STUDY OF ELECTRODE PROCESSES IN Pb/H$_2$SO$_4$ + ADDITIVE SYSTEMS

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Introduction

The polarization behaviour of lead has been studied in sulphuric acid solutions with various additions of sodium sulphate, cobalt sulphate, ammonium dichromate and phosphoric acid. The potential sweep of the working electrode, within given potential ranges, was intended to simulate the processes taking place at the positive and negative plates of the lead/acid battery during charge/discharge cycling. The characteristics of the polarization curves (*i.e.*, shape and height and potential range in which peaks appear), as well as the values of the kinetic parameters determined from such curves, enable conclusions to be drawn concerning the electrochemical characteristics of the Pb/PbSO$_4$ + additive system. The results also provide valuable information in attempts to elucidate the processes taking place at the Pb/H$_2$SO$_4$ interface.

Experimental

Experiments were carried out using the linear sweep voltammetric method with a low potential scan rate (5 mV s^{-1}). The scans were applied by means of a Model 173 Potentiostat–Galvanostat (Princeton Applied Research) provided with a Model 179 Digital Coulometer.

The working electrode was made from a pure lead cylinder with a surface area of 50 mm^2 exposed to the electrolyte solution. The counter electrode was a platinum net, and an Hg/Hg$_2$SO$_4$/SO$_4^{2-}$ electrode was used as reference. All potentials are reported with regard to this reference electrode. The working electrode potential was scanned within set potential ranges, namely, -1170 to -860 mV and $+700$ to $+1650$ mV. The working cell and the experimental method have been described in previous reports [1 - 6].

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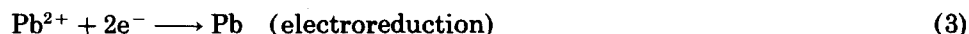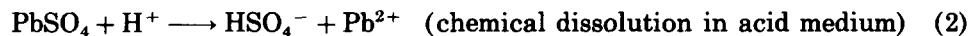
Results and discussion

Effect of sodium sulphate

The successive cycling of the potential of a lead electrode in sulphuric acid solution gives rise, after about 10 cycles, to the formation of a porous microelectrode with an adequate capacity and reproducible properties. It is important to form such a porous microelectrode since it is able to simulate the processes taking place at the positive and negative plates of the lead/acid battery. Therefore, prior to each experimental run, the lead electrode was cycled within the potential range under study and the polarization curve was recorded only after 10 such cycles had been completed.

The potential cycling of a lead electrode in sulphuric acid solution without additives over the range -1170 mV to -860 mV gives rise to a current peak [1 - 6], *i.e.*, an oxidation current maximum on the positive-going scan that corresponds to lead dissolution and formation of a passivating $PbSO_4$ layer. This process is equivalent to the discharge of the negative plate in a lead/acid battery according to the overall equation:

$$Pb \longrightarrow Pb^{2+} + 2e^- \xrightarrow{H_2SO_4} PbSO_4 + 2H^+ + 2e^- \tag{1}$$
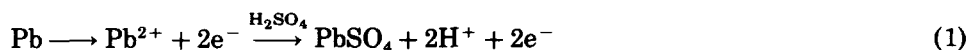
On the reverse potential sweep, a reduction current maximum occurs. This is associated with electroreduction of $PbSO_4$ to metallic lead. The conventional process of reduction takes place, as Popova and Kabanov [7] have shown, by a chemical dissolution of $PbSO_4$ to Pb^{2+} ions, followed by the electroreduction of Pb^{2+} ions to metallic lead, according to the following equations:

$$PbSO_4 + H^+ \longrightarrow HSO_4^- + Pb^{2+} \quad \text{(chemical dissolution in acid medium)} \tag{2}$$

$$Pb^{2+} + 2e^- \longrightarrow Pb \quad \text{(electroreduction)} \tag{3}$$

The potential difference between the anodic and cathodic peaks is about 60 mV. The height of the cathodic peak is much smaller than that of the anodic peak. Furthermore, a limiting current appears on the cathodic scan. This is due to diffusion control of the reduction process through the semipermeable membrane of $PbSO_4$. It has also been found that a considerable cathodic current is maintained, thus showing that at -1170 mV the reduction of the lead sulphate layer is not fully accomplished.

The polarization behaviour of the lead microelectrode in $H_2SO_4 + Na_2SO_4$ mixtures was studied, the sulphate ion concentration being maintained constant. The potential scan of the working electrode within the negative potential range mentioned above gave the following information:

● the general shape of the voltammograms is unaffected by the hydrogen-ion concentration;

● an increase in pH results in a decrease in the anodic and cathodic currents, in the diminution of the anodic and cathodic processes, and in a decrease in the anodic and cathodic peak potentials by about 60 mV per pH unit.

