Effect of polarisation mode, time and potential on the properties of the passive layer on lead–tin alloys

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Abstract

Taking into account the dynamic behaviour of the passive layer formed on lead and lead–tin alloys, this work emphasises the effect of the polarisation potential and the polarisation time on the electronic conductivity of the passivation layer. When the lead electrode was polarised in the passivity region (700 mV versus Hg/Hg_2SO_4 electrode), the polarisation resistance increased but decreased when tin was alloyed. This behaviour is interpreted by the increasing formation of semi-conducting PbO and conducting tin oxide. With a potential incursion in the PbO_2 region (1500–2000 mV), semi-conducting lead oxide, PbO_x, was formed. The decrease in polarisation resistance is explained by the electronic properties of PbO_x which is assumed to be less resistive than PbO, and, subsequently, the increase in polarisation resistance versus time is interpreted by the reduction of PbO_x at 700 mV.

Keywords: Alloys; Lead; Tin; Polarisation mode; Passivation layer

1. Introduction

Antimony-rich alloys have been extensively used in the lead/acid battery industry [1]. A problem associated with the utilisation of this type of alloy arises from the release of large quantities of hydrogen in valve-regulated batteries. The resulting water losses from the electrolyte must be minimised and new materials have been employed to make the grid: low-antimony (1–2 wt.% Sb) or antimony-free alloys (lead–calcium alloys or even pure lead). But other problems then appear [2]: (i) low charge acceptance for heavy-duty-cycle discharged batteries, (ii) low performance of the positive plates when processed at high temperatures, and (iii) rapid capacity loss on cycling.

All these phenomena are associated with the presence of a 'passivation' layer at the grid–lead dioxide interface. This layer acts as an energy barrier impeding electron transfer, leading to loss of capacity and a shortened cycle life of the accumulator. This layer has been identified as tetragonal lead oxide, noted as α-PbO [3–6]. The formation of this passivating α-PbO layer at the positive grid, during charging or discharging, is allowed by the presence of the sulfate layer, which acts as a semi-permeable membrane, leading to an increase of the local pH to a value close to 9 [7,8] at the grid–lead sulfate interface.

A solution to this passivation problem consists in the addition of tin, as an alloying element, to the lead. Tin has the property of decreasing the thickness of the PbO layer [9,10] and increasing the electronic conductivity of the passivation PbO layer [11,12].

In a previous paper [13], we first studied the action of tin on the electronic properties of the PbO layer using a redox couple added to an electrolyte (a borate solution) at pH 9.2. Passive layers were formed on lead–tin alloys (up to 2.5 wt.% Sn) by potentiostatic polarisation. The conductivity through the layer was evaluated by measuring the exchange-current density of the redox couple. The results showed that the layers formed on pure lead and low-tin alloys (< 1 wt.% Sn) were non-conducting. The conductivity increased sharply for alloys with 1–1.5 wt.% tin, and tended to a plateau for 1.5–2.5 wt.% Sn. A percolation mechanism was proposed to explain the modification of the conductivity of the passivation layers.

The same alloys were then polarised in 1 M H_2SO_4 solution at 400 mV versus a Hg/Hg_2SO_4 electrode. Electrochemical impedance spectroscopy studies showed that tin transformed the semi-conducting lead oxide layer (formed on a pure-lead electrode) into a highly conducting layer for tin-rich alloys ($\geq$ 1 wt.% Sn) [14].

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The objective of the present study, which takes into account the dynamic behaviour of the passivation layer, is to clarify the relationship between the electronic conductivity and the formation conditions of the passive layer for various polarisation times at different potentials.

2. Experimental

Pure lead (99.999%) and Pb–3wt.%Sn alloy were used in this work.

The growth of the passive film was monitored by a classical polarisation technique. All the potentials quoted in this study were referred to a Hg/Hg_2SO_4 saturated K_2SO_4 electrode, noted as SSE in the text.

The electrolyte was 4.5 M H_2SO_4 without and with a redox couple, which was ceric–cerous sulfates (0.01 M).

Cyclic polarisation of the electrodes were carried out with a potential scan rate of 1.1 mV/s.

The electrochemical impedance apparatus consisted of a Solartron Schlumberger 1250 frequency response analyser and a Solartron electrochemical interface. The data were processed by a Hewlett-Packard 9000 computer.

3. Results and discussion

3.1. Effect of polarisation time at 700 mV on the impedance characteristics

3.1.1. Forward polarisation

The electrodes were polarised from −1500 to +700 mV in a 4.5 M H_2SO_4 solution, with a scan rate of 1.1 mV/s. Passive layers were formed on pure-lead and Pb–3wt.%Sn electrodes by potentiostatic polarisation at 700 mV. Electrochemical impedance measurements were carried out after different polarisation times, up to 24 h.

Fig. 1(a) shows the Nyquist plots of the impedance of the pure-lead electrode. The polarisation resistance, R_p, obtained by extrapolating the semi-circle toward the real axis, increased strongly with increasing time, from 50 to 250 kΩ. At 700 mV, the pure-lead electrode can be described by the duplex structure $Pb/PbO/PbSO_4$ [2,8]. The increase of R_p can be related to the continuous growth of the PbO layer underneath the sulfate layer.

