Evaluation of the Effect of the Concentration of Sodium Hydroxide with and without Potassium Oleate on the Behavior of Lead by Cyclic Voltammetry

A. G. Berezhnaya*, M. A. Kaz'mina, and V. A. Volochaev

Southern Federal University, Rostov-on-Don, 344006 Russia
*e-mail: ber@sfedu.ru
Received March 15, 2016

Abstract—The effect of the concentration of sodium hydroxide with and without potassium oleate on electrochemical behavior of lead has been investigated using cyclic voltammetry. It has been shown that the number of anode and cathode peaks on the curve depends on the potential scan rate and the concentration of alkali. Anode peaks are related to the formation of lead compounds (PbO and PbO_2), the presence of which has been confirmed by X-ray phase analysis. It has been determined that the dissolution of lead in sodium-hydroxide solution with and without potassium oleate proceeds under diffusion-kinetic control. Potassium oleate facilitates lead passivation in the solutions with lower concentration of alkali decreasing the potential and current of active−passive transition and does not affect or restricts it in more concentrated solutions.

INTRODUCTION

Lead undergoes anodic passivation in alkaline media. Passive state is provided by the presence of oxides or hydroxides on its surface. Detailed analysis of the formation of lead compounds at different oxidation state with the change of potential is given in [1−3]. However, insignificant changes of experimental conditions, such as preliminary handling of the electrode surface, variation of anionic composition, and introduction of additives, which can form their own film, could significantly change the composition of surface compounds and the form of the voltammetric curve. Film-forming additives can also be represented by potassium oleate, which can inhibit and promote anodic dissolution [4−6].

The aim of this work was to determine the effect of the concentration of sodium hydroxide with and without potassium oleate on the electrochemical behavior of lead by cyclic voltammetry (CV).

PROCEDURE OF EXPERIMENT

Cyclic chronovoltammograms were recorded on an IPC-PRO potentiostat in a three-electrode thermostatted cell with catolyte and anolyte separated by glass filter. Potential sweep was carried out from −1.5 to 1.5 V (forward sweep) and from 1.5 to −1.5 V (reverse sweep) at the rates of $V = 1, 5, 10, 20, 50,$ and 100 mV/s. As a reference electrode, an EVL-1M saturated silver-chloride electrode was used, relative to which E values are given in the work. The auxiliary electrode represented platinum. All measurements were carried out at the temperature of 25 ± 0.5°C, which was maintained using an IT-2/77 thermostat.

X-ray diffractograms of specimens were recorded on an ARL X'TRA diffractometer using filtered Cu$K\alpha$-radiation ($\lambda = 0.154056$) at room temperature. X-ray diffractograms of the specimens were recorded in the angle range of $5° \leq 2\theta \leq 95°$ using stepwise scanning with a step width of a detector of $0.02°$ and exposure time of up to 4 s at each step, voltage of 40 kV, and anodic current of 30 mA. Energy-dispersion solid-state Si(Li) detector cooled by a Peltier element was employed for the filtration of Kβ and white radiation.

RESULTS AND DISCUSSION

In Fig. 1, CVA curves of lead at various potential sweep rates V in sodium-hydroxide solution with concentrations of 0.1, 1, and 5 mol/L are given.

