

EIS-in situ characterization of anodic films on antimony and lead–antimony alloys

M. Metikoš-Huković^{a,*}, R. Babić^a, S. Brinić^b

^a Department of Electrochemistry, Faculty of Chemical Engineering and Technology, University of Zagreb, PO Box 177, 10000 Zagreb, Croatia

^b Faculty of Technology, University of Split, N. Tesle 10, 21000 Split, Croatia

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Abstract

The behaviour of antimony as a function of the concentration of both H_2SO_4 and HSO_4^- ions, and the electrode rotation rate was studied by cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS). The rate of antimony dissolution is accelerated with the addition of HSO_4^- ions and with the increasing electrode rotation rate. Impedance measurements of antimony in the region of film formation, and lead and lead–antimony alloys in the region of PbO formation showed that the dissolution rate is controlled by the diffusion through the oxide layer. The diffusion coefficients (D) for protons in the case of antimony dissolution, and for oxygen ions in the case of lead and alloys, were estimated. Electric and dielectric properties of the anodic surface layer of the lead–antimony alloys are significantly influenced by the antimony content. © 2005 Elsevier B.V. All rights reserved.

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1. Introduction

Antimony is widely used as a constituent of lead alloys for lead/battery grids. Therefore, the electrochemical behaviour of antimony [1–8] and its influence on the electrochemical processes at lead electrode in sulphuric acid solutions [8–17] have been extensively studied. During the anodic polarization of antimony electrode in H_2SO_4 solution, at relatively low overvoltages, a gel-like anodic layer, as a result of primary passivation, is formed [5]. The properties of this layer, which acts as an ionic conductor, were studied using various polarization techniques [1–5,7,8], and impedance spectroscopy [3–8]. Since the anodic dissolution of antimony depends on acid concentration, Pavlov et al. [4] proposed that SO_4^{2-} , and even HSO_4^- may be involved in the mechanism.

It is well known that antimony has a beneficial effect on the performance of lead-acid battery positive plate. Its oxidation in Pb–Sb alloys begins at the potential values at which PbO formation takes place under the PbSO_4 perm-selective membrane. It was shown [9,10,13–17] that Sb oxidation in the alloy

changes the composition of the anodic layer; simultaneously to the formation of lead oxides, mixed lead and antimony oxides of various compositions, depending on the electrode potential, are formed [9,10].

In the previous papers, we have studied the electrochemical kinetics of anodic layer formation and reduction on antimony and antimonial lead [8]. Mostly we investigated the electrical properties of corrosion layers on the Pb–Sb alloys using EIS method [12,13]. In the present paper, we aimed at EIS examination of the transport processes in surface layers on pure antimony and on Pb–Sb alloys with low antimony content. Also, herein, we investigated the effect of HSO_4^- ions on the anodic dissolution of antimony.

2. Experimental

The study was performed on spectroscopically pure antimony (Johnson Matthey Co.), pure lead (99.998 wt.%) and Pb–Sb alloys with Sb content of 1.3 and 2.7 wt.%. The electrodes had a cylindrical form, and the lateral surface of the cylinder was coated with polyester, exposing only the plane of the cylinder base to the solution; the surface area was 0.46 cm^2 . The Sb electrode was polished mechanically, wiped with tissue

* Corresponding author. Tel.: +385 1 4597 140; fax: +385 1 4597 139.
E-mail address: mmetik@marie.fkit.hr (M. Metikoš-Huković).

Nomenclature

B	fitting parameter
c	molar concentration (mol dm^{-3})
C	capacitance ($\mu\text{F cm}^{-2}$)
d	film thickness (nm)
D_f	diffusion coefficient ($\text{cm}^2 \text{s}^{-1}$)
E	potential (V)
E	electric field strength (V cm^{-1})
j	current density (mA cm^{-2})
n	fractional exponent
q	charge density (mC cm^{-2})
Q	parameter which contains fractional characteristics of electrochemical system ($\Omega^{-1} \text{cm}^{-2} \text{s}^n$)
R_d	diffusion resistance (Ωcm^2)
R_Ω	ohmic resistance (Ωcm^2)
W	diffusion component
Z_W	impedance of diffusion component (Ωcm^2)

Greek letters

ε	relative dielectric constant
ω	rotation rate (rpm)

paper, dipped in ethanol to remove dust and grease from the surface. Prior to each measurements the electrode was polarized at -300 mV to remove oxides formed on the surface by contact with air. The Pb and Pb–Sb electrodes were polished with SiC paper (600 grit), degreased in ethanol and rinsed with distilled water. Prior to each measurement, the electrodes were polarized at -1.0 V for the same reason mentioned above. Measurements were performed mostly in $0.5 \text{ M H}_2\text{SO}_4$ solution. However, electrochemical behaviour of Sb was investigated also in H_2SO_4 solutions of lower and higher concentrations; the solutions were saturated with Sb_2O_3 in order to prevent greater dissolution of antimony.

