



Fundamental research on the role of alloying tin as a means to eliminate the passivation phenomena in lead/acid batteries.

N. Bui ^{*}, P. Mattesco, P. Simon, N. Pébère

Ecole Nationale Supérieure de Chimie, Laboratoire des Matériaux et Interfaces, ESA-CNRS 5071, 118 rte de Narbonne, 31077 Toulouse, France

Received 5 August 1997; accepted 10 October 1997

Abstract

Advances in the role of alloying tin on the electrochemical properties of lead alloys are reviewed. In recent studies, the effect of tin on the conductivity of the passive layer developed on lead alloys has been studied by various techniques, e.g., measurements of redox kinetics, cyclic polarization, a.c. impedance, chronopotentiometry, photoelectron spectroscopy. The results show that in pH 9 medium, the electron conductivity of the passivation layer, which is composed mainly of PbO, increases sharply when the tin content in the alloy is increased from 1 to 1.5 wt.%. In sulfuric acid, the tin content must be higher than 1 wt.% to ensure good electron conductivity of the passivation layer. A percolation mechanism is proposed to explain the modification of the conductivity. One of the effects of tin is to decrease the thickness of the PbO layer, during both the charge and discharge of lead-acid batteries. Tin dissolves slowly in sulfuric acid and this can explain the decrease in the conductivity of the passivation layer after long polarization times. Alloying tin appears to favour the formation of an intermediate oxide PbO_x, which is less resistive than PbO. © 1998 Elsevier Science S.A. All rights reserved.

Keywords: Lead alloys; Tin effect; Depassivation; Lead/acid battery

1. Introduction

Low-antimony and antimony-free alloys have been used in the manufacture of grids in order to minimize gassing in either maintenance-free or valve-regulated lead/acid batteries. Unfortunately, these alloys promote other problems such as loss of capacity on cycling, reduced performance of positive plates, and low charge-acceptance with deeply-discharged batteries [1,2]. These problems are associated with the formation of a passivation layer, identified as the poorly-conducting oxide α -PbO, that develops between the grid and the active material [3–5].

Tin has been shown to alleviate the passivation problem [6,7]. Fundamental research has been performed to elucidate the mechanism of the action of tin on the electronic properties of the PbO layer and to determine the optimum level of tin for the alloys. In this paper, the key research results are reviewed and recent studies are presented.

2. Significant investigations on the tin effect

Nelson and Wisdom [8] and Culpin et al. [9] have presented comprehensive reviews of studies up to 1992 on the effect of alloying tin in deep-cycling lead/acid battery applications and on the performance of positive plates. The nature of the passivation layer and the conditions of its formation have been well defined. The generally accepted view is that the passivation layer, namely α -PbO, acts like a semiconductor or an electrical insulator. The effect of tin on grid passivation has been known for a long time ago [9] but fundamental studies on the tin effect were stimulated by the investigations of Pavlov et al. [7] in 1989. The main topics of the research can be classified as follows.

2.1. How alloying tin affects the electron conductivity of the passivation layer

Using photoelectrochemical techniques, Pavlov et al. [7] proposed a mechanism for the action of tin namely, tin facilitates the process of oxidation of PbO to PbO_n ($1 \leq n \leq 2$) and lowers the potential at which this reaction starts.

^{*} Corresponding author.

The electron conductivity of lead oxide increases strongly with the value of n . PbO_2 is very electron conductive. PbO behaves like a semi-conductor, with a bandgap width of 1.9 eV and Sn does not affect this band gap. With tin-containing alloys, in the process of corrosion, Sn^{3+} ions are incorporated in the oxide crystal lattice and bring about an increase in hole concentration, and probably in hole mobility. In this way, Sn increases the oxidation rate of PbO to PbO_n and thus eliminates the formation of α - PbO .

Döring et al. [10] explained the cause of passivation in terms of a phase-junction model of the interfacial region in which PbO_n is p -conducting and PbO_2 is n -conducting and the resulting structure is like a n - p - n transistor. With tin incorporated in the alloy, PbO_n doped by tin and becomes n -type, thus presenting an ohmic character and higher conductivity.

