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KINETIC RESEARCHES AND ELECTROCHEMICAL BEHAVIOUR OF LEAD AT POLARIZATION ALTERNATING CURRENT

Abstract. In the present work the kinetics and electrochemical behavior of lead during polarization by alternating current that occur on the lead and graphite electrodes in an acid medium by using the potentiodynamic method were researched. Anode-cathode and cathodic-anode cyclic polarization curves were taken to clarify the mechanism of the electrode processes occurring during the polarization by an alternating current on a lead electrode. According to the polarization measurements the kinetic parameters were calculated: charge transfer coefficients (α), the heterogeneous constants of rate the electrode process (k_s), and the effective activation energy of the process (E_a). The results are based on the high electrochemical activity of a lead electrode and the prospects of their use in electrolysis with alternating current polarization for the synthesis of various lead compounds.

Key words: lead, electrode, alternating current, electrooxidation, electrical dissolution, kinetic parameters.

Introduction. Recently, the demand for various industries in non-ferrous metals is more satisfied by their production from recycled materials. For the issue of recycling of secondary raw materials and various types of industrial waste for valuable products of multi-purpose use is given great attention, since it allows expanding not only the raw material base, but also to solve economic and environmental problems.

According to the data of [1, 2], especially lead (21.3%) is found in the hazardous solid wastes of polymetallic plants that falls into the environment from rock dumps (53.8%) and existing tailing dumps (39.6%). The effect of lead on the environment has a dampening and multiplying character. Concentration of lead in polymetallic ores of different regions averages from 0.32 to 0.8% per ton, in rich to 1.5%, and in very rich to 2.5%, sometimes higher.

In tailing dumps, depending on the time of their formation, lead content varies from 0.4 to 0.7 and even up to 1.5%. At present, out-of-use lead-acid batteries, lead cables and other products are disposed of again. Lead-acid battery scrap, as a rule, contains about 61% of pasty material and 39% of lead plates. The paste contains 41% lead sulphate, as well as lead oxides and lead metal.

Known methods for extracting lead from the scrap of batteries include the use of a reflector furnace or a shaft furnace for the smelting of lead [3, 4]. In the implementation of these processes, large amounts of sulfur dioxide are formed, which is a danger to the environment. Increased control over the composition of waste gases leads to a significant rise in the cost of the process.

The introduction of processes for the integrated processing of lead-containing materials, their regulation and finding the optimal conditions for a particular process require the study of the electro-chemical behavior of lead and its compounds. It should be noted that in recent years, alternating current has been increasingly used in various branches of chemical technology, but the electrochemical behavior of lead and the ability to synthesize its compounds under polarization by alternating current has not been studied.

One of the most urgent tasks today is the preparation of lead compounds by an electrochemical method without additional reagents and additives [5, 6]. Technological schemes of isolation of lead used in recent years do not give high indicators. In this connection, the synthesis of the most important metal compounds using non-stationary electrolysis regimes is an urgent task. The peculiarity of the non-stationary mode of electrolysis is the production of metals and its compounds of high purity, reduction of reagent costs, the possibility of using wasteless and simplified technological processes [7, 8].

Studies of domestic and foreign scientists on the possibility of conducting electrochemical reactions at alternating current are very limited. Most of the researchers studied the dissolution of vanadium in aqueous solutions in electrolysis by alternating current, as well as the mechanism of its influence [9], the process of silver dissolution in nitric acid at an alternating current of [10], the electrochemical behavior of titanium and copper under alternating current polarization [11-13].

The electrochemical behavior of nickel in alkaline solutions was studied in [14, 15]. In the literature, there are studies on the electrochemical synthesis of metal oxides using an alternating current for this purpose. The author with co-workers [16] were studied the effect of the composition and concentration of electrolyte, current density and electrolysis temperature on the oxidation rate of metals (Cu, Cd, Ti, Zn, Sn, Ni, Al, Pb, Fe, Mo) under alternating current polarization with a frequency of 50 Hz.

Analysis of the literature data showed the prospects of using alternating current. Because of the lack of knowledge about the kinetics of the processes of electrical dissolution, the poor knowledge of the chemistry of metal dissolution, it became necessary to search for effective methods of investigation, to determine the optimum conditions for the dissolution processes. In connection with this, it was of interest to study the electrochemical behavior of lead in aqueous solutions when passing an alternating current.