The modulus versus frequency plots is presented in Fig. 1(b). At low frequencies, the increase of the modulus with increasing polarisation time can be related to the increase of R_p. At high frequencies, the modulus is still frequency dependent, and its value increases with increase of the polar-
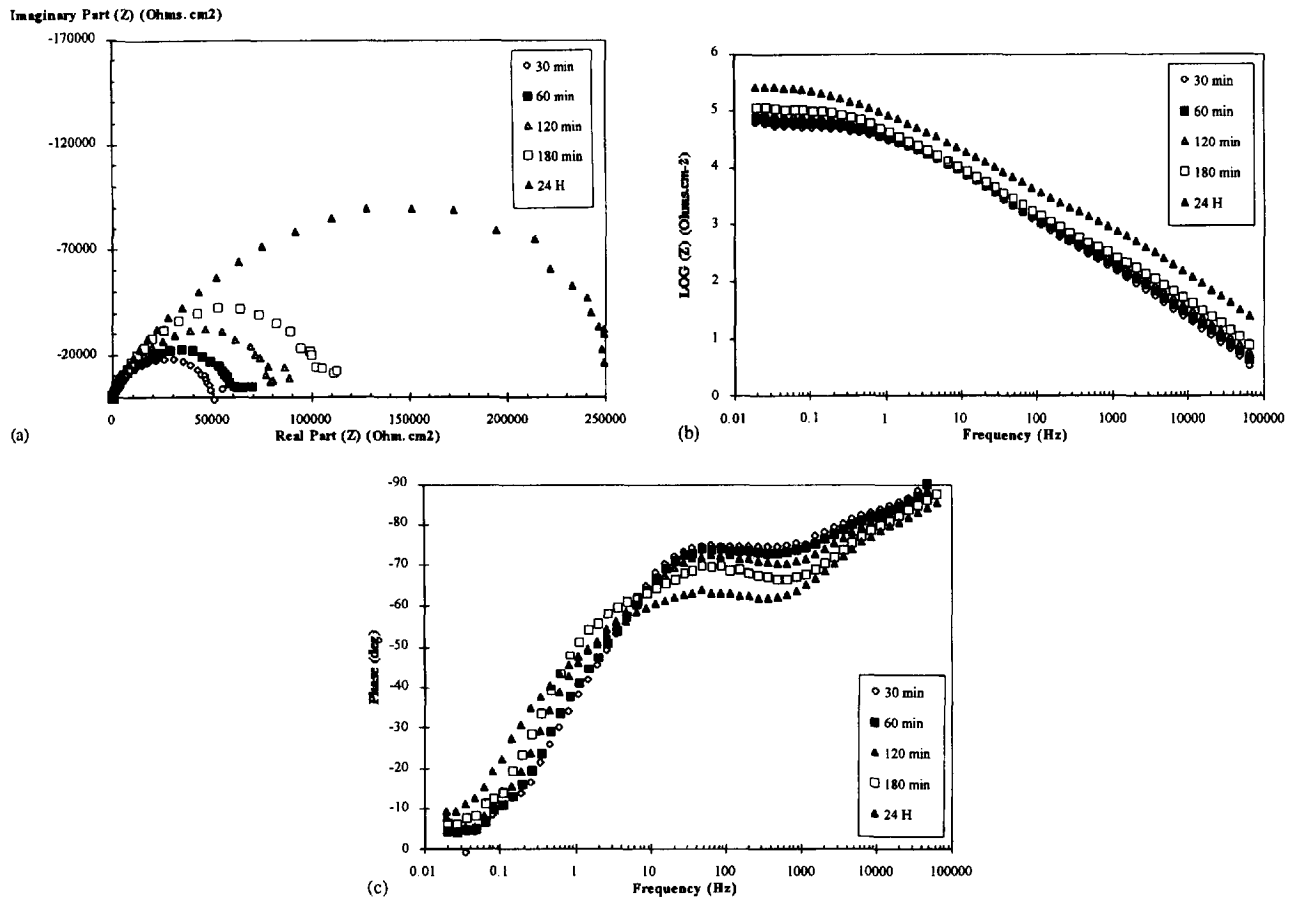

Fig. 1. Impedance plots for the pure-lead electrode, after polarisation in 4.5 M H_2SO_4 at 700 mV: (a) Nyquist plot; (b) modulus vs. frequency plot, and (c) phase angle vs. frequency plot.

isation time. This behaviour can be associated with the semi-conducting properties of the passivation layer, as shown in a previous study [15]. When the polarisation time is increased, more and more resistive PbO is formed in the layer, leading to an increase of the modulus.

Fig. 1(c) shows the phase angle versus frequency plots for the pure-lead electrode. At high frequencies, the high values of the phase angle can be also related to the semi-conducting properties of the PbO layer [15].

Fig. 2(a) presents the Nyquist plots for a Pb–3wt.%Sn electrode. Smaller values of R_p were obtained as compared with the lead electrode. R_p decreased slowly with increasing time roughly from 15 to 10 kΩ during the first three hours, and then there was a tendency for the impedance to increase at low frequencies at longer times (24 h).