Taking into account the significance of the two peaks, the pH increase results in a decrease of the chemical solubility of the lead sulphate layer formed on the positive-going sweep. This causes the $PbSO_4$ to form faster and to be more dense and compact. As a result, the anodic current intensity and, hence, the height of the anodic peak, is smaller. An explanation for the decrease in the cathodic peak with pH increase may be found in the mechanism of the electroreduction of the lead sulphate layer. Electroreduction of Pb^{2+} ions results from the chemical dissolution of the lead sulphate layer. At low pH values, this dissolution occurs rapidly and does not hinder the charge-transfer step. Simultaneously, with increase in the amount of Na_2SO_4, the pH of the solution increases and the chemical dissolution of the lead sulphate decreases, resulting in a decrease in the concentration of Pb^{2+} ions. Hence, there is a decrease in the height of the cathodic peak and in the capacity of the lead microelectrode.

The polarization behaviour of the lead electrode in $H_2SO_4 + Na_2SO_4$ mixtures was also studied as a function of temperature. Experiments were carried out at four different temperatures, namely, 15, 25, 35 and 45 °C. The kinetic parameters determined from the polarization curves showed that the intensity of the anodic and cathodic peak currents (and, hence, an intensification of the anodic and cathodic processes) increased with increasing temperature. At the same time, increase in temperature results in a shift in the potentials of the anodic and cathodic peaks. The thermal coefficient of the peak potential $(\partial E_p/\partial T)_p$ was $-0.40 \, mV \, °C^{-1}$.

A study was made of the polarization behaviour of lead in $H_2SO_4 + Na_2SO_4$ mixtures within the potential range $+700 \, mV$ to $+1650 \, mV$. Current peaks are observed on voltammograms obtained for electrodes cycled in H_2SO_4 both with, and without, additives. On positive-going scans, a small anodic peak (a shoulder, in fact) occurs within the potential range $+820$ to $+940 \, mV$; this represents the formation of basic lead oxides and sulphates. A larger peak is observed at higher potentials and is due to the formation of lead dioxide (α and β modifications). After this peak, oxygen evolution takes place and the current increases sharply. On the reverse (negative-going) sweep, a peak corresponding to the reduction of PbO_2 to $PbSO_4$ (of Pb^{4+} to Pb^{2+}) appears. The shape of the two peaks differs appreciably: the cathodic peak for PbO_2 to $PbSO_4$ reduction is very sharp (indicating that the cathodic process is under kinetic control), while the anodic peak for the oxidation of $PbSO_4$ and non-stoichiometric lead oxides and basic lead sulphates is smaller and is spread over a relatively wide potential range (indicating that the anodic process of PbO_2 formation is under diffusion control).

Voltammograms obtained in $H_2SO_4 + Na_2SO_4$ mixtures with the maintenance of the SO_4^{2-} concentration at a constant value of 1 M revealed that the general shape of curves does not change; there are only variations in the peak current values and the charge involved in the anodic and cathodic processes. The values of the kinetic parameters showed that in $H_2SO_4 + Na_2SO_4$ mixtures with a constant SO_4^{2-} concentration, the decrease

of H^+ concentration down to 0.6 M favours the anodic and cathodic processes. Furthermore, larger current peaks are obtained and the charge involved in the electrode processes increases so that the capacity of the lead microelectrode also increases. Decrease in the H^+ concentration below 0.6 M leads to a decrease in the anodic and cathodic peak currents, as well as to a decrease in the charge involved in the electrode processes. A diminution in anodic and cathodic processes takes place; less PbO_2 is formed and the capacity of the lead microelectrode decreases.

Again, increase in temperature gave rise to an enhancement in both the anodic and cathodic processes, as well as to a shift in the anodic and cathodic peak potentials. The thermal coefficient of the peak potential $(\partial E_p / \partial T)_p$ was -0.38 mV $°C^{-1}$. At the same time, an increase in the pH gave, in all cases, a decrease in the anodic and cathodic potentials by ~ 60 mV per pH unit.

Effect of cobalt sulphate

An examination was carried out into the influence of cobalt sulphate additions on the polarization behaviour of a lead microelectrode over the potential range $+700$ to $+1650$ mV. Analysis of the polarization curves and of the kinetic parameters determined from the curves showed that cobalt sulphate addition to a 4.15 M H_2SO_4 solution gave rise, in all cases, to a considerable increase in the electricity amounts involved in the anodic process (Q_a) but only a negligible decrease in those involved in the cathodic (Q_c) process. The peak current corresponding to the main anodic reaction $(Pb^{2+}$ to $Pb^{4+})$ increases while the peak cathodic current decreased with increase in Co^{2+} concentration. The formation of PbO_2 was not detectable beyond a certain cobalt sulphate concentration. The process was masked by the current for oxygen evolution which becomes the main reaction. It is remarkable that the potential corresponding to the lead dioxide reduction remains constant and is not influenced by the number of cycles or by the concentration of cobalt sulphate.

