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Effect of phosphoric acid concentration on conductivity of anodic passive film formed on surface of lead-indium alloy

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Abstract: The addition of phosphoric acid into sulfuric acid solution is mentioned to be helpful in the reduction of sulfation after deep discharge of lead-acid battery. The anodic behavior of Pb and Pb–In alloys was studied in pure phosphoric acid and sulfuric acid containing various concentrations of phosphoric. The electrochemical measurements were performed using potentiodynamic, potentiostatic and cyclic voltammetric techniques. The composition and morphology of passive layer formed on the surfaces of Pb and Pb–In alloys were characterized by X-ray diffraction (XRD), energy dispersive X-ray spectroscopy analysis (EDX) and scanning electron microscopy (SEM). The potentiodynamic study shows that the passive current density increases with increasing the indium content in the alloy in the examined solutions. The addition of 0.1 mol/L H_3PO_4 into the electrolyte is more effective to decrease the thickness of passive film on the surface of alloys containing higher indium content (10% and 15%). The XRD, EDX and SEM data reveal that the formation of PbSO₄ and PbO on the surface decreases with increasing the indium level in the alloy and is completely prevented at higher indium content (15%) in mixed acid.

Key words: lead-indium alloy; phosphoric acid; anodic behavior; passive film; lead-acid batteries

1 Introduction

Lead-acid battery has been played an active role with a long history of more than 150 years. Even though modern systems such as lithium-ion and nickel-metal hydride systems are coming up to replace lead-acid battery, however, it is still the main candidate for automotive, hybrid electric vehicles, uninterruptible power supplies, solar traffic lights, telecommunications and stationary applications [1,2]. The reason is the low abundance of lithium in the earth's crust which is a serious concern on the availability of lithium if electric vehicles become reality in the future and high efficient recycling technology is not developed [3,4]. However, up till now, there is no other battery able to compete with lead-acid battery on cost ground and recycling technology. The raw materials for their manufacture are practically unlimited, about 95% of the material can be recovered and reused. The advantages of lead-acid battery include low cost, high safety, low self-discharge and easy construction [5]. The main weaknesses of lead-acid battery system are low specific energy, negative plate sulfation and poor cyclability in partialstate of charge application. This behavior is due to the insufficient utilization of active mass and the discharge product of lead sulfate. Consequently, poor efficiency is converted back to its original form. Therefore, this leads to progressive accumulation of irreversible PbSO₄ on the negative active mass. This insulating material hinders the acid diffusion on the surface which is coupled with a loss of electrical connectivity and rapid decline in capacity. The cycle life of the batteries is determined by the reversibility of processes that proceed during charge/discharge [6]. It is important to remark that there is a number of experimental investigations in literatures, which have recently been envisaged the intimate role of the resulting microstructural array on the properties of Pb-based alloys used to manufacture various lead-acid battery components [7,8] as potential alternatives to alloys currently used. In this regard, much attention is now focused on the negative active mass which must be well combined with a conductive additive and possibility the effective means of eliminating these problems. The problem in using Pb-Sn alloys as grid material in the lead-acid battery is the observed decrease of conductivity for long periods of time. This behavior was explained by the slow dissolution of tin oxide in

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 H_2SO_4 [9]. Indium alloying with lead suppresses the growth of PbO phase. Accordingly, the corrosion of Pb into PbO can be controlled or can be prevented by incorporating indium in the lead [10]. Consequently, the conductivity of passivation layer on the Pb-In alloy is improved. Phosphoric acid is an interesting additive to H₂SO₄ solution used in lead-acid batteries to improve the performance [11-17]. H₃PO₄ is mentioned to be helpful in the reduction of the sulfation after deep discharge, increasing the life cycle and slowing down the discharge [18-21]. The overpotentials of both hydrogen and oxygen evolution reactions increase, while the capacity decreases with the addition of phosphoric acid [11,12]. Some electrochemical studies have indicated the improvement of formation of PbO₂ with the addition of H₃PO₄ [22], but the results of other studies supported the opposite effect [17,23]. The effect of H₃PO₄ on the nature of the products formed potentiostatically on Pb-1.7%Sb alloy and the self-discharge of the anode was studied by ABD EL-RAHMAN et al [24].

In our previous work [25], we have studied the effect of indium alloying with lead on the corrosion behavior of lead in phosphoric and sulfuric acids containing various concentrations of phosphoric acid. This study was conducted in the examined acid solution using Tafel plot extrapolation in the range of active region (\pm 200 mV) and electrochemical impedance spectroscopy measured at φ_{corr} . The authors aimed to study the effect of both indium content and concentration of phosphoric acid on the conductivity of the anodic passive film formed on the surface. This study is complementary to the previous work.

