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Electrotransformations at some lead-antimony alloy/ sulphuric acid interfaces

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The electrochemical behaviour of Pb-(0-8%)Sb alloys in H_2SO_4 solutions was studied using impedance and cyclic galvanostatic measurements. The experimental results indicated that the alloy containing 2.5% Sb is critical in many respects. The potential arrest corresponding to the formation of the sulphate layer was absent for the alloy containing 2.5% Sb while it was present for the other alloys. The efficiency of the charging was found to increase with decreasing anodizing current. The electrochemical transformations during cyclic galvanostatic polarization and self-discharge are discussed.

1. Introduction

The corrosion and polarization behaviours of lead-antimony alloys are of great importance due to their wide applications in lead acid batteries. The addition of antimony to lead not only improves the mechanical properties, but also affects the corrosion and charging and discharging characteristics [1-8]. The kinetics of the anodic film growth on some Pb-Sb alloys were studied in 4.5 M H_2SO_4 solutions by Weifang *et al.* [9-11]. They concluded that the major constituent of the anodic film was a porous PbO_2 film and the order of decreasing growth rate of the PbO_2 film was Pb > Pb-(7%) Sb-(0.3%) Ag > Pb-(7%) Sb > Pb-(5%) Sb-(0.2%) As. In previous work [12] the effect of alloying of Sb on the open circuit potential and impedance behaviour of lead in H_2SO_4 solutions was reported.

In the present work, the cyclic galvanostatic charging and discharging characteristics of some Pb-Sb alloys in H_2SO_4 solutions are studied.

2. Experimental details

The Pb-Sb alloys were prepared from pure lead and antimony metals from the Helwan Company of Non-Ferrous Industries, Helwan, Egypt. The electrode preparation, solutions, electrolytic cell and electrical circuit for polarization and impedance measurements are described elsewhere [13]. The electrodes were mechanically polished using successively finer grades of metallographic emery papers down to 4/0 until the surface appeared free of scratches and defects. The solutions were prepared from AnalaR grade sulphuric acid and triply distilled water. All potentials were measured against a Hg/Hg_2SO_4, saturated K_2SO_4 solution reference electrode and the cell capacitance and resistance were measured at a frequency of 1 kHz. All experiments were conducted at a temperature of $30 \pm 0.2°C$ in a double walled air thermostat.

3. Results and discussion

3.1. *Open circuit behaviour*

It has been observed in previous work [12] that lead and lead-antimony alloys passivate in sulphuric acid solutions to various extents depending on the acid concentration and antimony content of the alloy. Figure 1 shows the variation of the quasi-steady values of capacitance, C_m, resistance, R_m, and corrosion potential, E_{corr}, with the percentage of antimony in the Pb-Sb alloys. As can be seen there is a critical point at a composition of 2.5% Sb. At [Sb] < 2.5%, the steady E_{corr} values ($E_{corr} \simeq -0.95$ V against Hg/Hg_2SO_4 closely correspond to the $Pb/PbSO_4$ system in 0.5 M H_2SO_4; $E^0_{Pb/PbSO_4} = -0.996$ V [14]. This implies that the metal surface is covered by an insulating $PbSO_4$ layer which thickens with time and this accounts for the shift of the reversible potential to more positive values. At [Sb] = 2.5%, sharp changes, especially in E_{corr} and R_m, can be seen in Fig. 1. It seems that antimony begins to affect the electrochemical behaviour of the alloys. The steady E_{corr} values at [Sb] $\geqslant$ 2.5%, -0.51 V against Hg/Hg_2SO_4 corresponds to the Sb/Sb_2O_3 system in 0.5 M H_2SO_4 [15].

