text{H}_2\text{O} \rightarrow 2 \text{PbO}_2 + \text{SO}_4^{2-} + 6\text{H}^+ + 4e \)
\[ e = 1.468 - 0.0886 \text{pH} + 0.0148 \log a_{\text{SO}_4^{2-}} \]
\[ 1.422 - 0.0886 \text{pH} + 0.0147 \log a_{\text{SO}_4^{2-}} \] [4]

(13) \( 3 \text{PbO} \cdot \text{PbSO}_4 \cdot \text{H}_2\text{O} + 4 \text{H}_2\text{O} \rightarrow 4 \text{PbO}_2 + \text{SO}_4^{2-} + 10\text{H}^+ + 8e \)
\[ e = 1.325 - 0.0739 \text{pH} + 0.0074 \log a_{\text{SO}_4^{2-}} \]
\[ 1.285 - 0.0739 \text{pH} + 0.0074 \log a_{\text{SO}_4^{2-}} \] [4]

(14) \( \text{PbO} + \text{H}_2\text{O} \rightarrow \text{PbO}_2 + 2\text{H}^+ + 2e \)
\[ e = 1.107 - 0.0591 \text{pH} \] [2]

(15) \( 5 \text{PbO} \cdot 2 \text{H}_2\text{O} + 3 \text{H}_2\text{O} \rightarrow 5 \text{PbO}_2 + 10\text{H}^+ + 10e \)
\[ e = 1.070 - 0.059 \text{pH} \] [4]

If the active species is \( \text{HSO}_4^- \) instead of \( \text{SO}_4^{2-} \), the potential changes according to the relation:
\[ \log \frac{a_{\text{HSO}_4^-}}{a_{\text{SO}_4^{2-}}} = 1.92 - \text{pH}. \]