

THE EFFECT OF A LIGNOSULPHATE TYPE ADDITIVE ON THE LEAD-ACID BATTERY POSITIVE PLATE REACTIONS

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(Received July 30, 1988; in revised form May 10, 1989)

Summary

The electrochemical formation of lead dioxide has been investigated at a lead electrode in a 5 M sulphuric acid solution, and in the presence of phosphoric acid and lignosulphate-type additive. The formation of lead dioxide from lead sulphate, and the reverse reaction, have been investigated by the linear potential sweep method, by an impedance method in which the impedance was measured at the end of each pulse during a potential pulse train, and by a charging curve method in which the current and charge was measured during a similar potential pulse train. The charge measurements prove that the main effect of the additive is to decrease the accompanying oxygen evolution reaction. The impedance measurements, however, show that the additive has a small but significant effect on the structure of the solid lead sulphate and lead dioxide layers.

Introduction

The overall electrochemical reaction between lead sulphate and lead dioxide is a solid state electron exchange reaction:



To study the electrode kinetics of this reaction it would be necessary to vary the amount of each of the components and study the rate of conversion of lead sulphate and lead dioxide. Although the hydrogen, water, and sulphate ion concentration can be fixed in the solution, the lead sulphate and lead dioxide concentrations are not easy to control. Many of the features of this reaction which relate to lead-acid battery performance, however,

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have been investigated. If the lead sulphate and lead dioxide amounts are large, then experiments could be carried out, in principle, at constant composition of reaction and product. A particular problem is passivation of the lead sulphate. This has been investigated by the deep discharge cycling of lead-acid battery positive electrodes and seems to be due to three causes [1 - 7]: a formation, within the lead dioxide structure, of non-conducting lead sulphate; a passivation of the lead to lead dioxide interface; and the formation of other lead oxides (such as lead monoxide) in the lead dioxide layer.

The use of additives has been investigated as a means of controlling these effects.

Bullock *et al.* [7 - 9] have investigated the effects of phosphoric acid as an addition to sulphuric acid. Small additions of phosphoric acid, up to 0.2% in 5 M sulphuric acid, have an observable effect and modify the crystal growth of lead dioxide. The lead dioxide is less easily reduced to lead sulphate than is the case in the absence of the phosphoric acid.

Surface active substances have been extensively investigated as a means of controlling the structure of the lead dioxide layer. Dietz *et al.* [10], Dasoyan *et al.* [11], and Mahato [12, 13] have mentioned hundreds of possible additives, some of which have been patented. Carboxymethyl cellulose [10] seems to increase the surface area of the lead dioxide and prevent passivation at the lead dioxide interface but leads to reduced capacity of the lead dioxide layer. The addition of silica gel [10, 14] has the effect of increasing the battery capacity. A mixture of the two compounds has desirable characteristics.

These observations seem to indicate the need for more sophisticated additives to improve the structure of the lead dioxide layer, to allow access to the various components in reaction (1), and to maintain the efficient utilisation of the lead dioxide layer.

The present paper reports an investigation of the formation and reduction of a lead dioxide layer on lead using a single electrode. Similar experiments have been carried out on portions of an actual battery, but these will be reported later. The aim was to investigate reaction (1) in a controlled manner, using electrochemical methods, and to observe the effect of phosphoric acid and a lignosulphate-type molecule when these are added to the basic 5 M sulphuric acid electrolyte.

Experimental

The electrochemical experiments were carried out using computer controlled instrumentation. The current was always measured at the same time as the impedance. The latest version of this equipment will be described in the literature [15]. The impedance data were treated by curve fitting to an equivalent circuit to give the double layer capacitance, ohmic resistance, and charge transfer resistance, in the usual way. The electrode material, a

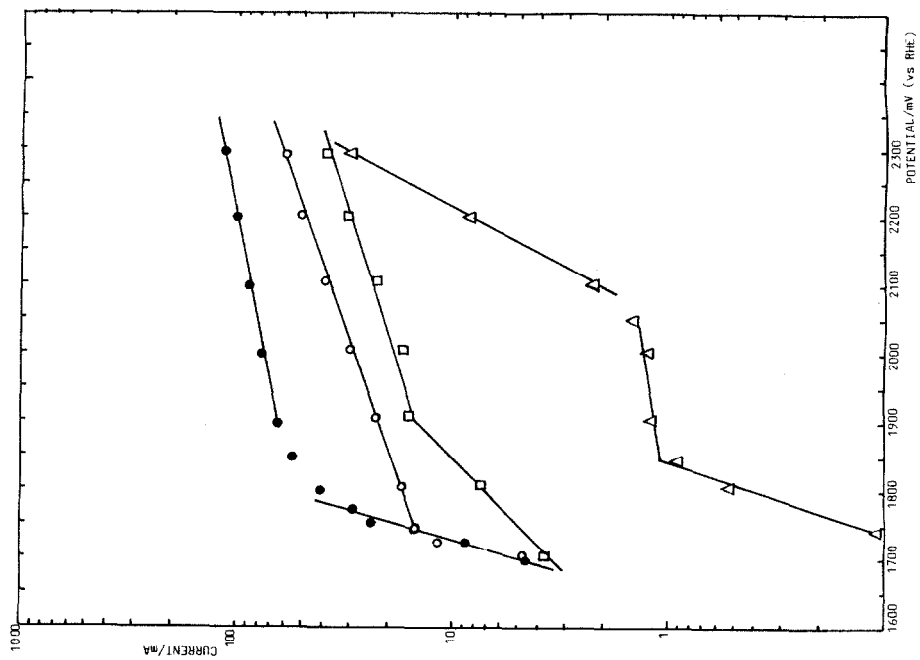
disc of pure lead, was retained in a PTFE holder by means of a neoprene O-ring. The holder was in the form of a standard ground glass joint and entered the cell from below. 0.64 cm^2 of electrode was exposed to the solution. Contact with the electrode was made by a soldered connection. The reference electrode was a hydrogen electrode in 5 M sulphuric acid to which all potentials are referred; it was in contact with the solution via a Luggin capillary. The solutions were prepared using AnalaR reagents and triply-distilled water.

