

## FUNDAMENTALS OF LEAD-ACID CELLS XVII. NEGATIVE ORGANIC EXPANDER ACTION AT LOW TEMPERATURES

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### Summary

The behaviours of porous lead electrodes containing, and free from, organic expander in 5M  $\text{H}_2\text{SO}_4$  are compared at temperatures down to  $-30^\circ\text{C}$ . It is shown that the behaviour of those electrodes containing the expander is significantly different from that of those free of the organic. Some possible explanations are discussed.

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### 1. Introduction

Deficiencies in the capacities of lead negatives of the lead cell to deliver their nominal charge on continued cycling have been known from early times [1, 2]. Organic expanders have been added in order to try to correct the deterioration in negative behaviour and the patent literature contains examples of almost every class of organic compound claimed as beneficial additive. Ritchie [3] has comprehensively reviewed all the listed expanders up to 1947. Since the 1950s all the organic expanders have been based on wood and cellulosic materials and there are very few instances of comprehensive investigations since pre-war years. One exception was the work of the Chloride Group Research Laboratories in the mid 1950s when a very comprehensive study was made under the direction of Barak [4]. That investigation underlined the importance of the condensed hexose structure in the constitution of an expander. Thus expander activity was quite pronounced in carboxymethylcellulose, although somewhat inferior to that of humic acid, obtained from peat or the aqueous extract from vandyke crystals. Today, all the commercially used expanders are based on lignosulphonic acid which is a complex material of uncertain structure [5, 6].

The specific action of the expander is clear to the battery manufacturer. Without the additive, discharge capacity is progressively lost, especially under

tests which impose a high demand on the battery such as high rates and low temperatures. It is of interest to note that the presence of an expander in the negative is reported not to be essential for the initial cycle [7]. It is not clear to the electrochemist how these effects arise.

Thermodynamically the principle of minimisation of free energy requires densification of the electrode if atoms on a porous lattice go through a stage where they have surface mobility. Such a state of affairs arises in the charge/discharge processes of cycling lead cells. This process would account for a gradual loss in discharge capacity on cycling. However, there seems to be more involved in the processes than that; for we have recently shown that in the absence of expander at low temperature a layer of lead sulphate overlying a lead electrode in some instances behaves as a polarisable system [8]. Further, we have shown that in dilute sulphuric acid solution the presence of a lignosulphonate expander (Indulin C) changes the current limiting process from cover passivity in the sense of Müller [9] to diffusion of ions through the passivating lead sulphate film.

It has been suggested by Archdale and Harrison [10] that adsorbed expander at lead surfaces hinders the diffusion of  $\text{Pb}^{2+}$  ions and delays the onset of solid phase passivation. There is certainly evidence for this [11]; however, this cannot be the whole explanation of expander action. There is also an effect on the solid state lead sulphate formation. Hampson and Lakeman [12] found that at room temperature the incorporation of a lignosulphonate expander into the paste increased the number of nucleation sites (*i.e.*, the active surface area) available for the crystallisation of  $\text{PbSO}_4$  on the lead during the discharge reaction. This process turned out to be the major difference between expander-containing and expander-free porous electrodes.

Further investigation of porous lead electrodes at low temperatures indicates that the formation of  $\text{PbSO}_4$  in 5M sulphuric acid at  $\sim -30^\circ\text{C}$  is a complicated process. Not only do the normal processes of phase formation occur but the picture may be complicated by phase ice formation when the concentration of solution in the pore structures is sufficiently reduced by the electrochemical reaction. To a potentiostatic step experiment the normal phase formation current response exhibits a stepped form [13].

It is timely to explore the effects of organic expanders in a porous electrode both incorporated in the porous structure itself (by reducing an expander-containing paste) and by dispersing expander material in the electrolyte.