2 Experimental

2.1 Materials and solutions

4 mol/L stock solutions of H₂SO₄ and H₃PO₄ (analytical grade) were prepared by dissolving appropriate volume of H₂SO₄ and H₃PO₄ in doubly distilled water, respectively. The mixed acids were prepared from 4 mol/L H₂SO₄ and various concentrations of H₃PO₄ (0.05, 0.1, 0.15, 0.2 mol/L). Pb and In of high purity (99.999%) were used to prepare Pb-In alloys as disk electrodes (A=0.196 cm²) in a muffle furnace using evacuated closed silica tubes at 500 °C for 24 h. The melts were shaken every 6 h to ensure the homogeneity of the molten. Finally, the molten was quenched in ice as previously reported [26]. Five samples of Pb-In alloys with different In contents (0.5%-15%, mass fraction) (Table 1) were prepared in the same procedures. The prepared alloys were analyzed using X-ray photoelectron spectroscopy (XPS). For each alloy, the fractions of Pb and In were found in accord with the fraction of mixing

Pb and In. The microstructure of alloy was investigated in our previous work [8] by X-ray diffraction (XRD) and scanning electron microscopy (SEM). The XRD peaks appear at the same positions as long as the indium content does not exceed 15%. The observed broadness of the peaks may be due to the lattice distortion or grain refinement. Noteworthy, such change in the morphology demonstrated by SEM beside the change in the microstructure due to the concentration of dilute lead–indium alloy has significant effect on both the microhardness and corrosion.

Table 1	Com	position	of Pb-	-In	alloy	vs
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Alloy No.	Composition	
Ι	Pb _{99.5} In _{0.5}	
II	Pb ₉₉ In _{1.0}	
III	Pb ₉₅ In _{5.0}	
IV	IV $Pb_{90}In_{10}$	
V	Pb ₈₅ In ₁₅	

2.2 Electrochemical measurements

The measurements were performed on planar disk electrodes embedded in an Araldite holder. Prior to each measurement, the electrodes were polished with sequacious grades of emery paper, degreased in pure ethanol and washed in running bidistilled water before being inserted in the polarization cell. A conventional three-electrode system was used; the counter electrode was a Pt sheet with an area of 1 cm \times 2 cm. The reference electrode was a saturated calomel electrode (SCE) to which all potentials were referred. To avoid contamination between electrolyte and the solution of calomel electrode, the reference electrode was connected to the working electrode through a jacket filled with the solution under test. The jacket was elongated in the form of a Haber-Luggin capillary provided with G₄ sintered glass, which was placed at a distance of about 0.1 mm from the working electrode. The cell description was given elsewhere [27]. To remove any surface contamination and air formed oxide, the working electrode was kept at -1.5 V for 5 min in the tested solution, disconnected, and was shaken free of adsorbed hydrogen bubbles. Then, each electrode was left in the solution (30 min) to reach steady state potential (φ_{ocp}) before the anodic polarization measurements. Potentiostat/galvanostat (EG&G Model 273) connected with a personal computer (IBM Model 30) was used for the measurements. Softwares 342 C and version 270 (used for cyclic voltammetric measurements) supplied from Princeton Applied Research were used for all the electrochemical measurements. Cyclic voltammograms of the pure Pb and Pb-In alloys as electrodes in 4 mol/L H_3PO_4 solution and potential region of -1.2 to 2.0 V (vs

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SCE) (-1.640 to 1.560 V vs SME) were obtained at various sweep rates.

In the case of potentiodynamic measurements, the potential was altered automatically in the positive direction from the open circuit potential (φ_{ocp}) up to 2 V (vs SCE) (1.560 V vs SME) and at scan rate of 1 mV/s. In some potentiostatic experiments, the anodic potential was fixed at required constant value and the variation of current density was recorded as a function of time (current density-time transients). The details of experimental procedure have been described elsewhere [28].

2.3 Surface characterization

The structure of the corrosion products formed on the surfaces of Pb and Pb-In alloys was detected by X-ray diffraction (Brucker AXS-D8 Advanced diffractometer) using Cu K_a radiation (λ =1.5418 Å). The compositions and morphologies of corrosion products formed on the surfaces of electrodes were examined by scanning electron microscopy (SEM) equipped with energy-dispersive X-ray spectroscopy (EDX) (SEM-EDX) (JEOL, model 5300). Each experiment was performed with freshly prepared solution and a clean set of electrodes. Measurements were conducted at 20 °C for each investigated electrode. For this purpose. ultrathermostat model Frigiter 600 382 (SELECTA) was used.

3 Results and discussion

3.1 Behavior in phosphoric acid solution

Figure 1(a) shows a comparison between the potentiodynamic anodic polarization curves of pure lead and its alloys in 4 mol/L H₃PO₄ solution. The polarization curves were swept from the steady state of open circuit potential (φ_{ocp}) up to 2 V (vs SCE) (1.560 V vs MSE) at scan rate of 1 mV/s and 20 °C. The curves reveal that the anodic excursion exhibits active-passive transition of both lead and lead-indium alloys. The active dissolution region involves two well-defined anodic peaks $A_{\rm I}$ and $A_{\rm II}$ in the case of pure lead and alloys I-III. However, additional peak A is observed for alloys IV and V (high In content). The curves show that the peak A_I is followed by passive region, which extends up to 1.2 V (vs SCE) (0.76 V vs SME) which showed slightly increase of current density with shifting the potential to more positive direction (up to the appearing of A_{II}). This means that partial dissolution of the passive layer in the solution occurs.

