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Studies on the anodic and cathodic polarization of lead in sodium sulphate solution

E.E. Abd El Aal

Chemistry Department, Faculty of Science, Zagazig University, Zagazig, Egypt

Abstract

Galvanostatic polarization of lead has been studied in 0.1 M Na_2SO_4 solutions at various current densities. It was found that, at relatively low current densities, the anodic polarization curve does not reach the oxygen evolution potential. This indicates that the anodic dissolution of lead could continue indefinitely at these rates. At high current densities, the anodic polarization curve is characterized by four distinct arrests corresponding to the formation of $PbSO_4$, PbO, PbO_n and PbO_2, respectively, followed by transformation of $PbSO_4$ to PbO_2 on the electrode surface before the evolution of oxygen. The cathodic reduction curve shows three distinct plateaux corresponding to the transformation of PbO_2 to $PbSO_4$, PbO_2 to PbO and the latter with $PbSO_4$ to spongy lead, successively, followed finally by the formation of PbH_2. The correlation between the current, i, and the passivation time, t, for lead in 0.1 M Na_2SO_4 solution was found to follow the relation: $\log t = A - n\log i$, where A and n are constants. The diffusion and migration of the SO_4^{2-} and Pb^{2+} ions through the micropores of the anodic film become the controlling step. © 1998 Elsevier Science S.A. All rights reserved.

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1. Introduction

The behaviour of lead in sulfate solutions has been studied extensively owing to the widespread use of lead–acid storage batteries [1]. Moreover, lead is used as a storage material for nuclear waste in deep underground vaults [2]. Relatively little work has been reported regarding the electrochemistry of lead in neutral sulfate media [3–6]. Therefore, it is important from fundamental and practical standpoint to study the electrochemical behaviour of lead in sulfate solutions.

The present study was undertaken to elucidate the conditions leading to the passivation of lead in sulfate solution. A procedure was applied in which an electrode was repeatedly subjected to cathodic and anodic polarization under constant current while the potential–time variation was observed. Special attention was paid to the influence of current density on the potential–time relationship.

2. Experimental

Spectroscopically pure Pb (Johnson-Matthey, UK) was used as the test material in the form of short rods, 0.94 cm in diameter. The electrodes were affixed to Pyrex glass tubes with Araldite so that the total exposed surface area was 0.69 cm². Electrical contact was achieved through a copper wire soldered to the end of the Pb rod but not exposed to the solution. Each electrode was successively polished mechanically with fine grades of emery papers, degreased with acetone, and finally washed with bidistilled water before it was used. Experiments were done in 0.1 M Na_2SO_4 solution (pH = 6). The solution was prepared using bidistilled water and deaerated with nitrogen gas.

The electrolytic cell used (capacity 250 ml) was described previously [7]. The lead electrode and the main bulk of the solution were separated from the counter electrode (Pt) by means of a G-3 sintered glass disc. Before anodization, the lead electrode was first subjected to cathodic pretreatment for 20 min in the deaerated solution with the same polarizing current density (until it had reached a constant potential). This process was done to reduce any oxides which could have formed spontaneously on the metal surface before the experiment. The polarizing current density was then reversed, and the potential recorded as a function of time (anodic polarization). When oxygen evolved, the current was reversed to check any

formed films (cathodic polarization). The potential of the working electrode was measured relative to a Hg/Hg_2SO_4, saturated K_2SO_4 reference electrode (0.680 V vs. NHE) via a salt bridge, filled with 0.1 M Na_2SO_4 solution, whose tip was close to the working electrode.

Each experiment was carried out in a freshly deaerated solution, using a newly polished electrode surface. The polarization curves were recorded on a recording potentiometer (type Cole Parmer Instruments, USA). All measurements were conducted at $25 \pm 0.2°C$ using an air thermostat.

3. Results and discussion

3.1. Anodic polarization

Fig. 1. shows the galvanostatic anodic polarization curves of lead in 0.1 M Na_2SO_4 solution at relatively high current densities. The variation of the potential of the lead electrode with time shows a rapid and almost linear change of potential due to the decay of hydrogen overpotential and the subsequent charging of the double layer at the metal–solution interface [7]. This process occurs over a potential range which depends on the magnitude of the polarizing current. Subsequently, the potential of the lead electrode changes more slowly, giving rise to four distinct arrests a_1 to a_4, and finally passing to the value characteristic for oxygen evolution. The potential corresponding to the different arrests a_1 to a_4 at all the imposed current densities are given in Table 1.