Takahashi et al. [11] also concluded that tin accelerates the formation of α - PbO_2 and retards the early failure of batteries that use lead–calcium grids. They also found that a high ratio of acid to positive active material (i.e., $\text{H}_2\text{SO}_4/\text{PbO}_2 > 0.6$) brought an effective remedy to the passivation phenomena in valve-regulated batteries after prolonged discharge. The authors demonstrated that a tin-rich surface layer on the grid offered the same benefit as a high-tin alloy.

Bojinov et al. [12] combined photoelectrochemistry and a.c. impedance with electrochemistry and a rotating ring-disc technique to study the influence of tin. They found that tin catalyses the oxidation of Pb(II) to Pb(IV) by 0.1–0.2 V, increases the amount of non-stoichiometric oxide, and facilitates the formation of a more highly conductive corrosion layer on lead.

Steyer [13] investigated the nature of tin in the PbO layer by Mössbauer spectroscopy, as well as the distribution of tin in the oxide by transmission electron microscopy and electron microprobe analysis. The results showed that the PbO layer has a columnar grain structure. Furthermore, most of alloying tin is in the form of tin(IV) segregated in the PbO grain boundaries, with a smaller amount of tin(II) substituted in the structure of PbO inside the grains. A percolation mechanism for the conductivity was proposed.

2.2. How tin affects the thickness of the passivation layer

It is generally observed that with the incorporation of tin in the alloys, formation of PbO is impeded and the thickness of the passivation layer decreases as the tin level increases. A commonly generally proposed mechanism is the catalytic oxidation of PbO to PbO_n or PbO_2 [7,11,12], as reported earlier. Another suggested mechanism [14] is a disproportionation reaction between SnO and PbO , i.e.,



Both Pb and SnO_2 are very conductive but their presence has not been confirmed with certainty. Without experimental support, it has been advanced [13,30] that tin ions, (i.e., Sn^{4+} from the oxidation of tin) have an acidic character and inhibit the nucleation and the growth of PbO which is stable only in alkaline medium.

2.3. Optimum level of tin in the alloy

Giess [6] found that alloying tin at a level as low as 0.3 wt.% is effective in providing recovery from deep discharge. But in cycling applications, it has been reported [15] that as much as 2.5 wt.% tin is required to avoid early failure. By contrast, Nelson and Wisdom [8] found that tin, at the level of about 0.7 wt.%, had only a temporary effect on capacity performance. They further concluded that a different process takes place in valve-regulated lead/acid batteries (VRLA batteries): the passivation layer ($\text{PbO}_x/\text{PbSO}_4$) is initially inhibited at grain boundary sites on the grid surface and these areas remain open for current flow. Thus, the corrosion sites will minimize the passivation but may also shorten the life of the grid by degradation. Valeriotte et al. [16] reported that the main influence of tin in grid alloys appeared to be related to the corrosion and growth characteristics of the grid. Under conditions whereby deeply cycled lead/acid plates are adequately recharged, tin-free alloys do not necessarily suffer rapid or premature capacity loss and tin is not required in the positive grid alloy. Tin may have provided some benefit in reducing the rate of capacity loss during the final stages of cycling failure with 115% recharge, but no clear benefit was found with 105% recharge.