Figure 1 shows that the increase in antimony content leads to an increase in C_m and a decrease in R_m. Such behaviour may be attributed to increasing corrosion of the alloys as the Sb content increases. Morphological investigations showed that the alloys suffered selective leaching, the extent of which was found to increase with increasing antimony content. Again, the attack was a minimum for the alloy con-

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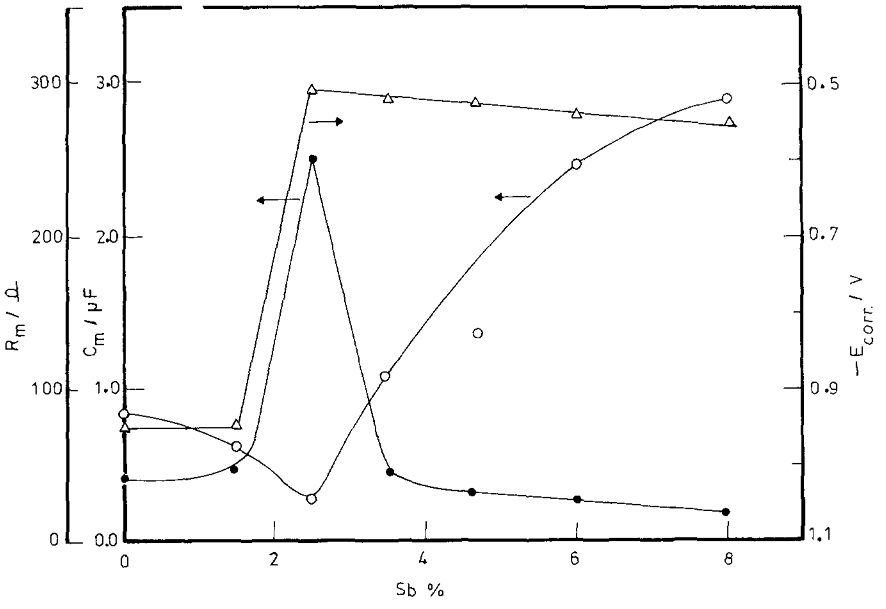

Fig. 1. Variation of the quasi-steady capacitance, C_m, resistance, R_m, and potential, E_{corr}, with the percentage of antimony in the alloy. The electrolyte was 0.5 M H_2SO_4, electrode area = 0.1963 cm^2. Key: (○) C_m, (●) R_m and (△) E.

taining 2.5% Sb. Figure 2 shows the microstructure of some Pb–Sb alloys after etching in solution contains 75 ml acetic acid and 25 ml H_2O_2 [16]. As can be seen the grain size and the amount of the intergranular Sb are at a minimum for the alloy containing 2.5% Sb. For other alloys the amount of intergranular Sb, as well as the grain deformations, seems to increase with increasing Sb, i.e. > 2.5%. It is reasonable to expect that the alloy with the minimum amount of intergranular Sb and the closest grain size is the least likely to corrode.

3.2. *Cyclic galvanostatic polarization*

The electrodes were cathodically polarized at a constant current of 100 µA until the steady potential values corresponding to hydrogen evolution were attained. Then the polarity was reversed in the anodic direction where the potential was traced with time until oxygen evolution. Thereafter, the polarity was again reversed in the cathodic direction up to hydrogen gas evolution.

Figure 3 shows the cyclic galvanostatic polarization curves for lead and some Pb–Sb alloys in 0.5 M H_2SO_4