Table 1

Dependence of the starting values of all potential arrests on the polarizing current

Current i ($\mu A\ cm^{-2}$)	E (V) (Hg/Hg_2SO_4, sat. K_2SO_4)			
Current 0	−0.9752	−0.810	−0.660	+0.980
	a_1	a_2	a_3	a_4
275	−0.970	−0.795		+1.000
290	−0.970	−0.795		+1.000
360	−0.970	−0.790	−0.600	+1.000
435	−0.960	−0.785	−0.550	+1.010
580	−0.950	−0.780	−0.530	+1.050
725	−0.955	−0.775	−0.520	+1.060
870	−0.940	−0.770	−0.510	+1.060
1000	−0.940	−0.765	−0.500	+1.065

As obvious from the data gathered in Table 1, the starting potential for the arrests a_1 to a_4 increases slightly but consistently with increasing the value of the imposed current density according to the following relation [8,9].

$$E = E_{i=0} + Zi \qquad (1)$$

where E is the measured electrode potential at the start of any of the arrests, i is the imposed current density, $E_{i=0}$ is the potential corresponding to $i = 0$ and Z is a constant. Plots of E vs. i, Fig. 2, gave rise to straight lines in accordance with Eq. (1). The intersection of such lines with the potential axis gives the values of $E_{i=0}$ which are collected in Table 2 in addition with the values calculated theoretically for each arrest [10,11].

It is obvious that the measured arrest potentials and calculated ones are similar. The four arrests could be
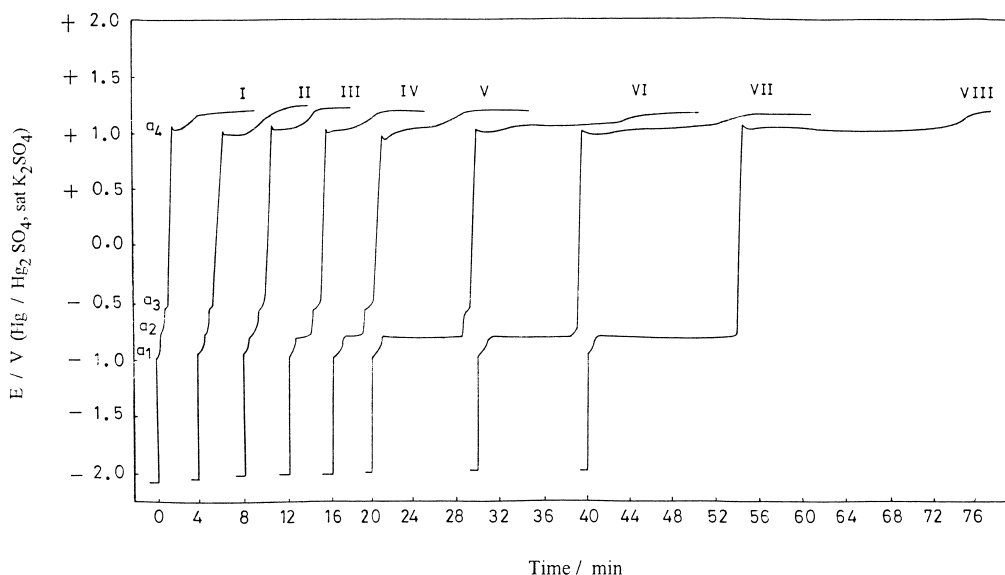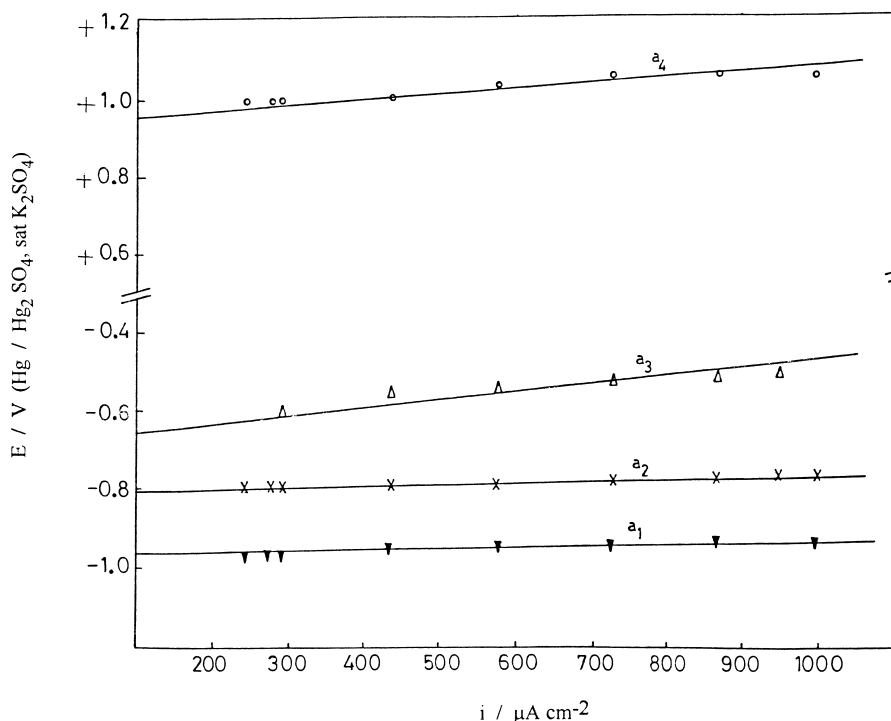