Linear potential sweep curves

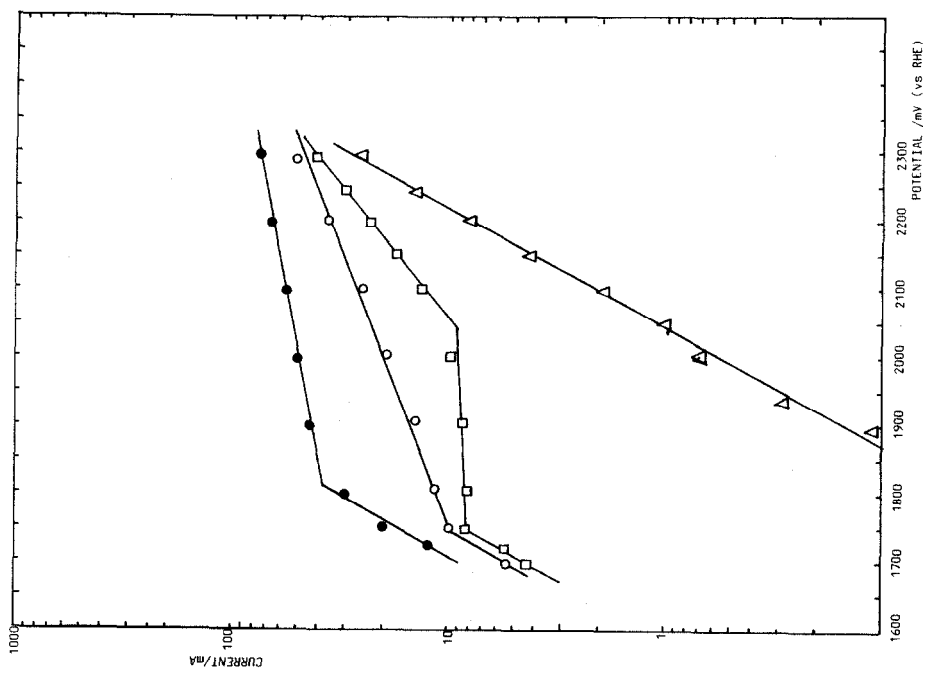
These experiments were undertaken to define the potential conditions for the subsequent pulsing experiments for the lead sulphate to lead dioxide transition. On smooth lead, the initially formed lead sulphate layer is very thin and its electrical resistance is large. For this reason the currents involved in the formation and reduction of lead dioxide are very small. If the surface area of the electrode is increased by repeatedly cycling an electrode to form, alternately, lead dioxide and then lead sulphate, however, the ohmic resistance decreases, presumably as the lead sulphate layer becomes disrupted and, hence, more conducting, and the current becomes appreciable. In this work the initially smooth electrode was cycled 50 times between a potential of 1700 mV (for 100 s) and 2100 mV (25 s) before the experiment started. As shown below, when charge as a function of the number of cycles was studied, the amount of lead sulphate after 50 cycles was about 170 mC cm^{-2} and was slightly less with the additive present. Single potential sweeps were carried out over this potential range, in the negative and positive potential directions, at various sweep rates. The potential sweep had a potentiostatic staircase waveform with the current measured at the end of each step, so high potential sweep rates can be recorded without the danger of a large capacitive component. This has an advantage over some previous work [9, 16] which was limited to low sweep rates. Figure 1(a) and (b) shows the result of potential sweep experiments in the positive direction, plotted as the $\log i-E$ curve, after standing at 1700 mV until no further current flowed and the reducible lead dioxide was fully converted to lead sulphate. Figure 1(a) is for 5 M sulphuric acid as the electrolyte, and in Fig. 1(b) 2 g l^{-1} of the lignosulphate compound has been added.

Depending on the sweep rate, the curves seem to have three features: up to about 1750 mV the current-potential curve is steep with a 40 mV Tafel slope, it then follows a limiting current which depends on sweep rate and additive, then, at low sweep rates, a new oxidation reaction occurs.

An explanation of this behaviour is that the current-potential curve at potentials below 1750 mV represents the electron exchange rate of reaction (1) at constant lead sulphate levels, the limiting current represents the oxidation of a decreasing amount of a lead sulphate layer, and the further current rise at high potential or low sweep rate represents the direct conversion of lead to lead dioxide. In addition, oxygen evolution is possible in this potential region. It will be shown below, however, that, on the basis

