

Anode Film Formation on Graphite Electrode

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Abstract

On the voltammograms of the electro-dissolution of sediments formed on a graphite electrode in solutions containing ferrous iron ions, one current peak is recorded. The authors compare the results of experimental studies and provide theoretical description of a solid electrode sediment amount's dependence from the parameters of electrodeposition. There is a linear dependence of the amount of sediment on the concentration of iron ions in the solution, which can be used for their analytical determination. Optimal conditions for electrodeposition and electro-dissolution of precipitation are recommended.

INTRODUCTION

Films of various compounds on the surface of metals or semiconductors are of great importance: 1) determine the chemical activity of such materials; 2) serve as protective and decorative coatings; 3) they are an integral part of various electronic devices; 4) they are the basis for creating nanodevices. A growing film at the phase boundary has its own peculiarities, namely: it occupies some intermediate position between solid and liquid phases, is a microheterogeneous system with its own, different from other phases, properties: porosity, diffusion coefficients, local concentrations, electrical conductivity, resistance.

Films of slow-soluble compounds formed in anode processes, or anode films, make up a separate class of sediments obtained from solutions of electrolytes. It is possible to choose film's growth and formation conditions, using an external EMF as a driving force: at constant potential, at constant current, applying the potential sweep of different configurations by varying the experimental conditions, depending on the requirements applied to the growing film, i.e. the process is easy to manage, knowing its features. The formation and electrical dissolution of anode films on an electrode can be accompanied by parallel and conjugated electrochemical and chemical reactions' behavior.

RESULTS AND DISCUSSION

We obtained equations describing the growth of the thin film growing on the surface of solid electrode [1] on the

electrodeposition stage parameters:

$$Q(t) = \frac{2}{\pi} nFDSc_0 (1 - \exp(-f\eta)) \left[\sqrt{\pi Dt} - \frac{nFDc_0}{i_0 \exp(+\alpha f \eta)} \ln \left(1 + \frac{i_0 \exp(+\alpha f \eta) \sqrt{\pi Dt}}{nFDc_0} \right) \right] \quad (1)$$

Equation (1) was obtained by a quasi-steady Stefan problem's solving method for electrochemical conditions [2]. The resulting equation (1) describes the dependence of the amount of sediment on the electrode from the electroaccumulation time, and ions concentration in the solution. Authors considered the case of thin films formation in condition of electrodeposition parameters changing.

Taking into account physical considerations, it follows that the equation (1) takes the form, ie the dependence $Q(t)$ - linear, $Q(c_0)$ - quadratic:

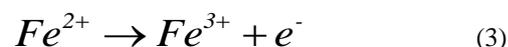
$$Q(t) = \frac{2}{\pi} nFDSc_0 (1 - \exp(-f\eta)) \sqrt{\pi Dt} \quad (2)$$

Electrodeposition of microquantities of a slow-soluble compound on the surface of metallic and indifferent electrodes is used to determine anions and ions of mixed valence by inversion voltammetry method [3-5].

To determine iron ions in water, two variants of electroconcentration have been suggested: in form of hydroxides of ferrous and ferric forms. In both cases, a mercury electrode was used [3].

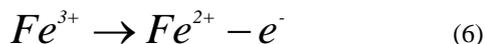
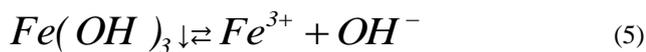
Graphite electrode has a number of advantages over mercury: it is non-toxic, easy to polish mechanically, and can be used in a wider range of pH and potentials. In the current study, the possibility and peculiarities of the formation and electro-dissolution of trace amounts of the sediment on the surface of a graphite electrode are investigated.

The process of electrodeposition of the electrode connection is represented by the following scheme:



The process of electrical dissolution of the connection from the surface of the electrode, with a linear sweep of the

potential, proceeds in the opposite direction:



A graphite disk electrode with an area of $(11.5 \pm 0.5) \cdot 10^{-2} \text{ cm}^2$ was made of spectrally pure graphite having the shape of a cylindrical rod, according to the method described in [3]. Before carrying out a series of measurements, the electrode was mechanically polished and thoroughly washed three times with distilled water.

Polarization curves for the electrodisolution of pre-formed precipitation on the electrode were recorded on a PU-1 polarograph with a three-electrode measurement scheme. A saturated silver chloride electrode was used as an auxiliary and reference electrode. Standard solutions containing ferrous form ions were prepared out of analytically pure reagents, background solutions - out of ACS reagents; to prepare the solutions, three times distilled water was used. The solution in the electrochemical cell was carefully deaerated with cp-grade argon, the rate of gas flow was controlled by a water manometer. To mix the solution and maintain constant hydrodynamic conditions, a magnetic stirrer was used.

Electrodeposition was carried out from solutions of sodium tetraborate containing $10^{-6} \div 10^{-4} \text{ M Fe}^{2+}$ by varying parameters: potential and electrodeposition time, pH of the solution. It is established that a slow-soluble compound on the electrode surface is formed at potentials more positive than -0.05 V and in the pH range equal to $7.0 \div 8.0$.