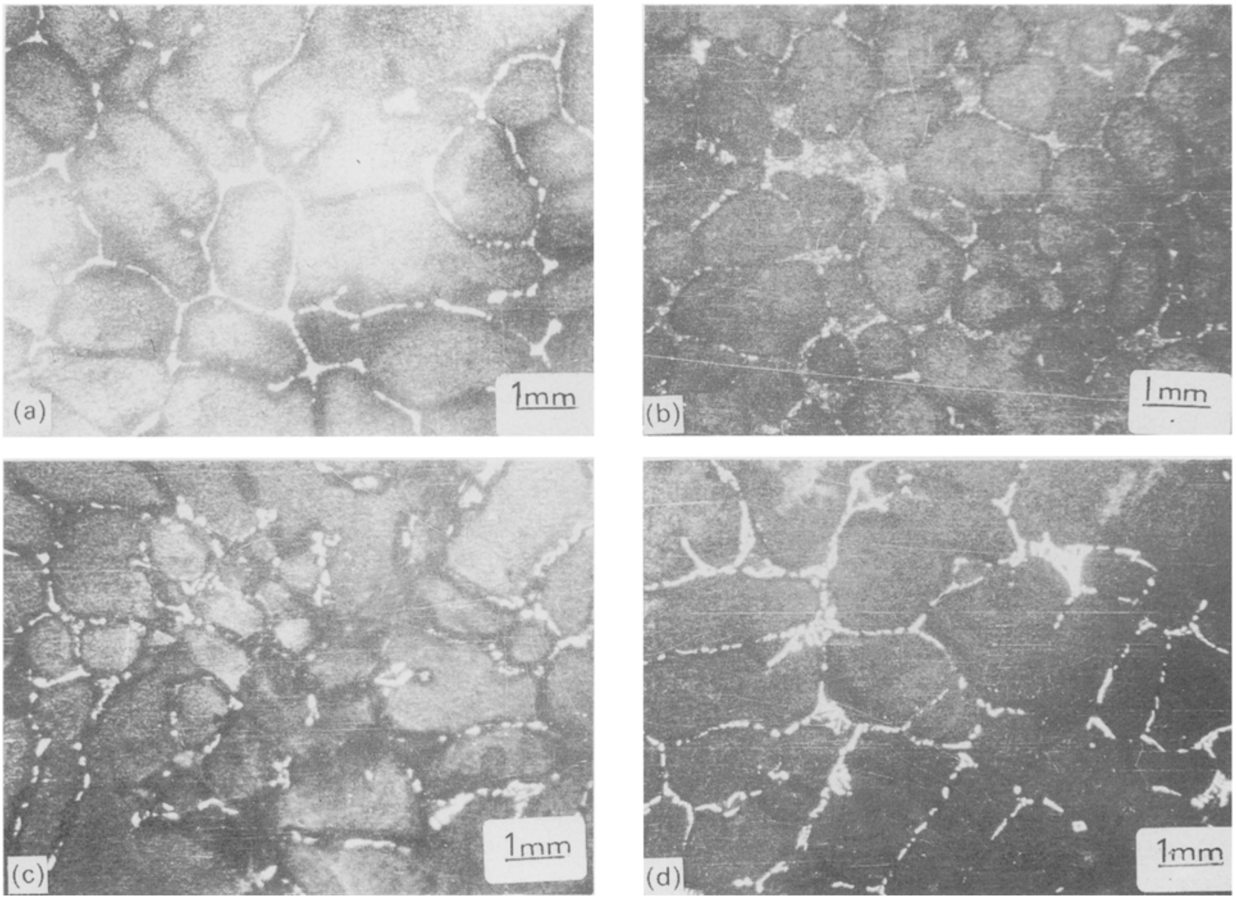

Fig. 2. Microstructure of Pb–Sb alloy containing different Sb%; (a) 1.5, (b) 2.5, (c) 3.5 and (d) 4.65.

