

# Study of oxide layers on metals and alloys by cyclic local voltammetry

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**Abstract.** The paper deals with the possibilities of local electrochemical analysis (LEA) in the investigation of anode properties and predicting corrosion behavior of metals and galvanic alloys. Our aim is to study changes in the surface composition in the process of anodic dissolution, determine the phase composition and quality of passive films on the surface of metals and alloys and control oxide nanofilm resistivity. We show the possibility of using the hybrid LEA method that combines cyclic local voltammetry and abrasive voltammetry to investigate the kinetics of oxide layer growth, determine their thickness, phase composition and resistivity. Analysis of one polarization curve makes it possible to monitor the process of oxide film formation on the metal surface (anode part) and estimate its phase composition and resistivity (cathode part). We propose a novel way of calculating the resistivity of the oxide film and an equation that describes its growth. The results of theoretical calculations are confirmed by the experimental data obtained in the course of analyzing the polarization of tin, lead and their alloys in an aqueous alkaline solution. The dependence of the oxide film thickness on the time of film growth is exponential.

## 1 Introduction

The variety of tasks that can be solved using electrochemical methods based on the use of solid-state electrochemical reactions determines their wide use in the study and control of various processes. Passive films can be formed on the surface of metals and alloys as a result of anodic polarization, corrosion in various aggressive media or due to long-term warehousing of products. The composition of passive films is very diverse – these are oxide and hydroxide layers, salt and sulfide deposits on the surface. Anode polarization of the metal surface in alkaline solutions is also used to produce oxide nanolayers characterized by certain functional properties [1]. To monitor the process of obtaining nanofilms various physical, physicochemical [2, 3], and electrochemical methods [4-12] are used.

Local electrochemical analysis (LEA) proved to be fairly efficient in solving such problems as controlling the thickness and composition of oxide layers on metals and alloys, predicting their corrosion behavior [13]. The method of local electrochemical analysis is based on anode or cathode polarization of individual small areas ( $S = 0.2-10.0\text{mm}^2$ ) of the surface of an object in an electrolytic press-on cell [9, 14, 15]. The role of the working electrode is performed by the surface of the material. LEA makes it possible to study the surface in its original form without disrupting its initial state. Therefore, metals can be used for the study of passive films formed under corrosion.

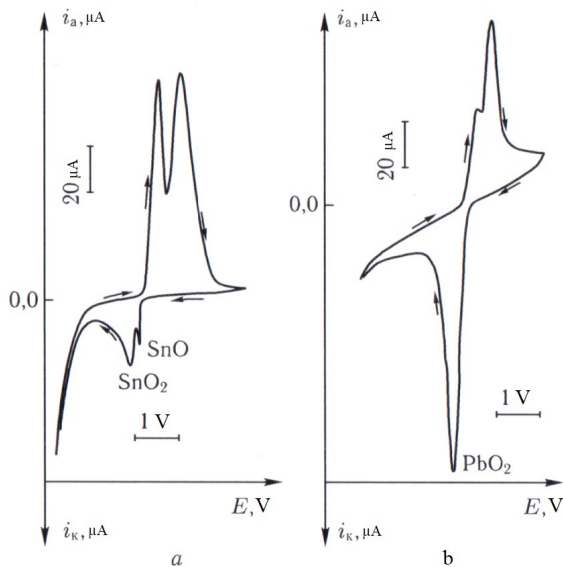
## 2 Experimental

Samples of protective coatings of metals and alloys were obtained on the cathode in an electrolysis bath [16]. The local electrochemical analysis of the coatings was performed with the following instrumentation: a potentiostat-galvanostat IPC-Pro M (St. Petersburg, Russia) in connection with a PC and a pressed cell made of graphite and with a well-defined hole. This cell has been described elsewhere in detail [9, 14]. Voltammograms and chronopotentiograms were recorded to obtain the desired information. Electrochemical dissolution of metals and alloys was carried out using aqueous electrolytes.