The anodic peak A_I is located at about -0.406 V (vs SCE) (-0.846 V vs SME) for pure lead, which can be associated with the active dissolution of Pb to Pb²⁺ species according to Reactions (1) and (2) [16]

$$Pb \rightarrow Pb^{2+}+2e$$



Fig. 1 Potentiodynamic anodic polarization curves of Pb and its alloys (a) and effect of indium content in alloy on passivation current density (b) in 4 mol/L H_3PO_4 solution at 20 °C

$$Pb^{2+} + HPO_4^{2-} \rightarrow PbHPO_4$$
(2)

where Pb2+ and HPO42- ions exceed the solubility product of PbHPO₄, it precipitates on the electrode surface and this current density drops, suggesting the onset of the primary passivation at a potential comparable with the equilibrium potential of the system Pb/PbHPO₄. However, the results show that the peak A_I potential of the alloy shifts towards more negative values with increasing the indium content in the alloy compared with that related to pure Pb. This behavior confirms that the tendency of the alloy towards passivity increases as a result of the presence of indium alloying with lead. This means that the formation of InPO₄ is responsible for the negative potential shift of the anodic oxidation peak A₁. This indicates that with the increase of alloying indium, the anodic layer formed on Pb-In alloys is more porous than that formed on pure lead. Consequently, the diffusion of phosphoric acid electrolyte to the inner of active material becomes more easier [16]. Accordingly, the peak A_I current density increases with increasing the In content in the alloy.

(1)

On the other hand, the small anodic peak A_{II} observed at about 1.223 V (vs SCE) (0.783 V vs SME) in the case of pure lead shifts to more positive values and the peak current density increases with increasing the In content. This peak may be attributed to the oxidation of Pb²⁺ and PbHPO₄ to β -PbO₂ according to the following reactions:

 $PbHPO_4 + 2H_2O \rightarrow \beta - PbO_2 + H_3PO_4 + 2H^+ + 2e$ (3)

and/or

$$Pb^{2+}+2H_2O \rightarrow \beta - PbO_2 + 4H^+ + 2e$$
(4)

This indicates that indium can promote the oxidation reaction and leads to the increase of oxidation peak current density. It is interesting to observe that small anodic peak A appears only in the case of alloys IV and V. This peak is attributed to the oxidation of In to $InPO_4$ or In_2O_3 , which is due to the higher content of indium. This peak is confirmed by XRD which will be discussed later.

The data in Fig. 1(b) show that, the passivation current density increases gradually with increasing the indium content. This exhibits that indium alloying with lead decreases the thickness of the passive film and increases the electric conduction of the corrosion layer, consequently, the conductivity of this layer increases. These results support the role of indium in the inhibition of the formation of PbO [29]. In other words, a thinner passive layer in the case of indium alloying with lead can form. This means that the passive layer is defective and facilitates the transport of the reactant and product species at higher indium content [24]. This behavior confirms that indium passivates Pb from its oxidation to PbO.

In order to establish that the current density of passivation increases with increasing the indium content in the alloy at passive region (1.3 V vs SCE, or 0.860 V vs SME), potentiostatic measurements of Pb and alloys I and V are examined. Figure 2 shows the current densitytime transient curves of Pb and alloys I and V in 4 mol/L H_3PO_4 solution at 20 °C. The data exhibit that the current density initially decreases gradually with increasing the time. This indicates that the oxides of Pb and In form on the surface of each electrode and the current density at this time may correspond to the film formation repairing the film material [30]. The curves exhibit that immediately after switching on the applied potential (1.3 V vs SCE, or 0.860 V vs SME), the value of current density of pure Pb is low compared with those of the two alloys. Accordingly, the current density of the alloy V remains at a maximum value. Finally, the data exhibit that the steady state value of current density in the case of alloy V is higher than that of pure lead and alloy I. The results suggest that the alloy surface is less protected, maybe due to the formation of another type of oxide

semi-conducting, but less resistant than PbO. These results support the potentiodynamic behavior of the investigated electrodes at the same applied potential.



Fig. 2 Curves of potentiostatic transients's current density vs time for Pb alloys I and V in 4 mol/L H_3PO_4 solution at passive region (1.3 V) and 20 °C

Figures 3(a) and (b) shows typical voltammograms of Pb and alloy V in 4 mol/L H_3PO_4 solution measured at different scan rates, each electrode was kept for 60 s at -1.5 V, then the potential was swept from -1.2 V up to 2 V (vs SCE) (-1.64 V up to +1.56 V vs SME) with different scan rates (5 to 40 mV/s). The data reveal that on the positive going sweep, a small cathodic current



Fig. 3 Cyclic voltammograms of Pb (a) and alloy V (b) in 4 mol/L H_3PO_4 solution at various scan rates and at 20 °C