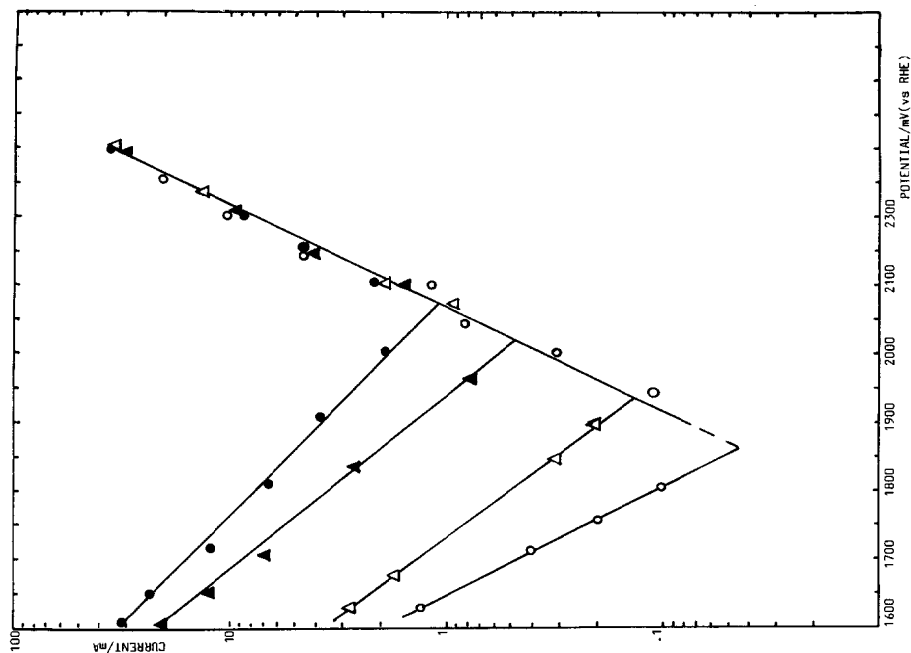


(b)



(a)

Fig. 1. Single linear potential sweep curves taken under various starting potentials and sweep rates after cycling an initially smooth lead electrode for 50 cycles between 1700 mV (100 s) and 2100 mV (25 s). The lead electrode was in a solution of 5 M sulphuric acid. Electrode area 0.64 cm^2 . (a) After standing at 1700 mV for 10 min and then sweeping in a positive direction in the absence of the additive. Δ , 2 mV s^{-1} ; \square , 100 mV s^{-1} ; \circ , 1000 mV s^{-1} ; \bullet , 10000 mV s^{-1} . (b) After standing at 1700 mV for 10 min and then sweeping in a positive direction in the presence of the additive. Δ , 2 mV s^{-1} ; \square , 100 mV s^{-1} ; \circ , 1000 mV s^{-1} ; \bullet , 10000 mV s^{-1} . (c) After standing at 2100 mV for 10 min and then sweeping in a negative direction with additive. Δ , 2 mV s^{-1} ; \bullet , 1000 mV s^{-1} . Without additive: \circ , 2 mV s^{-1} ; \blacktriangle , 1000 mV s^{-1} .



(c)

of the comparison of oxidation and reduction charge, oxygen evolution only becomes apparent at about $E = 2200$ mV. This interpretation of sweep curves conflicts with that given in the literature [9, 16].

Based upon this interpretation, it can be seen in the 2 mV s^{-1} curve that the third potential region where lead is directly oxidised is not well separated from the region where only preformed lead sulphate is oxidised. This suggests that when the lead sulphate layer is fairly thin, after the 50 cycles used here, the two mechanisms of formation of lead dioxide will operate. This is confirmed by the form of the charge-cycle number curves, shown below.

In general, at potentials more positive than 1750 mV, with the additive present, the currents at a fixed potential are higher. There is either slightly more lead sulphate present or the lead sulphate is more rapidly oxidised to lead dioxide. As the charge-cycle number curves indicate only small differences in the charge amount, these experiments indicate that the lead sulphate can be more rapidly oxidised, possibly as a result of structural changes.

On the other hand, when the electrode is held at 2300 mV until a steady state current is reached, the results shown in Fig. 1(c) are obtained for the negative-going potential sweep. This experiment cannot be controlled as precisely as the preceding experiment as the lead dioxide layer grows continuously.

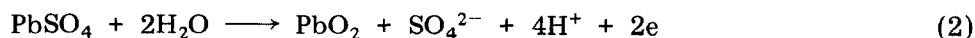
Similar measurements were made in a sulphuric acid solution containing an additive. The electrode was first cycled 50 times, as above, in the presence of the additive, and then the potential sweep experiment was carried out. The part of the curve from 2300 mV is due to the formation of lead dioxide from lead until, at some potential, the reduction of the lead dioxide to lead sulphate starts. The reduction of the lead dioxide is characterised by an approximately 120 mV slope and curves which depend on sweep rate and whether the additive is present. In the presence of the additive the reduction currents appear to be higher.

The 40 mV Tafel slope for the oxidation of lead sulphate, and the 120 mV for the lead dioxide reduction, are consistent with an overall two-electron exchange reaction.

Charge-discharge curves

These experiments were carried out by pulsing the potential alternately to form lead sulphate and then lead dioxide. The potential sweep curves indicate that under these conditions the following reactions will occur during the oxidation pulse:

- (i) at low positive potentials, lead sulphate to lead dioxide



- (ii) at high potentials, lead to lead dioxide



(iii) ultimately, water to oxygen



The pulse experiments were designed to investigate the way in which the anodic and cathodic charges and currents changed with time and to investigate whether a steady state was reached at long times.

The initial charging pulses should reflect reaction (3) and, in the later stages, when the lead sulphate layer has become thicker, should, more strongly, reflect the rate of reaction (2). The inequality of the anodic and cathodic charges should give a quantitative measure of the extent of reaction (4). The time (100 s) of the reduction pulse was chosen, in all cases, so that the lead dioxide formed in the oxidation pulse (25 s) was completely reduced to lead sulphate by the reverse reaction (2). This was checked by observing that at the end of the cathodic pulse the current was zero.