In most cases, regardless of V during scan of potential from −1.5 to 1.5 V, two clear peaks are resolved on anodic curve of CV of lead. The former corresponds to
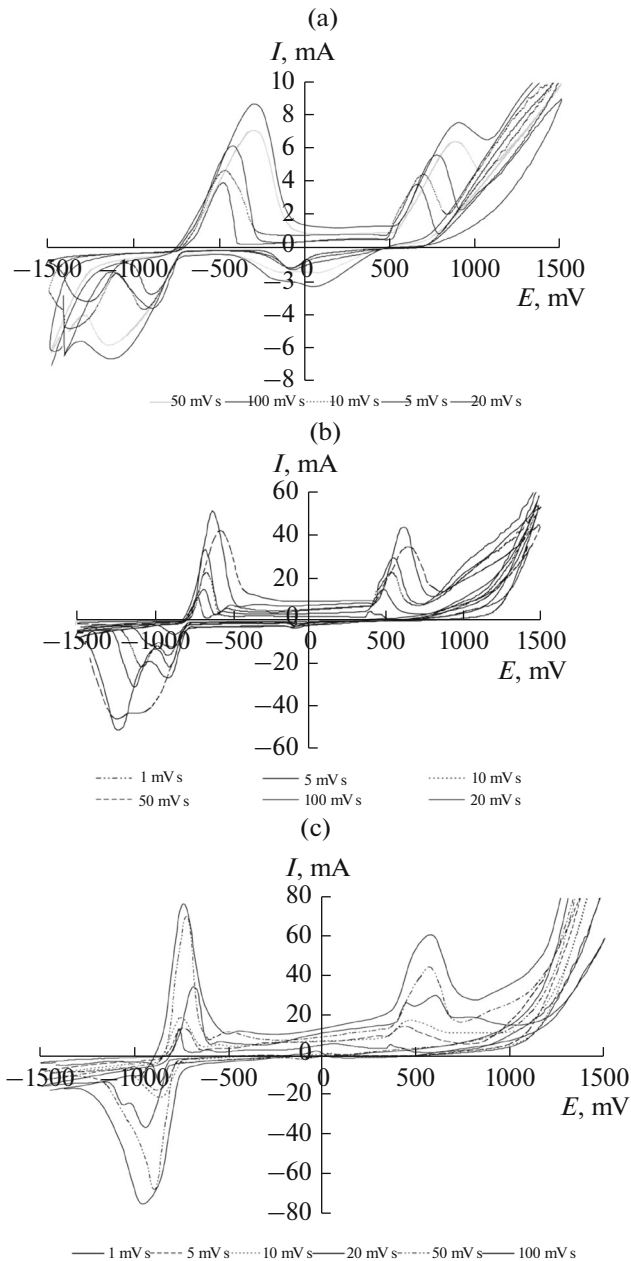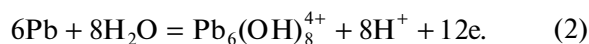
Fig. 1. Cyclic voltammograms of lead at various potential sweep rates and C_{NaOH}: (a) 0.1, (b) 1, and (c) 5 M.

Fig. 2. X-ray diffractogram of lead electrode maintained in (a) 0.1 and (b) 5 M alkaline solution, $E = 0.45$ V, $\tau = 1$ and 2 h, respectively.

the formation of PbO and/or hydroxide form $Pb_6(OH)_8^{4+}$ at the lowest potential sweep rate:

$$Pb + H_2O = PbO + 2H^+ + 2e, \qquad (1)$$

$$6Pb + 8H_2O = Pb_6(OH)_8^{4+} + 8H^+ + 12e. \qquad (2)$$

The rate in anode peak exceeds the rate of full passivation by less than a factor of 5. This indicates low protective action and porosity of the layer. With the growth of th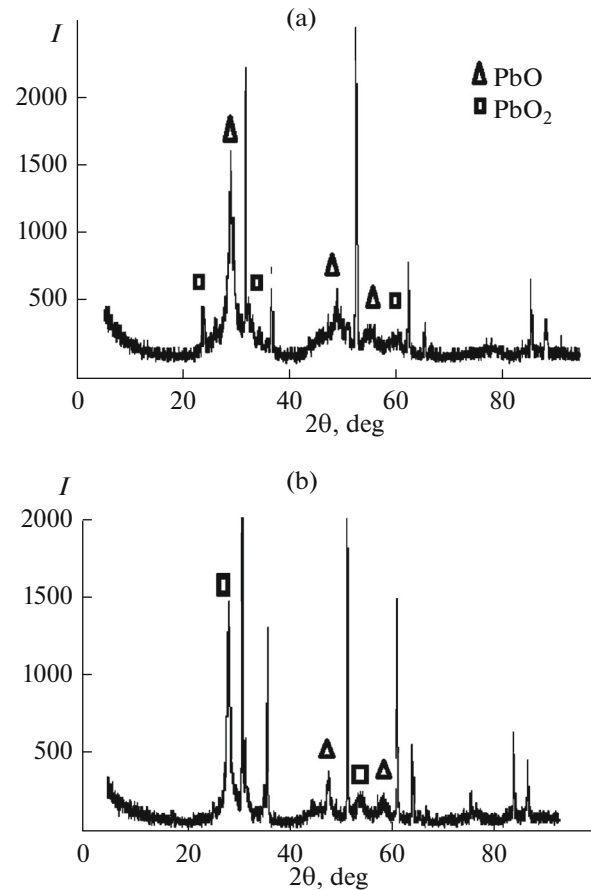e potential scan rate, the peak becomes broader and the corresponding potential ($E_{ap, 1}$) and current ($i_{ap, 1}$) increase (Fig. 1a). At potentials that are higher than -0.5 V (versus RHE), lead compounds at higher oxidation state (Pb_3O_4 and PbO_2) can be formed in the pores of existing oxide layer, which can be the reason for peak broadening. The passive state of lead is observed up to $E = 0.5$ V, after which the rate of the process increases. The second anode peak is most likely caused by the oxidation of lead(II) compounds into highly hydrolyzed form $Pb(OH)_6^{2-}$ [2]. Further growth of current on the curve is related to release of oxygen.

