The effect of temperature on the anodic oxidation of lead in 1 M sulphuric acid solutions

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The results of linear sweep experiments on lead in 1 M sulphuric acid solutions with and without saturation by an organic lignosulphonate (expander) have shown that one mode of expander action is to change the mechanism of current limitation in the passivation process.

1. Introduction

The influence of temperature on the electrochemistry of lead in sulphuric acid is important to the automotive battery industry, for it is the lead (negative) electrode which limits the low-temperature performance of the lead–acid battery. It has become the practice to add materials known as expanders in order to promote the low-temperature oxidation (discharge) of lead in sulphuric acid. Additives are usually mixtures of carbon black, barium sulphate and lignin material: the effects of these have been reviewed in [1]. Barium sulphate provides nucleation centres for the formation of lead sulphate, with which it is isomorphous; carbon black has apparently no effect other than to increase the conductivity of the porous electrode during the early stages of the electrochemical conversion of lead sulphate to lead.

The effect of the lignin organic expander material is apparently complex. Adsorption on the electrode surface leads to a larger specific electrode area, probably via the agency of a finer-grained lead sulphate phase in which small crystals predominate. However, other effects due to lignin have been suggested. Thus expander action may be via the suppression of the solid-state pathway for the oxidation of lead [2]. In agreement with this, Brennan and Hampson [3] found that an organic

lignosulphonate tended to suppress the nucleation step in the lead electrocrystallization process. Evidence was also found for the inhibition of the solution phase dissolution reaction [4].

All the above work was done with 5 M H_2SO_4, that is, battery-strength sulphuric acid. In this solution, the solution-controlled dissolution of lead as lead sulphate is extremely small by comparison with the solid-state reaction. The reason for this is the very low solubility of lead sulphate in 5 M H_2SO_4. The solubility of lead sulphate rises to a very sharp maximum in 1 M H_2SO_4; consequently, it was considered of interest to explore the effect of lignosulphonate on the anodic electrochemistry of lead in 1 M H_2SO_4. The most technologically interesting region for investigation is at low temperature where the beneficial effects of lignin additives are known to apply. This paper describes linear sweep voltammetry (LSV) experiments in which the results of our investigation in this area of the electrochemistry of lead are reported.

2. Experimental details

The electrode was a lead disc (diameter = 0.3 cm, 99.999%) shrouded in Teflon which could be rotated at a known constant speed. The electrochemistry was performed using the computer-controlled potentiostat recently described [5].

Electrolyte throughout was 1 M sulphuric acid made by diluting Analar sulphuric acid with triply distilled water. The electrolyte system was thermo-stated in a methanol bath the temperature of which could be controlled to within $\pm 1°$ C down to $- 40°$ C. All potential measurements were made with an Hg_2SO_4/Hg electrode disposed in the same cell and operating through a Luggin system, thus eliminating any thermoelectric effects.

Linear sweep experiments were made at a series of sweep rates in the temperature range from ambient down to $- 5°$ C, which was found to be the effective slushing point of the electrolyte solution. The series of experiments was then repeated after saturating the electrolyte solution with Indulin 'C' which is a lignosulphonate widely used in lead–acid battery applications.