The potentials for oxidation (2100 mV) and reduction (1700 mV) were chosen from the linear potential sweep curves, so that a reasonable amount of oxidation occurred in a reasonable time. The results also show that 2100 mV is the potential at which the oxygen evolution reaction is just absent.

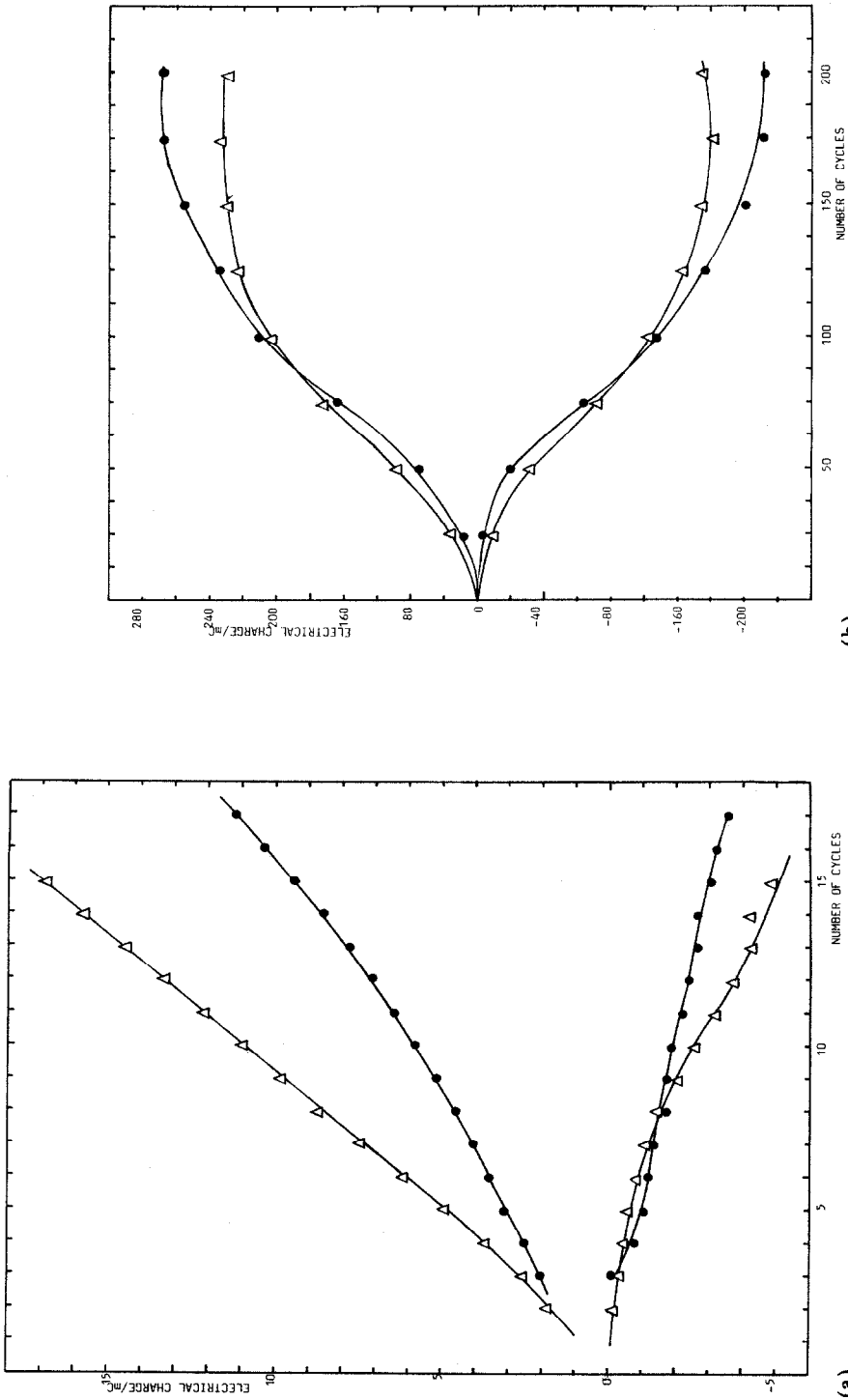
The results of the charging experiments are shown in Figs. 2 and 3. In Fig. 2 the results for lead in 5 M sulphuric acid with, and without, additive are shown. The results are divided into the early part of the curves (Fig. 2(a)) and the later portion (Fig. 2(b)). Figure 3 shows a more extensive set of results in which, during the run, the potential was changed, at 50 cycles, to 2200 mV and back to 2100 mV. These experiments were to investigate the contribution to the charging curves of the oxygen evolution reaction at various stages during the formation of lead dioxide. Only lead dioxide is reduced at 1700 mV and not the oxygen. The salient features of the curves are (i) in the early stages of cycling the charge to form lead dioxide increases progressively with time. Under these conditions, the additive decreases the charge to form lead dioxide, although the reduction charge is less affected; (ii) at later stages of cycling the charge to form lead dioxide reaches a limit and then decreases.

In Fig. 3 the effects of the additive and the phosphoric acid can be seen. The additive has an effect on the oxygen evolution reaction and depresses it by a small amount. It also seems to increase the charge slightly due to lead dioxide and lead sulphate formation. On the other hand, in contrast to some reports in the literature [9, 16], the phosphoric acid has little effect on the oxygen evolution reaction. It does, however, significantly increase the lead dioxide and lead sulphate charge.