The purpose of this work was to study the mechanism and kinetic regularities of lead electro-oxidation processes in acidic solutions by the method of pull off potentiodynamic polarization curves, and also to study the effect of the basic electrolysis parameters on the current output of lead dissolution and the synthesis of lead(II) nitrate.

Methods. In the work electrochemical behavior of lead electrodes at polarization by industrial non-stationary current of 50 Hz without separation of the electrode space in a glass electrolyzer was investigated. Sinusoidal alternating current was supplied using a B-24 current source. The current strength was measured with an E-538 ammeter. To analyze the mechanism of electrochemical processes occurring on the surface of electrodes, electrolysis was carried out under certain conditions. To produce non-stationary current of different frequencies, the generator of GZM-231286 brand was used.

In order to study the mechanism of metal dissolution during the polarization of the lead electrode by an alternating current, cyclic potentiodynamic curves on the potentiostat SVA-1BM were pull off. The polarograms were recorded on a self-biased two-coordinate potentiometer PDS-021. The reference electrode was chlorine silver ($E^0 = +0.203$ V), and an auxiliary electrode was made of platinum. When pulling off the polarization curves, an electrode of a special design was used [17]. The investigations were carried out in a thermostatic cell of YSEC-2 using a TGL8U thermostat.

The behavior of the lead electrode in solutions of nitric acid in the concentration range 0.5-3.0 M, at solution temperatures of 20-80 °C and potential sweep rates of 10-100 mV/s has been studied. Anodic-cathodic and cathodic-anode cyclic polarization curves were pull of to clarify the mechanism of the electrode processes occurring on the lead electrode.

Results and discussions. In the background solution ([HNO$_3$] = 10 g/l), on the lead electrode on the cathodic branch of the cyclic polarization curve in the potential range minus 0.4 V a wave of reduction of lead(II) ions is observed, and the anode branch corresponds to the dissolution of metallic lead. On the cathode curve, hydrogen is observed in the potential range of minus 1 V, and on the anode curve oxygen is released at a potential E = +1.8 V.

As well as, cyclic polarization curves were measured in nitric acid solutions of lead nitrate ([Pb^{2+}] = =10 g/l, [HNO$_3$] = 10 g/l). Recovery of lead in the cathode region passes through a maximum at a potential of minus 0.5 V (figure 1), and at a potential «minus» of 0.8 V, hydrogen liberation is observed. On the anodic-cathodic cyclic polarization curve (figure 2), the basic electrode processes remain the same.