The modulus versus frequency plots are given in Fig. 2(b). Here again, smaller values of the modulus are obtained as compared with the pure-lead electrode. This must be related to a decrease of the electronic resistance of the passive layer due to the presence of tin in the film, in an ionic or oxide form [11,16]. The phase angle versus frequency plots (Fig. 2(c)) confirm the same behaviour at high frequencies: first a slight increase then a decrease of the electronic conductivity.

The polarisation of pure-lead and Pb–3wt.%Sn electrodes at 700 mV showed that with increasing polarisation time more and more PbO was formed on pure lead, leading to an increase of R_p. In the presence of alloying tin, increasing amounts of

conducting tin oxide were mixed with PbO, lowering the resistance of the electrode.

3.1.2. Backward polarisation after a + 1500 mV incursion

The electrodes were polarised from − 1500 to + 1500 mV in backward direction down to + 700 mV at which the potential was kept constant and impedance measurements were carried out at various times.

The Nyquist plots for the lead electrode are presented in Fig. 3(a). The features of the impedance spectra are similar to those presented in Fig. 1(a), but R_p, which always increased with polarisation time, has smaller values, e.g. $R_p = 80$ kΩ compared with 250 kΩ (24 h at + 700 mV).

The modulus versus frequency plots, shown in Fig. 3(b), exhibit the same characteristics as those in Fig. 1(b). The effect of the polarisation time on the resistance of the passive layers can be seen at high frequencies: here again, the resistance of the films increased when the polarisation time increased. It can be assumed that between 900 and 1500 mV during the forward polarisation, PbO and PbSO₄ are partially oxidised to a less resistive, non-stoichiometric oxide PbO_x ($1 < x \leq 1.5$) [11]. On reverse sweep, when the electrode is polarised at 700 mV, PbO_x is slowly reduced to PbO. The longer the polarisation time, the more PbO is formed, thus leading to an increase of the resistance of the passive layers.

The semi-conducting properties of the films can be seen in Fig. 3(c) which presents the phase angle versus frequency
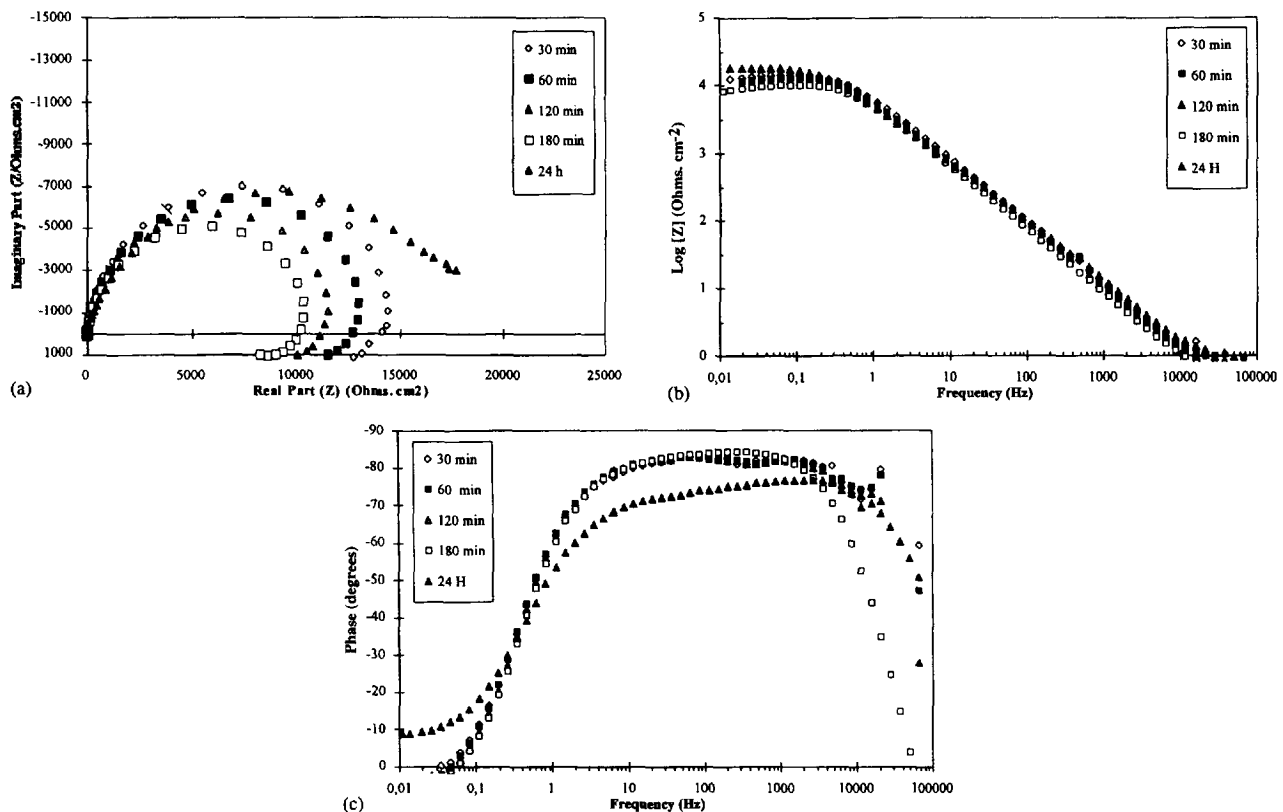