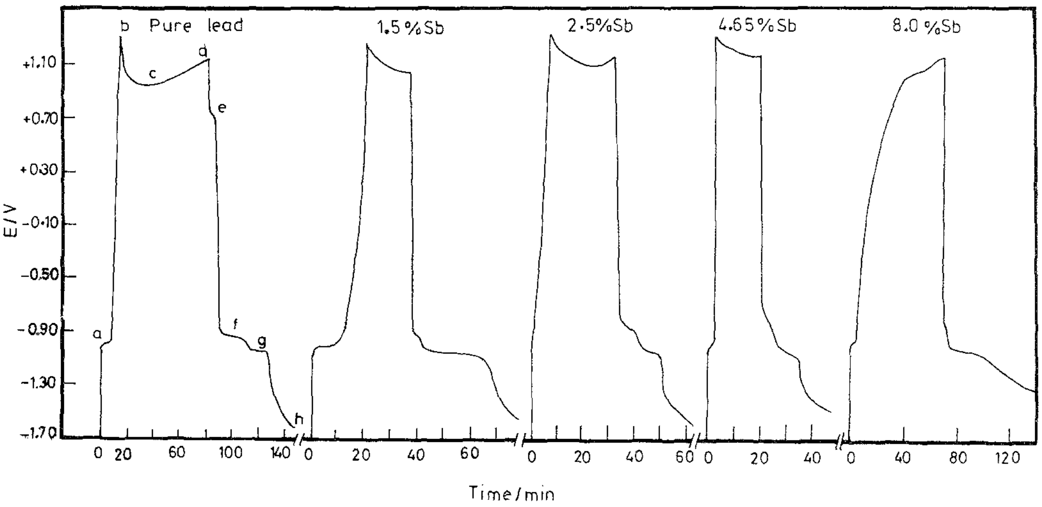

Fig. 3. Cyclic galvanostatic polarization curves for lead and Pb-(0-8%) Sb alloys in 0.5M H_2SO_4 solutions at 100μA. Electrode area = 0.1963 cm^2.

solutions. The main features of these curves can be summarized as follows [1, 17-26]:

(i) the formation of a lead sulphate layer at $\simeq$0.998 V (arrest a);

(ii) the start of formation of PbO_2 (maximum b);

(iii) the transformation of $PbSO_4$ into PbO_2 (minimum c);

(iv) the oxygen-evolution (maximum d);

(v) the reduction of PbO_2 to Pb(II) (arrest e);

(vi) the reduction of basic lead sulphate to lead metal (arrest f);

(vii) the reduction of the $PbSO_4$ layer to lead (arrest g); and

(viii) hydrogen evolution (arrest h).

No arrests corresponding to the oxidation of antimony could be traced for the Pb-Sb alloys. Arrest (a) for the alloy containing 2.5% Sb is absent but is present for the other alloys and lead metal. The arrest (c) corresponding to the reduction of PbO_2 to Pb(II) is very small for the Pb-Sb alloys as compared to the Pb metal. Such behaviour indicates that the amount of reducible PbO_2 on the alloy surface is less than that on the pure lead surface. For Pb-8.0% Sb alloy, the potential rises gradually after the arrest reaching a quasi-steady value of $\simeq$1.05 V (without showing the shoulder (b) and rises again due to oxygen gas evolution. The use of smaller current density make it possible to trace the arrests (a) and (c) for the alloy containing 2.5% Sb as can be seen in Fig. 4. The figure also shows an additional arrest, c*, which is not detected at higher current densities. Arrest c* at potential $\simeq$0.84 V corresponds to the oxidation of Pb(II) species to PbO_2 [14].

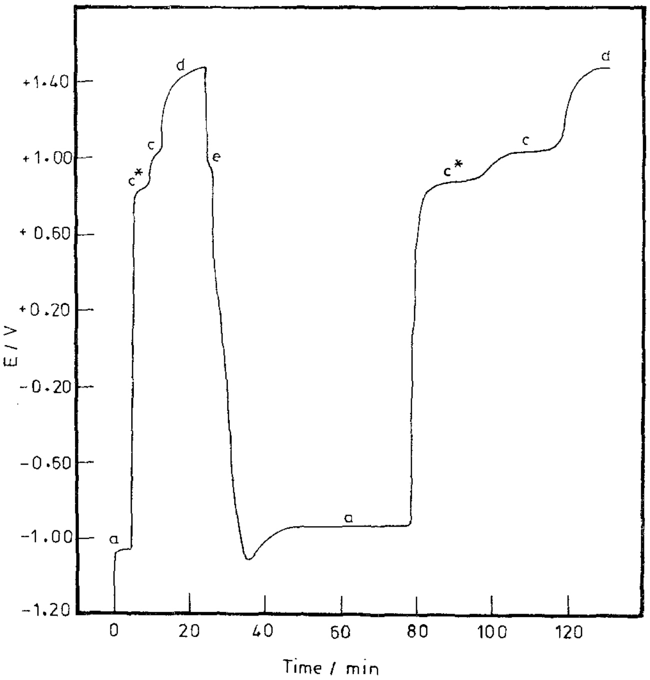

Fig. 4. Cyclic galvanostatic polarization curve for Pb-2.5% Sb alloy in 0.5M H_2SO_4 at 25μA. Electrode area = 0.1963 cm^2.