## 2. Experimental

The electrode was prepared by pasting a recess formed by shrouding a lead rod ( $\phi = 0.3$  cm, 99.999%), sectioned at right angles to the long axis, with Teflon so that the end of the shroud ( $\phi = 1.6$  cm) projected 0.076 cm below the lead. The end of the shroud was perpendicular to the long axis

and polished flat. The paste contained 'leady' oxide, sulphuric acid and, if necessary, expander. The paste was allowed to set in 100% humidity prior to drying at 21 °C (70 °F) and electroreduced. Porous electrodes were subsequently formed, in an inverted position (facing upwards), by reduction at 18 mA cm<sup>-2</sup> for a period of 72 h in 0.5M H<sub>2</sub>SO<sub>4</sub> upon which hydrogen was freely evolving from the electrode. The resulting electrodes had a nominal density of 3.35 g cm<sup>-3</sup> (~ 70% voids) and a theoretical recoverable capacity of 16.8 C. The electrochemical system was thermostatted in a methanol bath the temperature of which could be controlled ( $\pm 1$  °C) in the range ambient down to -40 °C. All potential measurements were made with an Hg<sub>2</sub>SO<sub>4</sub>/Hg electrode disposed in the same cell and operating through a Luggin system — this eliminated any thermoelectric effects.

The electrochemistry was carried out using a computer (Kemitron 3000) controlled potentiostat (Kemitron P-03) system, the experimental data being recovered from a digital plotter (Watanabe WX 4671) and a dot matrix printer (Heathkit H14) after monitoring on a digital storage oscilloscope (Gould OS 4100).

### 3. Results and discussion

#### 3.1. Porous electrodes free from organic expander

Figure 1 shows a stable L.S.V. curve corresponding to a newly produced electrode immediately after formation and stabilisation in 5M H<sub>2</sub>SO<sub>4</sub>. The currents involved were about two orders of magnitude greater than similar experiments on solid lead in less concentrated acid [8] and the shape of the L.S.V. curve was quite similar.

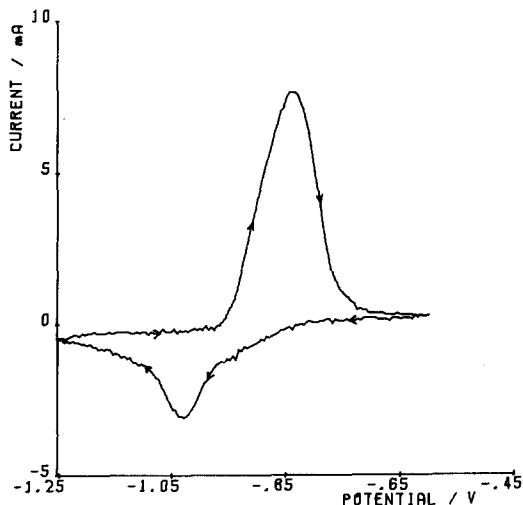


Fig. 1. L.S.V. curve for the porous Pb/PbSO<sub>4</sub> system in 5M H<sub>2</sub>SO<sub>4</sub>. 17 °C. Electrode area 0.0707 cm<sup>2</sup>, depth 0.76 mm (free of organic expander) sweep speed 100 mV s<sup>-1</sup>. Stabilised sweep after ~ 100 cycles.

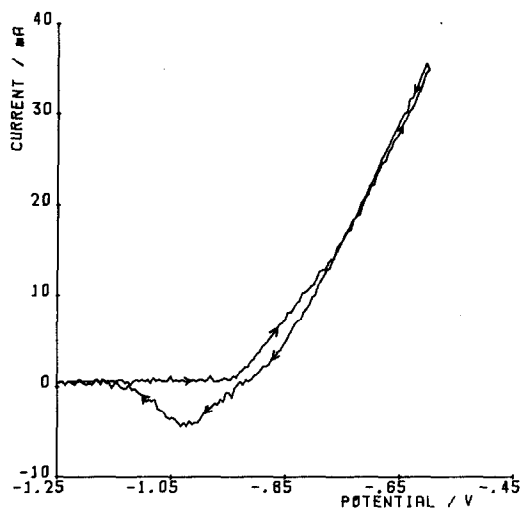


Fig. 2. System immediately after withdrawing from formation circuit (0.5M  $\text{H}_2\text{SO}_4$ ) and introducing into 5M  $\text{H}_2\text{SO}_4$  solution. Other details as Fig. 1.