Dependences of the maximum current of electrical dissolution formed on the electrode of the compound from the potential of preliminary electrolysis are shown in Fig. 1. As the electrolysis' potential increases, amount of the compound at the electrode and height of the peak of electrodisolution first increase, and then tend to a constant value corresponding to the limiting diffusion current of Fe^{2+} ions to the electrode surface. Further, there is a slight decrease in the magnitude of the peak of the electrodisolution of the sediment, apparently connected with the possibility of a competing process of oxygen evolution on the electrode surface [6]. The potential of the peak and the width of the half-peak of the electrodisolution remain practically constant when the electrolysis potential is changed, from which it can be concluded that the composition of the sediment formed on the electrode does not change when the electrolysis potential is changed. The pH of the solution may have a significant effect on the potential region of electroconcentration. In particular, when the pH was changed from 8.0 to 7.5, the optimal electrodeposition potential of the compound was shifted by $50 \div 100 \text{ mV}$.

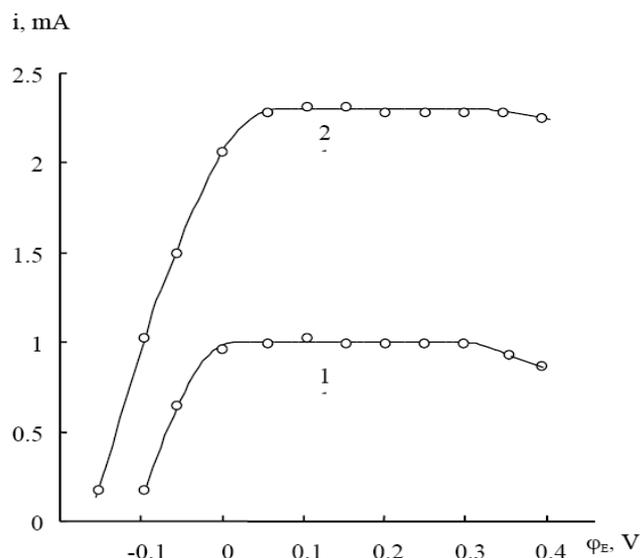


Figure 1: The dependencies of maximum current of electrodisolution of sediment formed on electrode on potential of preliminary electrolysis $0.02 \text{ M Na}_2\text{B}_4\text{O}_7 + x \text{ M H}_2\text{SO}_4$ (pH=8), containing different quantities of ions Fe^{2+} . $t_s=200 \text{ s}$; $w=2 \text{ mV/s}$; C, M: 1 – $7 \cdot 10^{-6}$; 2 – $1.5 \cdot 10^{-5}$.

An increase in the concentration of Fe^{2+} ions in the solution first leads to an increase in the amount of compound formed at the electrode and the maximum current of its electrodisolution. (Fig. 2). At sufficiently low concentrations ($10^{-6} \div 10^{-5} \text{ M}$) for $q < 100 \div 200 \text{ uC}$ these dependencies have linear range. In the region of high concentrations at $q > 500 \div 600 \text{ uC}$, a decrease in the film growth rate on the surface of the electrode is observed.

Figure 3 shows the results of studying the influence of electrodeposition time on the formation of a slow-soluble sediment on the electrode. An increase in this parameter also leads to an increase in the amount of the compound formed at the electrode and the maximum current of its electrodisolution. A decrease in the rate of precipitate formation and appreciable deviations of the dependences from linear precipitates also occur at $q > 500 \div 600 \text{ uC}$. Further film growth occurs according to a quadratic law, which is described by equation (2).

The amount of the compound on the electrode surface necessary to stop the film growth considerably depended on the pH of the solution and was $1500 \div 2000 \text{ uC}$ at pH=8 and $2000 \div 3000 \text{ uC}$ at pH=7.5.

The nature of the dependencies described above can be explained as follows. When the amount of sediment on the electrode is small, it is most likely distributed over the surface in the form of separate nucleating seeds. Under these conditions, the total process speed is determined by diffusion of Fe^{2+} ions to the electrode surface. With an increase in the amount of compound on the electrode, their growth and then

overlapping occurs, resulting in the formation of a film on the surface. Inhibition of the electrodeposition process of iron hydroxide with increasing amount of sediment at the electrode can be explained by the fact that under conditions when a slow-soluble compound completely covers the surface of the electrode, the slow process of substance transfer in the film

has a noticeable effect on the overall process speed. The total process speed will depend on the thickness and porosity of the film. It should be noted that these regularities also correspond to the theoretical conclusions obtained in modeling the processes of electrodeposition of slow-soluble compounds on a solid electrode [1, 2].