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density plateau P₁ appears just before the corrosion potential. This plateau corresponds to hydrogen evolution reaction on the electrode surface. After the corrosion potential, the voltammograms show an active-passive behavior. The passivity region extends after the formation of PbHPO₄ until the apparent of oxygen evolution at ~1.7 V (vs SCE) (1.260 V vs SME). The active dissolution region involves one anodic peak A_I for pure Pb, and two for alloy V. The peak A_I of both Pb and alloy V can be attributed to the formation and growth of PbHPO₄ and Pb oxide on the surface. However, the additional peak A which is observed in the case of alloy V can be attributed to the oxidation of indium to InPO₄ (Fig. 3(b)). Moreover, the peak (A_{II}) potential of both pure lead and alloy V appears at reverse scan (at a potential close to 1.130 V vs SCE) (0.690 V vs SME), but the current density of this peak A_{II} is observed in the positive anodic direction. This criterion is very important and has a strange behavior, which can be interpreted on the basis of reactivation peak. This observation can be due to the rupture of the passive film and active dissolution of the metal in the presence of that film [27]. In more details, the rupture of the film can be attributed to the formation of a large molar volume of PbHPO₄ on the surface, which leads to surface cracks exposing the bare metal [31]. These parts of the pare surface are then oxidized at reverse scan potential. Also, at a continuous negative-going scan, a small peak C_{II} appears at -0.7 V (vs SCE) (-1.14 V vs SME) corresponding to the reduction of PbO underneath the passive layer only in the case of pure lead. At more negative potential (C_I) , PbHPO₄ is reduced to Pb metal. However, it is interesting to observe that the peak (C_{II}) related to the reduction of PbO at negative back scan is not observed in the case of alloy V. This indicates that the formation of PbO on the alloy surface is completely hindered with the addition of indium to lead. In addition, more negative cathodic peak (C) of alloy V is observed, and may be related to the reduction of indium oxide into indium. It is believed that indium oxidation in the alloy changes the composition of the anodic layer. Consequently, the anodic layer on the lead-indium alloy surface is more porous than that on pure Pb.

It is observed that the current density of anodic peaks increases, while the peak potentials shift to more positive values with increasing the scan rate. This observation can be discussed on the basis that, during the cyclic voltammogram tests, electroactive species are progressively removed in the vicinity of the electrode, somehow causing a current limitation [32]. The anodic reaction Pb+HPO₄²⁻→PbHPO₄+2e is apparently limited by the depletion of HPO₄²⁻ ions in the neighborhood of the electrode. A slow scan rate increases this limitation, thereby reducing the height of peak. However, a fast scan

rate decreases the current limitation, thus increasing the magnitude of peak.

The anodic peak current density J_p versus $\upsilon^{1/2}$ (υ is the scan rate) shows linear behavior (Fig. 4) in agreement with the following equation [28]:

$$J_{\rm p} = abZ^{1/2}CD^{1/2}\upsilon^{1/2}$$
(5)

where a and b are constants, Z is the number of exchanged electrons, C is the concentration and D is the diffusion coefficient of the species into the solution. This result suggests that the dissolution of Pb and its alloys is under diffusion control by mass transport into the solution.

Cyclic voltammograms of pure Pb, Pb-0.5% In and Pb-15% In alloys in 4 mol/L H₃PO₄ solution at scan rate of 10 mV/s are compared (the curves are not presented here). Generally, the anodic oxidation peak A₁ slightly shifts to more positive potential, and the peak current density of alloy V is higher compared with that of pure Pb and alloy I. Thus, it can be established that the formation of passive layer of lead oxide on the alloy surface requires a larger over-potential than that on pure lead [33]. This behavior can be ascribed to that alloying indium decreases the thickness of passive PbO layer on the alloy surface. MUKHOBADHYAY et al [34] reported the anodic oxidation of Pb-In alloys in the alkaline solution. They found out that the oxidation of Pb into PbO or PbO₂ can be retarded or even prevented by indium alloying with lead. As mentioned above, small anodic peak A is observed only in the case of alloy V (15% In). By increasing the indium content (up to 15%), the peak related to the reduction of PbO at negative back scan was not observed compared with that of pure Pb and low indium content alloys (0.5% to 10%). This indicates that the formation of PbO on the alloy surface is completely hindered by reaching high indium content in the alloy.

3.2 Anodic behavior in mixed acid

The curves in Fig. 5 show the comparison between potentiodynamic anodic polarization of Pb with its alloys in 4 mol/L H_2SO_4 solution containing 0.05 mol/L H_3PO_4 at 20 °C. The anodic sweep exhibits active/passive behavior. The active dissolution region shows two anodic peaks A_1 and A_{II} prior to the permanent passive region in the case of Pb. The first peak is located at about -0.506 V (vs SCE) (-0.946 V vs SME), and can be associated with the active dissolution of Pb to PbSO₄ according to Reactions (1) and (6):

$$Pb^{2+} + SO_4^{2-} \rightarrow PbSO_4 \tag{6}$$

while the peak A_{II} appears at about -232 mV which can be related to the electro-oxidation of Pb to PbO. PbO is insoluble and precipitates [35] on the lead surface, giving