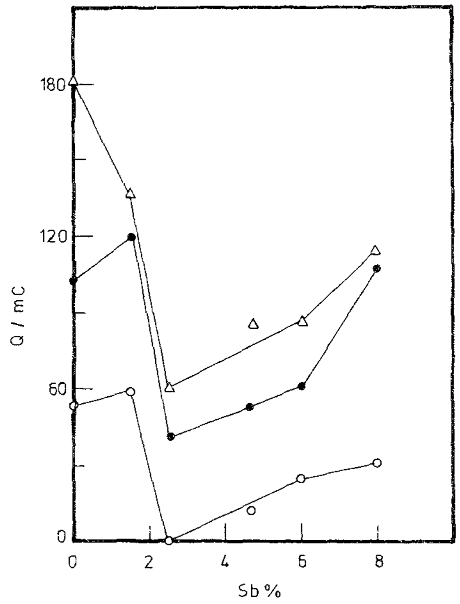

Fig. 5. Amount of charge, Q, against the percentage of antimony in the alloy; (○) charge for formation of $PbSO_4$, (×) charge for reduction of $PbSO_4$, and (△) charge for reduction of both basic $PbSO_4$ + $PbSO_4$. Details in Fig. 3.

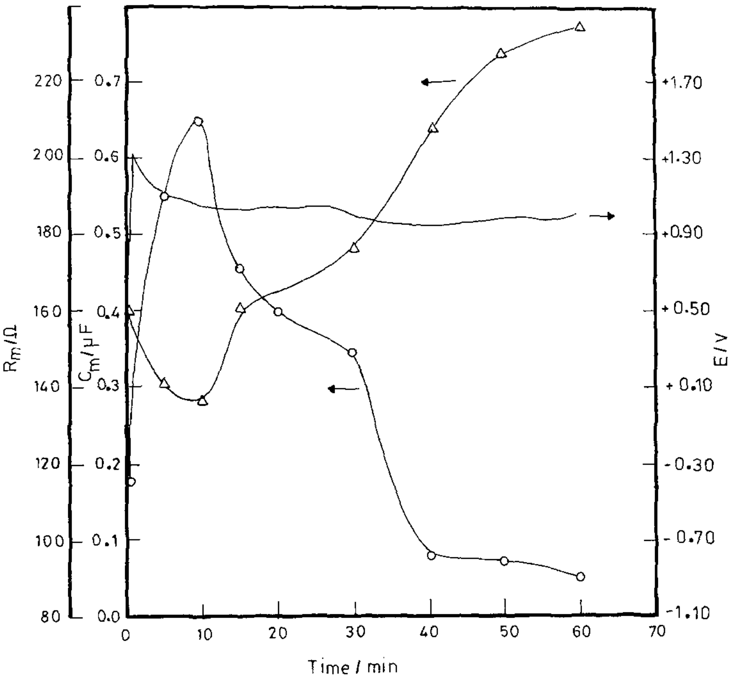

Fig. 6. Variation of capacitance, C_m (△), resistance, R_m (○), and potential, E ——, during anodization of the Pb–(2.5%) Sb alloy in 0.5 M H_2SO_4 solutions at 100 μA. Electrode area = 0.1963 cm^2.

The reduction of $PbSO_4$ to metallic lead, arrest (g), occurs for all the alloys and pure lead at the same potential, -1.04 ± 0.01 V against Hg/Hg_2SO_4. This value is about 40 mV more cathodic than the reversible potential of $PbSO_4$ formation; -100 V. On the other hand, the potential corresponding to the reduction of basic lead sulphate, arrest (f), depends on the alloying antimony content; being higher and having a shorter duration with increasing antimony percent.

The dependence of the amount of charge, Q, involved in the formation and reduction of $PbSO_4$ on the percentage of Sb in the alloy is shown in Fig. 5. The total amount of charge required to reduce both the basic salt and $PbSO_4$ is also shown in the figure. Q for the electrotransformation of $PbSO_4$ is minimum for the Pb–2.5% Sb alloy and maximum for the alloy containing 1.5% Sb. Further, the amount of charge, Q, for the Pb–1.5% Sb alloy is slightly higher than that for pure lead metal. Generally, these charges Q, increase as the antimony percentage shifts from 2.5% to lower or higher values.