The results of the investigation of electrode processes by pulling off cyclic polarization curves are shown, that the electrochemical reactions proceeding in the cathodic and anodic half-cycle under the polarization by industrial alternating current, differ substantially from the reactions proceeding on the cathode and anode at the polarization by direct current.
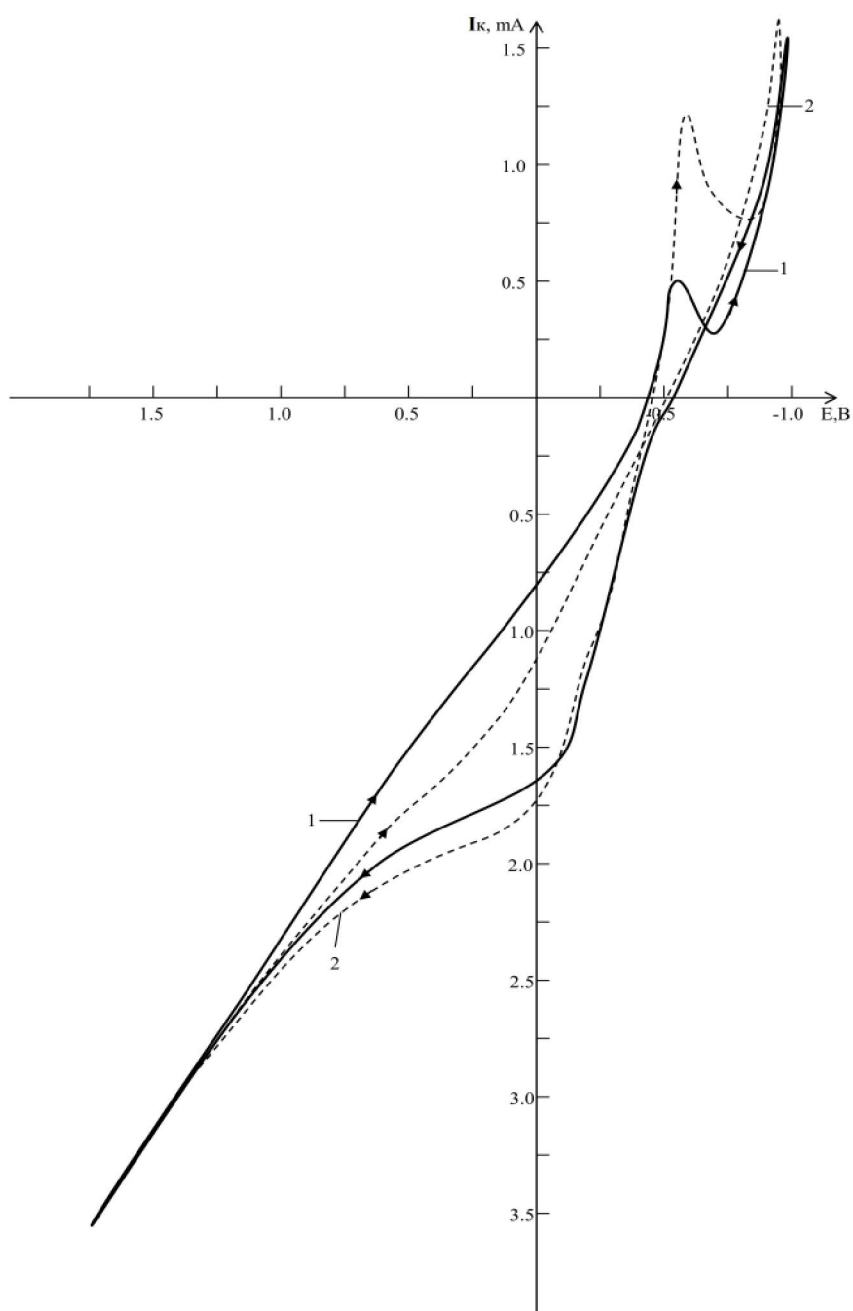
Figure 1 – Cathode-anode (1) and anodic-cathodic (2) cyclic polarization curves of a lead electrode:
$[Pb^{2+}]$ = 10 g/l, $[HNO_3]$ = 10 g/l; v = 10 mV/s; t = 20 °C

During the polarization of the lead electrodes by a nonstationary current in an acidic medium in anode half-period, the lead electrode dissolves according to the following reaction:

$$Pb^0 - 2e \rightarrow Pb^{2+} \qquad E^0 = -0.13 \text{ B} \tag{1}$$

At the same time, the hydrogen ion reduction reaction proceeds:

$$2H^+ + 2e^- \rightarrow H_2\uparrow \tag{2}$$

Perhaps, in the solution, lead(II) ions interact with nitrate ions by the reaction:

$$Pb^{2+} + 2NO_3^- \rightarrow Pb(NO_3)_2 \tag{3}$$
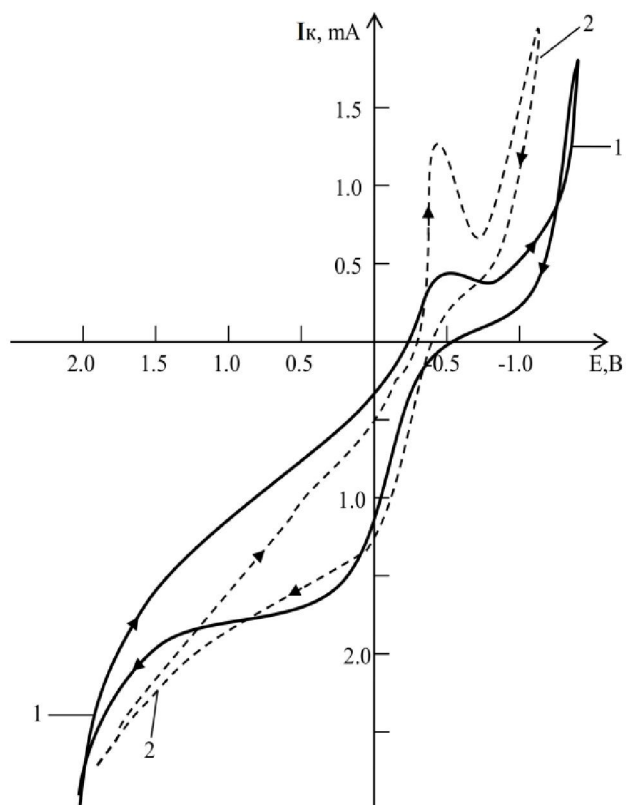
Figure 2 – Anodic-cathode (1) and cathodic-anode (2) cyclic polarization curves of a lead electrode:
$[Pb^{2+}] = 10$ g/l, $[HNO_3] = 10$ g/l; $v = 10$ mV/s; $t = 20$ °C