Fig. 4 Relation between anodic peak current density J_p and $v^{1/2}$ (v is scan rate) of Pb (a), alloy I (b) and alloy V (c) in 4 mol/L H₃PO₄ at 20 °C

rise to a passivation film. However, the current density starts to slightly increase again at potentials between -0.1 and 0.250 V (vs SCE) (-0.540 and -0.190 V vs SME). This behavior is attributed to the partial dissolution of PbSO₄ in the solution at this region. A partial stabilization on the current density is observed between 0.250 and 1.400 V (vs SCE) (-0.190 and 0.960 V vs SME). The passive region extends after the formation of lead oxides until the apparent onset of oxygen evolution at about 1.420 V (vs SCE) (0.980 V vs



Fig. 5 Potentiodynamic anodic polarization curves of Pb and its investigated alloys in 4 mol/L H_2SO_4 solution containing 0.05 mol/L H_3PO_4 at 20 °C

SME). However, these curves of the alloys reveal that indium alloying with lead has influence of increasing the peak current density. The peak AI current density gradually increases, while the peak A_{II} current density gradually decreases with increasing the In content. In addition, peak A_{II} completely disappears at higher indium content (15%). This behavior can be attributed to the presence of indium with lead, retarding the formation of PbO on the surface. Here, it can be concluded that indium inhibits the oxidation of Pb into Pb²⁺, which is completely prevented at higher In content. However, the current density of the passive region increases with increasing the In content. These results suggest that the alloy surface is less protected, most probably by the formation of more porous anodically formed films of mixed oxides from both indium and Pb [36]. Furthermore, it can be assumed that the presence of indium as alloying element decreases the passive film. This indicates that higher indium content in the alloy prevents the formation of both PbSO₄ and PbO [10]. Therefore, it can be concluded that the electrochemical conduction of this oxide is largely enhanced by the presence of In₂O₃ at high content. This indicates a significant change in the composition of passive layer in the presence of indium, most probably via the thinning of PbSO₄ layer and/or co-deposition of PbHPO₄. This suggestion is supported by increasing the passive current density with indium content. These changes indicate a thinner and less protective PbSO₄ layer in the presence of H₃PO₄ on the alloy surface. It is assumed that the formation of PbHPO₄ and InPO₄ in addition to the decrease of PbSO₄ is the reason behind the significant changes, especially the diffusion characteristic of passive layer. The previous studies on the oxidation of Pb alloys in H₃PO₄ have showed that the passive layer containing PbHPO₄ was porous [1,15]. Therefore, this indicates that

the effective diffusion coefficient of soluble species through the passive layer containing $PbHPO_4$ is higher than that in the H_3PO_4 free solution.

The starting potential of oxygen evolution shifts to more positive direction with increasing the indium content up to 1%, and then starts to relatively shift to less positive direction with increasing the In content more than 1% (but still higher than that of pure Pb). This indicates that the addition of indium to Pb delays the oxygen evolution reaction. This means that In alloying with Pb has an influence on the increase of oxygen over-potential. This exhibits that the presence of indium in the alloy significantly inhibits the oxygen evolution reaction [37]. The most pronounced effect of In alloying with lead is the disappearance of the fluctuation recorded in the case of Pb (Fig. 5). This behavior may be attributed to the nucleation and growth of In₂O₃ together with the deposition of PbHPO₄ on the alloy surface. A similar trend is observed for Pb and its alloys in other investigated different mixed acids (4 mol/L H₂SO₄ with each of 0.1 mol/L, 0.15 mol/L and 0.2 mol/L H_3PO_4).

The data in Fig. 6 show the relation between the passivation current density and indium content in H₂SO₄ solution containing various concentrations of H₃PO₄ at 0.500 V (vs SCE) (0.060 V vs SME) and 20 °C. Generally, the data exhibit that the passivation current density (J_{passive}) increases gradually with increasing the In content. This indicates that indium improves the conductivity of the passive film on the alloy surface by promoting the formation of β -PbO₂, having lower resistance values than those of both PbSO₄ and PbO [38]. It is suggested that, with the incorporation of indium in the Pb, the formation of PbO is impeded and the thickness of the passivation layer decreases as the indium level increases. The general proposed mechanism can be suggested as disproportion reaction according to the following reaction:

$$2In+3PbO \rightarrow In_2O_3+Pb \tag{7}$$

This study exhibits that indium ions have an acidic character and inhibit the nucleation and the growth of PbO which is stable in alkaline medium [39]. Therefore, indium alloying with Pb increases the amount of nonstoichiometric oxide and facilitates the formation of a more highly conductive corrosion layer on lead. Higher J_{passive} values are obtained in H₂SO₄ solution containing 0.1 mol/L H₃PO₄, particularly for alloys containing higher In contents more than 1%. However, the lower values of the passive current density are obtained with the addition of 0.2 mol/L H₃PO₄. These data show that, the addition of 0.1 mol/L H₃PO₄ to the electrolyte becomes more effective to decrease the passive film. But, the phosphate anions act as a passivity promoter in the presence of 0.2 mol/L H₃PO₄. This indicates that, the addition of higher concentration (0.2 mol/L) of H_3PO_4 leads to the improvement of the passivation properties of the barrier PbSO₄ layer [40]. Therefore, one can conclude that the addition of 0.1 mol/L H_3PO_4 decreases the resistance of the oxide layer on the alloy surface. Thus, 0.1 mol/L H_3PO_4 is the optimum concentration to be added to sulphuric acid in order to improve the efficiency of the lead acid batteries.