Recently, Giess [17] has shown that large-grained alloys with a composition of 0.07 wt.% Ca–0.7 wt.% Sn are desirable for long-life VRLA batteries. Pongaman [18] found that the highest mechanical properties were achieved for lead–calcium–tin alloys with 0.07 wt.% Ca and high tin levels of about 2.0 wt.%, and that a high tin level may also prove to be beneficial in imparting improved conductivity to the corrosion layer. Wrought tubular grids for VRLA batteries produced from these high-tin alloys should be suitable for both gel and AGM designs. Miraglio et al. [19] investigated the limit for the tin level at which the passivation phenomenon is suppressed. This limit was found to be between 1 and 2 wt.%. In accelerated corrosion tests, the weight loss passes through a minimum at about 1.3 wt.% Sn. Higher tin levels (> 2 wt.%) are not desirable because of over-ageing problems and intergranular corrosion. From field tests of VRLA batteries in taxis, Takahashi et al. [20] reported that batteries with grids of high tin content (1.25 wt.%) gave much longer lifetimes than those with low tin contents (0.25 wt.%) at high temperatures (up to 75°C). To improve the recovery after over-discharge, a tin-rich alloy (Pb-5 wt.% Sn) clad to wrought sheet was developed and proved to be effective for VRLA batteries.

2.4. Effect of tin (as Sn^{2+} ions) on the active material

Salmi and Sundholm [21], using a ring-disc technique and potential decay measurements, showed that Sn dissolves from or through the corrosion layer as Sn(II) ions, and that tin inhibits the formation of PbO_2 during the early stages of the oxidation of lead. The effect of tin ions dissolved in the acid solution appears to be similar to that of tin as an alloying element. The effect of tin ions in the positive active material has been reviewed by Voss et al. [22]. The active-material structure can be regarded as an aggregate of spheres ('Kugelhaufen' model) and the improvement in capacity due to tin is explained by an increase in the connectivity between the spheres and, hence, in the conductivity of the active material.

Pavlov [23] developed the concept of a gel-crystal structure for the positive active-material (PAM). Additives, such as Sb and Sn were thought to connect the polymer chain of lead dioxide into a network that maintains a high electric conductivity of the corrosion layer/PAM interface and, accordingly, suppresses the phenomenon of premature capacity loss.

Wei and Wang [24] studied the electrochemical behaviour of Sn^{2+} (dissolution of SnSO_4) in sulfuric acid and found that reduction of Sn^{2+} to tin metal on the negative plates will improve the charge-discharge properties. The oxidation of Sn^{2+} to SnO_2 , which may be incorporated in the PAM, increases the electronic conductivity of the gel zones proposed in Pavlov's gel-crystal model.

3. Recent research on the tin effect

The electrical properties of the passivity of $\alpha\text{-PbO}$ have been studied in situ by using a redox couple (ferro- and ferricyanide, 0.025 M) in 0.1 M tetraborate solution of pH 9.1 [25–27]. In this solution, PbO and tin oxide are very stable. Passive layers are formed on lead with incorporation of tin to up to 2.5 wt.%. The electron conductivity through the layer has been evaluated by measuring the exchange current density of the redox couple. The result show that the layers formed on pure lead and low-tin alloys (< 1 wt.% Sn) are non-conducting. By contrast, the conductivity increases sharply for alloys with 1–1.5 wt.% Sn and tends to a plateau for 1.5–2.5 wt.% Sn. A percolation mechanism has been proposed to explain the modification of the conductivity of the passive layers.

X-ray photoelectron spectroscopy (XPS) [26] has been used to perform both qualitative and quantitative analysis of the passive layers formed on the lead-tin alloys. It is found that for alloys with more than 1.5 wt.% Sn, the passive layers include positively charged zones because of low conductivity. When the tin content is higher than 1.5 wt.% Sn, only uncharged zones are assumed to be present in the passive layer. The concentration of tin in the passive

layer formed at pH 9.1 is 44, 28, 14, 13 and 3 wt.% for 2.5, 1.5, 1.3, 1 and 0.5 wt.% Sn alloys, respectively.

The same alloys have been examined in 1 M H_2SO_4 solution by electrochemical impedance spectroscopy. For tin-rich alloys (> 1 wt.% Sn), tin transforms the semi-conducting lead oxide layer (formed on pure-lead and low tin alloys) into a highly conducting layer.