Fig. 2. Impedance plots for the Pb–3wt.%Sn electrode after polarisation in 4.5 M H₂SO₄ at 700 mV: (a) Nyquist plot; (b) modulus vs. frequency plot, and (c) phase angle vs. frequency plot.
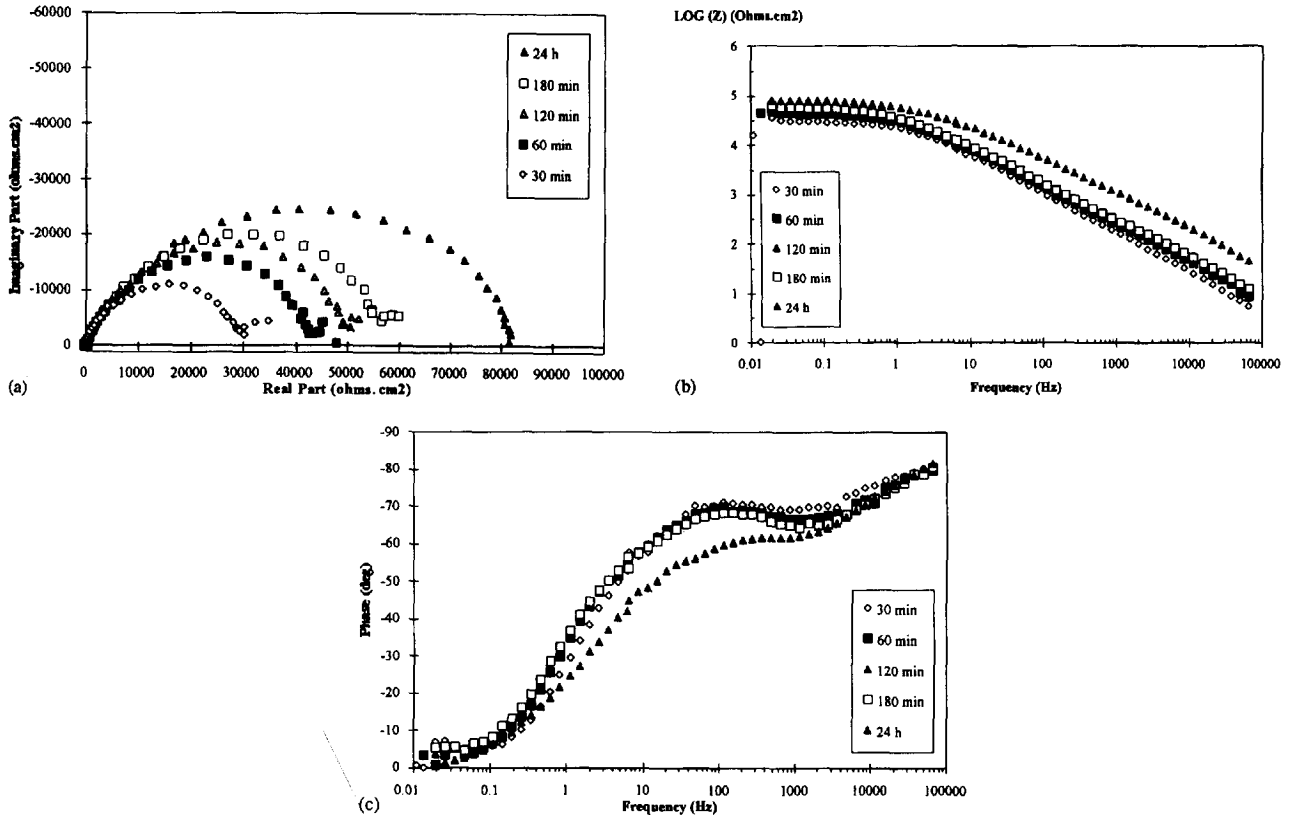
Fig. 3. Impedance plots for the pure-lead electrode polarised at 700 mV for various times, after backward polarisation from 1500 mV: (a) Nyquist plot; (b) modulus vs. frequency plot, and (c) phase angle vs. frequency plot.
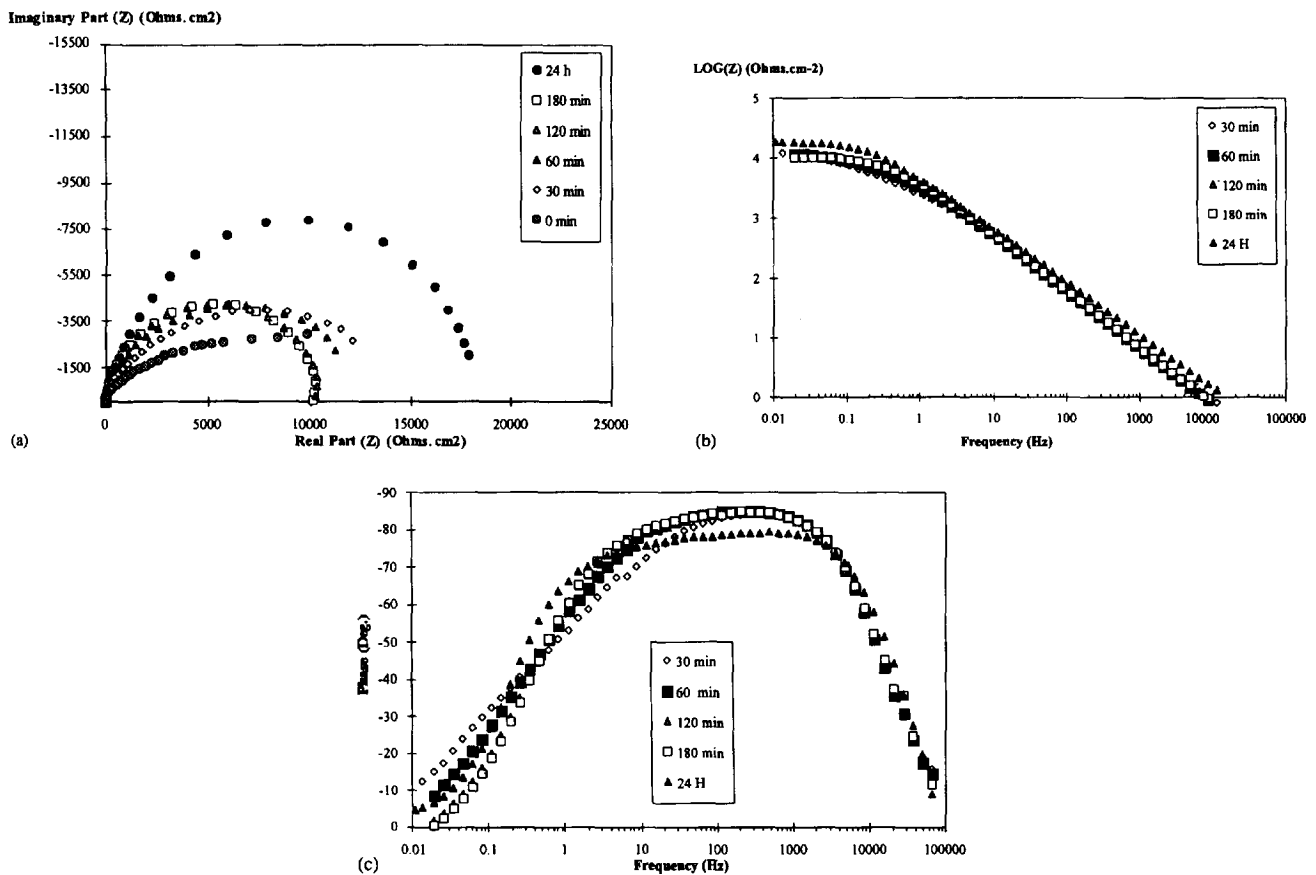