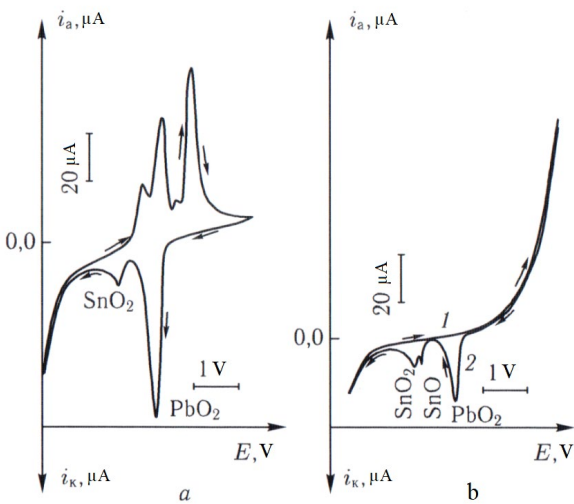
To investigate the phase composition of oxide layers formed on metals and alloys in the process of anodic dissolution a hybrid LEA method was developed which combines cyclic local voltammetry (CLVA) [9] and abrasive voltammetry (AV) [17, 18]. The essence of the CLVA + AV hybrid method is as follows. First, we register the cyclic current-voltage curve (Fig. 1, 2) of the surface of the alloy in the press-on cell filled with the appropriate electrolyte. To determine the nature of the oxides formed synthetic oxides supposed to be present in the oxide film are deposited on the rough surface of the abrasive material (normally spectrally pure graphite) according to a known method [17, 18]. Then a cathode polarization curve is registered in the same cell with the same electrolyte (Fig. 2 curve 2b). The abrasive polarization curve is combined with the cyclic

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polarization curve and the phase composition of the oxide film formed on the alloy surface during anodic dissolution is determined by the cathode maxima potentials.



**Fig. 1.** Polarization curves of tin (a) and lead (b) in 0.1 M NaOH.



**Fig. 2.** Polarization curves of tin-lead alloy (a), impregnated spectrally pure graphite (1, b) and synthetic oxides (2, b) of tin and lead in 0.1 M NaOH.

### 3 Results and discussion

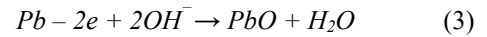
As can be seen from the cyclic polarization curves in figures 1 a and 1 b, the dissolution of tin and lead in 0.1 M NaOH solution proceeds in two stages in accordance with the equations



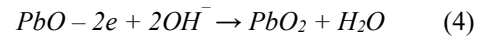
and



for tin,



and



for lead. Therefore, the mechanisms of the process of anodic dissolution of tin and lead are different from each other. In the event of tin dissolution two oxides, SnO and SnO<sub>2</sub>, are formed on the metal surface. They are shown in the cathode part of the cyclic curve in Figure 1a. In the case of lead dissolution lead oxide PbO formed at the first stage is almost completely converted into PbO<sub>2</sub> oxide, therefore there is one cathode maximum in the cathode part of the cyclic curve in Figure 1 b.

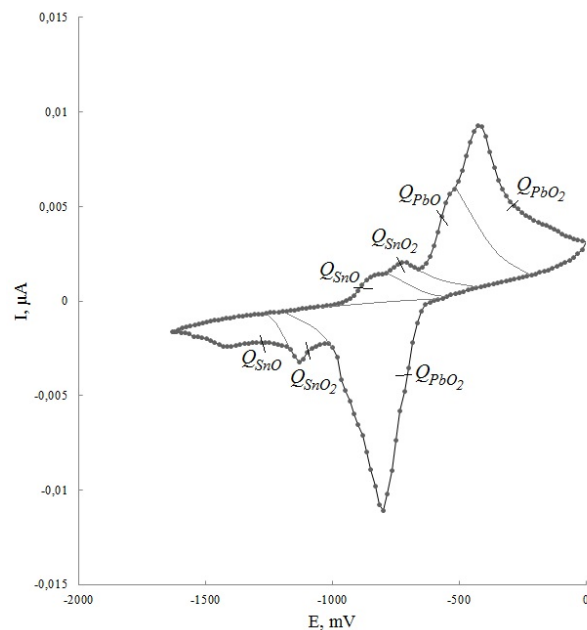
The process of dissolution of the tin-lead alloy (Figure 2 a) is similar to those mentioned above. All the anode and cathode maxima that were present in the polarization curves of pure metals manifest themselves in the polarization curve of the alloy. The phase composition of the oxides is found by abrasive voltammetry (Figure 2 b).

Thus, passive layers on tin-lead alloys in the case of their anodic polarization in a solution of NaOH are composed of three types of oxides, SnO, SnO<sub>2</sub> and PbO<sub>2</sub>.