Fig. 6 Effect of indium content in alloy on passivation current density in 4 mol/L H_2SO_4 solution containing various concentrations of H_3PO_4 at 500 mV (vs SCE) and 20 °C

Figure 7 represents the current density-time transient curves of Pb, Pb-0.5%In and Pb-15%In alloys in 4 mol/L H₂SO₄ solution containing 0.05 mol/L H₃PO₄ at 1.3 V (vs SCE) (0.860 V vs SME) and 20 °C. It is observed that the current densities of the investigated electrodes initially decrease gradually with increasing the time. This exhibits that the thickness of the passive film on the surfaces of Pb and the two investigated alloys (I and V) tends to increase with increasing the time. In other words, the passive film becomes more resistive and



Fig. 7 Potentiostatic transient's current density vs time curves of Pb, Pb–0.5%In and Pb–15%In alloys in 4 mol/L H_2SO_4 solution containing 0.05 mol/L H_3PO_4 at passive region (1.3 V) and 20 °C

inhibits the transport of the corrosive species [15]. The curves in Fig. 7 exhibit that, immediately after switching on the applied potential (1.3 V vs SCE or 0.860 V vs SME), the value of the current density of Pb–15%In alloy is high compared with those of both pure Pb and alloy containing lower indium content (0.5% In). Consequently, the current density remains at a maximum value for the alloy containing 15% In. These results show that the presence of indium in the alloy decreases the thickness of the passive film, consequently, the film becomes more conducting with increasing the indium content. This clearly indicates the transformation of PbO to the conducting β -PbO₂ with the addition of indium to lead which has a resistance lower than those of both PbSO₄ and PbO.

The increase of passive current density with the addition of indium to lead may be discussed on the basis that, the liquid among the gaps in β -PbO₂ is the main ion transport [41], which further enhances the corrosion process in the presence of In alloying with lead. As a result of the enhancement of both ion and electrontransportation, the passive current density increases with increasing the indium content. It may be that indium is segregated at the grain boundaries, leading to severe intergranular corrosion. Consequently, the intergranular corrosion destroys the integrity of the passive layer, causing the increase of passive current density [42]. The data suggest that the content of indium alloying with Pb in the mixed acid does not take part in the electrochemical reaction, but indium can promote the oxidation reaction and leads to the increase of passivation current density. The porosity-producing effect of indium in anode should probably be the main reason for the capacity increase in lead-acid battery. In₂O₃ as an alkaline oxidant comes into the alloy surface, and then dissolves in the mixed acid solution, and the apertures lead to the increase of passive current density compared with that of Pb. LIANG and WANG [43] showed that indium alloying with zinc improves the anodic activity of zinc electrode and delays the possibility of passivation. For this reason, it is interesting to see that, both of the initial and steady state current densities of the investigated alloys increase with increasing the In content. Similar behavior is observed in the presence of higher additions of H_3PO_4 (0.1, 0.15 and 0.2 mol/L) in some studied electrodes. These results clearly show that the higher concentration of H_3PO_4 has the ability to decrease the breakdown of passive layer. This indicates that, in the potential region of β -PbO₂ formation (>1.0 V), diffusion is more difficult in the presence of higher concentration of H₃PO₄ [3].

This behavior confirms that the tendency of the alloy towards passivity decreases as a result of the presence of indium in the alloy. This behavior displays the beneficial effect of the indium alloying with lead, which decreases the formation of oxide film on the alloy surface. This indicates that the addition of indium into Pb improves the charge efficiency and self-discharge of Pb, which can be used as anodes in batteries. Consequently, this work gives rise to improve battery grids alloys which are stronger and more corrosion resistance than conventional Pb-Sn alloy. Due to their advantages, these new grid materials will initiate many new lead-acid battery designs. Accordingly, they may be developed to replace the traditional Pb-Sn alloys which have been used for many years. Significantly, one can conclude that indium alloying with lead provides a good acid battery with the addition of H₃PO₄ to the electrolyte solution, which is due to its more conductivity in the passive region compared with that of pure lead.