Figure 4 shows a plot of the current at the end of each oxidation pulse (the current at the end of the reduction pulse is zero).

Impedance measurements of the charge-discharge reactions

Impedance measurements were made under similar conditions to the charge-discharge experiments. At the end of a given charging time the



(a) Fig. 2. Charge vs. cycle number for an experiment in which the potential was 1700 mV for 100 s (negative charge) and 2100 mV for 25 s (positive charge). The lead electrode (electrode area 0.64 cm^2) was in a solution of 5 M sulphuric acid. (a) For up to 18 cycles: ●, with additive; △, without additive. (b) For up to 200 cycles: ●, with additive; △, without additive.

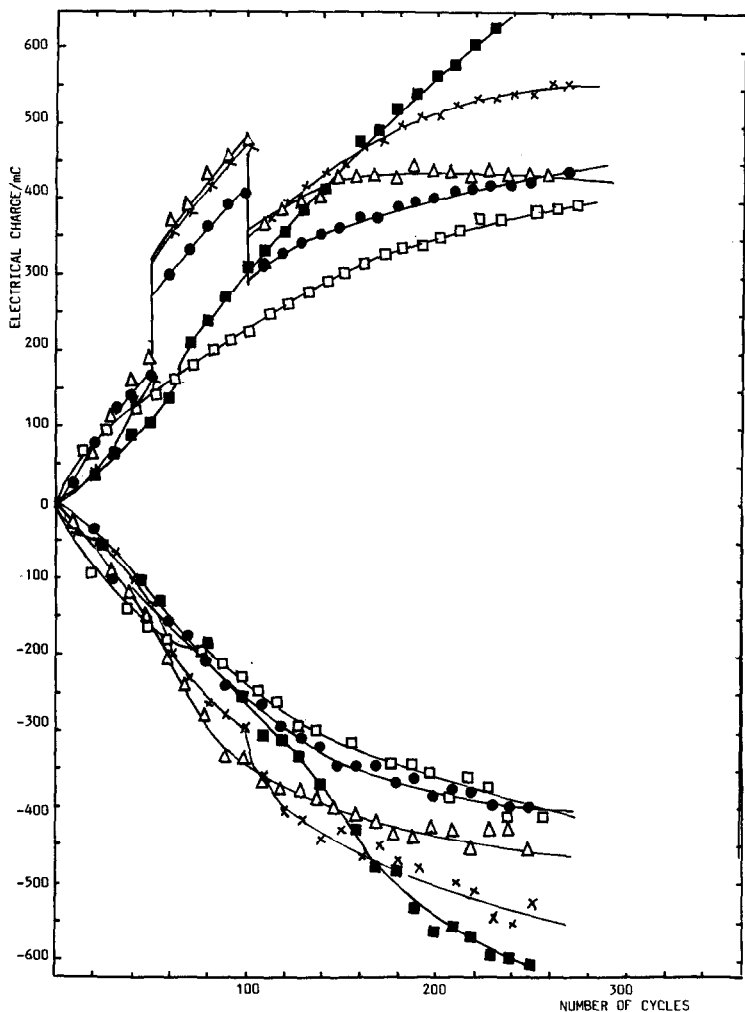


Fig. 3. Charge vs. cycle number for a lead electrode (area 0.64 cm^2) in 5 M sulphuric acid in which the potential was 1600 mV for 100 s (negative charge) and then either 2100 mV for 25 s (positive charge) or 2200 mV for 25 s. In the particular experiment shown here, the first 50 cycles of the formation of lead dioxide proceeded at 2100 mV, the next 50 cycles at 2200 mV, and then at 2100 mV for the rest of the run. The electrolyte was 5 M sulphuric acid: \triangle , without additive; \times , with 0.01 M phosphoric acid; \bullet , with additive; \square , without additive and a potential of formation of lead dioxide of 2100 mV; \blacksquare , with 0.01 M phosphoric acid and a potential of formation of lead dioxide of 2100 mV.

impedance for a small amplitude a.c. potential was measured as a function of frequency in the usual way. Immediately after measuring the impedance the potential was switched to the discharge potential.

These experiments are to be considered in conjunction with the charge experiments, and were undertaken to give further information about the surface of the lead dioxide and lead sulphate layers, as measured by the