3. Results

Fig. 1 shows the results of an LSV experiment at room temperature. In the potential range investigated the currents were independent of rotation speed and consequently the reaction rates are independent of diffusion in solution. The potential range was limited so that only the Pb(II)/Pb redox reaction was observed to any great extent. The increase in current near the negative limit of the negative-going sweep is due to hydrogen evolution on the product lead; the residual current
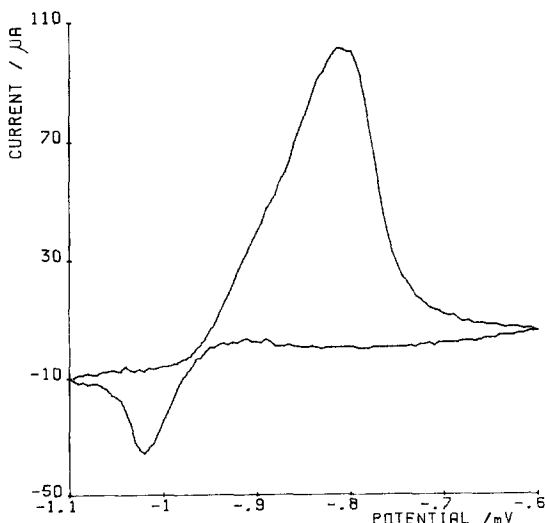
at the positive limit of the positive-going sweep is due to the residual high-field conduction current through the passivating lead sulphate layer. As the temperature was lowered the current in the voltammogram everywhere reduced (Fig. 2).

This trend continued as far as $\sim - 2°$ C. At this point gross changes occurred on repetitively cycling the electrode around the potential region. Fig. 3 shows a quasi-stable voltammogram produced on continued prolonged cycling (~ 30 cycles) at $- 2°$ C. This shape further degenerated on cycling to a linear shape with virtually no separation between the positive- and negative-going sweeps, as shown in Fig. 4. The shape is redolent of a polarizable system in spite of the clear electrochemistry exhibited in earlier sweeps. The current at the most negative potential (when the current is mainly due to the hydrogen reaction) is very small, considerably less than when the electrode is 'active', and confirms that the system is $Pb/PbSO_4(s)/H_2SO_4(1 M)$ and not Pb/H_2SO_4 (1 M). This behaviour can be explained by the transformation of the lead sulphate layer at the end of the positive sweep from a relatively randomly orientated layer through which electricity is readily able to pass to a much more ordered layer in which a considerable overpotential is required in order to effect the reduction of the $PbSO_4$ layer. The electrode therefore behaves in a quasi-polarizable manner over the narrow potential range.

At temperatures slightly in excess of $- 2°$ C the initial open voltammogram after degeneration to a single line on cycling was re-established by further prolonged cycles over the experimental region, the electrode behaviour apparently randomly switching between the two states. This indicates that the temperature is crucial, probably with local slight changes due to instrumental effects determining the precise form of the voltammogram.

The current in the anodic peak was related to the sweep rate and Fig. 5 shows that the i_p versus $v^{1/2}$ relationship for current control by a diffusion process holds over the whole temperature range. The controlling diffusion cannot be in the solution phase, for, using the theoretical equation connecting i_p and $v^{1/2}$ for a solution process

Fig. 1. Linear sweep voltammogram of the Pb(II)/Pb system in 1 M H_2SO_4 at 18° C.