Fig. 1. Anodic polarization of lead electrode in 0.1 M Na_2SO_4 solutions at relatively high current densities: (I) 1000, (II) 870, (III) 725, (IV) 580, (V) 435, (VI) 360, (VII) 290 and (VIII) 275 $\mu A\ cm^{-2}$.

Fig. 2. Dependence of all arrest potential on the imposed current densities.

ascribed to the formation of $PbSO_4$, PbO, PbO_n and PbO_2, respectively, on the electrode surface before oxygen evolution. The first arrest potential a_1 ($E_{i=0} = -0.975$ V vs. Hg/Hg_2SO_4, sat. K_2SO_4), corresponds to the oxidation of Pb to $PbSO_4$ according to the reaction [3–6].

$$Pb + SO_4^{2-} = PbSO_4 + 2e^- \qquad (2)$$

where the calculated potential value [10,11] for the $Pb/PbSO_4$ couple at the prevailing SO_4^{2-} ion concentration is -0.963 V. The $PbSO_4$ layer grows to a critical thickness [12]. Since the $PbSO_4$ layer is highly ion-selective, being nonpermeable for SO_4^{2-} or Pb^{2+} ions, but being permeable for H^+ and OH^- ions [13,14]. Thus the lead ions generated at the lead surface during the polarization will react with the OH^- ion, diffusing through the

pores of the $PbSO_4$ layer, to produce PbO, according to the reaction [3–6,15,16].

$$Pb + 2OH^- = PbO + H_2O + 2e^- \qquad (3)$$
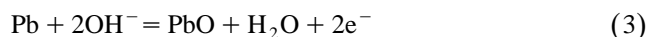
The calculated potential value for the Pb/PbO is -0.814 V. This value coincides with the measured potential arrest a_2 ($E_{i=0} = -0.810$ V). Hence, one might conclude that PbO is formed at this potential. The next arrest, a_3, which was noticed at higher current densities is assumed to correspond to the formation of a nonstoichiometric lead oxide, PbO_n (where $1 < n < 2$) [17,18]. The latter could not be formed at lower current densities. After the formation of PbO_n, arrest a_3, the potential rises quickly towards more positive values, arrest a_4. The arrest potential recorded at $E_{i=0} = +0.980$ V is assumed to the formation of PbO_2. The latter is formed from the oxidation of $PbSO_4$ to PbO_2:

$$PbSO_4 + 2H_2O = PbO_2 + SO_4^{2-} + 4H^+ + 2e^- \qquad (4)$$
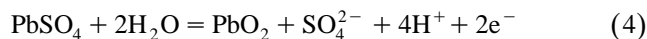
It is also of interest to note that after the formation of PbO_2 according to Eq. (4), the potential starts to decrease slightly with time. This may be attributed to an increase in the electrochemically active surface area, that is an increase in PbO_2 present [19,20]. Finally, the potential rises to that corresponding to the evolution of oxygen.

The relation between the polarizing current, i, and the passivation time, t, (time to the onset of oxygen evolution) is represented graphically in Fig. 3a. The passivation of the

Table 2
Experimental and calculated[a] starting potentials for lead oxides in 0.1 M Na_2SO_4 solution (pH = 6)

Arrest	Electrode system	E (V) (Hg/Hg_2SO_4, sat. K_2SO_4)	
		Experimental, $E_{i=0}$	Theoretical, E
a_1	$Pb/PbSO_4$	-0.975	-0.963
a_2	Pb/PbO	-0.810	-0.814
a_3	PbO/PbO_n[b]	-0.660	-0.664
a_4	PbO/PbO_2	$+0.980$	$+0.950$