Taking into account that:

$$Q_a = Q_{PbO_2} + Q_{O_2} = Q_c + Q_{O_2} \tag{4}$$

where:

$$Q_{PbO_2(\text{anodically formed})} = Q_{PbO_2(\text{cathodically reduced})} = Q_c \tag{5}$$

Hence:

$$Q_{O_2} = Q_a - Q_c \tag{6}$$

the coulometric ratios R_1, R_2, R_3 and R_4 have been calculated as follows:

$$R_1 = \frac{Q_{O_2}}{Q_{O_2}^0} \times 100 = \frac{Q_a - Q_c}{Q_a^0 - Q_c^0} \times 100 \tag{7}$$

$$R_2 = \frac{Q_{PbO_2}}{Q_{PbO_2}^0} \times 100 = \frac{Q_c}{Q_c^0} \times 100 \tag{8}$$

$$R_3 = \frac{Q_{PbO_2}}{Q_{O_2}} \times 100 = \frac{Q_c}{Q_a - Q_c} \times 100 \qquad (9)$$

$$R_4 = \frac{Q_{PbO_2}}{Q_{total}} \times 100 = \frac{Q_c}{Q_a} \times 100 \qquad (10)$$

where the [0] superscript refers to H_2SO_4 solution free from $CoSO_4$.

The values of the coulometric ratios R_1 - R_4 are presented in Table 1. It can be seen that the R_1 ratio increases markedly with the amount of $CoSO_4$; at the maximum concentration R_1 is about 8 times higher than that for H_2SO_4 without $CoSO_4$ addition. From analysis of the data in Table 1, and taking into account the meaning of the coulometric ratios, it can be concluded that $CoSO_4$ addition results in a remarkable decrease in the oxygen overvoltage, thus favouring the oxygen evolution within the working range of the positive electrode of the lead/acid battery. Since the Co^{2+} ion is an electrocatalyst for the oxygen evolution reaction, its presence in the solution will lead to a significant decrease in the oxygen evolution overvoltage. This behaviour could have advantageous effects on the functioning of the Pb/H_2SO_4 battery grid by hindering the corrosion rate. It is also possible that $CoSO_4$ addition will influence the behaviour of the grid but not that of the active mass [8]. The amount of the latter is very much greater than the amount of $CoSO_4$ in solution. Thus, the decrease in the $PbO_2/PbSO_4$ electrode capacity, as observed in the experiments reported here, is unlikely to have a negative influence on the active-mass capacity of the battery. It has been confirmed [9] that an addition of only 0.02 M $CoSO_4$ is sufficient to cause a considerable decrease in the oxygen overvoltage.

Within the -1170 to -860 mV potential range, $CoSO_4$ addition to the electrolyte did not change the shape of the voltammogram but did increase both the anodic and cathodic peak currents. Hence, $CoSO_4$ again intensifies both the anodic and cathodic processes at the electrode. As a result of experiments with a very wide range of $CoSO_4$ concentration (from 3.5 ppm to

TABLE 1

Coulometric parameters of voltammograms obtained on pure lead (for 10th cycle) in H_2SO_4 with $CoSO_4$
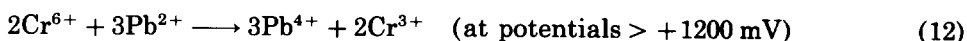Scan rate = 400 mV min^{-1}.

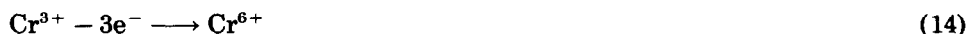| $CoSO_4$ (M × 10⁴)	Q_a (C)	Q_c × 10 (C)	R_1	R_2	R_3	R_4
0	2.303	1.993	100	100	9.47	8.65
4	2.645	1.504	118.6	75.4	6.03	5.68
18	3.518	1.438	160.4	72.1	4.26	4.08
36	10.490	1.400	492.1	70.2	1.35	1.33
89	11.100	1.370	521.3	68.7	1.24	1.23
178	15.923	1.320	750.9	65.3	0.82	0.81
356	16.620	0.945	785.8	47.4	0.57	0.56