$$i_p = 2.72 \times 10^5\, n^{3/2} D^{1/2} C\, v^{1/2} \qquad (1)$$
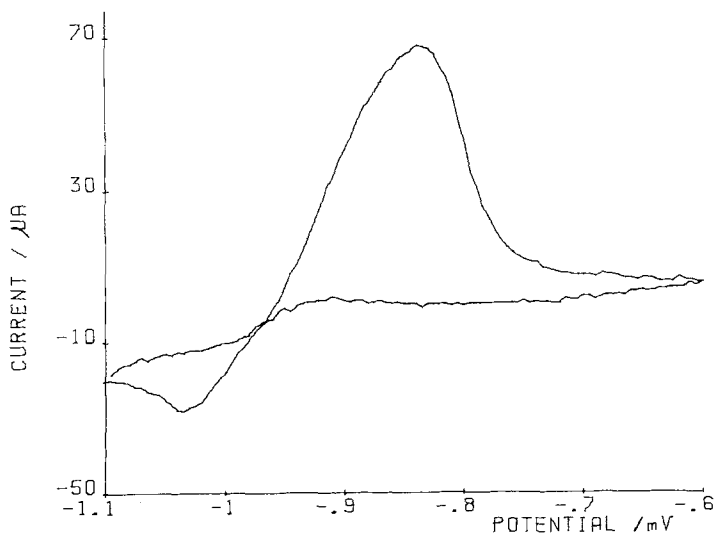
Fig. 2. Linear sweep voltammogram of the Pb(II)/Pb system in 1 M H_2SO_4 at 4° C.
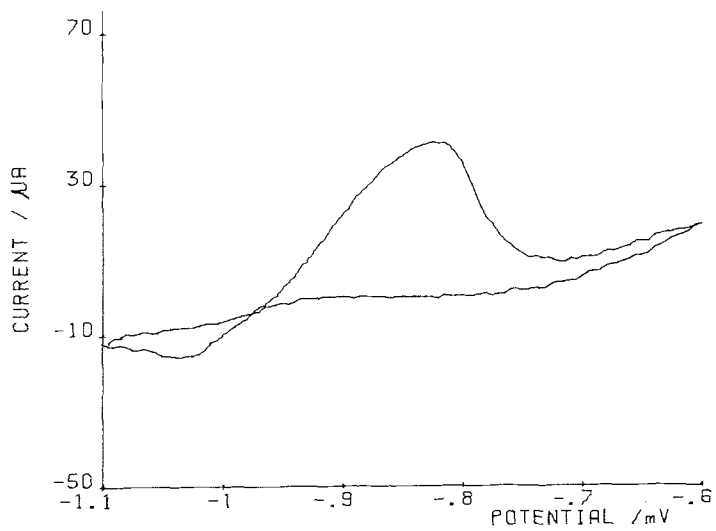
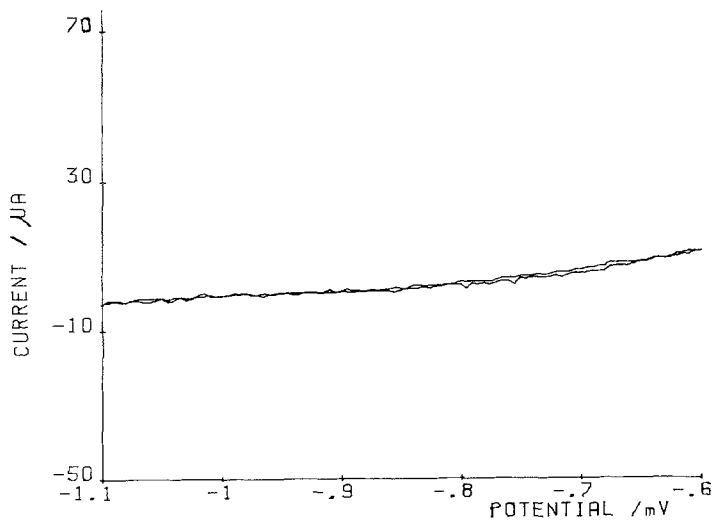Fig. 3. Linear sweep voltammogram of the Pb(II)/Pb system in 1 M H_2SO_4 at $-2°$ C.