[a]Calculated using Refs. [10,11].
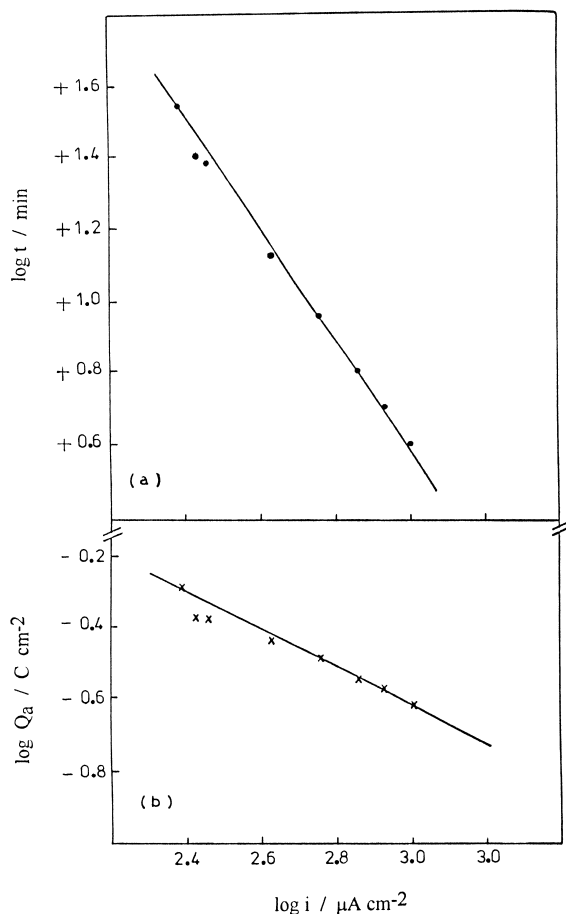[b]This value is obtained considering oxidation of PbO to Pb_3O_4.

Fig. 3. Variation of the passivation time (a) and the quantities of electricity required for passivation (b) of lead electrode in 0.1 M Na$_2$SO$_4$ solutions with the imposed current densities.

lead electrode in 0.1 M Na$_2$SO$_4$ solutions can be satisfactorily represented by the relation [8,9,15].

$$\log t = A - n \log i \qquad (5)$$

where A and n are constants. The slope, n, of the straight line of Fig. 3a, is found to be about 1.7. This value indicates that the diffusion and migration of H$^+$ or OH$^-$, during plateaus a$_2$ and a$_3$, and diffusion and migration of SO$_4^{2-}$ and Pb^{2+} ions during plateau a$_4$ through the micropores of the anodic film become the controlling step [21,22].

Fig. 3b, shows the relation between the quantities of electricity consumed during the anodic arrests (Q_a) up to oxygen evolution with the imposed current densities, i. A straight line relationship is obtained satisfying the following [15].

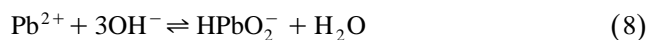$$\log Q_a = \alpha - \beta \log i \qquad (6)$$

where α and β are constants which depend on the nature of solution and the metal under test. From Fig. 3b, it is of great interest to note that when the imposed current density increases from 246 to 1000 μA cm^{-2}, the passivation time, t, decreases from 35 to 4 min. Also, it is clearly

demonstrated that the quantity of electricity, Q_a, required for passivation decreases from 0.52 to 0.24 C cm^{-2}. Therefore, the length of potential arrests decreases with the increase of the imposed current densities.

The galvanostatic polarization behaviour of the lead anode in 0.1 M Na$_2$SO$_4$ solution at lower current densities are shown in Fig. 4. At current densities ≤ 100 μA cm^{-2}, after the arrest corresponding to the formation of PbSO$_4$ layer, the potential was found to rise until it reached a steady value, at the Pb/PbO potential. The potential along this arrest remained constant and did not change appreciably even after 2 h, cf. Fig. 4I and II. This behaviour is assumed to be due to formation of soluble HPbO$_2^-$, at rate equal to that of oxide formation (oxidation of Pb to PbO). The reactions taking place are assumed to be [15,23].

$$Pb = Pb^{2+} + 2e^- \qquad (7)$$

The Pb^{2+} ions are reacting to form either HPbO$_2^-$ or PbO as follows

$$Pb^{2+} + 3OH^- \rightleftharpoons HPbO_2^- + H_2O \qquad (8)$$

or

$$Pb^{2+} + 2OH^- \rightleftharpoons PbO + H_2O \qquad (9)$$

followed by

$$PbO + OH^- \rightarrow HPbO_2^-$$

The OH$^-$ ions required for these processes are supplied by diffusion through the available pores of the lead sulphate layer, which previously formed on the Pb electrode [3,4].

It is worth mentioning here that when the current density is increased to 145 μA cm^{-2} (Fig. 4III), the time corresponding to the formation of the PbSO$_4$ layer is decreased. The electrode potential rises then to the steady value of the Pb/PbO couple for a certain time, depending on the current density. Thus one may assume that the PbO dissolution continued at a rate equal to that of PbO formation. This process continued until the concentration of Pb^{2+} ions in the solution reached a critical value [24]. Then, the anode potential rises rapidly to more positive value corresponding to the formation of PbO$_2$ on the electrode surface. Due to a nucleation overpotential for PbO$_2$ formation, a potential peak is produced. The potential then decreases due to an increase in active surface, as the transformation of PbSO$_4$ into PbO$_2$ proceeds. The potential then remains constant and does not change up to oxygen evolution. A part of the formed PbO$_2$ could possibly dissolve as plumbate [11] ions PbO$_3^{2-}$. In Fig. 4IV, it becomes apparent that the minimum current density required to reach oxygen evolution is 217 μA cm^{-2}.