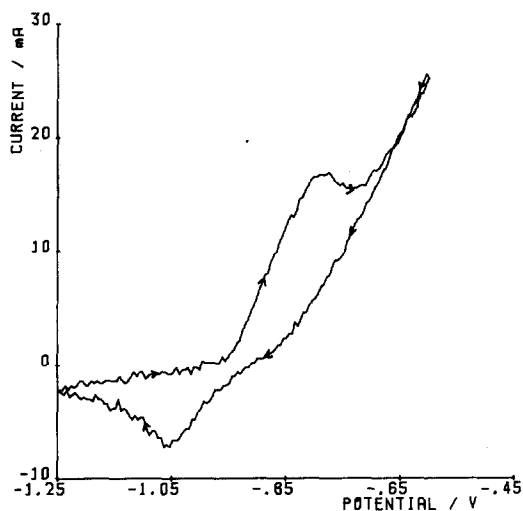


Fig. 3. As Fig. 2 but with 5 min o/c period in 5M  $\text{H}_2\text{SO}_4$  to partially replace 0.5M  $\text{H}_2\text{SO}_4$  with 5M  $\text{H}_2\text{SO}_4$ .

The effect of the porous structure in modifying the behaviour of electrodes is illustrated by Fig. 2. Here, the porous electrode was withdrawn from dilute ( $< 0.5\text{M}$ ) forming acid and immediately cycled to a constant response. The electrochemical process contains very much less charge than in the experiment with the 5M  $\text{H}_2\text{SO}_4$  initially disposed throughout the porous system, and shows quite clearly how restricted diffusion in the porous structure results in capacity loss, presumably the dilute electrolyte solution becomes entrapped in the porous structure at stages in the oxidation to lead

sulphate (discharging) when the front of the pores are blocked with electrode product. Confirmation of this explanation is obtained from Fig. 3 which represents an intermediate case (5 min allowed for partial electrolyte replacement) showing increased charge recovery by the effective provision of additional electrolyte. With reduced sweep speed the peak heights were reduced and Fig. 4 shows the rectilinear relationship between the peak current  $i_p$ , and the sweep speed  $\nu$ . The curve, within the limits of experiment, passes through the origin. This behaviour is typical for a solid electrode over which a uniform insoluble insulating film is being formed by the electro-oxidation of the lattice. We must conclude therefore that this electrode is behaving simply as one of planar characteristics and large surface area. This conclusion is neatly confirmed by the data of Table 1 which show charges calculated from the L.S.V. curves (integrated area/sweep speed) to be independent of sweep speed for a fixed temperature, that is, the passivating  $\text{PbSO}_4$  layer is the same for all the sweep speeds, which can only hold for a surface process.

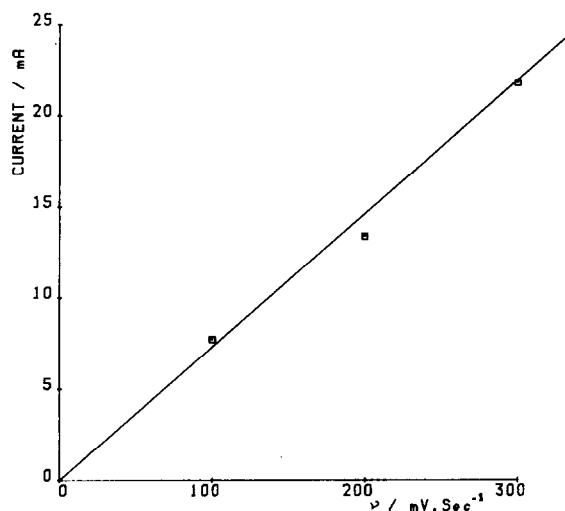


Fig. 4. The relationship between peak current and sweep speed. Other details as Fig. 1.