Fig. 4. Impedance plots for the Pb–3wt.%Sn electrode polarised at 700 mV for various times, after backward polarisation from 1500 mV: (a) Nyquist plot; (b) modulus vs. frequency plot, and (c) phase angle vs. frequency plot.

plots, with high values of the phase angle (near 90°) at high frequencies.

For the Pb–3wt.%Sn alloy, the Nyquist plots presented in Fig. 4(a) show that the effect of potential incursion in the PbO_2 and oxygen evolution region (+ 1500 mV) led to a decrease of R_p which has a tendency to increase slightly from 10 to 18 kΩ after long polarisation times (24 h).

The Bode plots present the same features as the plots obtained for the electrode during the forward sweep in Fig. 2. At high frequencies, the modulus versus frequency plots, see (Fig. 4(b)), show lower values as compared with the pure-lead electrode. This can be explained by an increase of the electronic conductivity of the passive layers formed on the lead–tin alloy. This result is confirmed by the phase angle versus frequency relationship presented in Fig. 4(c), indicating that at high frequencies the phase angle values tend toward 0.

From the above results, it can be stated that when the electrodes are polarised in the PbO_2 region with oxygen evolution, there is evidence of formation of another type of oxide, named PbO_x [11,12]. This type of oxide is semi-conducting but has less resistance than PbO. It was reduced slowly at + 700 mV to PbO.

3.2. Effect of high oxidation potential up to + 2000 mV

3.2.1. Cyclic voltammetry

In order to determine the influence of the anodic limit of the potential scan on the properties of the passive films formed on pure-lead and Pb–3wt.%Sn electrodes, cyclic voltamme-

try measurements were carried out from − 1500 to + 2000 mV, then back to − 1500 mV. The electrodes were removed from the experimental cell, polished with SiC paper ending with grade 1200; another potential scan was performed in the presence of a redox couple, ceric–cerous sulfate (0.01 M), dissolved in a sulfuric solution.

