Analysis of tin in lead oxide by Mössbauer spectrometry and transmission electron microscopy

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Abstract

Tin present in the PbO layer growing on lead–calcium–tin alloys under deep-discharge conditions (0.7 V versus SSE) has been characterized by Mössbauer spectroscopy and transmission electron microscopy. After polarization, tin is present in PbO in two valencies. Sn(IV) is predominant and in oxides probably precipitated at the grain boundaries, whereas Sn(II) could be weakly incorporated in the PbO lattice. On the other hand, the crystallization of PbO is very fine, in contrast to that of PbSO$_4$.

Keywords: Alloys; Lead; Tin; Calcium; Lead/acid batteries; Passivation; Mössbauer spectroscopy; Transmission electron microscopy

1. Introduction

Most manufacturers of lead/acid batteries have opted for Pb–Ca–Sn ternary alloys in applications such as starting, lighting and ignition (SLI) of vehicles. The Sn content must be at a level that is sufficient to avoid passivation, mainly under conditions of deep-discharge, during which a duplex coating is formed. It consists of an outer thin PbSO$_4$ film and a thick inner layer of tetragonal PbO (α-PbO). It was recently demonstrated that Sn increases the conductivity of the corrosion layer and, in particular, of the α-PbO oxide [1]. The objective of this study is to determine the valence of Sn present in the PbO layer after having simulated the battery's deep-discharge.

2. Experimental

The selected Pb–Ca–Sn alloys are listed in Table 1. Alloys A1, A3 and A4 were prepared by Metaleurop whereas the second alloy was synthesized at Nancy by adding adequate amounts of ^{119}Sn granules (83% enriched) to alloy A1. Each alloy was rolled, corrosion tests were performed in 0.5 M H$_2$SO$_4$ (20 °C) at an applied potential of 0.7 V versus a Hg/Hg$_2$SO$_4$, K$_2$SO$_4$ saturated reference electrode during one week except for alloy A4, polarized during two weeks (Fig. 1). After oxidation of a 30 cm^2 area, corrosion products

Table 1
Composition of Pb–Ca–Sn alloys

Alloys	Ca (wt.%)	Sn (wt.%)	^{119}Sn (wt.%)	Al (wt.% ($\times 10^{-4}$))
A1	0.1	0.58	0.05	160
A2	0.1	~0.5	~0.5	160
A3	0.1	2		~160
A4	0.08	0.6		~130

formed on both A1 and A2 samples were removed by scratching, then ground and analysed by Mössbauer spectroscopy at different temperatures.

^{119}Sn Mössbauer spectra were obtained in transmission geometry with an Elscint spectrometer at 80 K (alloy A2), at room temperature (alloys A1, A2) using a 10 mCi calcium stannate source. The spectrometer was operated in the conventional constant acceleration mode. The Sn Mössbauer spectra were fit with a standard least-squares program using Lorentzian lines.

Three techniques were used to prepare samples for analysis by transmission electron microscopy using a CM 2000 Philips TEM/STEM:

1. microcleavage of the oxidized surface with a diamond point (A3);
2. microtome method of rolled alloys embedded in epoxy resin to obtain thin foils of 150 nm in thickness [2], and
3. argon-ion milling of specimens showing corrosion scales in transverse cross sections [3].
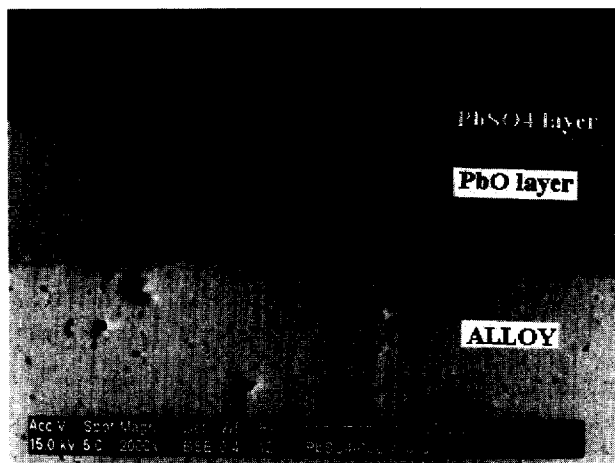
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Fig. 1. Metallographic cross section of Pb–0.08wt.%Ca–0.6wt.%Sn after polarization at 0.7 V for two weeks in 0.5 M H₂SO₄ at 20 °C.