The conductivity of the passivation layers on lead-tin alloys in 4.5 M H_2SO_4 has been studied in situ by the measurements of the reaction rates of the ceric-cerous redox couple and by electrochemical impedance spectroscopy [28]. The electronic conductivity of the passivation layers is evaluated by comparing cyclic voltammograms for pure lead and lead alloys with/without the redox couple. The redox reaction is possible only if the passivation layer is electron conducting. The potential at which a sharp change occurs in the polarization current is denoted as E_{i0} while the equilibrium potential of the redox couple on platinum is denoted as $E_{o\text{redox}}$. The closer E_{i0} is to the equilibrium potential $E_{o\text{redox}}$, the higher the conductivity of the passivation layer. The inverse of $E_{o\text{redox}} - E_{i0}$, viz., $\sigma = 1/(E_{o\text{redox}} - E_{i0})$, gives an indication of the conductivity. Fig. 1 shows the conductivity of the passivation layer as a function of the level of tin in lead-tin alloys. There is a sharp increase in the electronic conductivity when the tin level is greater than 1.0 wt.%.

Electrochemical impedance spectroscopy allows the determination of the polarization resistance, R_p , which is related to the inverse of the corrosion rate. The change of the modulus and the phase angle of the impedance versus the frequency of the alternative voltage can give an indication of the semi-conductivity or the electron conductivity. The variation of R_p versus the level of tin in the alloys is presented in Fig. 2. The passivation layer comprises lead

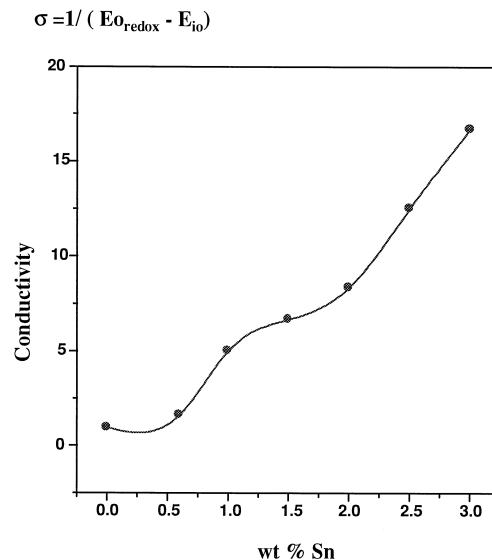


Fig. 1. Effect of tin level on conductivity parameter $\sigma = 1/(E_{o\text{redox}} - E_{i0})$ of lead-tin electrodes in 4.5 M H_2SO_4 from cyclic polarization between -1500 and +1500 mV.

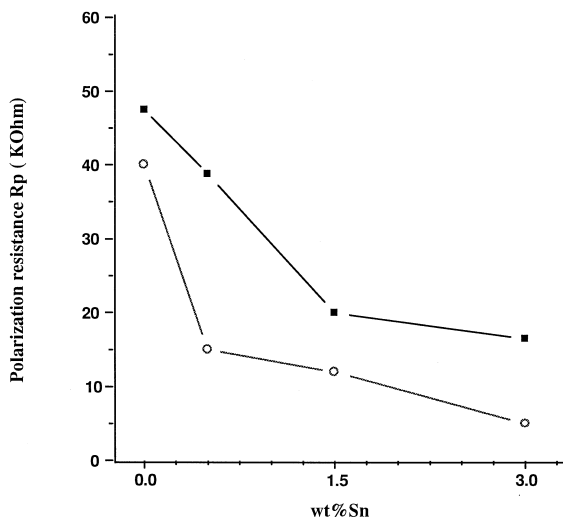


Fig. 2. Effect of tin level on polarization resistance R_p of lead–tin alloys in 4.5 M H_2SO_4 . -■- electrodes polarized at 700 mV for 30 min after forward polarization from -1500 mV. -○- electrodes polarized at 0 mV for 30 min after backward polarization from -1500 mV.

sulfate and PbO formed at $+700$ mV for 30 min. The decrease of R_p , when the tin level increases, can be explained by the dissolution of tin in sulfuric solution leading to an increase in ionic conductivity of the layer.