Fig. 5 presents the cyclic voltammograms obtained for the pure-lead electrode, with and without the redox couple. The polarisation curves of the redox system alone on a platinum electrode are also given. During the backward polarisation in the passivity range, from 700 to − 700 mV, the cathodic current was roughly 10 μA/cm². In this potential range, the electrode can be described by the $Pb/PbO/PbSO_4$ system. In the presence of the ceric–cerous couple, the cathodic current in the passivity range was the same as that previously observed without the redox couple. This means that no electron transfer occurred through the passivation layer: the layer is non-conducting.

For the Pb–3wt.%Sn alloy, cyclic polarisation curves with and without the redox couple are presented in Fig. 6. During the backward polarisation, without the redox couple, between 700 and − 700 mV, the cathodic current attained 2×10^{-4} A/cm². With the redox system, the cathodic current was 2×10^{-3} A/cm², the same value for the reduction of ceric ions on platinum. This means that the passive layer was highly electron-conducting. The increase of the conductivity can be related to the presence of tin in the PbO layer, in cationic or oxide form [11,16].
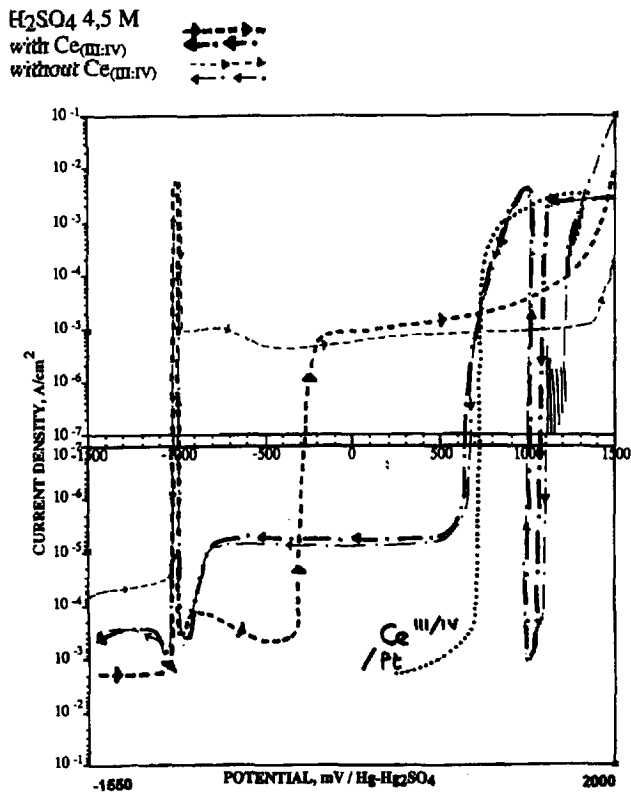

Fig. 5. Cyclic polarisation of pure lead in 4.5 M H_2SO_4 with and without a ceric–cerous redox couple (0.01 M).
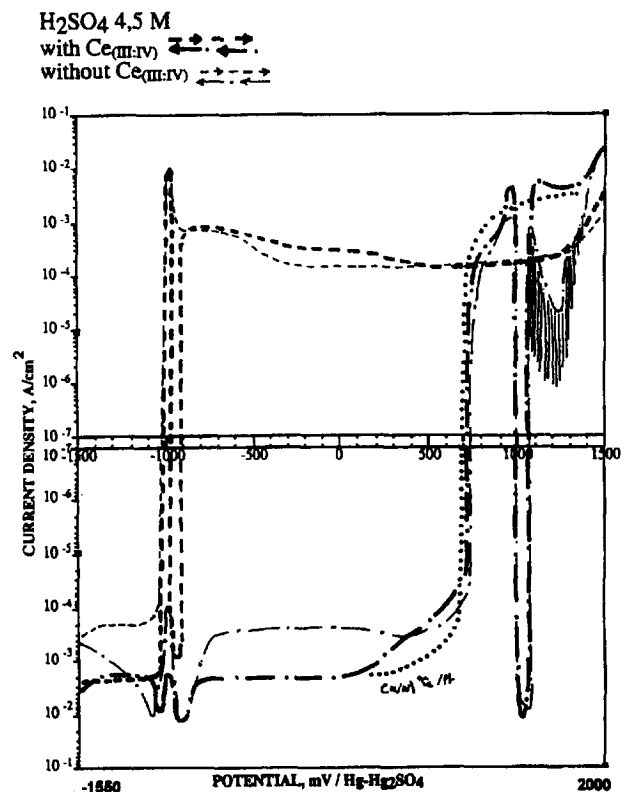