The variation with time of both C_m and R_m for the alloy containing 2.5% Sb during anodic polarization in 0.5 M H_2SO_4 is shown in Fig. 6. As the polarization proceeds, C_m decreases to a minimum and R_m increases to a maximum, then the situation is reversed, i.e. C_m increases and R_m decreases. Such behaviour reflects the different electrotransformation during the anodic polarization. During the first 10 min, the insulating $PbSO_4$ layer grows and thickens. Thereafter, the electrotransformation of $PbSO_4$ layer to conducting PbO_2 layer causes an increase of C_m and decrease of R_m. A comparison between the potential on one hand, and C_m and R_m on the other, indicates that a $PbSO_4$ layer must be formed before its oxidation to PbO_2. Part of such a layer is formed at potentials where PbO_2 may be formed.

3.3 *Electrotransformations during the self-discharge*

The electrodes were anodically polarized at constant current for a certain time, then the circuit was switched off and the open circuit potential, capacitance and resistance were followed with time. Such a process involves the self-discharge of the anodic PbO_2 layer into $PbSO_4$. Figure 7 shows the potential decay for anodized lead and Pb–2.5% Sb alloy in 0.5 M H_2SO_4 solutions. The potential decays rapidly at first, then gradually to reach steady values, -0.99 V, which are very close to the reversible potential of the $Pb/PbSO_4$ system. During the decay, some arrests, A, B, C and D are observed. The duration of each arrest depends on the alloying Sb percent and the polarizing current and time. These arrests may be explained thus: (i) arrest A at $+0.85$ V corresponds to the reduction of

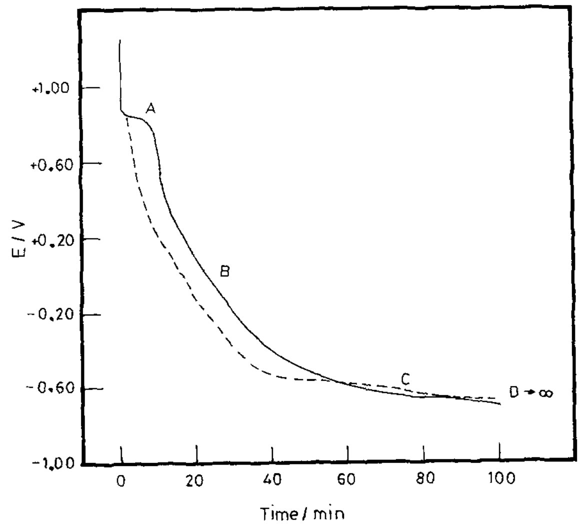

Fig. 7. Potential decay curves for pure lead and Pb–(2.5%) Sb alloy after their anodization at 100 μA in 0.5 M H_2SO_4 solutions. Electrode area = 0.1963 cm^2. (——) 0.0% Sb; (– – –) 2.5% Sb.