For the characterizing of the mechanism of lead electrooxidation process based on processing of polarization curves the following kinetic parameters have been determined: charge transfer coefficients (α), heterogeneous rate constants (k_s) of the electrode process (table 1) and effective activation energy of the process (E_a). Calculation of kinetic parameters (α, k_s) was carried out at temperatures of 20-25 °C and sweep speeds of 20-80 mV/s.

Table 1 – The values of transfer coefficients (α) and heterogeneous rate constants (k_s) of lead oxidation

t, °C	V, mV/s			
	20	40	60	80
Transfer coefficients (α)				
20	0.31	0.24	0.21	0.17
25	0.38	0.26	0.22	0.21
Heterogeneous rate constants ($k_s \cdot 10^3$, cm·s^{-1})				
20	2.93	3.20	2.98	3.14
25	2.79	4.61	2.61	4.30

By the values of the potential peak E_P and the half-peak $E_{P/2}$ of the voltammograms, the transfer coefficient (α) of the electrons for the anode process was calculated by the Matsuda and Ayabe equation [18]. Calculation of heterogeneous rate constants of electrode processes is carried out by the Matsuda equation [19].

An increase in the sweep rate of the potential, as can be seen from table 1, determines a decrease in the value of α at temperatures of 20-25 ° C to 0.17-0.21, respectively, characteristic of irreversible processes. Small values of the rate constants of electrode processes also indicate the irreversibility of the

electrochemical reaction proceeding from equation (1). The calculated value of the activation energy as a function of temperature according to the Arrhenius equation is 23.53 kJ/mol. Analysis of the obtained results and calculated kinetic parameters of electrode processes showed that the electrooxidation process of lead has a mixed nature of control, which allows us to draw a conclusion about the diffusion-kinetic regime of the electrode process.

It is established that in the case of the polarization with alternating current of two electrodes, they dissolve in a very small amount. During replacing one of the electrodes with a graphite electrode, dissolution of a second electrode made from a lead plate is observed. At the same time the graphite electrode is in the cathode half-cycle, the lead electrode is in the anode half-period and dissolves, forming divalent lead(II) ions.

In the work the influence of various parameters of electrolysis: the current density on lead and graphite electrodes, the concentration and temperature of the electrolyte, the duration of electrolysis, the frequency of alternating current on the electrochemical behavior of lead electrodes in a nitric acid medium under alternating current polarization is studied.

The influence of current density of a lead electrode in the range of 400-1000 A/m^2 was investigated, and a graphite electrode with a constant current density of 40 kA/m^2 used as an auxiliary electrode. When the current density on the lead electrode is increased, the current yield decreases from 98.1 to 20.3%. A decrease in the current output is probably due to the oxidizing properties of nitrate ions at high current densities, an oxide film is formed on the surface of the electrodes and passivation of the lead electrode is observed.

The effect of the current density of a graphite electrode under polarization by the alternating-current the current output of dissolving a lead electrode was also investigated. The current density at the lead electrode was kept constant – 400 A/m^2, and on graphite it varied in the range of 20-120 kA/m^2. By increasing of the current density on the graphite electrode, the yield of the lead electrode dissolution current decreases (table 2).

Table 2 – Effect of the current density of a graphite electrode on the current output of dissolving the lead electrode
(i_{Pb} = 400 A/m^2, C_{HNO3} = 1 M, τ = 0.5 h, t = 20 °C, v = 50 Hz)

i, kA/m^2	20	40	60	80	100	120
Current output, %	93	87	70	51	48	46

In the work, the effect of the electrolyte concentration on the current output of lead(II) ions has also been studied. By increasing the molar concentration of nitric acid to 3.0 M, the current output of the formation of lead(II) ions increases. An increase in the current output when polarized by a non-stationary current of the industrial frequency is due to simultaneous chemical dissolution of the lead electrode (table 3).