On the reverse-sweep curve, cathode peaks are observed, the number of which depends both on V and C_{NaOH}. At the lowest concentration of alkali, as well as low and medium V (1–20 mV/s), three cathode peaks are realized, whereas at high V four peaks can be distinguished (Fig. 1a). The larger number of cathode peaks as compared to anode ones is related to the reduction of lead compounds at higher and intermediate oxidation states, as well as hydrogen. X-ray phase analysis data confirm the presence of lead oxide compounds (PbO and PbO_2) on the lead surface (Fig. 2).
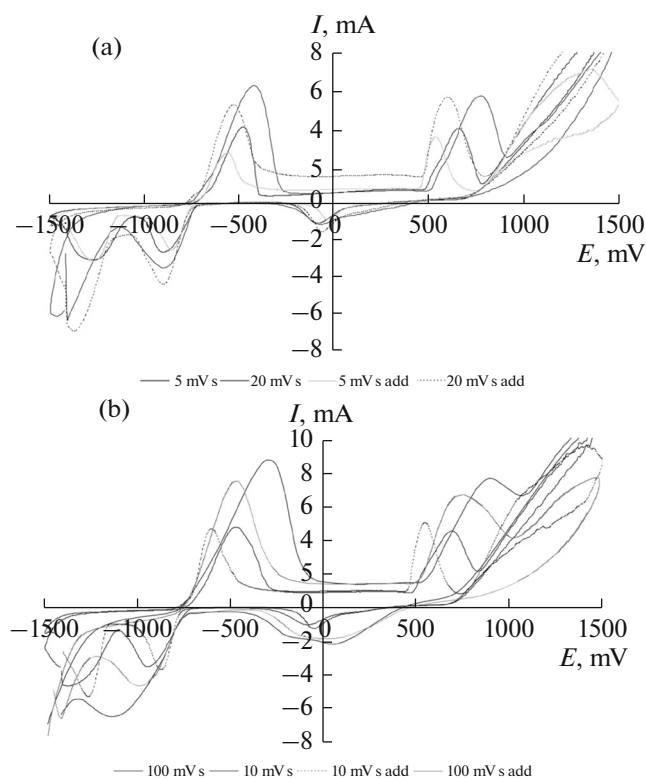
Fig. 3. Cyclic voltammograms of lead in 0.1 M alkaline solution in the presence of potassium oleate, $C_{PA} = 0.001$ M.
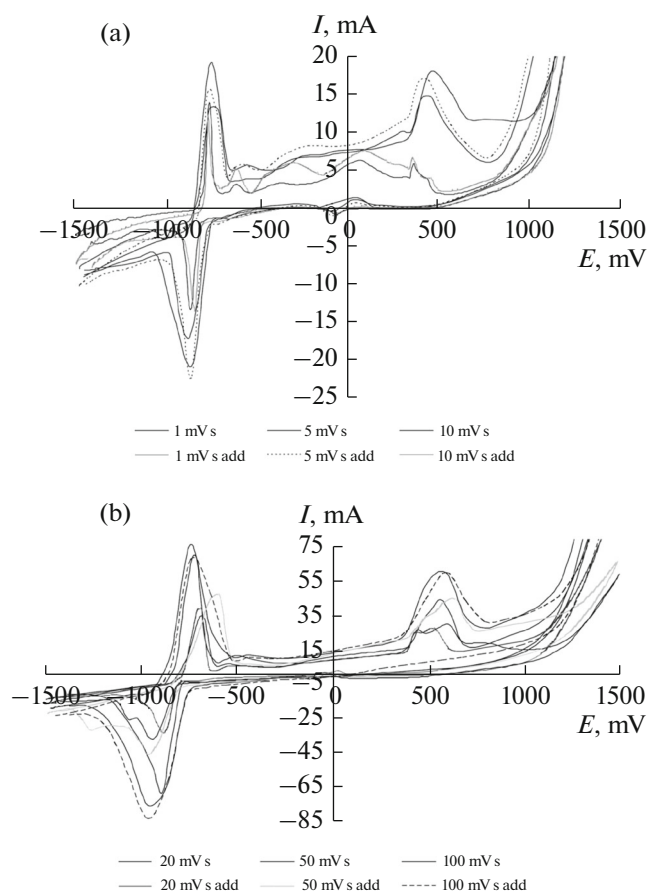