3.3 Composition and properties of passive film

3.3.1 X-ray diffraction

Figures 8(a) and (b) represent the XRD patterns of passive film formed on the surfaces of Pb and alloy V (15% In) after anodic potentiostatic polarization treatment in 4 mol/L H_3PO_4 solution for 20 min at the potential of passive region (0.250 V vs SCE or -0.190 V



Fig. 8 XRD patterns of passive films on surfaces of Pb (a) and Pb-15%In alloy (b) formed anodically in 4 mol/L H_3PO_4 solution at 20 °C

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vs SME). The data for the composition nature of passive film on the Pb surface confirm the existence of Pb, β -PbO₂, PbO and (Pb)₃(PO₄)₂. This indicates that the passive film formed on the Pb surface is β -PbO₂, PbO and (Pb)₃(PO₄)₂. However, the data in Fig. 8(b) for alloy V indicate that the surface is covered by β -PbO₂, In₂O₃ and InPO₄. By comparing the results in Fig. 8(a) with those in Fig. 8(b), it is interesting to see that the peaks related to PbO disappear in the case of alloy V. This observation supports our suggestion that In alloying with Pb, particularly at high In content, prevents the formation of semiconducting PbO. The XRD analysis is used to establish that the small peak A which appears at potential for anodic potentiodynamic polarization of alloy V in 4 mol/L H₃PO₄ is related to the oxidation of In to indium oxide. The data reveal that the surface contains Pb, In₂O₃ and InPO₄. This result implies that the peak (A) potential can be attributed to the oxidation of In to In₂O₃ and InPO₄. This indicates that the high In content in the alloy (15%) leads to the appearance of this peak.

The XRD data of Pb and alloy V (not represented here) treated potentiostatically in mixed acid (4 mol/L H₂SO₄ + 0.1 mol/L H₃PO₄) at passive potential region show that the surface of pure Pb is covered by a mixture of PbSO₄, (Pb)₃(PO₄)₂, β -PbO₂ and PbO. However, the data obtained for alloy V show the existence of β -PbO₂, In₂O₃ and InPO₄. It is very interesting to observe that PbO and PbSO₄ disappear in the case of alloy V (15% In). This further confirms that PbO and PbSO₄ can not form at higher In content.

3.3.2 SEM images and EDX spectroscopy

Figures 9(a)-(c) represent the SEM images of Pb, Pb-0.5% In and Pb-15% In alloys, respectively, where the anode surface is obtained from experiments performed at anodic potential (1.2 V vs SCE or 0.760 V vs SME) for 20 min in 4 mol/L H₃PO₄ solution. Figure 9(a) shows that the surface of pure Pb seems to be completely covered by the passive film. However, the particles formed on the alloy surface (0.5% In, Fig. 9(b)) are lager in size and the vacancies between them become wider compared with those on the surface of pure Pb (Fig. 9(a)). Figure 9(c) shows that the presence of higher In content in the alloy retards the formation of Pb oxides on the surface. It is clear that the particles formed on the surface are few in number, and their size is much bigger compared with those of both Pb and alloy I. These results show that high In content alloying with Pb aids in the dissolution of passive film and increases the reversibility of anodic reaction. In addition, with increasing the In content in the alloy, the surface becomes more porous in nature, consequently, the electrolyte can easily penetrate into the oxide film and reach the underlying substrate [44].

Figures 10(a)-(c) show the SEM images of the



Fig. 9 SEM images of passive film on Pb (a), Pb–0.5%In (b) and Pb–15%In (c) alloys surface formed anodically (1.2 V vs SCE) in 4 mol/L H_3PO_4 solution at 20 °C

anodic passive films formed potentiostatically on the surfaces of the same mentioned electrodes at 1.8 V (vs SCE) (1.360 V vs SME) (at oxygen evolution reaction). Generally, it would be seen that the surfaces of the investigated electrodes are covered with thin passive layers compared with those at less positive potential (1.2 V vs SCE or 0.760 V vs SME). In addition, the distortion of particles formed on the surface is observed, may be due to oxygen evolution reaction in this region. On the other hand, the surface of Pb exhibits that the concentration of particles formed on the surface is higher compared with those of two studied alloys. This indicates that at higher positive potential (1.8 V vs SCE or 1.360 V vs SME), the formation of β -PbO₂ overlaps with the oxygen evolution reaction [45]. Consequently, at low applied potential (1.2 V vs SCE or 0.760 V vs SME),



Fig. 10 SEM images of passive films on Pb (a), Pb–0.5%In (b) and Pb–15%In (c) alloys surface formed anodically (at 1.8 V vs SCE) in 4 mol/L H₃PO₄ solution at 20 °C

only the oxides of the passive layer form, while in the case of high applied potential (1.8 V vs SCE or 1.360 V vs SME), the formation of the oxides and the oxygen evolution reaction occur at the same time, making the amount of oxides formed decreases [46]. The oxygen evolution reaction not only makes the metal oxides thin films non-uniform, but also distorts the structures of the thin films.