Using Faraday's law

$$h = \frac{M \cdot Q}{n \cdot F \cdot S \cdot \rho}, \quad (5)$$

where  $h$  is the thickness of the oxide film;  $M$  is the molecular weight of the oxide;  $Q$  is the quantity of electricity spent for the dissolution of the oxide layer (Fig. 1, and 2);  $n$  is the number of electrons involved in the process;  $F$  is the Faraday number;  $S$  is the surface area specified by the cell;  $\rho$  is the oxide density, one can estimate the thickness of the oxide phase layer.



**Fig. 3.** Polarization curves of tin-lead alloy: 19.3 % mas. Sn in 0.1 M NaOH.

**Table 1.** Results of determining the thickness of nanolayers of tin and lead oxides in the case of anode and cathode polarization of galvanic coatings with tin-lead alloys under conditions of CLVA.

Alloy composition % mass.		Thickness of oxide film, nm							
Sn	Pb	Anode part				Cathode part			
		SnO	SnO <sub>2</sub>	PbO	PbO <sub>2</sub>	SnO	SnO <sub>2</sub>	PbO	PbO <sub>2</sub>
7.5	92.5	1.4	2.5	23.5	61.1	1.6	1.0	39.7	
19.3	80.7	1.1	4.2	13.5	60.8	2.2	0.4	32.4	
31.5	68.5	2.0	5.2	16.0	28.3	2.1	1.6	20.0	
58.6	41.4	4.9	18.0	4.9	19.6	2.3	4.6	9.4	
64.1	35.9	7.7	19.1	6.3	14.0	1.8	6.6	8.9	
77.3	22.7	9.0	25.8	8.1	17.3	3.9	5.9	6.2	

From Figure 3 and Table 1 it is evident that anode and cathode maxima are disparate. Consequently, the reduction process involves only part of oxides that contact directly with the substrate. Hence it follows that oxide films formed on the surface of metals and alloys have a loose structure and poor adhesion to the substrate. In the case of anode polarization of the metal surface (Sn, and Pb) in alkaline solutions under LEA conditions the current density in the electrochemical circuit is determined by the Butler-Volmer equation [19]:

$$i = i_0 \left[ \exp\left(\frac{\beta n F}{RT} \cdot \eta\right) - \exp\left(-\frac{\alpha n F}{RT} \cdot \eta\right) \right], \quad (6)$$

where  $i_0$  is the exchange current density;  $\alpha$  and  $\beta$  are the transfer coefficients of the cathode and anode processes;  $\eta$  is the overvoltage of the electrochemical reaction.

On the other hand, the Faraday equation in the integral form has the following form with respect to the thickness of the resulting oxide layer [9]:

$$\int_0^h dh = \frac{A}{nF\gamma S} \int_0^t i(t) dt, \quad (7)$$

where  $A$  is the molecular weight of the oxide, g/mol;  $\gamma$  is the oxide density, g/cm<sup>3</sup>;  $h$  is the thickness of the oxide layer, cm.

Then the Faraday equation with regard for (6) takes the following form:

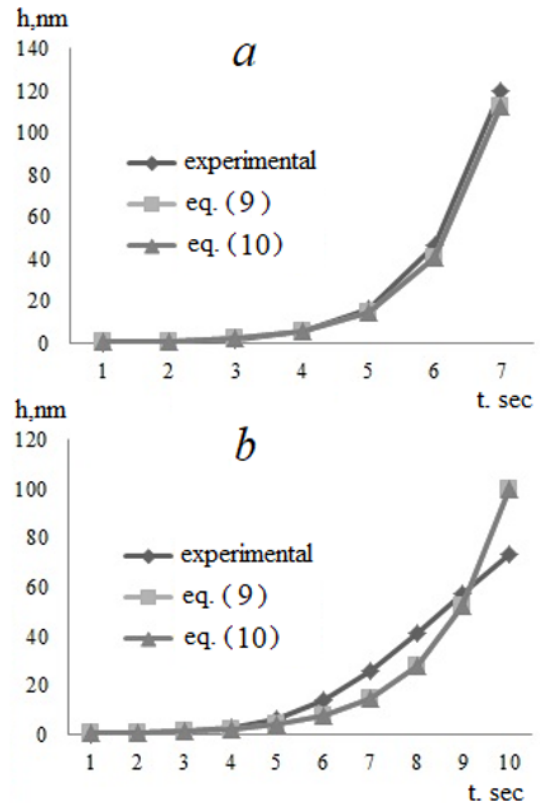
$$\int_0^h dh = \frac{A \cdot i_0}{nF\gamma S} \int_0^t \left[ \exp\left(\frac{\beta n F}{RT} vt\right) - \exp\left(-\frac{\alpha n F}{RT} vt\right) \right] dt. \quad (8)$$