TABLE 1

Temperature (°C)	Sweep rate (mV s <sup>-1</sup> )	Charge (C)
17	300	$9.84 \times 10^{-3}$
	200	$10.27 \times 10^{-3}$
	100	$9.35 \times 10^{-3}$
-18	300	$1.363 \times 10^{-3}$
	200	$1.336 \times 10^{-3}$
	100	$1.477 \times 10^{-3}$
-31	300	$1.509 \times 10^{-4}$
	200	$1.585 \times 10^{-4}$
	100	$1.448 \times 10^{-4}$

Figure 5 shows a typical L.S.V. experiment at a temperature lower than ambient. The current in the L.S.V. curve is everywhere reduced in accordance with previous investigations using different techniques [12, 14]. The shapes of the L.S.V. curves remain the same, however, as do the direct relationships between current and sweep rate. The Arrhenius plot of slope  $di_{(\max)}/d\nu$  is

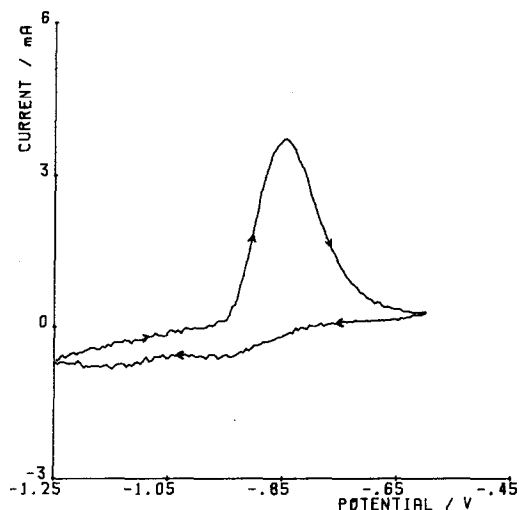


Fig. 5. As Fig. 1 but  $-10^{\circ}\text{C}$ .

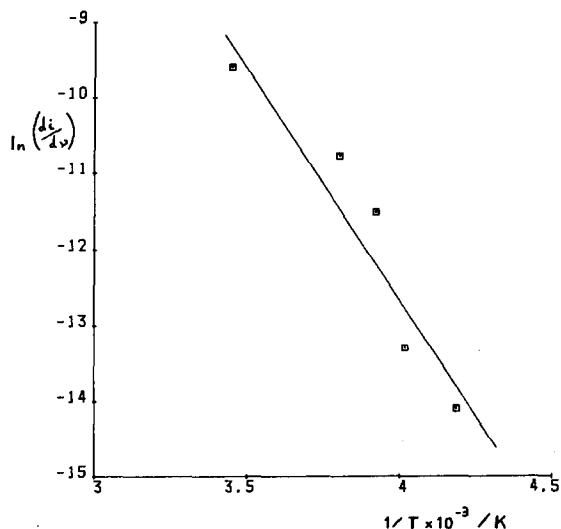


Fig. 6. Arrhenius plot ( $di_{\max}/d\nu$ ) vs.  $1/T$  for electrode systems corresponding to Fig. 1.

shown in Fig. 6. The slope of this line contains the enthalpy of activation\* for film formation in the form  $\Delta H_f/R$  and this was found to be  $52 \text{ kJ mol}^{-1}$ .

Figure 7 shows the Arrhenius plot of the charge in the anodic process (discharge); this too contains essentially the same information as the temperature dependence of the slope. The enthalpy for film formation from this plot was found to be  $47.5 \text{ kJ mol}^{-1}$ . In view of the uncertainties inherent in these experiments the agreement is quite reasonable. These values are very close to those observed for solid lead and strengthen our conclusion that the same passivating process is occurring; the effect of the porous structure is simply to provide an electrode of large area, in this case about a hundredfold.

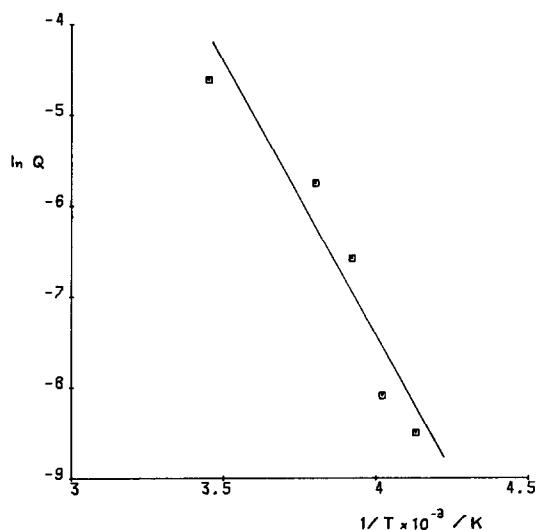


Fig. 7. Arrhenius plot (passivating charge) vs.  $1/T$  for electrode systems corresponding to Fig. 1.