Fig. 4. Cyclic voltammograms of lead in 0.1 M alkaline solution in the presence of potassium oleate, $C_{PA} = 0.001$ M.
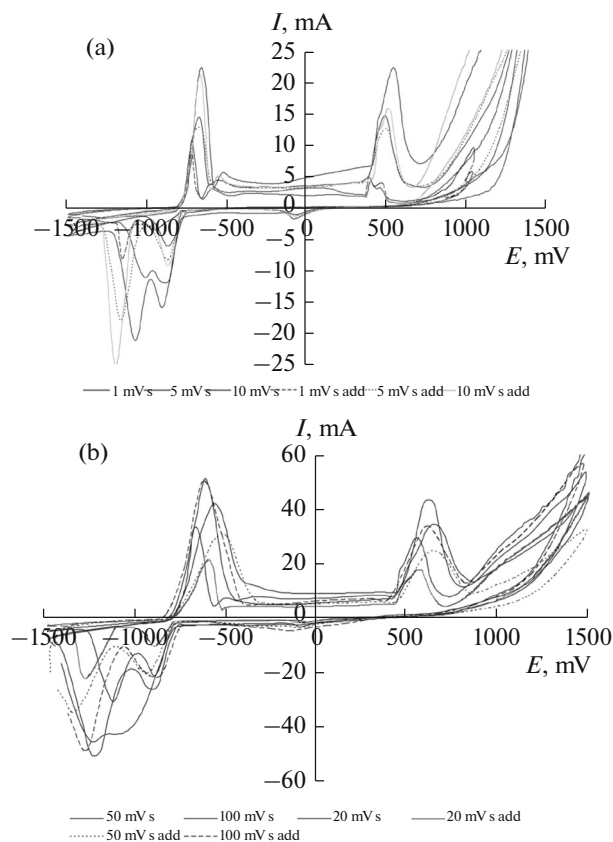

Fig. 5. Cyclic voltammograms of lead in 0.1 M alkaline solution in the presence of potassium oleate, $C_{PA} = 0.001$ M.

An increase in the concentration of alkali leads to the decrease in corrosion potential, growth of the rate of process, and the appearance of additional poorly resolved additional peaks (Figs. 1b, 1c). In 5 M alkali solution, multiple-peak anodic curve is observed at low sweep rates E, which indicates a large number of reactions [2]. They should include the formation of highly hydrolyzed lead(II) compounds, because according to XPA data there are only lead(II) and lead(IV) oxides in the specimens held in 0.1 and 5 M solutions (Fig. 2). During the reverse sweep of the curve, with the growth of C_{NaOH}, the currentless potential ($E_i = 0$) decreases and the third cathode peak, which is realized in the potential range close to 0 V, almost disappears. In the most concentrated solution, the first two cathode peaks merge (Fig. 1c).