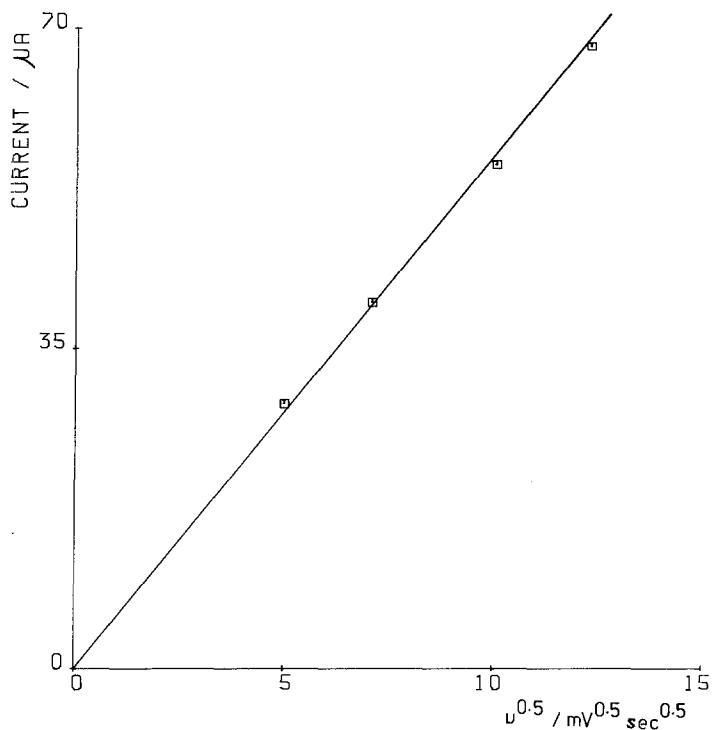Fig. 4. Linear sweep voltammogram of the Pb(II)/Pb system in 1 M H_2SO_4 at $-2°$ C and with cycling.

Fig. 5. The i_p versus $v^{1/2}$ relationship for the Pb(II)/Pb system in 1 M H_2SO_4.

the value of D, the diffusion coefficient, is found to be 2.5×10^{-8} cm^2 s^{-1} at $18°$ C. This implies current control by diffusion of ions through the lead sulphate film which will be very incompletely formed, which probably accounts for the observed magnitude. This is in agreement with previous work [6]. The value of the diffusion coefficient is found to be lower at the lower temperatures as expected.

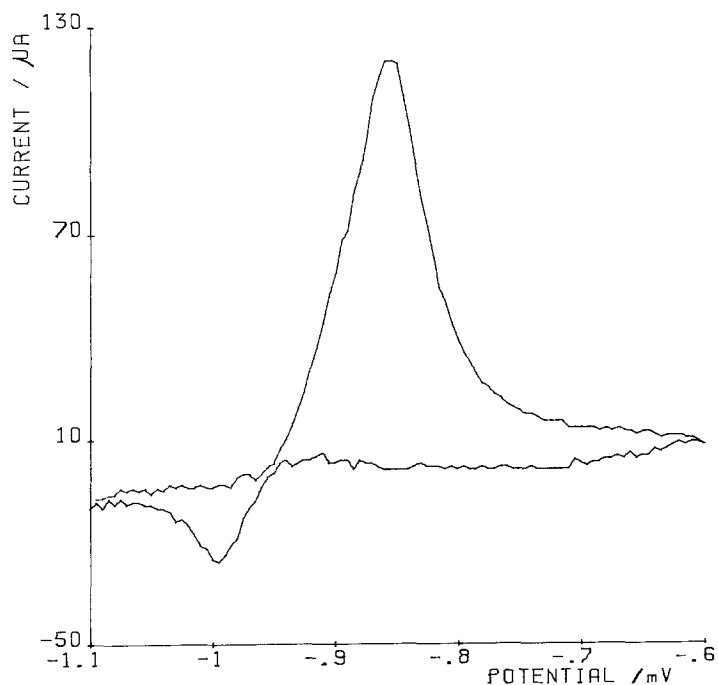When Indulin 'C' is added to the electrolyte

Fig. 6. Linear sweep voltammogram of the Pb(II)/Pb system, in 1 M H_2SO_4 saturated with Indulin 'C' expander, at $18°$ C.

phase the height of the reduction peak is significantly reduced, over all temperature ranges; indicative of a thinner $PbSO_4$ film being initially deposited. The separation of the oxidation and reduction peaks is also noticeably decreased. Fig. 6 shows the data corresponding to a saturated 1 M H_2SO_4 solution of Indulin 'C'. This method of solution preparation was used due to the great insolubility of Indulin 'C' in sulphuric acid, the saturated solution containing a barely detectable amount of the organic material although the solution was a very pale yellow colour. When the temperature was lowered the voltammogram current was everywhere reduced but the degeneration of the shape into a single line for a quasi-polarizable system was not observed. Even reducing the temperature to $-6°$ C (at which the onset of electrolyte slushing was observed) did not produce the quasi-polarizability. We are forced to the conclusion that the presence of Indulin 'C' inhibited the formation of a highly ordered, completely passivating lead sulphate film.