### 3.2. Porous electrodes containing 0.01% organic expander (Indulin C)

Figure 8 shows an L.S.V. curve for a system containing organic expander. The effect of the expander is considerable. There is much more current in the voltammograms and the discharge (oxidation) peak is considerably broadened. The reduction peak which is quite well defined for the expander-free systems is very poorly defined here and convoluted with a continuously increasing hydrogen current. It was desirable to extend the negative limit in these sweeps beyond  $-1.25 \text{ V}$ , but this was not done in view of the possibility of saturating the porous mass with gaseous product. If the limit was extended, however, there was an increase in the quantity of hydrogen evolved, whilst the lead sulphate formation peak remained unaf-

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\*Strictly speaking these enthalpies are not true enthalpies of activation since the variation of equilibrium potential is not considered. This cannot be assessed since attempts at measurement fail because of the presence of an unknown thermo-liquid junction potential.

fect. The limit of  $-1.25$  V was chosen because the reduction peak had closed up completely by the time this limit was reached, in addition to there being no evolution of hydrogen gas. If the electrode was maintained at  $-1.25$  V, gas evolution was apparent even though it was not in the sweeping experiments. This evidence was considered to be sufficient to show that at the zero current potential on the anodic sweep the electrode was completely reduced to lead.

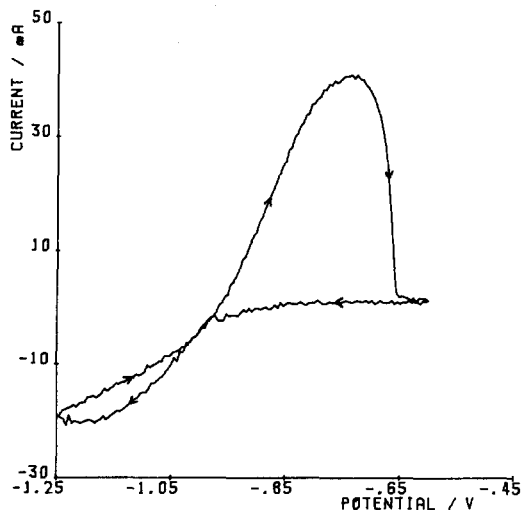


Fig. 8. As Fig. 1 but containing 0.01% Indulin C incorporated in the porous structure (paste).

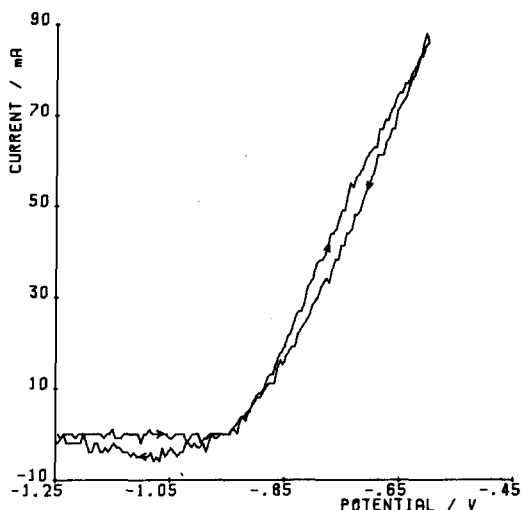


Fig. 9. As Fig. 2 but with electrode containing 0.01% Indulin. Sweep speed  $300 \text{ mV s}^{-1}$ .

The porous characteristics of the expander containing electrodes were demonstrated by sweeping electrodes which had been immediately withdrawn from the formation circuit (containing 0.5M  $\text{H}_2\text{SO}_4$ ) and sweeping in 5M  $\text{H}_2\text{SO}_4$ . The result shown by Fig. 9 confirms that similar porous characteristics in the sense of diffusion apply to both expander-containing and expander-free electrodes. The intermediate condition illustrated in Fig. 10 is markedly different from Fig. 3 and indicates that the expander characteristics of a broad oxidation peak and poorly defined reduction peak begin to develop as soon as the more concentrated sulphuric acid begins to diffuse into the porous mass. Thus we can confirm that expander action is not simply the provision of a more open porous structure.