The aforementioned differences in CV of lead depending on the concentration of sodium hydroxide also remain with the introduction of potassium oleate, which forms its own film on the lead surface [6] (Figs. 3–5).

In 0.1 M NaOH, potassium oleate facilitates passivation almost at all potential sweep rates decreasing

Table 1. Parameters and correlation coefficient of linear equations

Parameter Y	a, Y_0, and R values at C_{NaOH}, mol/L								
	0.1			1			5		
	a	Y_0	R, %	a	Y_0	R, %	a	Y_0	R, %
$i_{ap,1}$, mA	0.67	2.25	96	4.7	6.3	96	8.3	−1.0	98
$i_{ap,2}$, mA	0.59	2.10	95	4.0	4.8	93	6.2	0.9	99
$i_{cp,1}$, mA	−0.56	−2.1	89	−4.9	−4.8	94	−8.9	−0.7	77
$i_{cp,2}$, mA	−0.50	−1.4	95	−3.1	−6.6	68	—	—	—
$E_{ap,2}$, mV	46	511	89	23	430	90	21	394	96
$E_{ap,1}$, mV	39	−604	93	12	−696	75	3.8	−728	75
$E_{cp,1}$, mV	−42	−1140	77	−29	−989	95	−9.6	−1851	92
$E_{cp,2}$, mV	−33	−846	96	−12	−887	53	—	—	—
E_{cor}, mV	1.8	−730	50	−0.96	−805	40	−4.9	−805	57
$E_{i=0}$, mV	−8.9	489	67	−20	476	55	60	−590	96
a, Y_0, and R values in the presence of potassium oleate									
$i_{ap,1}$, mA	0.43	−0.45	84	4.7	3.0	97	6.6	3	97
$i_{ap,2}$, mA	0.73	−0.56	94	3.6	3.8	99	6.0	0.9	99
$i_{cp,1}$, mA	—	—	—	−3.9	−6.8	97	—	—	—
$i_{cp,2}$, mA	−0.43	0.28	95	−1.8	−1.6	97	−7.4	−0.39	97
$E_{ap,1}$, mV	36	−655	73	−1.2	−522	—	5.4	−754	47
$E_{ap,2}$, mV	49	451	97	22	426	82	11	478	56
$E_{ap,1}$, mV	—	—	—	−19	−1147	75	—	—	—
$E_{cp,2}$, mV	−90	−256	66	3.8	−923	33	−15	−805	97
E_{cor}, mV	5.4	−752	50	−2.9	−788	58	−2.9	−783	57
$E_{i=0}$, mV	−25	526	76	−14.9	345	62	28	−406	90

$E_{ap,1}$ and $i_{ap,1}$, almost does not affect the rate of the process between the first and the second anode peaks, and decreases the values of $E_{ap,2}$ and $i_{ap,2}$. On the reverse-sweep curves, a decrease in the rate of the process and currents in cathode peaks is also observed.

At higher concentrations of alkali, either an increase in the potentials of anode peaks is observed or they occur at the same E as in the solution without potassium oleate. When there is potassium oleate, cathode peaks are clearer at $C_{NaOH} = 1$ M, while at $C = 5$ M, one cathode peak is realized (Figs. 4, 5).

According to the theory of CV method, the dependence of anode and cathode peaks, as well as their potentials, on the potential sweep rate was processed at all concentrations of alkali, as well as in the presence of potassium oleate (Figs. 6, 7). As follows from criterial plots of $i_a(i_c)$, $V^{1/2}$, the dependences are linear and are not extended to the reference point. In most cases, they are described by the following equation:

$$Y = aX \pm Y_0, \qquad (3)$$

where $Y = i_{ap}$, i_{cp}, E_{ap}, E_{cp}, E_{cor}, and $E_{i=0}$, $X = V^{1/2}$.