The conductivity of the PbO layer can also be related to its thickness. The reduction at low current density, 10^{-6} A cm^{-2} , led to chronopotentiometric curves which gave an indication of the thickness (proportional to the duration of reduction) and the nature of the oxide (arrest potential of reduction). The reduction time versus tin level in the alloys is shown in Fig. 3. The thickness of the PbO layer decreases when the tin level in the alloys increases.

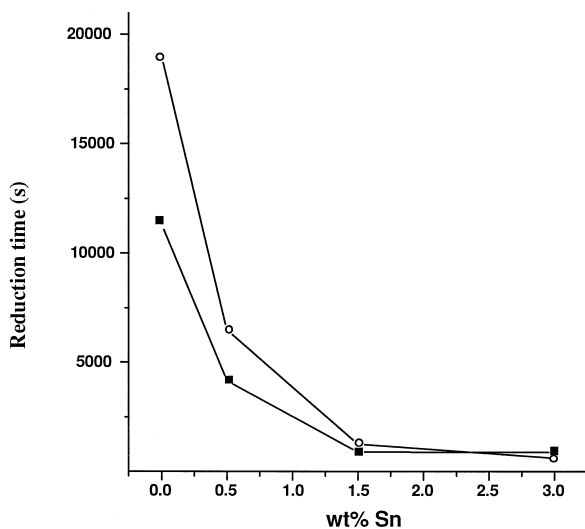


Fig. 3. Effect of tin level on reduction time of PbO layer formed on lead–tin alloys in 4.5 M H_2SO_4 . -■- electrodes polarized at 700 mV for 30 min after forward polarization from -1500 mV. -○- electrodes polarized at 0 mV for 30 min after backward polarization from -1500 mV.

Chronopotentiometric studies also show that at a high oxidation potential (1500 mV for 30 min), a high tin level (3.0 wt.%) favours the formation of PbO_2 and a non-stoichiometric oxide PbO_x .

The effect of the polarization time and polarization potential on the properties of the passivation layer on lead–tin alloys has been investigated by a.c. impedance and cyclic voltammetry [29]. The data in Fig. 4 show that when the lead electrode is polarized in the passivity region (700 mV), the polarization resistance R_p increases with time (increasing amount of semi-conducting PbO). In the presence of alloying tin (3.0 wt.% in this case), R_p decreases slowly during the first three hours and then increases slightly at longer times (24 h). This change in the resistance of the electrode can be explained by a competition mechanism between an increase in the thickness of the resistive PbO layer and an increase in the amount of conducting tin oxide. With long polarization times, the effect of the thickness prevails and, possibly, some conducting tin oxide may be dissolved in the sulfuric solution. The effect of a high oxidation potential ($+1500$ mV) is presented in Fig. 5. The polarization resistance of a pure-lead electrode increases with polarization time but has smaller values, $R_p = 80$ k Ω as compared with 250 k Ω , after 24 h at 700 mV. For a Pb-3 wt.% Sn alloy, the effect of potential in the PbO_2 and oxygen evolution region (1500 mV) leads to an initial decrease of R_p which again displays a tendency to increase slightly after long polarization times (24 h).

The tin effect in lead–calcium (0.08 wt.%) alloys, under simulated conditions of deep discharge (700 mV in 0.5 M H_2SO_4) has been investigated by measurements of the polarization resistance, the oxidation rate of ferric ions added to the electrolyte, the potential decay with/without