The effect of temperature on the L.S.V. curve is shown in Fig. 11. The current (and charge) in the anodic peak decreased as the temperature was lowered and the shape of the L.S.V. curve changed somewhat to become more redolent of the expander-free electrode.

The typical relations between peak current and sweep speed are shown in Fig. 12. At each temperature the same behaviour was observed: a fairly horizontal line. This behaviour is mirrored in the data of Table 2 which show the charges obtained to be very dependent upon sweep speed. This behaviour is what we would expect from an ideal porous electrode [15]; as the sweep speed becomes slower the reaction is driven ever more deeply into the porous electrode. At very high sweep speed the front of the electrode accounts for the majority of the electrochemical reaction, penetration depth in the sense of Frumkin [16] increasing as the sweep speed is reduced (analogous to the greater penetration of a porous electrode by a low frequency a.c. signal). In spite of this pronounced dependence of passivating charge on sweep rate the expander-containing electrode provides, in all cases, more charge than the expander-free electrode.

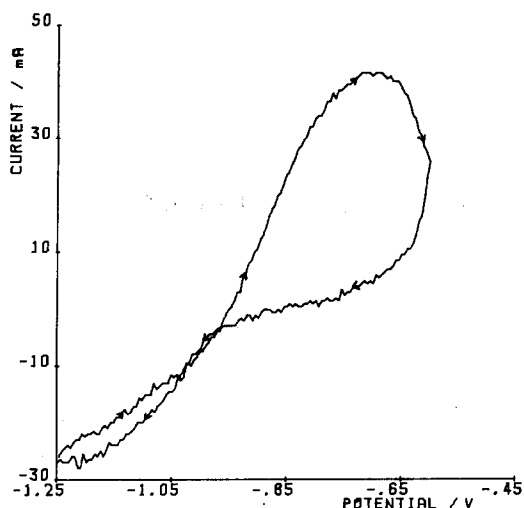


Fig. 10. As Fig. 3 but with electrode containing 0.01% Indulin. Sweep speed  $300 \text{ mV s}^{-1}$ .

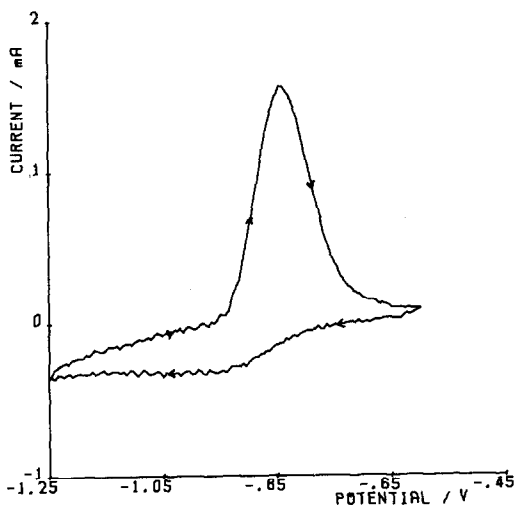


Fig. 11. As Fig. 8 but  $-30^{\circ}\text{C}$ .

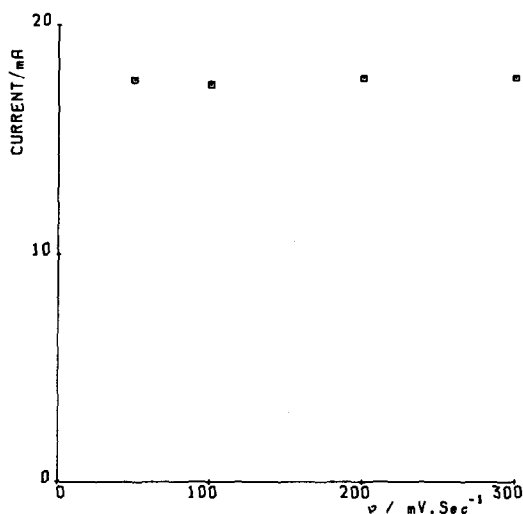


Fig. 12. The relationships between peak current and sweep speed at  $\sim 0^{\circ}\text{C}$  for electrodes as Fig. 8.