Table 3 – Chemical dissolution of lead electrode in nitric acid

$C_{M, HNO3}$	0.5	1.0	1.5	2.0	2.5	3.0
Δm, g	0.0003	0.0106	0.0505	0.0861	0.0955	0.0723

For the determining of the order of the reaction, the influence of the concentration of lead(II) ions on various electrodes is studied. The rectilinear dependences lg i - lg [Pb(II)] are obtained, according to which the order of the reaction was calculated equal: 0.5 on a lead electrode, 0.8 on a graphite electrode, and -1.0 on platinum.

The effect of temperature on the electrochemical behavior of a lead electrode in an acidic medium under polarization by a nonstationary current was also investigated. Based on the results of the research, it is shown that with an increase in the temperature of the solution from 20 to 80 °C and a constant current density on a lead electrode of 400 A/m^2, the lead dissolution current output rises from 31% to 160%. It is likely that an increase in the temperature of the electrolyte leads to an increase in the activity of the acid

molecules, as a result of which both the mobility of the ions and the rate of formation of the final products of electrolysis increase.

In a solution of nitric acid at a constant current density of 400 A/m^2 and a variation in the duration of electrolysis in the range 0.25-1.25 h, the lead current dissolution rate of the lead electrode decreases from 98% to 12%. The decrease in current output with increasing duration of electrolysis is probably due to a decrease in the concentration of lead(II) ions in the volume of the electrolyte.

The influence of current frequency as one of the main electrochemical parameters is also studied in the paper. Of particular interest, the study of the influence of the frequency of the current in the interval 500-3000 Hz on the electrical dissolution of lead in a solution of nitric acid had. An increase in the value of the frequency of the alternating current leads to a decrease in the output current of dissolving the lead electrode from 89.2% to 4%. This decrease is due to the shortage of the time of the electrooxidation reaction in the anode half-period, that is, the rate of oxidation reaction of lead ions slows down according to equation (1) as the frequency of the current increases, and the hydrogen ion reduction process according to equation (2) is mainly observed.

As a result of carrying out electrolysis during the polarization of the lead electrode, the main product of electrochemical synthesis is lead(II) nitrate. X-ray phase analysis (ASTM 36-1461) was carried out, which proves the identification of this compound [20]. All the reflections correspond to the phases of lead nitrate $Pb(NO_3)_2$: 4.5 Å; 3.92 Å; 3.5 Å; 2.78 Å; 2.37 Å; 2.27 Å; 1.97 Å; 1.75 (figure 3).
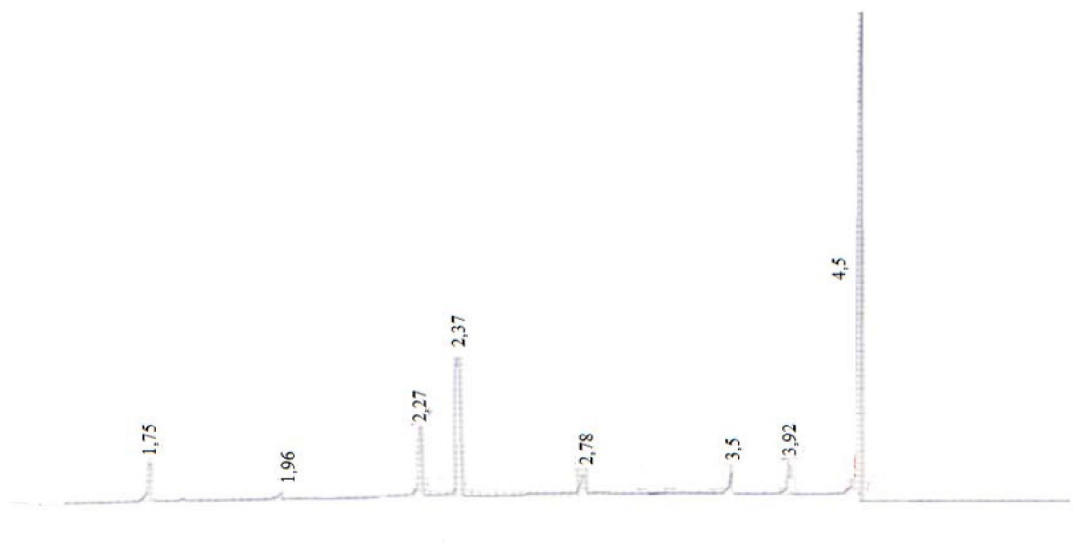