3.2. Cathodic polarization

Fig. 5 illustrates the cathodic polarization curves obtained on reversing the polarization current just after the anodic half cycle at oxygen evolution potential. Four dis-
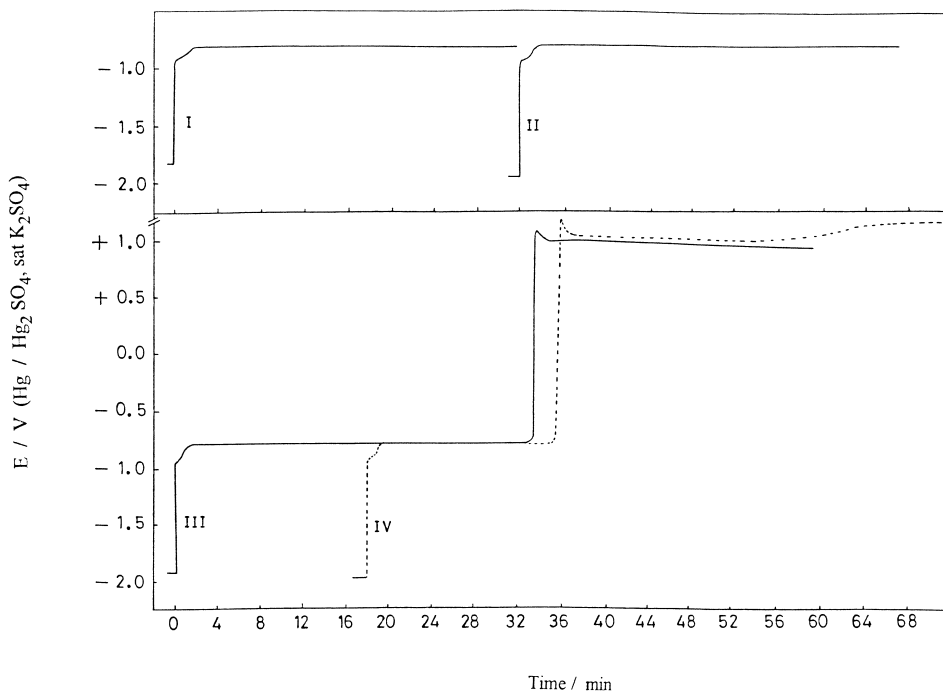
Fig. 4. Anodic polarization of lead electrode in 0.1 M Na_2SO_4 solutions at relatively lower current densities: (I) 73, (II) 100, (III) 145 and (IV) 217 μA cm^{-2}.

tinct cathodic plateaux were observed. The duration as well as the starting potential of each plateau depends on the imposed current density. The potential falls first rapidly, then gradually, with time to give the first reduction plateau c_1. In the potential region of plateau c_1, PbO_2 is electro-

chemically reduced to $PbSO_4$ [19,20]. The surface becomes covered with a layer of $PbSO_4$. Further reduction of PbO_2 to $PbSO_4$ is inhibited, because the slow diffusion of SO_4^{2-} anion into the $PbSO_4$ layer [13,14]. The potential then decreases to the level where unreduced PbO_2, beneath
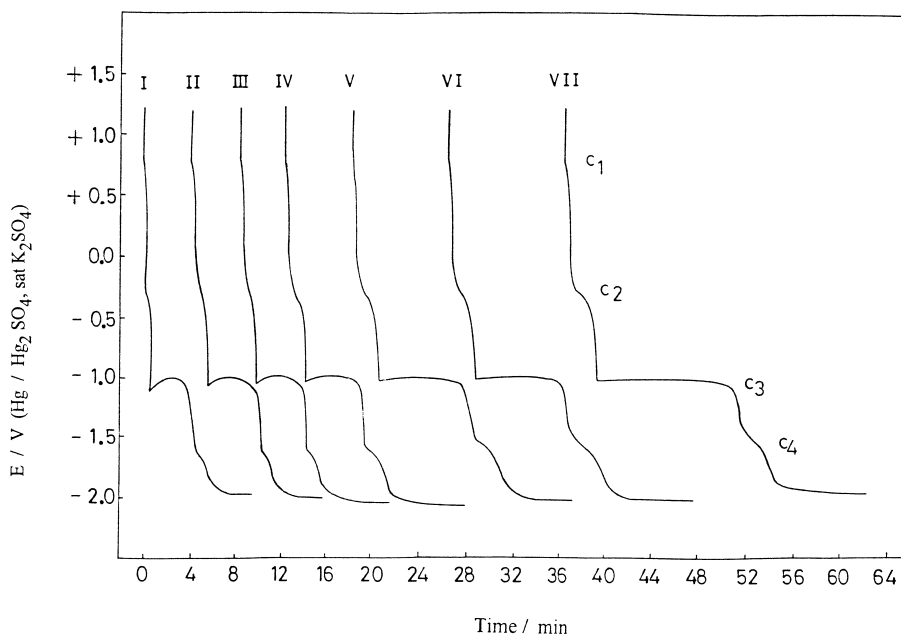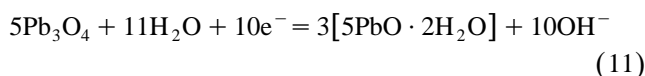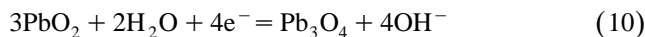