Fig. 6. Cyclic polarisation of Pb–3wt.%Sn in 4.5 M H_2SO_4 with and without a ceric–cerous redox couple (0.01 M).
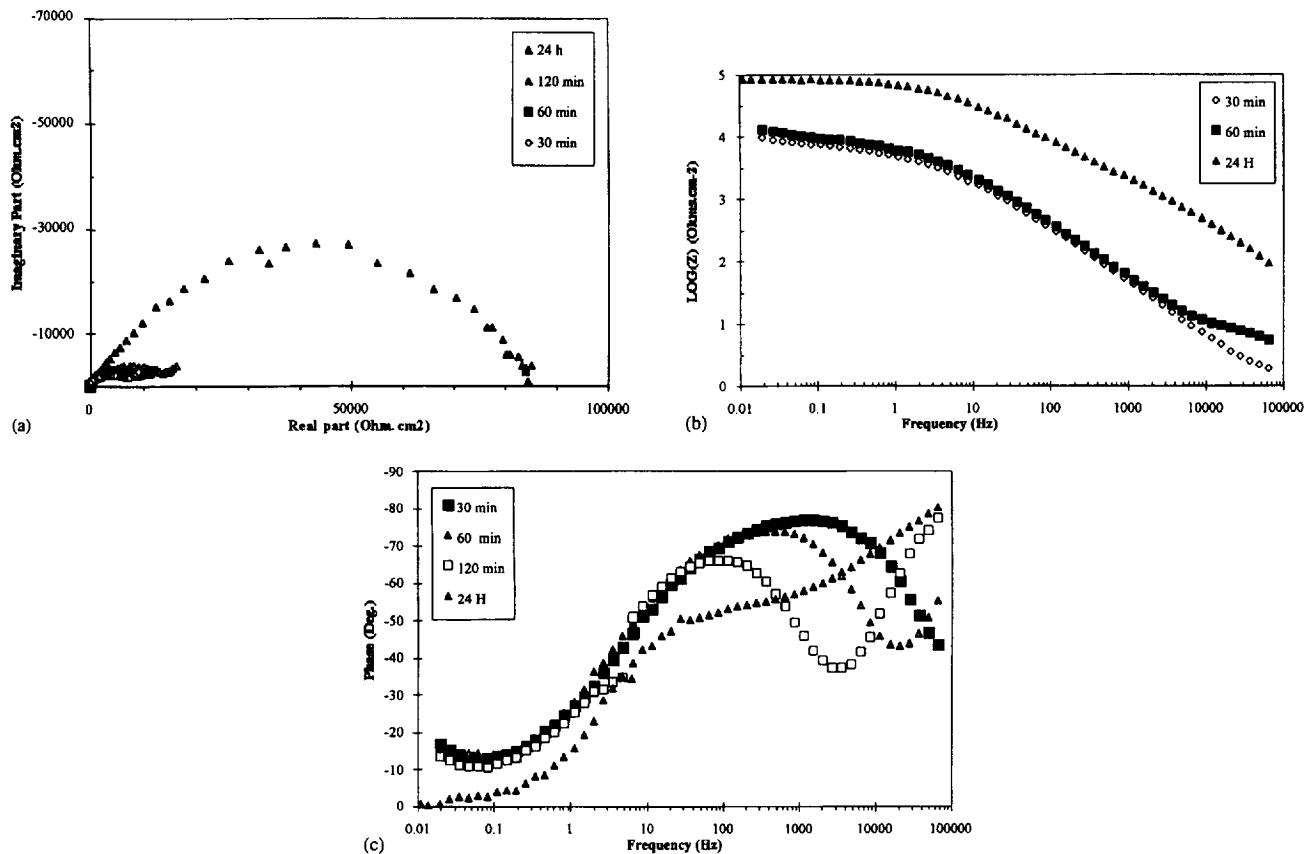
Fig. 7. Impedance plots for the pure-lead electrode polarised at 700 mV for various times, after backward polarisation from 2000 mV: (a) Nyquist plot; (b) modulus vs. frequency plot, and (c) phase angle vs. frequency plot.

3.2.2. Impedance measurements

The electrodes were polarised from − 1500 to + 2000 mV then polarised backward to + 700 mV, the electrode impedance being determined at various times.

Fig. 7(a) presents the Nyquist plots for the pure-lead electrode. The polarisation resistances were low (10–15 kΩ) during the first three hours, but increased to ∼ 80 kΩ for 24 h. A diffusion control can be seen for short polarisation times (≤3 h).

The modulus versus frequency plots (Fig. 7(b)) show the same influence of the polarisation time. For the first three hours, the moduli were two orders of magnitude lower than that obtained after 24 h of polarisation. This is clear that the conductivity of the passivation layers, observed at high frequencies, decreases when the polarisation time is increased from 3 to 24 h.

The phase angle versus frequency plots given in Fig. 7(c) indicate the evolution from a conducting layer for short polarisation time (≤3 h) to a more resistive semi-conducting one after longer polarisation times.

The Nyquist plots for the Pb–3wt.%Sn alloy shown in Fig. 8(a) are not semi-circles; a diffusion control seems to proceed through the passive layer.

The modulus versus frequency plots presented in Fig. 8(b) show the high conductivity of the passivation layer formed

on the electrode. In contrast to the behaviour of the lead electrode, the effect of the polarisation time on the conductivity of the films appears to be very small. This result is confirmed by the phase angle versus frequency plots (Fig. 8(c)) which show low values for the phase angle at high frequencies.

It is likely that after the incursion into the high potential region (2000 mV), non-stoichiometric oxide PbO_x was formed in greater quantities, leading to a greater decrease of the resistance of the passive layer. The reduction of PbO_x to PbO justifies the cathodic currents and the trends toward higher resistance with long polarisation time. When tin was present in the alloy, more tin oxide was incorporated in the PbO_x, leading to a great increase of the electronic conductivity of the passive layer. There was also a slight decrease of the conductivity for longer polarisation times, probably from the slow dissolution of tin oxide.