The parameters of Eq. (3) for the aforementioned characteristics are given in Table 1.

The absence of extension to the reference point indicates mixed diffusion-kinetic control of the process, while the difference in the potentials of anode and cathode peaks (significantly higher than 23 mV) shows the irreversibility of processes [7]. However, it should be noted that anode peaks in this case are
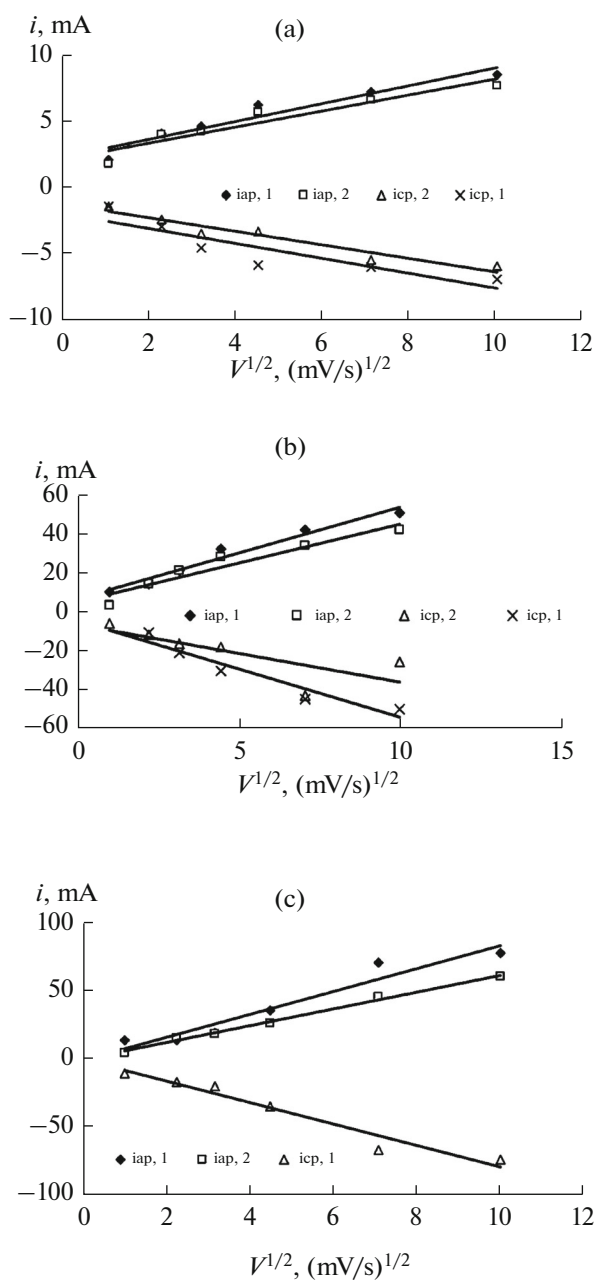
Fig. 6. Dependence of currents of anode and cathode peaks on potential sweep rate in (a) 0.1, (b) 1, and (c) 5 M NaOH.
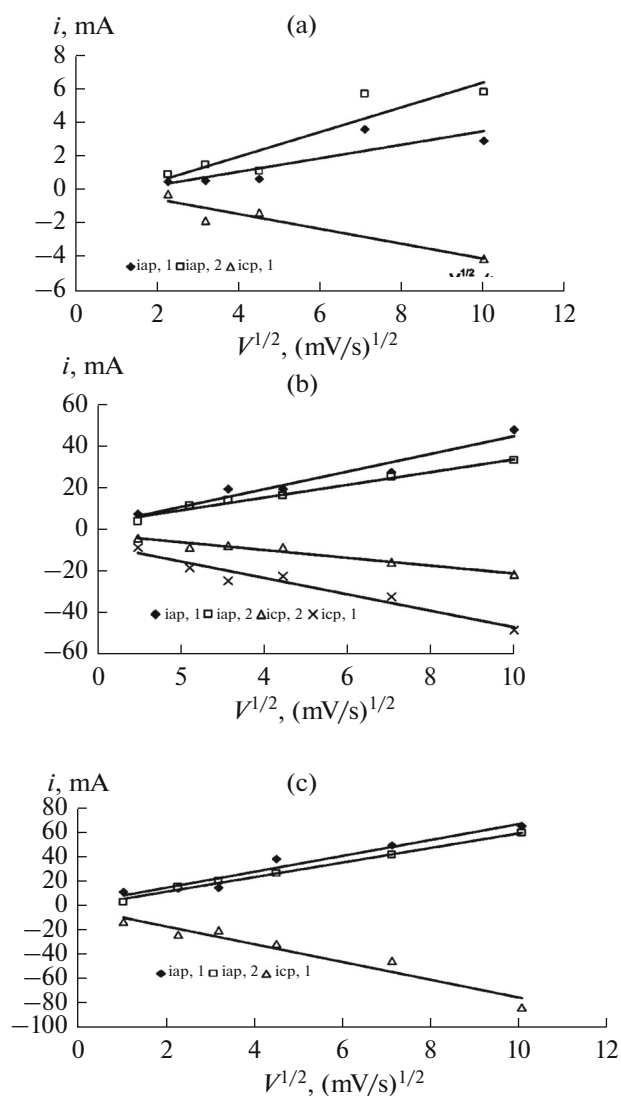