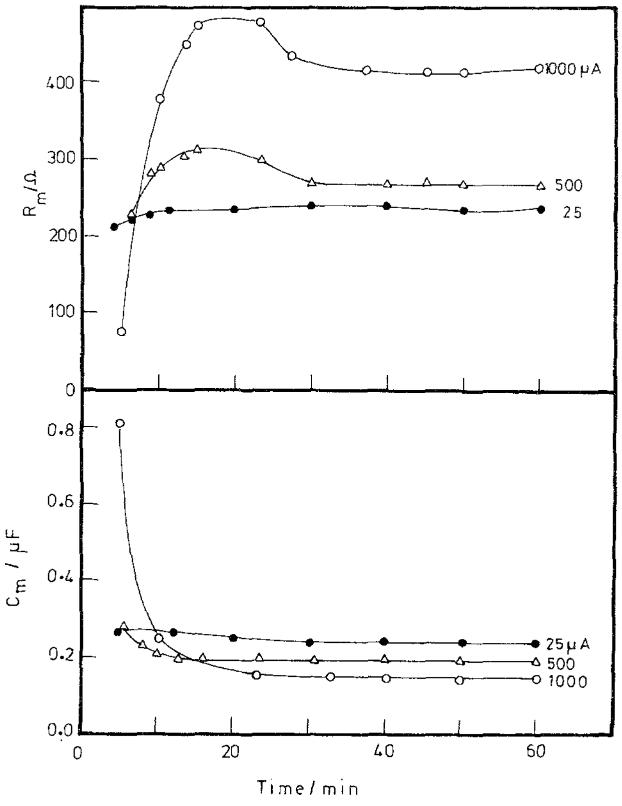

Fig. 8. Variation of capacitance, C_m, and resistance, R_m, with time during self-discharge of the Pb–(2.5%) Sb alloy in 0.5 M H_2SO_4 solutions after anodization for $\frac{1}{2}$ h at: (×) 25, (△) 500 and (○) 1000 μA. Electrode area = 0.1963 cm^2.

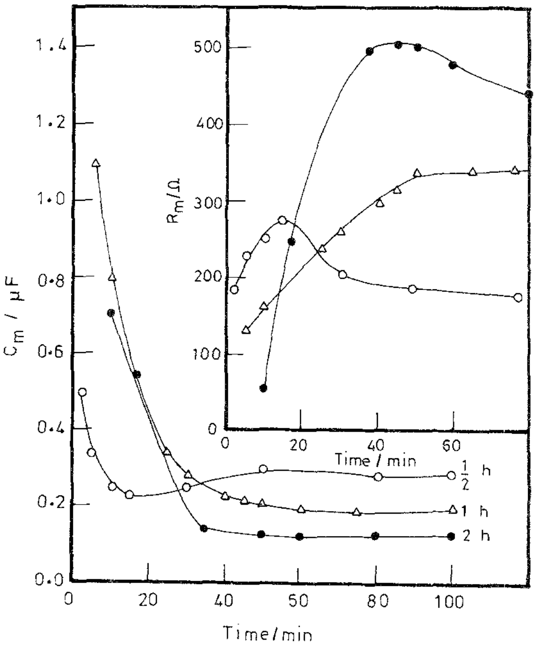

Fig. 9. Variation of capacitance, C_m, and resistance, R_m, with time during self-discharge of the Pb–(2.5%) Sb alloy in 0.5 M H_2SO_4 solutions after anodization at 100 μA for: (○) 0.5, (△) 1.0 and (×) 2.0 h. Electrode area = 0.1963 cm^2.

PbO$_2$ to PbSO$_4$; (ii) arrest B at +0.02 V corresponds to the reduction of the inner α-PbO$_2$ layer via a solid-state mechanism to PbO [26]; and (iii) arrest C at −0.60 V corresponds to the reduction of PbO to metallic lead.

3.4. *Effect of anodization current and time on the self-discharge characteristics*

Figures 8 and 9 show the variation of open circuit C_m and R_m for anodized Pb-2.5% Sb alloy in 0.5 M H_2SO_4 solutions under different anodization conditions. Generally, the self-discharge process is accompanied by a decrease in C_m to a minimum and an increase in R_m to a maximum. Thereafter, C_m increases and R_m decreases slowly. The initial decreases in C_m and increase in R_m are attributed to the transformation of the conducting PbO$_2$ layer into the insulating PbSO$_4$ layer. The reverse behaviour observed thereafter may be due to the reduction of the poor conductor PbO into metallic lead. The minimum capacitance values, C_{min}, decrease with increase of the anodization current and time while the maximum resistance values, R_{max}, increase. The increase in the thickness of the sulphate layer formed during the self-discharge process is proportional to $(C_{min})^{-1} - C_s^{-1}$ where C_s is the steady capacitance before polarization.

Figure 10 shows the variation of $(C_{min})^{-1} - C_s^{-1}$ and $(R_{max} - R_s)$ with anodization current and time. As can be seen, the thickness of the sulphate layer increases with increasing anodization current and time. This means that the thickness of the PbO$_2$ layer formed by anodization increases with increasing amount of charge passed.