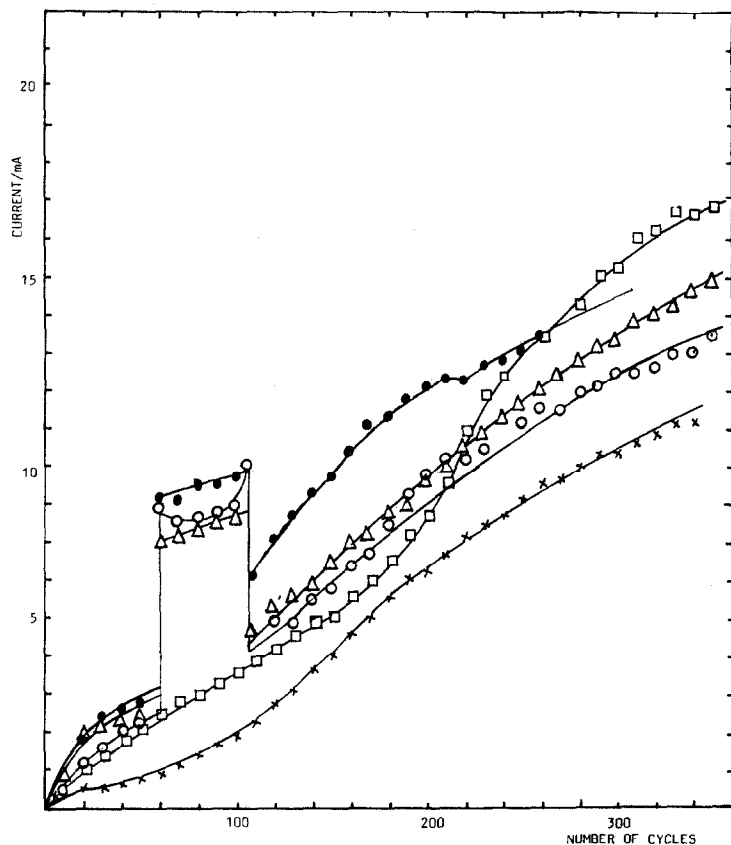


Fig. 4. Current at the end of each potential pulse *vs.* cycle number for a lead electrode (0.64 cm^2) in 5 M sulphuric acid in which the potential was 1600 mV for 100 s (zero current) and then either 2100 mV for 25 s (positive current) or 2200 mV for 25 s. In the particular experiment shown here, the first 50 cycles of the formation of lead dioxide proceeded at 2100 mV, the next 50 cycles at 2200 mV, and then at 2100 mV for the rest of the run. The electrolyte was 5 M sulphuric acid: ○, without additive; ●, with 0.01 M phosphoric acid; △, with additive; ×, without additive and a potential of formation of lead dioxide of 2100 mV; □, with 0.01 M phosphoric acid and a potential of formation of lead dioxide of 2100 mV.

double layer component of the impedance. The data were analysed using an equivalent circuit in which a charge transfer resistance is in parallel with a double layer capacitance, and both are in series with an ohmic resistance. The only technical problem in this case was the very high value of the double layer component, reflecting the roughness of the lead dioxide and lead sulphate layers. This means that a large a.c. current flows. Because the measurement of the impedance takes a long time (determined by the integration time at each frequency), it was necessary to make the charge and impedance measurements together with current, under somewhat different time conditions. A complete set of the parameters: charge transfer resistance, double layer capacitance, and ohmic resistance, were obtained as a

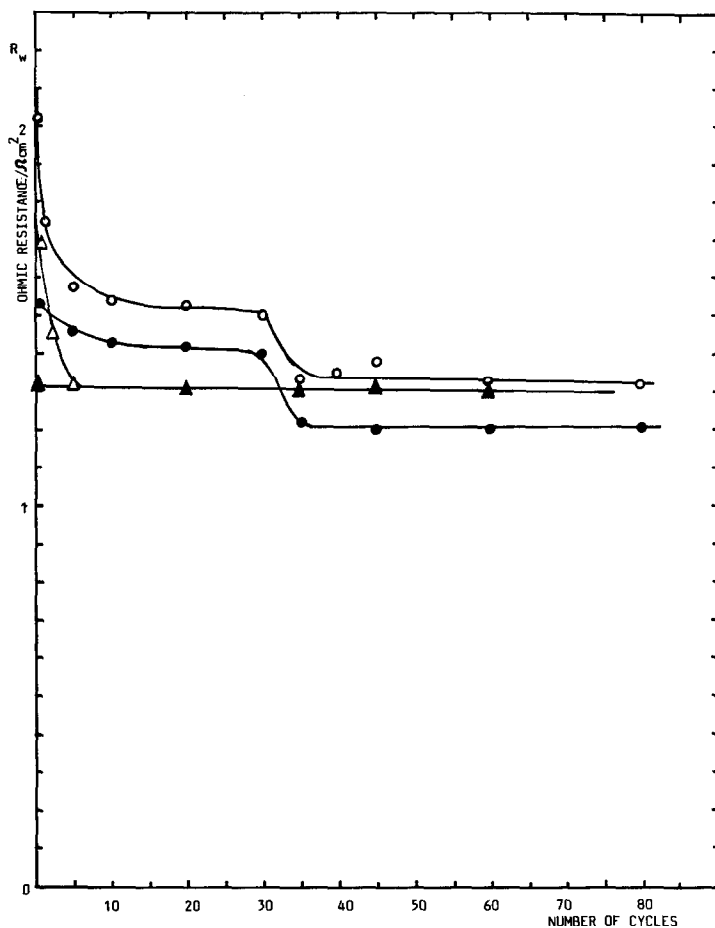
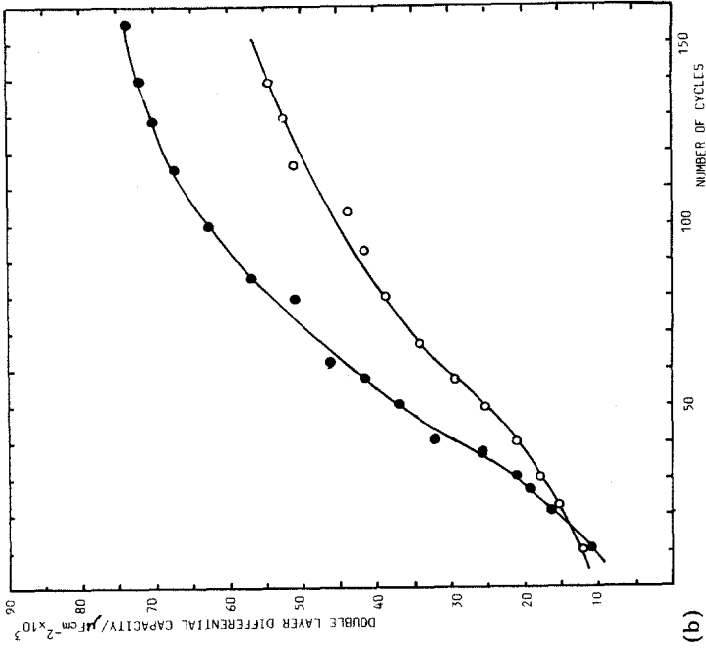
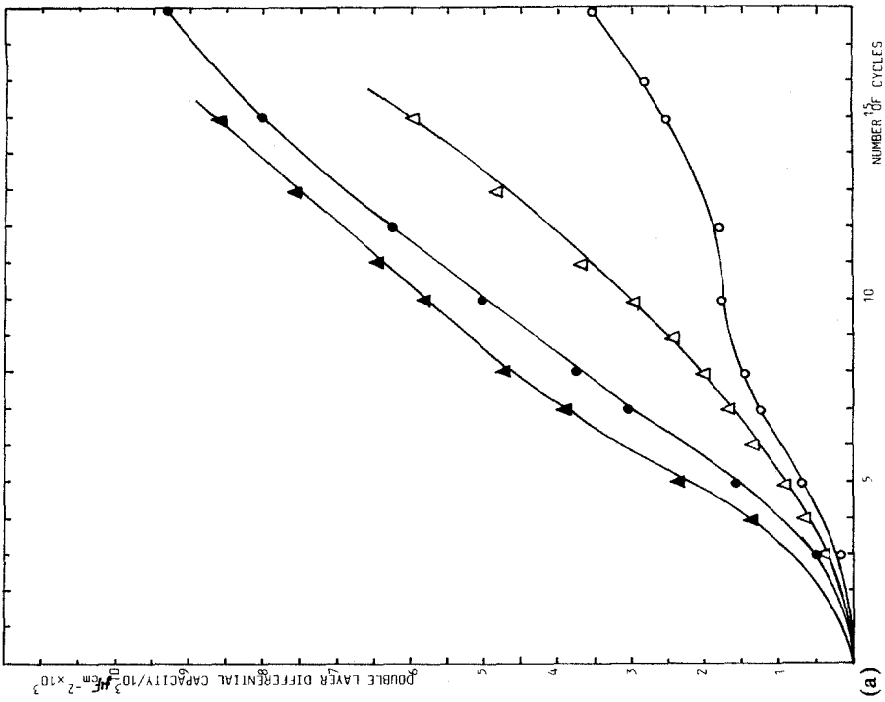