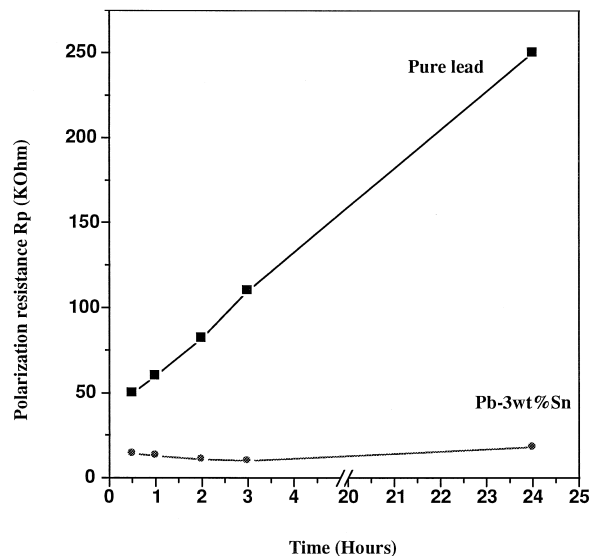


Fig. 4. Effect of polarization time on polarization resistance R_p of pure lead -■- and Pb-3 wt.% Sn -●- at 700 mV, after forward polarization from -1500 to 700 mV, in 4.5 M H_2SO_4 .

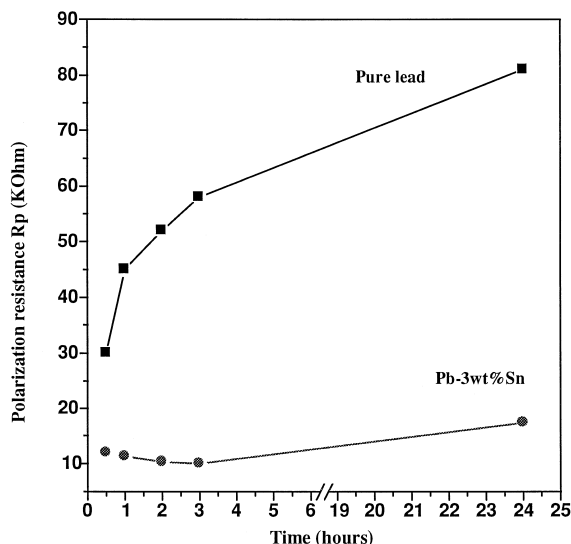


Fig. 5. Effect of polarization time on polarization resistance R_p of pure lead -■- and Pb-3 wt.% Sn -●- at 700 mV, after backward polarization from +1500 to 700 mV in 4.5 M H_2SO_4 .

applied cathodic current, surface analysis, and visual inspection [30]. Over a period of seven days, a linear relationship has been observed between the thickness of the PbO layer and the oxidation time at +700 mV. The effect of alloying tin on the thickness can be seen in Fig. 6. It is interesting to note that for low-tin alloys, the increase in the thickness with oxidation time is very large. Particularly, the alloy with 0.6 wt.% Sn exhibits the greatest thickness.

The conductivity of the passivation layer, as determined by measurements of the polarization resistance or by the rate of oxidation of added ferric ions, increases with time.

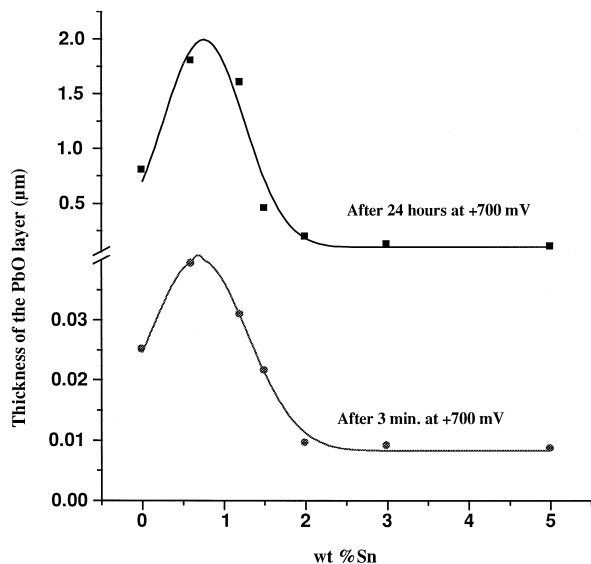


Fig. 6. Effect of tin level and of oxidation time on thickness of PbO layer formed on lead-tin alloys: -●- after polarization at 700 mV for 3 min and -■- after polarization at 700 mV for 24 h in 4.5 M H_2SO_4 .