Fig. 5. Cathodic reduction of lead dioxide in 0.1 M Na_2SO_4 solutions at different current densities: (I) 1000, (II) 870, (III) 725, (IV) 580, (V) 435, (VI) 360 and (VII) 290 μA cm^{-2}.

the $PbSO_4$ layer, will be reduced at plateau c_2 to PbO. This could be explained on the basis that PbO_2 will be reduced first to Pb_3O_4 and the latter to PbO according to the following equations [12,15,18].

$$3PbO_2 + 2H_2O + 4e^- = Pb_3O_4 + 4OH^- \qquad (10)$$

$$5Pb_3O_4 + 11H_2O + 10e^- = 3[5PbO \cdot 2H_2O] + 10OH^- \qquad (11)$$

Once the above process is completed, the potential falls rapidly to approach the plateau c_3. Within this potential region the inner layer of PbO which formed during the reduction of PbO_2 and the outer $PbSO_4$ layer would be reduced simultaneously to give spongy lead (as seen later). Pavlov and Iordanov [25] and Valeriote and Gallop [26] have pointed out that the H^+ and OH^- ions can diffuse and migrate through the $PbSO_4$ layer. So in the reduction process of the PbO, OH^- ions must diffuse away from the PbO layer to the bulk solution and H^+ ions must diffuse in the opposite direction. Since PbO is stable only under alkaline conditions [27], the concentration of the OH^- ions is much greater than that of the H^+ ion within the PbO layer. Therefore, the process of PbO reduction will be limited by the diffusion of OH^- ions passing through the $PbSO_4$ layer [25–27].

The plateau c_4 which appears immediately before hydrogen evolution was attributed to the formation of lead hydride, PbH_2, Fig. 5. The potential of this process depends on the pH of the solution according to [11]: $E = 1.54 - 0.06$ pH. An interesting feature of the cathodic curves is that, the reduction of the oxide film takes place at potentials considerably far from their formation values (shifted in the negative direction). This indicates the irreversibility of the process [7,18].

3.3. Limited polarization

To obtain further insight into the oxidation and reduction processes, the following experiments were carried out. The lead electrode was first polarized cathodically at 435 $\mu A\ cm^{-2}$ in 0.1 M Na_2SO_4 solutions to reduce the air-formed oxide film. Then the current was reversed and the electrode polarized anodically until the potential reached a pre-determined value, after that, the current was reversed again cathodically, to reduce the oxides which formed during previous anodic polarization (Fig. 6). If the lead electrode was polarized anodically to the $PbSO_4$ arrest, Fig. 6I, the subsequent cathodic reduction curve showed one reduction plateau c_3, corresponding to reduction of $PbSO_4$ to Pb. When the lead electrode was polarized anodically to the PbO arrest, curve II, the cathodic reduction curve showed also only one single reduction plateau c_3. This indicates a simultaneous reduction of both $PbSO_4$ and PbO to Pb [28]. According to Varela et al. [29] the electroreduction of the composite $PbSO_4$–PbO layer can be explained on the basis of a complex mechanism which takes into account the contribution of each single species.