Fig. 5. The measured ohmic resistance as a function of cycle number. The potential was 1700 mV for 135 s (Δ), and 2100 mV for 153 s (\blacktriangle) without the additive, and the potential was 1700 mV for 135 s (\circ), and 2100 mV for 153 s (\bullet) with the additive. The lead electrode was in a solution of 5 M sulphuric acid.

function of cycle number, for comparison with the charge-discharge curves. Examples of some of these measurements are shown in Figs. 5 and 6. The simultaneously measured current is shown in Fig. 7, in a longer run. These Figures have the following characteristics:

(i) the differential capacitance against cycle number shows a progressive increase at small cycle numbers. The values are of the order of $1000 \mu\text{F cm}^{-2}$. The surface formed, therefore, is rough (assuming that a smooth lead surface has a differential capacitance of $100 \mu\text{F cm}^{-2}$). The additive has an interesting effect. It depresses the capacitance strongly in the early stages, but the effect becomes smaller as the lead dioxide layer grows;

(ii) the differential capacitance, at later stages of growth, reaches a limit. The limiting value is higher when the additive is present.



(a) For up to 18 cycles, 2100 mV (●) and 1700 mV (▲) without additive. (b) For up to 200 cycles, 2100 mV (●) with additive, 2100 mV (○) without additive. (a) For up to 18 cycles, 2100 mV (●) and 1700 mV (▲) without additive. (b) For up to 200 cycles, 2100 mV (●) with additive, 2100 mV (○) without additive.

Fig. 6. The differential capacitance, measured by impedance-frequency measurements at the end of the formation of lead sulphate (135 s) and the end of the formation of lead dioxide (153 s), as a function of cycle number. The lead electrode was in a solution of 5 M sulphuric acid.

Discussion

In general, the charge curves rise continuously up to about 200 cycles. The corresponding reduction reaction at 1600 or 1700 mV also reflects this rise. After 200 cycles, the anodic and cathodic charges remain in a steady state or decay slightly to a new steady state. This means that the results can be considered in two sections. In the early stages the main reaction must be lead going to lead dioxide, which is reduced to lead sulphate on the cathodic pulse. This reaction is similar to the grid corrosion reaction in a lead-acid battery. When the charges approach the steady state, the layer of lead dioxide is now so thick that the supply of lead from the electrode is unimportant and the main reaction is the formation of lead dioxide from lead sulphate.

The early stages

The first experiments were carried out at 2000 mV for the applied formation potential and 1700 mV for the reduction potential.