The enthalpy of activation for the passivation processes can be measured only at constant sweep speed as a consequence of the above observations. These data are obtained from the passivating charges at each sweep speed. The results of the inverse temperature plots are shown in Fig. 13. The enthalpies of activation for the passivation process are 48.6, 50.5 and 50.2 kJ mol<sup>-1</sup>, respectively, for the sweep speeds 100, 200 and 300 mV s<sup>-1</sup>. The magnitudes of the enthalpies are similar to the values for the expander-free systems. When we investigated the effect of dissolved expander in the electrolyte on the passivation process on solid lead in dilute sulphuric acid it was

TABLE 2

Temperature (°C)	Sweep rate (mV s <sup>-1</sup> )	Charge (C)
17	300	$29.6 \times 10^{-3}$
	200	$43.5 \times 10^{-3}$
	100	$81.4 \times 10^{-3}$
0	300	$8.97 \times 10^{-3}$
	200	$12.2 \times 10^{-3}$
	100	$23.7 \times 10^{-3}$
-10	300	$4.135 \times 10^{-3}$
	200	$6.1696 \times 10^{-3}$
	100	$12.1 \times 10^{-3}$
-20	300	$1.522 \times 10^{-3}$
	200	$1.726 \times 10^{-3}$
	100	$2.871 \times 10^{-3}$
-30	300	$7.298 \times 10^{-4}$
	200	$9.901 \times 10^{-4}$

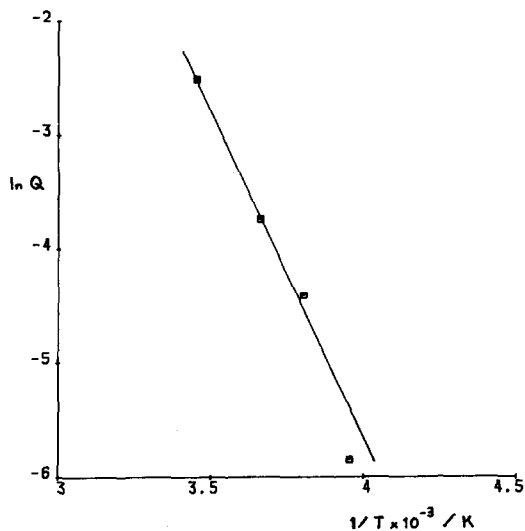
found that the presence of dissolved expander effectively changed the rate control from a simple cover passivity to diffusion through a thickening layer of PbSO<sub>4</sub>. In the cases of the porous electrodes a difference in mechanism is quite clear from the electrochemical behaviours (from a large planar electrode-unexpanded, to a 'truly porous' electrode-expanded). From the energetics the passivation process is apparently the same in both the expander-free and expander-containing matrices and this reaction-limiting process is apparently (from the magnitude of the enthalpy) a cover passivity within the porous matrix.

### 3.3. Expander additions to the electrolyte

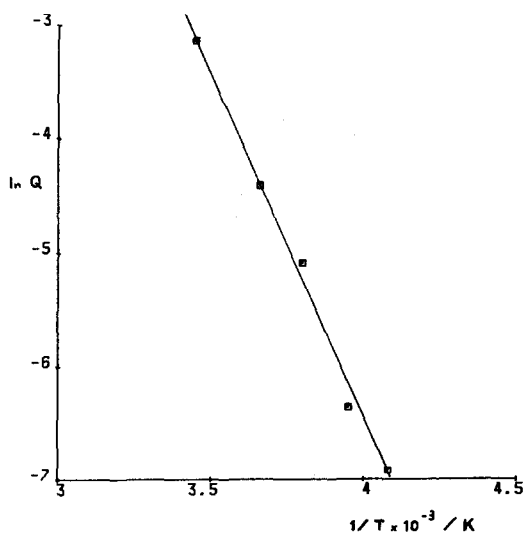
For the case of expander-free electrodes the 5M sulphuric acid solution was saturated with Indulin C. This did not produce the characteristic pale straw coloured solution observed with the dilute electrolyte solution [8]; rather a crude suspension was produced. The electrolyte solution therefore contained a negligible amount of dissolved organic. Consequently the solution was agitated for 24 h before experiments and then continuously stirred whilst L.S.V. experiments were carried out. Figure 14 shows the results of a typical experiment; there is no effect due to the dissolved expander. This is likely to be a result of the fact that in 5M H<sub>2</sub>SO<sub>4</sub> Indulin C is insoluble.