Figure 3 – Radiograph of lead(II) nitrate
(i_{Pb} = 400 A/m^2, $i_{graphite}$ = 20 kA/m^2, C = 2 M, t = 20 °C, τ = 0.5 h)

The experimental results obtained during the polarization of the lead electrode by an industrial alternating current in a solution of nitric acid showed the possibility of electrosynthesis of nitric acid compounds of various metals. As a result of carried out studies developed of favorable conditions of electrolysis: i_{Pb} = 400 A/m^2; $i_{graphite}$ = 20 kA/m^2; C = 2 - 2.5 M; τ = 0.5 h; t = 20 °C; v = 50 Hz. Electrolysis measurement data allow achieving high values of the current output of lead(II) ions up to 96-98%.

Conclusion. Thus, on the based of the potentiodynamic polarization curves, the mechanism of electrooxidation lead established and the kinetic parameters of the electrode process, which proceeds in the diffusion-kinetic regime, estimated. Investigations of the basic parameters of electrolysis made it possible to determine the optimum conditions for the preparation of the nitrate-acid salt of lead(II).

In the non-stationary mode of electrolysis, lead electrodes exhibit electrochemical activity and dissolve in nitric acid with the formation of lead(II) nitrate compounds. On the basis of the obtained results, the possibility of electrosynthesis of nitrate salts of metals used in various sectors of the national economy is shown by electrochemical treatment of environmentally harmful metal waste.

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АЙНЫМАЛЫ ТОКПЕН ПОЛЯРИЗАЦИЯЛАУ КЕЗІНДЕ ҚОРҒАСЫННЫҢ КИНЕТИКАЛЫҚ ЗЕРТТЕУЛЕРІ МЕН ЭЛЕКТРОХИМИЯЛЫҚ ҚАСИЕТТЕРІ

Аннотация. Потенциодинамикалық әдіспен қышқылдық ортада қорғасын және графит электродтарын айнымалы токпен поляризациялау кезінде қорғасынның электрохимиялық қасиеттері мен кинетикасы зерт-телген. Қорғасын электродында айнымалы токпен поляризациялау кезінде жүретін электродты процестердің механизмін анықтау үшін анод-катодты және катод-анодты циклді поляризациялық қисықтар түсірілді. Поляризациялық өлшеулердің мәліметтері бойынша кинетикалық параметрлер: заряд тасымалдау коэф-фициенттері (α), электродты процестің гетерогенді жылдамдық константасы (k_s) және эффективті активтену энергиясы (E_a) есептелген. Зерттеулер нәтижелері бойынша қорғасын электродының электрохимиялық белсенділігі және айнымалы токпен поляризациялау кезінде оның әртүрлі қосылыстардың синтезін жүргізуге болатыны анықталды.

Түйін сөздер: қорғасын, электрод, айнымалы ток, электртотығу, электрлік еру, кинетикалық параметр-лер.

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КИНЕТИЧЕСКИЕ ИССЛЕДОВАНИЯ И ЭЛЕКТРОХИМИЧЕСКОЕ ПОВЕДЕНИЕ СВИНЦА ПРИ ПОЛЯРИЗАЦИИ ПЕРЕМЕННЫМ ТОКОМ

Аннотация. В работе исследованы кинетика и электрохимическое поведение свинца при поляризации переменным током, протекающих на свинцовом и графитовом электродах в кислой среде потенциодинамическим методом. Для выяснения механизма электродных процессов, протекающих при поляризации переменным током на свинцовом электроде, были сняты анодно-катодные и катодно-анодные циклические поляризационные кривые. По данным поляризационных измерений рассчитаны кинетические параметры: коэффициенты переноса заряда (α), гетерогенные константы скорости электродного процесса (k_s) и эффективная энергия активации процесса (E_a). Приведенные результаты указывают на высокую электрохимическую активность свинцового электрода и перспективность их использования в электролизе при поляризации переменным током для синтеза различных соединений свинца.

Ключевые слова: свинец, электрод, переменный ток, электроокисление, электрорастворение, кинетические параметры.

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