At, say, 10 cycles, on increasing the potential for the formation of lead dioxide by 100 mV, there is a twofold increase of the oxidation charge without the lignosulphate additive. The disappearance of the ohmic effects by cycle 10 (see above) suggests that diffusion or transport effects are operating in the formation kinetics. It is impossible to say which of the following species: sulphate ions, hydrogen ions, lead ions, and water, control the transport. The analysis of the impedance results in Figs. 5 and 6 gives a clue to this behaviour. Figure 5 shows that, in the early stages, the ohmic resistance of the lead dioxide and lead sulphate layers depends on whether the lignosulphate additive is present. This suggests that the lignosulphate additive is incorporated in the layer in such a way that it retains the structure of the lead sulphate layer. Lead sulphate in pure form is known to be an insulator. It seems, therefore, that the charge curves can be understood in terms of the ohmic resistance behaviour, and the fact that the applied potential is decreased. The double layer capacitance results in Fig. 6, however, show a further effect. The lignosulphate additive only affects the double layer capacity of the lead sulphate layer. This must be attributed to a surface effect; that is, the lignosulphate is absorbed on the lead sulphate layer and not on the lead dioxide. This effect, however, only operates in the early stages and, as seen below in connection with the oxygen evolution reaction and the results at higher cycle numbers, the lignosulphate additive eventually appears on the lead dioxide surface.

The later stages

Figure 3 shows the charge variation with cycle number up to about 280 cycles. In a typical experiment the potential was advanced from 2100 mV to 2200 mV to test the charge balance. As can be clearly seen, at 2100 mV the changes in the positive and negative directions are approximately equal and opposite when the charging voltage is 2100 mV, but not at 2200 mV. This implies that at 2100 mV there is virtually no oxygen evolution effect.

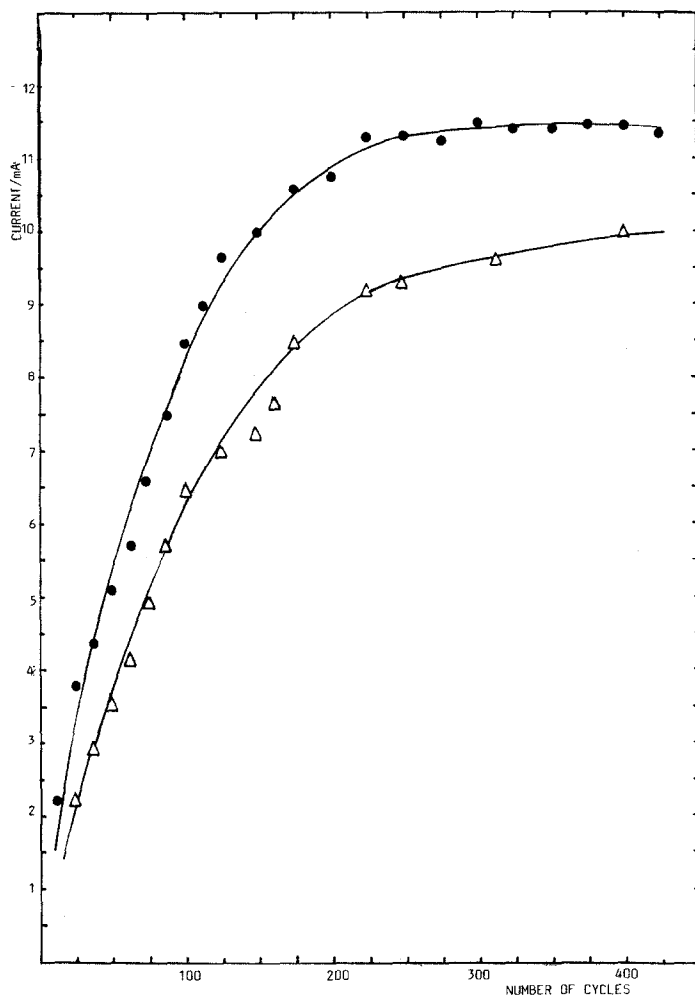


Fig. 7. Current measured at the end of the formation of lead sulphate (135 s) and at the end of the formation of lead dioxide (153 s), as a function of cycle number. The current at the end of lead sulphate formation is close to zero and is not shown here. The lead electrode was in a solution of 5 M sulphuric acid. For up to 380 cycles, (●) with additive, (△) without additive.

It is seen, however, that at 2200 mV oxygen evolution becomes significant. These results allow an investigation of the effect of phosphoric acid and the liginosulphate additive on the oxygen evolution reaction. The liginosulphate additive inhibits the oxygen evolution reaction. Addition of phosphoric acid has no effect. Other effects can be seen: for example, the charge curves tend to be higher in the phosphoric acid solution. This confirms the observation in the literature [9] that the lead dioxide layer has a rougher structure in the presence of phosphoric acid.

Conclusions

The charge curves given in this paper relate to the charging behaviour and utilisation expected in a lead-acid battery. Because only small amounts of lead dioxide have been formed, the method is a rapid means of testing the effect of different conditions. In the present investigation the main effect of adding a lignosulphate additive to the battery electrolyte is to reduce the oxygen evolution reaction. There are, however, more subtle effects on the lead dioxide and lead sulphate structures which can be seen in the studies of the double layer capacitance and charge and current as a function of the cycle number. This paper is exploratory in nature, but it is clear that measurements of the current, impedance, and charge during prolonged cycling could be carried out that would bring further information about the long term changes which take place in the lead dioxide and lead sulphate layers.

Acknowledgements

S.E.O. is indebted to the Association of Commonwealth Universities and the British Council for supporting this work. Prof. F. Goodridge and the Department of Chemical and Process Engineering are also thanked for the provision of facilities that made this project possible.

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