Thin foil TEM graphs, X-ray diffraction (XRD) patterns, energy dispersive spectroscopy (EDS) and parallel electron-energy loss spectroscopy (PEELS) spectra have led to the characterization of PbSO₄ and PbO.

3. Results

At room temperature, one broad line is observed whose Mössbauer parameters are characteristic for Sn(IV); a better
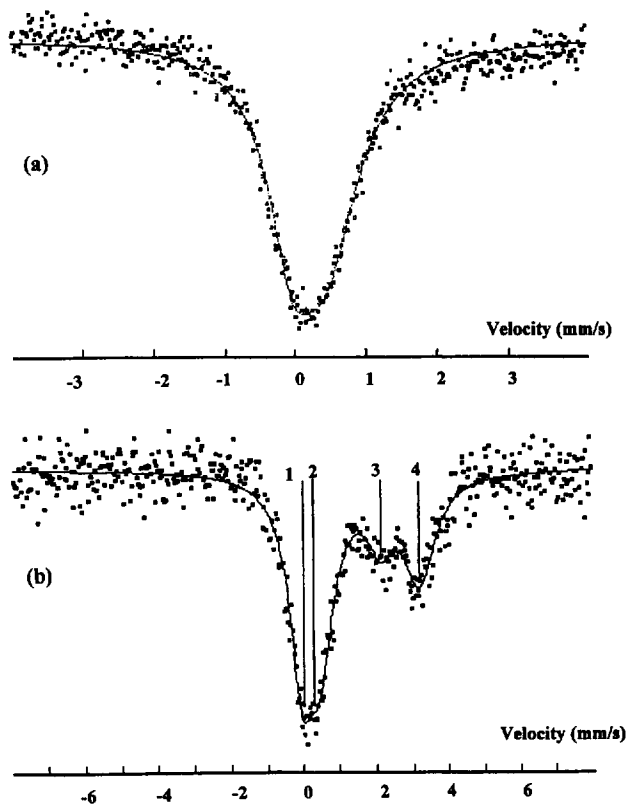

Fig. 2. Characteristic Mössbauer spectra for PbO 'doped with tin' after polarization during one week at 0.7 V in 0.5 M H₂SO₄ of Pb–0.1wt.%Ca–0.5wt.%¹¹⁸Sn–0.5wt.%¹¹⁹Sn: (a) at room temperature, and (b) 80 K.

signal to noise ratio is obtained with samples prepared from alloy A2, enriched with ¹¹⁹Sn. Nevertheless, the spectrum shows a weak asymmetry which suggests the presence of Sn(II), Fig. 2(a). A new experiment was carried out at 80 K since the Lamb–Mössbauer factor, f, increases when the temperature decreases. More important, the ratio $f(\mathrm{Sn}^{4+})/f(\mathrm{Sn}^{2+})$ may be unfavourably large for a clear observation of the Sn²⁺ contribution at room temperature compared with that in SnO$_x$ ($f(\mathrm{Sn}^{4+})/f(\mathrm{Sn}^{2+}) = 1.88 \pm 0.35$ [4]). It will
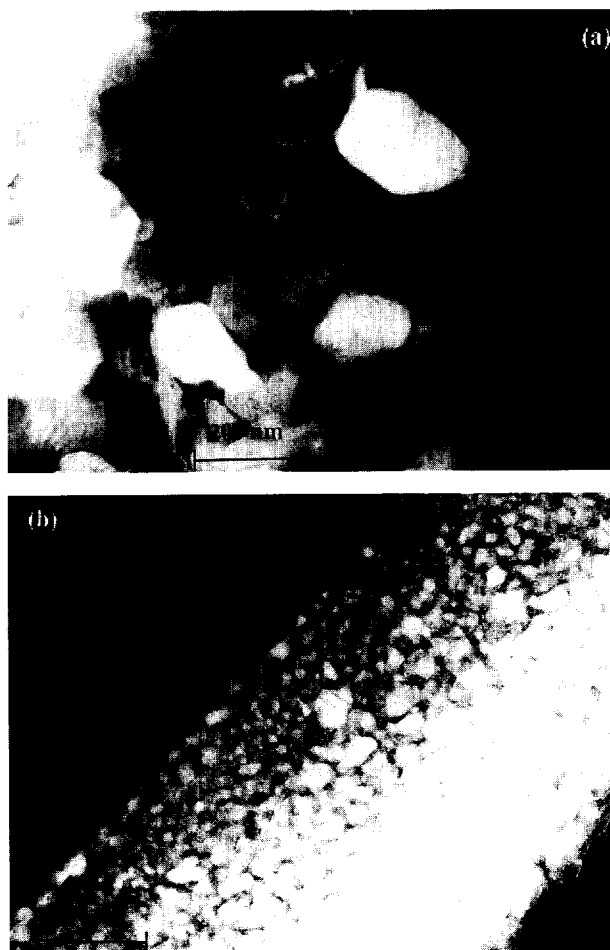