Figures 11 and 12 represent the EDX spectroscopies of Pb and alloy V (15% In) surfaces exposed to passive film formed anodically at both 1.2 and 1.8 V (vs SCE) (0.760 and 1.360 V vs SME), respectively, in 4 mol/L H₃PO₄ solution. Figures 11(a) and 12(a) exhibit the characteristic peaks which are related to Pb, O and P elements. This indicates that the corrosion layer on pure



Fig. 11 EDX spectra of passive films on Pb (a), Pb-0.5%In (b) and Pb-15%In (c) alloys surface formed anodically at 1.2 V (vs SCE) in 4 mol/L H₃PO₄ solution at 20 °C

Pb surface is $(Pb)_3(PO_4)_2$ and Pb oxides. However, the data in Figs. 11(b) and 12(b) show additional peaks of In element. These exhibit that InPO₄ or In₂O₃ forms in addition to $(Pb)_3(PO_4)_2$ and Pb oxides on the alloy surface (15% In). However, the higher fraction of Pb element (14.7%, mole fraction) on the surface of Pb compared with that of alloy V (7.7%, mole fraction), indicating that In alloying with Pb decreases the



Fig. 12 EDX spectra of passive films on Pb (a), Pb-0.5%In (b) and Pb-15%In (c) alloys surface formed anodically (1.8 V at vs SCE) in 4 mol/L H₃PO₄ solution at 20 °C

formation of Pb oxides in the passive film. On the other hand, it is interesting to see that the fraction of Pb (4.24%) element on the surface of alloy at 1.8 V (vs SCE) (1.360 V vs SME) is low compared with that at 1.2 V (vs SCE) (0.760 V vs SME) (7.77%). This result confirms that the amount of Pb oxides on the alloy surface significantly decreases. This behavior supports the SEM images (Figs. 9(c) and 10(c)) that the particles of the passive layer formed at oxygen evolution reaction region (1.8 V vs SCE or 1.360 V vs SME) are few in number compared with those observed in the passive region formed at 1.2 V (vs SCE) (0.760 V vs SME).

4 Conclusions

1) The potentiodynamic curves exhibit two peaks $(A_{I} \text{ and } A_{II})$ in the pure $H_{3}PO_{4}$ for Pb and its investigated alloys, and the current densities of two peaks increase with increasing the indium content in the alloy. This indicates that peak A_I can be associated with the active dissolution of Pb to Pb^{2+} species. While peak A_{II} can be attributed to the oxidation of Pb²⁺ and PbHPO₄ to β -PbO₂. Additional small peak is observed in the case of high indium content alloying with Pb (10% and 15%) can be attributed to the oxidation of indium to In_2O_3 . However, the active dissolution region involves two anodic peaks (A_I and A_{II}) prior to the permanent passive region and oxygen evolution reaction in H₂SO₄ containing various concentrations of H₃PO₄ for Pb and its investigated alloys (except alloy V, one peak only). This behavior can be attributed to the active dissolution of Pb to $PbSO_4(A_I)$, and electro-oxidation of Pb to PbO (A_{II}) . Also, the current density of the first peak (A_{I}) increases, while that of peak AII decreases gradually with increasing the In content in the alloy and completely disappear at its higher level (15% In). It can be concluded that indium alloying decreases the oxidation of Pb into PbO.

2) With the increase of alloying In content, the passive current density gradually increases in pure H₃PO₄ and H₂SO₄ containing various concentrations of H₃PO₄. This indicates that In alloying with Pb decreases the thickness of the passive film, consequently, its conductivity increases. The data show that the addition of 0.1 mol/L H₃PO₄ to the electrolyte (H₂SO₄) becomes more effective to decrease the thickness of passive layer on the surface of alloys containing higher In content (10% and 15%), but the higher concentration (0.2 mol/L) of H₃PO₄ has ability to decrease the breakdown of passive layer. This indicates that the addition of 0.1 mol/L H₃PO₄ decreases the resistance of the oxide layer on the alloy surface, and this is the optimum concentration which will be added to H₂SO₄ in order to improve the efficiency of the lead-acid batteries.

3) The cyclic voltammetric measurements exhibit that the anodic oxidation (A_I) shifts to more positive, and the peak current density of alloys is higher compared with that of pure Pb. This indicates that alloying In decreases the thickness of passive PbO layer which is completely hindered at high In content (15%). This behavior is confirmed by the peak related to the reduction of PbO at negative back scan which is not observed in the case of pure Pb and alloy containing low In content.

4) The XRD, EDX and SEM data show that the formation of semi-conducting $PbSO_4$ and PbO layer on the surface decreases with increasing the In level in the alloy, and which is completely prevented at higher In content in mixed acid.

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H₃PO₄浓度对 Pb-In 合金表面阳极钝化膜导电性的影响

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摘 要:将H₃PO₄加入H₂SO₄溶液有助于降低铅酸电池深放电后的硫化作用。研究Pb和Pb-In合金在纯H₃PO₄和含不同浓度H₃PO₄的H₂SO₄溶液中的阳极行为。使用动电位法、恒电位法和循环伏安法进行电化学测试。通过X射线衍射(XRD)、X射线能谱分析(EDX)和扫描电镜(SEM)对Pb和Pb-In合金表面钝化膜的成分和形貌进行表征。动电位研究表明测试溶液中的钝化电流密度随合金中In含量的增加而增加。向电解液中添加0.1 mol/LH₃PO₄对减小In含量更高(10%和15%)的合金表面的钝化膜厚度更有效。XRD、EDX和SEM数据表明在混合溶液中,PbSO₄和PbO在合金表面的生成随合金中In含量的增加而减弱,且当In含量更高时(15%)完全停止。 关键词:Pb-In合金;H₃PO₄;阳极行为;钝化膜;铅酸电池

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