4. Conclusions

The study of the effect of polarisation mode (time and potential) on the properties of the passive layers formed on pure-lead and Pb–3wt.%Sn electrodes led to the following conclusions:
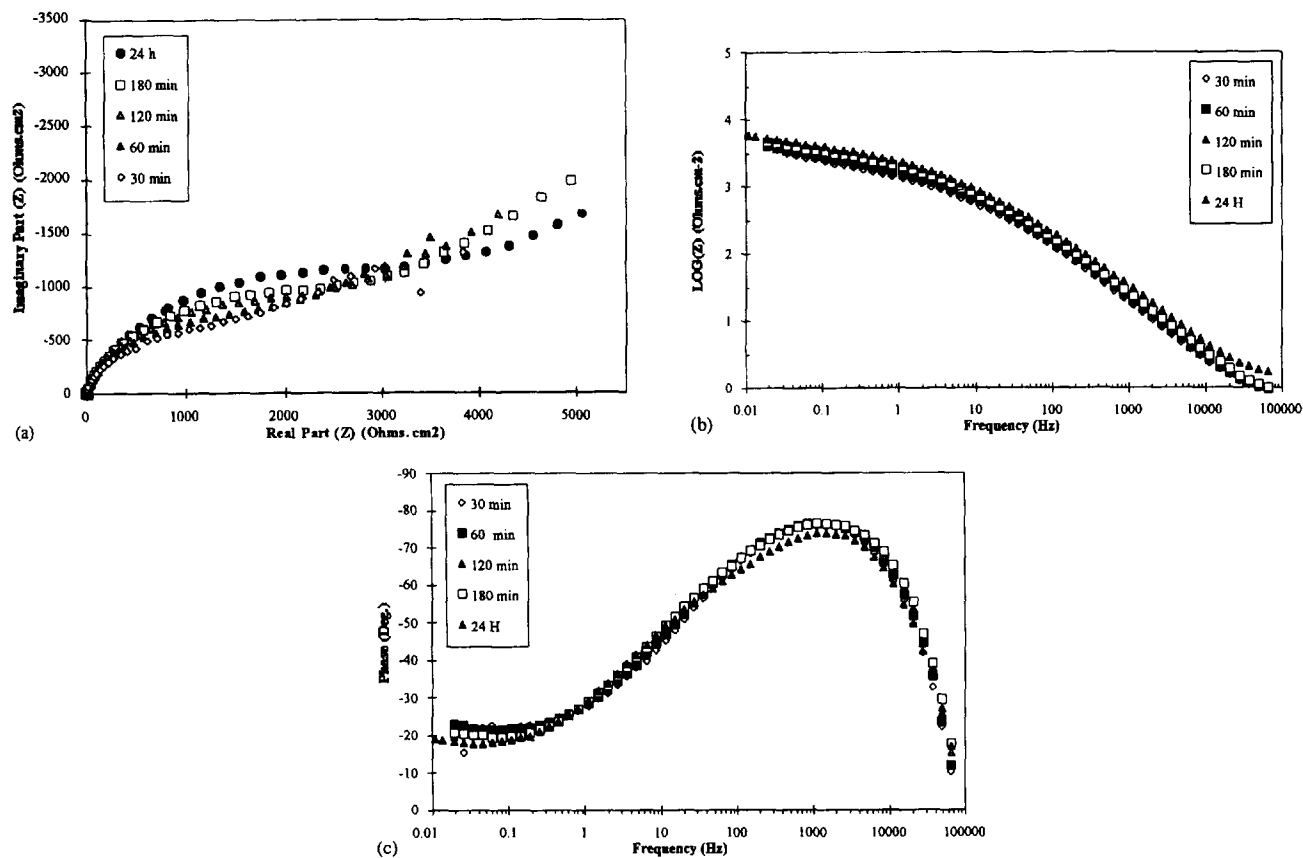
Fig. 8. Impedance plots for the Pb–3wt.%Sn electrode polarised at 700 mV for various times, after backward polarisation from 2000 mV: (a) Nyquist plot; (b) modulus vs. frequency plot, and (c) phase angle vs. frequency plot.

1. The resistance of the passivation layer, R_p, increased with increasing polarisation time in the PbO region (700 mV) probably due to the increase of the thickness of the semi-conducting PbO layer.

2. Alloying tin had the effect of increasing the electron conductivity of the passivation layer, possibly through the process of percolation with conducting tin oxide, but for long polarisation times, a decrease of the conductivity was observed. This behaviour can be explained by the slow dissolution of tin oxide in sulfuric acid.

3. After a polarisation incursion of the electrodes in the high potential region (1500–2000 mV), there was evidence of the formation of a semi-conducting PbO_x which is less resistant than PbO.

4. With increasing polarisation time at 700 mV, PbO_x was reduced slowly to PbO, leading to an increase of the resistance of the passivation layer.

Acknowledgements

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