Integration of equation (8) yields the dependence of the thickness of the oxide film on the time:

$$h = \frac{A \cdot i_0}{nF\gamma S v} \left[ \frac{RT}{\beta n F} \exp\left(\frac{\beta n F}{RT} \cdot vt\right) - \frac{RT}{\alpha n F} \exp\left(-\frac{\alpha n F}{RT} \cdot vt\right) \right]. \quad (9)$$

With significant values of the polarizing voltage, the cathode component of the equation (8) can be neglected. Then:

$$h = \frac{A \cdot i_0}{nF\gamma S v} \left[ \frac{RT}{\beta n F} \exp\left(\frac{\beta n F}{RT} \cdot vt\right) \right]. \quad (10)$$



**Fig. 4.** Dependence of the thickness of SnO (a) and PbO (b) oxide films on the time of polarization of metals in 0.1 M NaOH.

Figures 4 a and 4 b show the kinetic dependences  $h = f(t)$  for the process of formation of SnO and PbO oxides, derived from experimental polarization curves of Figure 1, according to Faraday equation (5). It is obvious that the dependence  $h = f(t)$  is exponential. The results of theoretical calculations made according to equations (9) and (10) that agree satisfactorily with the experimental data. The presented data also show that the cathode side in the equation (9) can be neglected and the kinetics of the oxide film growth on the metal surface is described by equation (10).

Resistivity of oxide films is their important characteristic which determines the rate of corrosion. The control of this parameter presents a problem. The resistivity of nanofilms produced electrochemically on the metal surface can be controlled by the potentiometric method [11, 12]. We examine the CLVA method that makes it possible, using one polarization curve, to follow the process of oxide film formation on the metal surface (the anode part of the curve), as well as to assess the phase composition and resistivity by the cathode part of the curve.

The expressions for the oxide dissolution cathode current can be presented by the following equation [20]:

$$i = i_o \exp \frac{anF}{RT} \left[ vt - i \left\{ R_o + \frac{A \cdot \rho_{ox}}{nF\gamma\delta^2} (Q_m - Q_i) \right\} \right], \quad (11)$$

where  $\rho_{ox}$  is the resistance of the oxide layer, ohm·cm;  $h$  is the thickness of the oxide layer, cm;  $Q_m$  is the quantity of electricity used to dissolve the entire oxide layer formed on the surface of the electrode in the anode part of the polarization curve (corresponding to the maximum in the cathode part of the voltage-current curve);  $Q_i$  is the quantity of electricity used to dissolve the oxide layer, coulombs.

**Table 2.** Results of analyzing the process of reduction of PbO<sub>2</sub> in 0.1 M NaOH ( $A=239.2$  g/mol;  $n=4$ ;  $\gamma=9.38$  g/cm<sup>3</sup>;  $S=0.00385$  cm<sup>2</sup>;  $i_o=2.0 \cdot 10^{-6}$  A;  $R_o=600$  ohm;  $Q_m=625 \cdot 10^{-6}$  coulombs;  $\alpha=0.32$ ).

Voltage sweep $vt$ , V	0.025	0.050	0.075	0.100	0.125	0.150
$\rho_{ox} \cdot 10^{-5}$ , ohm·cm	1.61	1.60	1.52	1.06	0.92	0.93

The correctness of the proposed equation is confirmed by the calculation of resistivity of the PbO<sub>2</sub> oxide layer by equation (11) (Table 4) transformed relative to  $\rho_{ox}$ .

$$\rho_{ox} = \frac{vt - iR_o - \frac{RT}{anF} \ln \frac{i}{i_o}}{\frac{i \cdot A}{nF\gamma\delta^2} (Q_m - Q_i)}. \quad (12)$$

## 4 Conclusions

It is found that the local electrochemical analysis (LEA) can be successfully used to study the kinetics of growth of oxide layers on metals and alloys in the process of their anodic polarization in the appropriate electrolyte. Theoretical calculations were confirmed by experimental studies of anodic polarization of tin, lead and their alloys. Tin-lead alloys oxidation in an aqueous alkaline solution and its protection from corrosion has to be monitored.

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