If the lead electrode was polarized anodically to the PbO_n arrest, Fig. 6III, the following cathodic reduction curve showed a composite plateau which may correspond to the reduction of PbO_n to PbO, c_3*, and the latter with $PbSO_4$ to Pb, c_3, respectively. Oxidation of the electrode to a potential of $\simeq +1.00$ V, Fig. 6IV and V, showed the same subsequent reduction curve, as shown by curve III. This indicates that, during the anodic polarization from $\simeq -0.55$ V up to $\simeq +1.00$ V, no chemical transformation takes place. On the other hand, when the electrode was polarized anodically to a potential of $+1.2$ V or more,
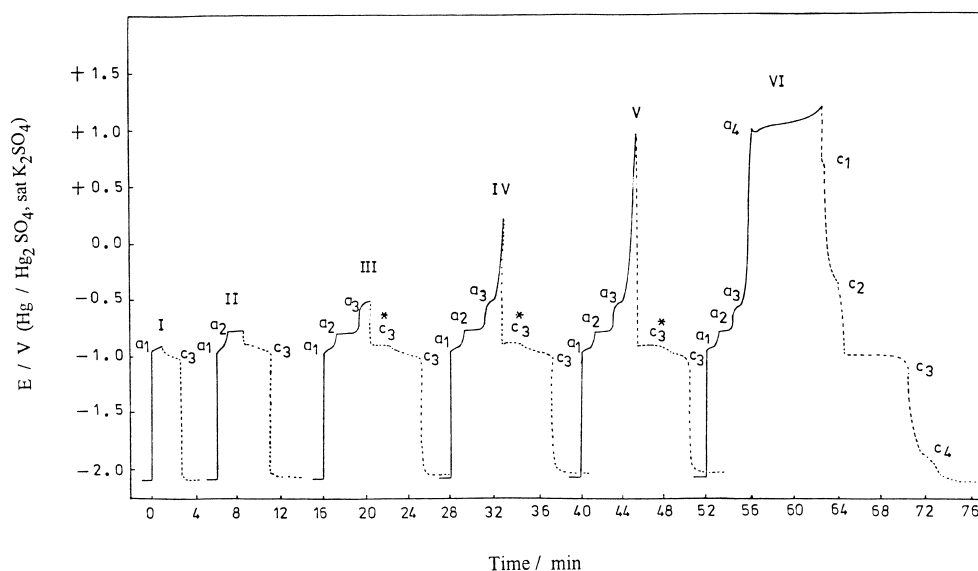

Fig. 6. Anodic polarization of lead electrode in 0.1 M Na_2SO_4 solutions at different potential values (solid lines) and their reduction curves (dashed lines), polarizing current density = 435 $\mu A\ cm^{-2}$.
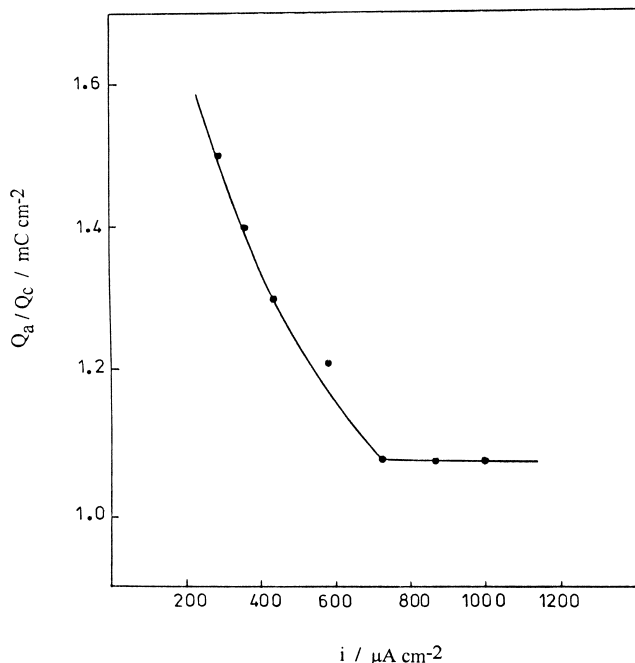
Fig. 7. Plots of Q_a / Q_c vs. the imposed current densities.

curve VI, the subsequent cathodic curve showed the same behaviour as discussed above in Fig. 5.

A distinctive feature of Fig. 6 is that the reduction plateau, c_4, was observed only if the polarization of the lead electrode had previously reached the oxygen evolution potential. The plateau c_4 could thus possibly be due to the electrochemical reduction of oxygen. The plateau c_4 became more pronounced with cycling, due to an increased amount of absorbed oxygen. In general, electrochemical reduction of the oxides occurred at potentials considerably more negative than the thermodynamic potentials. The degree of irreversibility seemed to depend on the anodization potential.