Throughout the experimental temperature range the current in the voltammogram increased with increasing sweep speed. However, this this relationship for the Indulin 'C' systems is

for i_p to be rectilinear with the sweep speed. We can interpret this if the electrode passivates when a completed layer of $PbSO_4$ is formed on the surface. Since charge (q_p) in the voltammetric peak is simply the peak area (A_p) divided by the sweep rate (v), then, if the peaks remain the same shape at all sweep rates,

$$i_p = Cv \qquad (2)$$

where C is a constant proportional to the film thickness. Fig. 7 shows that Equation 2 adequately describes the behaviour.

The value of C depends on the temperature, and the lower slopes of the i_p and v lines as the temperature is lowered indicates that at lower temperatures the thickness of the film required to passivate the electrode is reduced.

4. Discussion

The influence of Indulin 'C' in suppressing the transformation of the electrode cycling behaviour from the active to the quasi-polarizable condition is a new aspect of expander behaviour. We suggest that the specific effect is the creation by the expander of lattice defects in the $PbSO_4$ phase
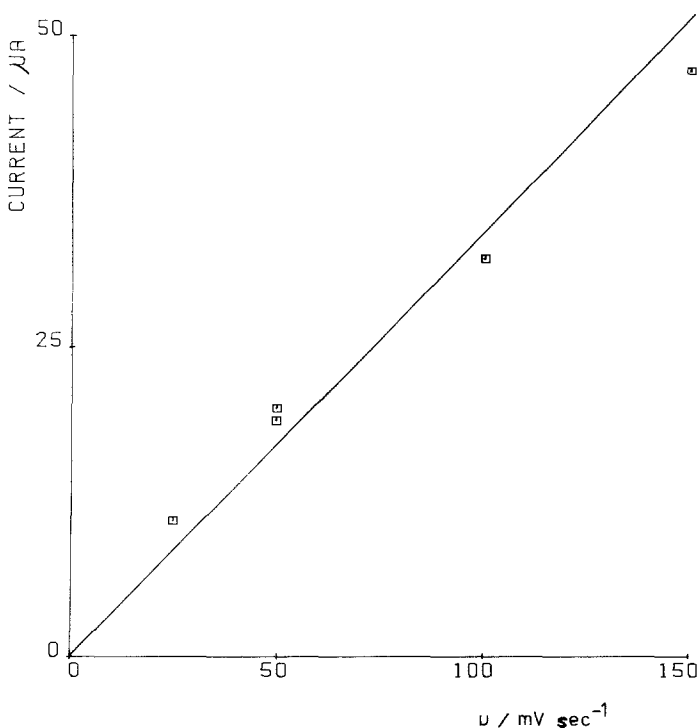