The experiments were performed in a two-compartment glass cell at 298 K . The counter electrode was a large Pt-plate, and the reference electrode was a saturated calomel electrode (SCE). All potential values are reported in $V(\text{mV})$ versus SCE. Voltammetric measurements were carried out using an EG&G Princeton Applied research Model 273 potentiostat/galvanostat and an EG&G PAR Model 616 rotating disc electrode. The EIS measurements were done using an EG&G M5315A lock-in amplifier in the frequency range from 100 kHz to 30 mHz with the ac voltage amplitude $\pm 5 \text{ mV}$. The impedance spectra were analyzed using the software for complex non-linear least squares (CNLS) fitting developed by Boukamp [18].

3. Results and discussion

3.1. Cyclic voltammetry on pure antimony

Cyclic voltammograms of an antimony electrode, obtained within the potential range from -0.5 to 1.0 V in H_2SO_4 solutions of different concentrations, are presented in Fig. 1. Electrode

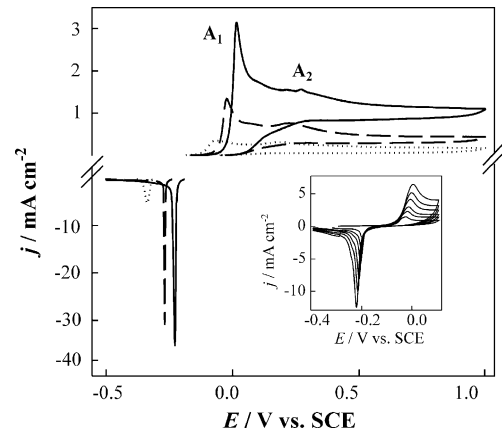
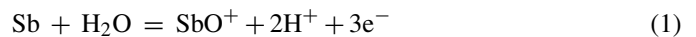


Fig. 1. Cyclic voltammograms on Sb in 0.05 M (····), 0.5 M (---) and 5 M (—) H_2SO_4 ; $\nu = 20 \text{ mV s}^{-1}$. The inset: cyclic voltammograms recorded in $0.5 \text{ M H}_2\text{SO}_4$; $\nu = 10, 20, 30, 50, 100$ and 200 mV s^{-1} .

processes in the anodic and cathodic portions of the Sb voltammetric response have already been discussed in details [3–5,8] and here will be only briefly covered. The anodic portion of the voltammograms starts with a sharp increase in the current density due to the antimony oxidation:

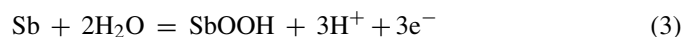


This is a process of active dissolution of antimony. In order to preserve the electroneutrality at the nearby electrode surface, the sulphate ions come from the bulk of the solution, and hydrogen ions leave the surface causing an increase in pH and the formation of a gel-like layer of basic sulphate:

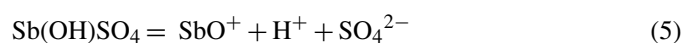


The formation of the $\text{Sb}(\text{OH})\text{SO}_4$ layer at the electrode surface corresponds to the first current maximum, A_1 . With an increase in the acid concentration, partial passivation of the electrode occurs at higher anodic currents, i.e. a higher concentration of SbO^+ ions near the electrode surface is needed for the formation of an anodic layer.

After the formation of the surface layer, the antimony dissolution continues, and when the rate of anodic generation of antimony ions becomes greater than that of the sulphate ions diffusing from the bulk of the electrolyte into the surface layer, the formation of an antimony hydroxide sublayer starts:



When the entire electrode surface is covered with the SbOOH sublayer, the current maximum A_2 appears at the cyclic voltammogram. With a further potential increase the current decreases slowly showing a current plateau whose height increases with increasing acid concentration. The fairly high currents are accompanied by the high ionic conductivities of the anodic film, and the SbOOH layer grows at about the same rate as it dissolves. This process may be best described by the following reactions:



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