The reasons for the behaviour are not clear. In the absence of expander the penetration into the porous electrode is limited, possibly due to a reduced porosity *vis-à-vis* expander-containing electrodes. Certainly the results shown in Figs. 2, 3 and 9, 10 leave no room for doubt that there is restricted solution movement in the porous matrices. What we cannot be so certain of is the shape of the pores. A possible explanation of the observed behaviour would be if the pores in the expander-free electrodes were mainly of the

“ink-bottle” form with restricted openings near the front of the pore, whereas in the presence of expander a more uniform pore structure is engendered. Work is presently in progress on this aspect.



(a)



(b)

Fig. 13. (For legend please see facing page.)

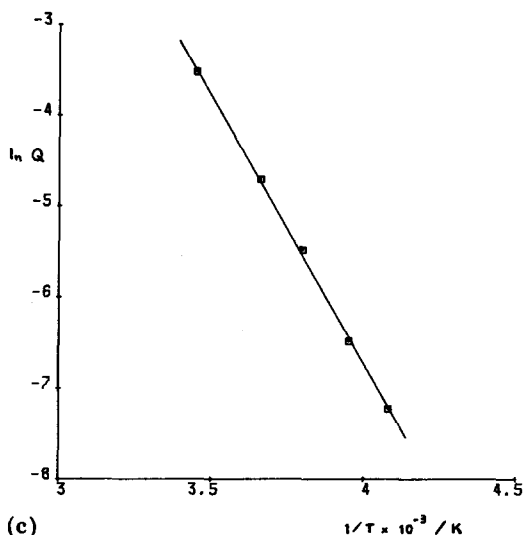


Fig. 13. Arrhenius plots (passivating charge,  $Q$ ) vs.  $1/T$  for electrode systems corresponding to Fig. 8. a,  $100 \text{ mV s}^{-1}$ ; b,  $200 \text{ mV s}^{-1}$ ; c,  $300 \text{ mV s}^{-1}$ .

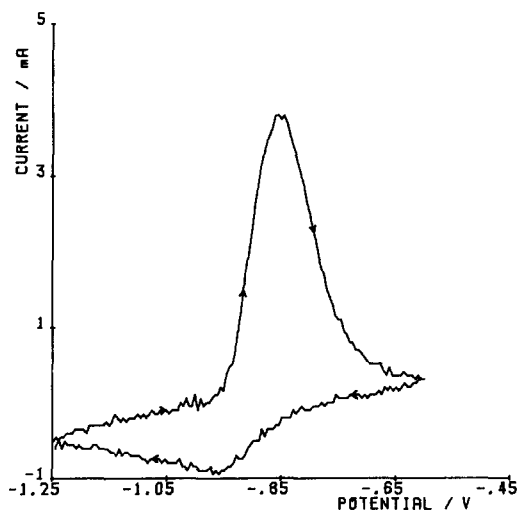


Fig. 14. As Fig. 1. Indulin-C saturated solution.  $300 \text{ mV s}^{-1}$ .

#### 4. Conclusion

The incorporation of Indulin C into a porous electrode fundamentally changes its electrochemical behaviour. The anodic reaction is able to penetrate more deeply the expander-containing porous electrode (as would be expected of an ideal porous electrode) as the sweep speed (reaction rate) is decreased. The expander-free electrode behaves as a simple electrode of large area.

It should be noted that these conclusions apply to very high rates of reaction and low temperatures. It is to improve performance under these conditions that organic expanders are added to negative electrodes. The conclusions may be different under different conditions.

### Acknowledgments

We thank the Directors of Joseph Lucas for financial support (to P.J.M.). Dr Monty Barak is thanked for his interest in the work at Loughborough extending over many years.

### Dedication

This paper is dedicated to our friend of many years standing, Mr Derek Collins, as a contribution to his Festschrift.

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