300 ppm), it was found that both the life-time index, $\eta = (Q_f - Q_0)/Q_0$ (where Q_0 and Q_f represent the initial and the final capacity of the electrode), and the peak current, have the highest values for a $CoSO_4$ concentration of 250 ppm. At concentrations above 250 ppm, both the life-time index and the peak currents decrease slowly but still maintain much higher values compared with those obtained in H_2SO_4 solution free from $CoSO_4$. The intensification of the anodic and cathodic processes with $CoSO_4$ addition can be explained by the fact that although Co^{2+} ions participate to only a negligible extent in the anodic and cathodic currents (because of their very low concentration), the ions activate the electrode surface by means of a change in its structure. Analysis showed that the normal electrode potentials of the $Pb/PbSO_4$ and Co/Co^{2+} couples are very close, both being within the potential range under study. Hence, the $Co^{2+} \rightleftharpoons Co$ process occurs simultaneously with the $Pb^{2+} \rightleftharpoons Pb$ process; the difference is that $PbSO_4$ is practically insoluble and forms a passivating layer on the electrode surface, while $CoSO_4$ is completely soluble. It is possible that this cyclic process of cobalt deposition–dissolution increases the porosity of both the $PbSO_4$ layer and, in turn, the spongy lead that forms on the microelectrode. In other words, $CoSO_4$ additions are considered to increase the real surface of the electrode and, hence, its working capacity. At concentrations of $CoSO_4$ higher than 250 ppm, it is possible that the deposition of Co^{2+} ions occurs not only on the free sites of the spongy lead but also on $PbSO_4$, thus hindering dissolution of the latter and inhibiting both the anodic and cathodic processes.

The conclusion is that $CoSO_4$ addition activates the $PbSO_4$ layer on the electrode surface, increases the thickness of the active layer and, hence, increases the microelectrode capacity. Because a $Pb/PbSO_4$ microelectrode cycled over the -1170 to -860 mV potential range simulates the functioning of the negative electrode in the lead/acid battery, it can be concluded that the addition of small amounts of $CoSO_4$ increases the service life of the negative electrode by hindering sulphation processes.

Effect of ammonium dichromate

The influence of small additions of ammonium dichromate, $(NH_4)_2Cr_2O_7$, on the polarization behaviour of the lead electrode was studied in H_2SO_4 solutions within the $+700$ to $+1650$ mV potential range. It was found that the additive does not change the shape of the polarization curve, but causes a considerable increase in the height of both the anodic and the cathodic peaks as well as in the amounts of electricity involved in these processes. These features indicate that ammonium dichromate intensifies both the processes. It is suggested that the electrode processes occurring in the presence of the dichromate ion during the positive-going scan from $+700$ to $+1700$ mV are:

$$2Cr^{6+} + 3Pb \longrightarrow 3Pb^{2+} + 2Cr^{3+} \quad \text{(at potentials: } +800 \text{ to } +1200 \text{ mV)} \tag{11}$$

$$2Cr^{6+} + 3Pb^{2+} \longrightarrow 3Pb^{4+} + 2Cr^{3+} \quad \text{(at potentials} > +1200 \text{ mV)} \tag{12}$$

$$Pb^{2+} \longrightarrow Pb^{4+} + 2e^- \tag{13}$$

$$Cr^{3+} - 3e^- \longrightarrow Cr^{6+} \tag{14}$$

On the negative-going scan from $+1700$ to $+800$ mV, reduction of the formed PbO_2 takes place, *i.e.*,

$$Pb^{4+} + 2e^- \longrightarrow Pb^{2+} \tag{15}$$

The coulometric ratios (defined by eqns. (4) - (10)) indicate that the capacity of the lead microelectrode increases with increase in both the number of cycles and the ammonium dichromate concentration.

Effects of phosphoric acid

The influence of phosphoric acid, H_3PO_4, addition on the polarization behaviour of the $PbSO_4/PbO_2$ electrode was studied over the potential range $+700$ to $+1650$ mV. Analysis of the voltammograms as well as the coulometric data showed that the main effect of the H_3PO_4 addition is to passivate strongly all the electrode processes in the potential range under study. For example, the amounts of anodic (Q_a) and cathodic (Q_c) electricity are 5 - 10 times smaller than these obtained in H_2SO_4 solution free from H_3PO_4. Phosphoric acid also caused a marked increase in the oxygen-evolution overvoltage. Taking into account the ratio between the added amount of H_3PO_4 and the PbO_2 active mass per unit plate surface area, it can be concluded that small additions of H_3PO_4 do not decrease the capacity of the positive active mass of the battery, but can hinder the formation of insulating films (*i.e.*, $PbSO_4$) between the active mass and the grid. Thus, phosphoric acid can exert a beneficial effect on the service life of lead/acid batteries.

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