Fig. 7. The i_p versus v relationship for the Pb(II)/Pb system in 1 M H_2SO_4, saturated with Indulin 'C' expander.
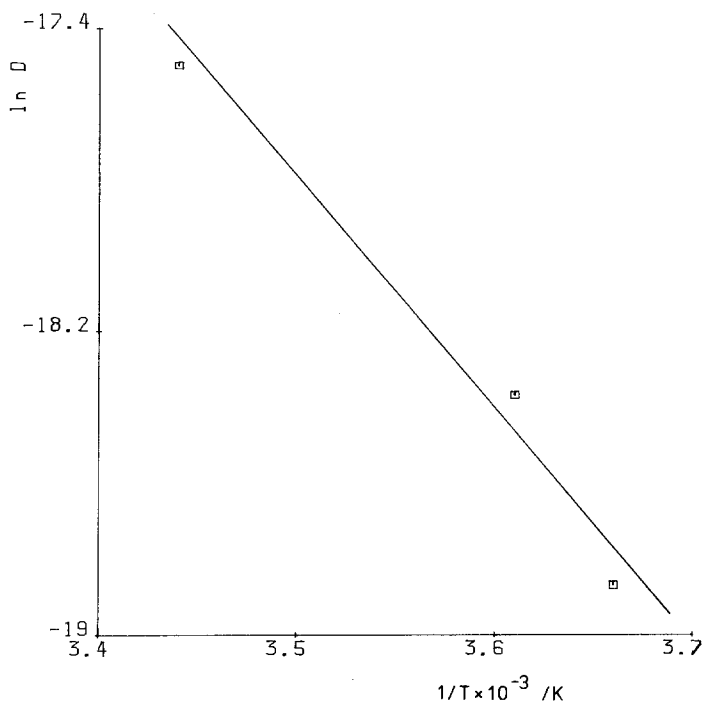
Fig. 8. Arrhenius plot of ln$D$ versus $1/T$ for the Pb(II)/Pb system in 1 M H_2SO_4.

which inhibit the formation of the ordered structure at low temperatures. Thus, in the presence of the Indulin 'C', the current is not controlled via the passage across and through the lead sulphate film, whereas in the Indulin 'C' free system it is.

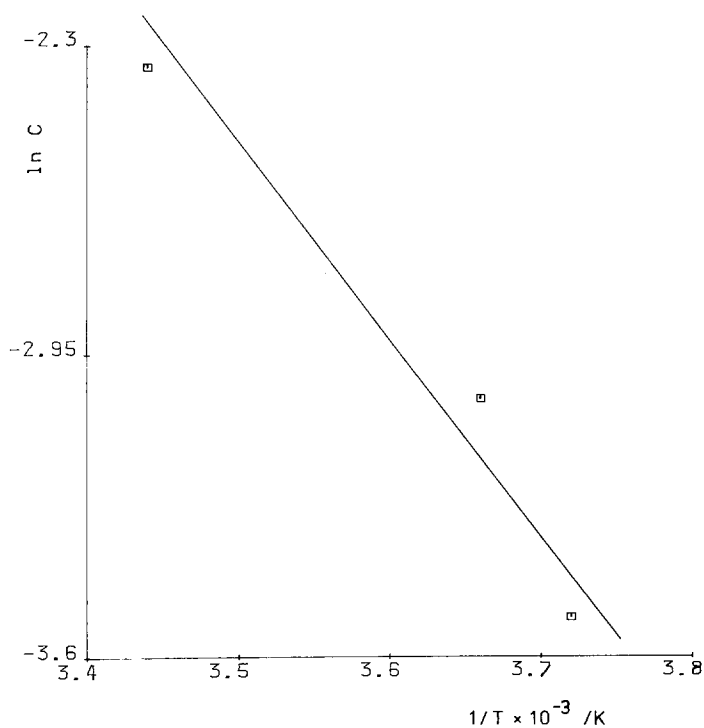An Arrhenius plot for diffusion in the $PbSO_4$ film is shown for the diffusion-controlled systems

Fig. 9. Arrhenius plot of ln$C$ versus $1/T$ for the system saturated with expander.

in Fig. 8. The enthalpy of activation for the diffusion process is 52 kJ mol^{-1}. This value is in excess of the value expected for simple diffusion in solution and supports the conclusion that the controlling diffusion is in the solid phase.

Fig. 9 shows the Arrhenius plot for the system containing Indulin 'C', where ln$C$ from Equation 2 is plotted against $1/T$. The enthalpy of activation for the formation of the passivating film is 27 kJ mol^{-1}, sufficiently close to the diffusional enthalpy above to enable the Indulin 'C' to exert a control over which mechanism (solid-state diffusion or film formation) controls the current.

References

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