The effect of charging rate on the charging efficiency can be inferred from the study of the decay curves for alloys anodized to a certain amount of charge using

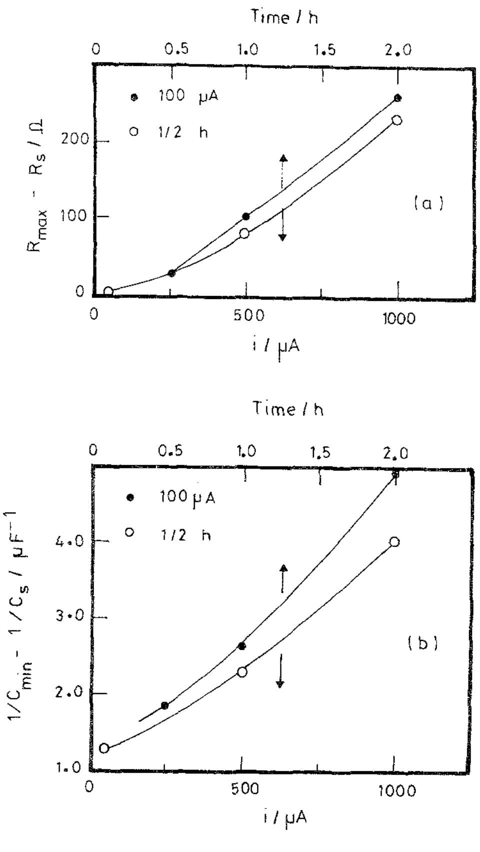

Fig. 10. $(C_{min}^{-1} - C_s^{-1})$ and $(R_{max} - R_s)$ against the anodization current at constant time = $\frac{1}{2}$ h) and anodization time (at constant current = 100 μA). Details in Figs 8 and 9.

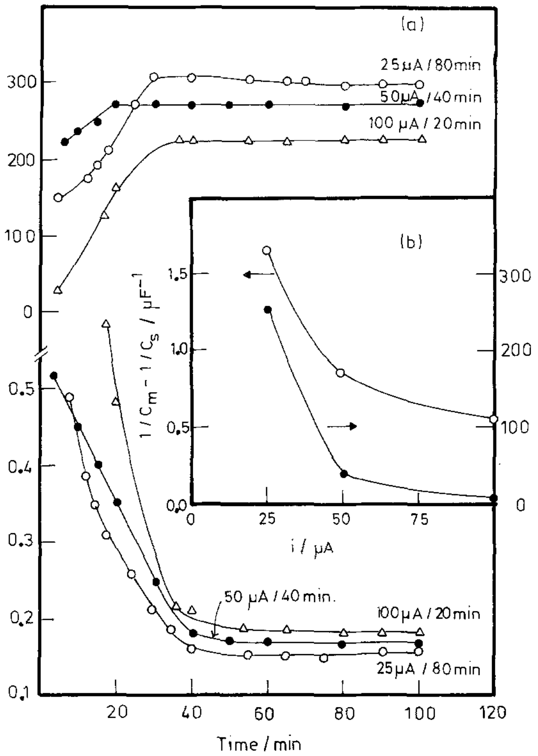

Fig. 11. (a) Variation of capacitance, C_m, and resistance, R_m, with time during the self-discharge of the Pb-(2.5%) Sb alloy after anodization until constant charge ($Q = 0.12\,\mathrm{mC}$) using different current densities. (b) ($C_{min} - C_s^{-1}$) against the anodizing current.

different current densities. Figure 11 shows the variation of both C_m and R_m with time during the self-discharge of the alloy containing 2.5% Sb after its anodization up to $Q = 0.12\,\mathrm{mC}$ using 25, 50 and 100 μA. As can be seen, R_{max} increases as the anodizing current decreases, whereas C_{min} decreases. Thus, the thickness of the sulphate layer formed during self-discharge (or the PbO_2 layer formed on charging) decreases as the charging rate increases. This means that the charging efficiency decreases with increasing charging rate.

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