Fig. 7. Dependence of currents of anode and cathode peaks on potential sweep rate in (a) 0.1, (b) 1, and (c) 5 M NaOH in the presence of potassium oleate, $C_{PO} = 1$ mmol/L.

related to passivation processes and do not fully correspond to the peaks of conventional CV.

A significant decrease in the currentless potential on the reverse-sweep curve with an increase in the concentration of alkali in the solution should be noted. At low potential sweep rates, the difference in $E_{i=0}$ in 0.1 and 5 M NaOH takes values up to 1 V and the sensitivity (a) of this parameter to V also changes (table). The sensitivity of E_{cor} to V changes less significantly and in a different direction.

In most cases, the sensitivity of CV parameters to the change of the potential sweep rate in solution with and without potassium oleate almost does not change. Only the section on the coordinate axis (Y_0) is different. In the solutions with and without potassium oleate, dissolution of lead proceeds under mixed control conditions. At low potential sweep rates, the contribution of the diffusion component is higher, in particular, in alkaline media without potassium oleate.

Thus, the number of anode and cathode peaks on CV of lead depends on the concentration of alkali and the potential scan rate. The largest number of anode peaks is realized at low potential sweep rates in 5 M alkaline solution, while that of cathode is in 0.1 M solution. Due to the formation of the intrinsic film, potassium oleate facilitates lead passivation in 0.1 M

solution; however, it does not affect or restricts it in solutions with higher concentration of alkali. Dissolution of lead in sodium-hydroxide solution with and without potassium oleate proceeds irreversibly under mixed diffusion-kinetic control. Potassium oleate increases the contribution of diffusion control due to the formation of the own film.

REFERENCES

1. Nguen, D.K. and Sukhotin, A.V., *Zh. Prikl. Khim.*, 1990, vol. 63, no. 8, pp. 1821−1824.
2. Nguen, D.K. and Sukhotin, A.V., *Zashch. Met.*, 1988, vol. 24, no. 5, pp. 822−826.
3. Nguen, D.K. and Sukhotin, A.V., *Zh. Prikl. Khim.*, 1990, vol. 63, no. 8, pp. 1824−1828.
4. Berezhnaya, A.G., Ogarev, P.I., and Ekilik, V.V., *Korroz.: Mater., Zashch.*, 2012, no. 2, pp. 16−21.
5. Ekilik, V.V., Tikhomirova, K.S., and Berezhnaya, A.G., *Kondens. Sredy Mezhfaznye Granitsy*, 2012, vol. 14, no. 1, pp. 104−113.
6. Berezhnaya, A.G. and Kaz'mina, M.A., *Korroz.: Mater., Zashch.*, 2016, no. 2, pp. 32−40.
7. Galus, Z., *Fundamentals of Electrochemical Analysis*, Chichester: Ellis Horwood, 1976.

Translated by A. Muravev