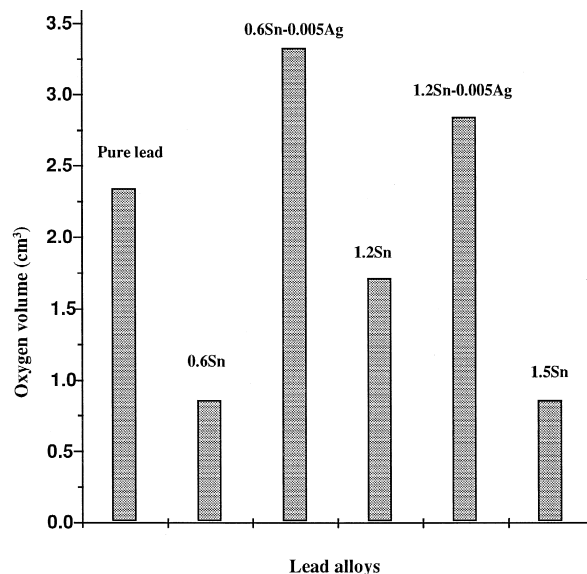


Fig. 7. Effect of alloying with tin and silver on oxygen gassing for Pb-0.08 wt.% Ca electrodes polarized at +1500 mV for 5 h.

It then decreases as the thickness of the PbO layer increases and as tin is dissolved in the sulfuric solution. These results suggest that the alloyed tin level must be higher than 1.5 wt.% to reduce the thickness of the PbO layer and to increase the conductivity of this layer.

The effect of tin on the oxygen over-voltage has been investigated further by direct measurement of the volume of evolved oxygen. The oxygen gassing is very limited when the electrodes are polarized at +1300 mV. At +1500 mV, the rate of oxygen evolution is much more rapid, and this rate increases with time to attain a stationary value. The oxygen volume collected after 5 h at 1500 mV is reported in Fig. 7. In general, tin decreases the oxygen gassing, or, in other words, increases the oxygen over-voltage. The particular behaviour of the 0.6 wt.% Sn alloy can be seen again: it exhibits the highest oxygen over-voltage. It has been found that tin also increases the hydrogen over-voltage [30].

4. Conclusions

An overview of fundamental research on the effect of tin on the depassivation of lead alloys provides the following conclusions.

(i) There is an unanimous observation that alloying tin decreases the thickness of the passivation PbO layer. On the other hand, the mechanism of this reaction remains uncertain. The propositions are: a disproportionation reaction between PbO and SnO, catalytic oxidation of PbO to PbO_n or PbO_2 , inhibition of PbO formation by the acidity of Sn^{4+} ions.

(ii) The electron conductivity of the passivation layer increases with the tin level in lead alloys. The mechanisms

proposed comprise the doping of PbO_n ($1 < n < 1.5$) by tin, the action of tin ions Sn^{3+} on the catalytic oxidation of PbO to conductive PbO_2 , the conduction by percolation through conductive paths of tin oxide in the passivation layer, a reduced thickness of the PbO layer.

(iii) The optimal level of tin in lead alloys varies greatly depending on the service life and the states of discharge and charge. It is shown that good conductivity of the passivation layer is attained when the tin level is higher than 1.5 wt.% and, in this respect, it is not necessary to increase the tin level above 2.0 wt.%.

(iv) Tin dissolves slowly from alloys in sulfuric solution and produces tin ions, Sn^{2+} , which can be reduced to tin metal on the negative plates and oxidized to conductive SnO_2 on the positive plates. The improvement in capacity is explained by the increase in conductivity of the active material, especially in the zones connecting the PbO_2 .

(v) Tin in the alloy decreases oxygen and hydrogen gassing at the positive and negative electrodes, respectively.