3.4. The ratios of oxide formed to oxide reduced

A comparison of the quantity of charge under the anodic oxidation arrests, Q_a, and the cathodic plateaus of

the oxides, Q_c is a useful method for detecting the formation of soluble reaction products [7,18]. On the basis of Figs. 1 and 5, the change of the ratio Q_a/Q_c with the applied current densities, i μA cm^{-2}, was derived and depicted in Fig. 7. The quantity of electricity was integrated, excluding however the charge involved in the arrest corresponding to oxygen evolution, and the plateau c_4, corresponding to oxygen reduction. The Q_a/Q_c ratio decreases linearly with increasing current density, until it approaches a constant value of 1.08 at high current densities, which indicates that the oxidation products almost completely reduced. However, at low current densities some of the products formed during anodic oxidation are lost by diffusion into the bulk of the solution, before becoming reduced at the electrode surface on reversing the electrode potential [18]. The soluble reaction products, namely the biplumbite ion $HPbO_2^-$, might result from the electrochemical reaction [15,18,23].

$$Pb + 3OH^- \rightleftharpoons HPbO_2^- + H_2O + 2e^- \qquad (12)$$
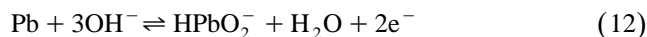
or from dissolution of PbO according to

$$PbO + OH^- \rightleftharpoons HPbO_2^- \qquad (13)$$

It should be noted that the dissolution of some PbO_2 as the plumbate ions PbO_3^{2-} could also be considered as a plausible explanation [18].

3.5. Effect of cyclization

Fig. 8 shows the anodic (A) and cathodic (C) potential–time curve of the lead electrode in 0.1 M Na_2SO_4 solution at a current density of 435 μA cm^{-2} and the open circuit decay curve D. On repeated anodic and cathodic cycling, the anodic oxidation seems to have the general features reported previously in Fig. 1, except that the total quantity of electricity prior to oxygen evolution increases with every new anodic half-cycle. This might be attributed to an increase in the thickness of the corrosion layer which progresses with the number of cycles.

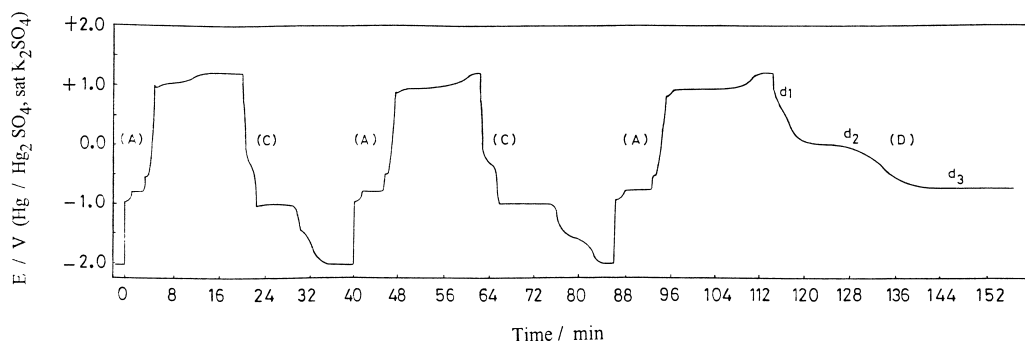Fig. 8 shows that the overshoot accompanying the formation of PbO_2 is gradually disappearing during cy-

Fig. 8. Cyclic anodic A and cathodic C polarization curves of lead electrode in 0.1 M Na_2SO_4 solution and anodic decay D, polarizing current density = 435 μA cm^{-2}.

cling. It is probably due to a decrease of the nucleation overvoltage for PbO_2 formation.

The anodic decay curve D, Fig. 8, is recorded by switching off the polarizing current after the electrode had reached the oxygen evolution potential. The potential falls rapidly to that of the $PbO_2/PbSO_4$ reaction, polarized to a potential of $\simeq +0.700$ V (d_1). This is followed by a gradual change over a considerable length of time to the PbO_2/PbO potential at $\simeq +0.050$ V (d_2). The potential finally decreased to the equilibrium value of PbO/Pb reaction, at -0.820 V (d_3). It is interesting to note that the potential during open circuit decay was slightly higher than the theoretical, calculated plateau potentials. This is may be due to polarization effects or resistive effects. A detailed analysis of the influence of Na_2SO_4 concentration on lead dissolution and passivation will be presented in a future publication.

4. Summary

The electrochemical behaviour of lead has been studied in 0.1 M Na_2SO_4 solutions at various current densities. The results of these experiments revealed the following.

(I) The shape of the anodic polarization curves depends on the applied current densities.

(II) At relatively low current densities, the anodic polarization does not reach the oxygen evolution potential. It indicates the dissolution of Pb and/or lead oxides.

(III) At high current density, the anodic polarization curves shows four distinct arrests corresponding to the formation of oxidation $PbSO_4$, PbO, PbO_n and PbO_2, respectively, followed by transformation of $PbSO_4$ to PbO_2 on the electrode surface oxygen evolution.

(IV) The cathodic reduction curves shows three distinct plateaux corresponding to reduction of PbO_2 to $PbSO_4$, PbO_2 to PbO and the latter with $PbSO_4$ to spongy lead, successively, followed by the formation of PbH_2 before hydrogen evolution.

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