Fig. 3. Thin-foil transmission electron micrographs of (a) PbSO₄ and (b) PbO of a Pb–0.08wt.%Ca–0.6wt.%Sn alloy polarized at 0.7 V during two weeks in 0.5 M H₂SO₄ solution.
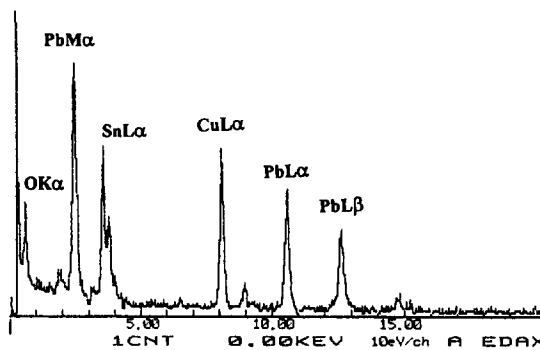

Fig. 4. EDS spectrum of an Sn-rich particle in Pb–0.08wt.%Ca–2wt.%Sn alloy polarized during seven days at 0.7 V in 0.5 M H₂SO₄ solution. (The copper peak originates from the copper grid on which the sample is put.)

Table 2
Mössbauer spectra parameters for Sn present in PbO (at 80 K), compared with data determined at room temperature [5] and 100 K [6]

Compounds	Isomer shift, δ, relative to BaSnO$_3$ (mm/s)	Quadrupole splitting, Δ (mm/s)
Compound 1 peaks 1 and 2	0.1	0.5
Compound 2 peaks 3 and 4	2.56	1.06
SnO$_2$ [5]	0	0.5
SnO orthorhombic [6]	2.7	2.2
SnO tetragonal [6]	2.8	1.6
SnO crystalline [5]	2.68	1.36

decrease and become close to unity when the temperature decreases, as shown for Sn^{2+} and Sn^{4+} [5]. In these conditions the right part of the spectrum, at positive velocities, is much better defined and two new peaks are detected (Fig. 2(b)), leading to the data given in Table 2.

Some typical literature data on both divalent and tetravalent tin oxides also are mentioned in this Table [5,6]. Comparison of all these data proves the presence of two tin oxidation states in the PbO layer (no tin has been detected by microprobe in PbSO$_4$).

Combining the results of the three previously described TEM preparation methods we clearly identify the duplex layer, in which the sulfate appears to be porous and formed by crystals bigger than those of PbO, see Fig. 3.

Furthermore, EDS spectra indicate heterogeneous distribution of Sn in PbO (Fig. 4), in contrast to that determined by microprobe [7], analysing a greater volume. Finally, TEM as well as electron probe microanalysis (EPMA) have detected no traces of Sn in PbSO$_4$.

4. Conclusions

The corrosion layer formed on Pb–0.1wt.%Ca–(0.6–2)-wt.%Sn polarized under deep-discharge conditions consists of a duplex layer (PbSO$_4$/PbO). Although the superficial PbSO$_4$ layer appears to be porous, PbO can grow under the sulfate 'barrier' according to the model proposed by Ruetschi [8].

Tin is only present in the PbO layer and in two valencies. Mainly oxidized at the highest oxidation state, Sn(IV), it is probably present in SnO$_2$ or (and) Pb$_2$SnO$_4$ oxides, precipitated at grain boundaries. It is difficult to differentiate these oxides because of their very close Mössbauer parameters. Moreover, Sn(II) would be subtituted for Pb(II) in the tetragonal PbO lattice to a lesser extent; it can be assumed that this (Pb$_{1-x}$Sn$_x$O) limited solid solution modifies less the conduction properties of the PbO layer than the precipitates containing Sn(IV).

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