Acknowledgements

The authors are indebted to the European Economic Community and to the Advanced Lead-Acid Battery Consortium (Brite Euram Project BE 7297) for financial support.

References

- [1] K.R. Bullock, M.A. Butler, *J. Electrochem. Soc.* 133 (1986) 1085.
- [2] J. Burbank, *J. Electrochem. Soc.* 106 (1959) 359.
- [3] D. Pavlov, N. Iordanov, *J. Electrochem. Soc.* 117 (1970) 1103.
- [4] P. Rüetschi, *J. Electrochem. Soc.* 120 (1973) 331.
- [5] D. Pavlov, R. Popova, *Electrochim. Acta* 15 (1970) 1843.
- [6] H.K. Giess, in: K.P. Bullock, D. Pavlov (Eds.), *Advances in Lead-Acid Batteries*, Proc. Vol. 84-14, The Electrochemical Society, Pennington, NJ, USA, 1984, p. 241.
- [7] D. Pavlov, B. Monahov, M. Maja, N. Penazzi, *J. Electrochem. Soc.* 136 (1989) 27.
- [8] R.F. Nelson, D.M. Wisdom, *J. Power Sources* 33 (1991) 165, and references therein.
- [9] B. Culpin, D.A.J. Rand, A.F. Hollenkamp, *J. Power Sources* 38 (1992) 63, and references therein.
- [10] H. Döring, J. Garche, H. Dietz, K. Wiesener, *J. Power Sources* 30 (1990) 41.
- [11] K. Takahashi, N. Hohihara, H. Yasuda, T. Ishii, H. Jimbo, *J. Power Sources* 30 (1990) 23.
- [12] M. Bojinov, K. Salmi, G. Sundholm, *Electrochim. Acta* 39 (1994) 719.
- [13] P. Steyer, Thesis, University of Nancy, France, 1997.
- [14] M. Terada, S. Saito, T. Hayakawa, A. Komaki, *Prog. Batt. Solar Cells* 8 (1989) 214.
- [15] K. Wiesener, J. Garche, N. Anastasijevic, in: J. Thompson (Ed.), *Power Sources* 9, Academic Press, London, 1983, p. 36.
- [16] E.M.L. Valeriotte, A. Heim, M.S. Ho, *J. Power Sources* 33 (1991) 187.
- [17] H.K. Giess, *J. Power Sources* 53 (1995) 31.
- [18] R.D. Prengaman, *J. Power Sources* 53 (1995) 207.
- [19] R. Miraglio, L. Albert, E.A. Ghachcham, Steinmetz, J.P. Hilger, *J. Power Sources* 53 (1995) 53.
- [20] K. Takahashi, H. Yasuda, H. Hasegawa, S. Horie, K. Kanetsuki, *J. Power Sources* 53 (1995) 137, and references therein.
- [21] K. Salmi, G. Sundholm, *J. Power Sources* 40 (1992) 217.
- [22] E. Voss, U. Hullmeine, A. Winsel, *J. Power Sources* 30 (1990) 33.
- [23] D. Pavlov, *J. Power Sources* 42 (1993) 345.
- [24] G.L. Wei, J.R. Wang, *J. Power Sources* 52 (1994) 81.
- [25] P. Simon, N. Bui, F. Dabosi, *J. Power Sources* 50 (1994) 141.
- [26] P. Simon, N. Bui, F. Dabosi, G. Chatainier, M. Provincial, *J. Power Sources* 52 (1994) 31.
- [27] P. Simon, N. Bui, N. Pebere, F. Dabosi, L. Albert, *J. Power Sources* 55 (1995) 63.
- [28] P. Mattesco, N. Bui, P. Simon, L. Albert, *J. Electrochem. Soc.* 144 (1997) 443.
- [29] P. Mattesco, N. Bui, P. Simon, L. Albert, *J. Power Sources* 64 (1997) 21.
- [30] N. Bui, P. Mattesco, P. Simon, J. Steinmetz, E. Rocca, to be published in *J. Power Sources*, 1997.