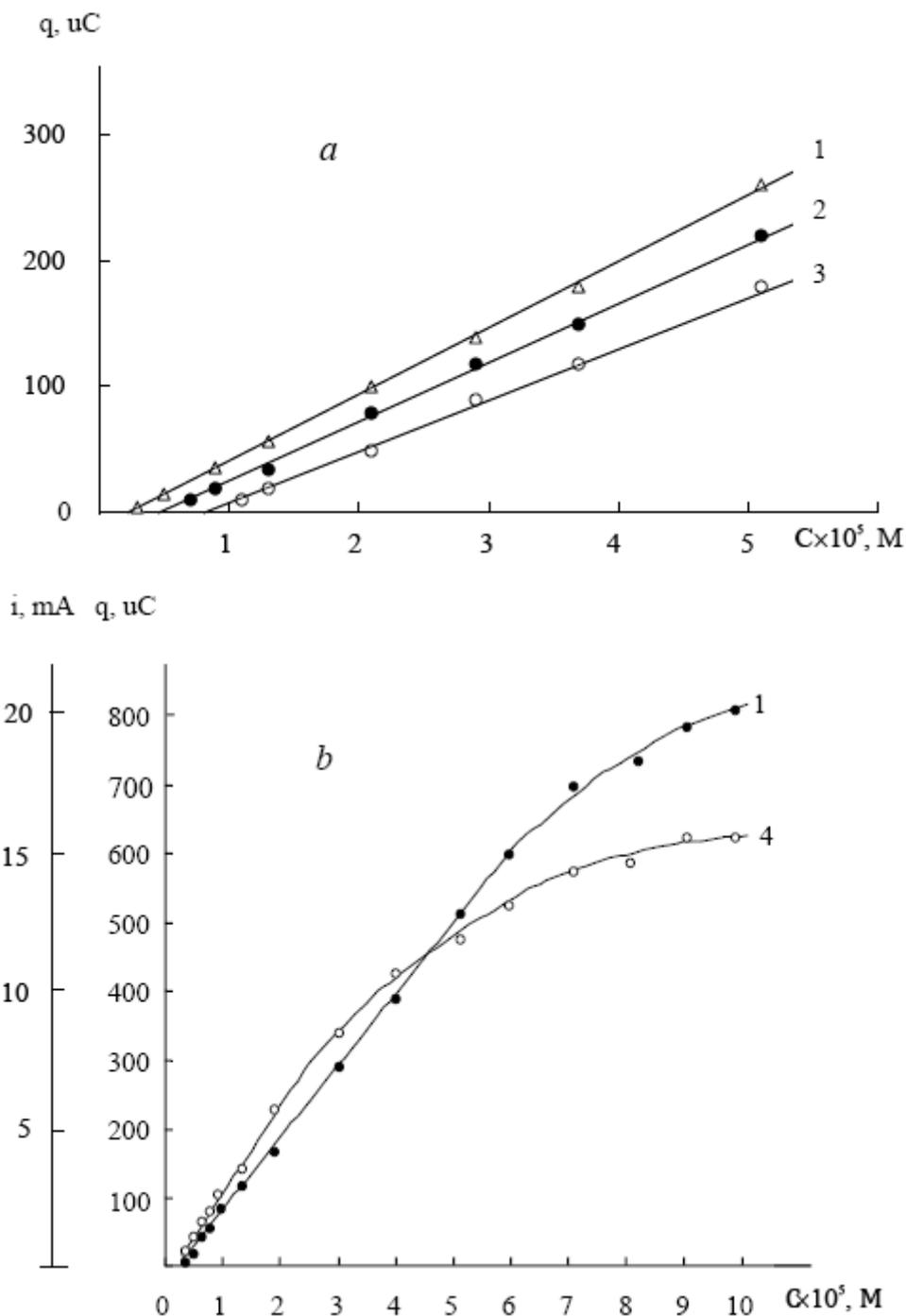


Figure 2: The dependencies of quantity of sediment formed on electrode (1, 2, 3) and maximum current of its electrodisolution (4) from concentration of ions Fe^{2+} in solution $0.02 M Na_2B_4O_7 + x M H_2SO_4$ (pH=8). $W = 2 mV/s$; a) $t_E=300 s$; φ_E, V : 1 – 0,17, 2 – 0,15, 3 – 0,13; б) $t_E=400 s$; $\varphi_E=0.15 V$.

CONCLUSION

The investigations conducted made it possible to recommend sediment electrodeposition and electro-dissolution' conditions, which are optimal for determining Fe^{2+} ions in aqueous solutions.

The area under the electrodissoolution peak depends linearly on the concentration of iron (II) ions in the solution and can be used to determine them. As the optimum conditions for the determination of Fe^{2+} ions in aqueous solutions, the following conditions for electrodeposition and sediment dissolution can be recommended:

- Indifferent electrolyte – 0.02 M $\text{Na}_2\text{B}_4\text{O}_7 + x$ M H_2SO_4 ($\text{pH} = 7.8 \div 8.2$).
- Potential of preliminary electrolysis $\varphi_e = 0.10 \div 0.20$ V relative to the potential of a saturated silver chloride electrode.
- The duration of preliminary electrolysis is $t_e = 2 \div 15$ min, the cathode sweep rate of the potential $w = 2 \div 5$ mV / s,
- The current peak potential is recorded in the range - 0.28 \div -0.42 V.

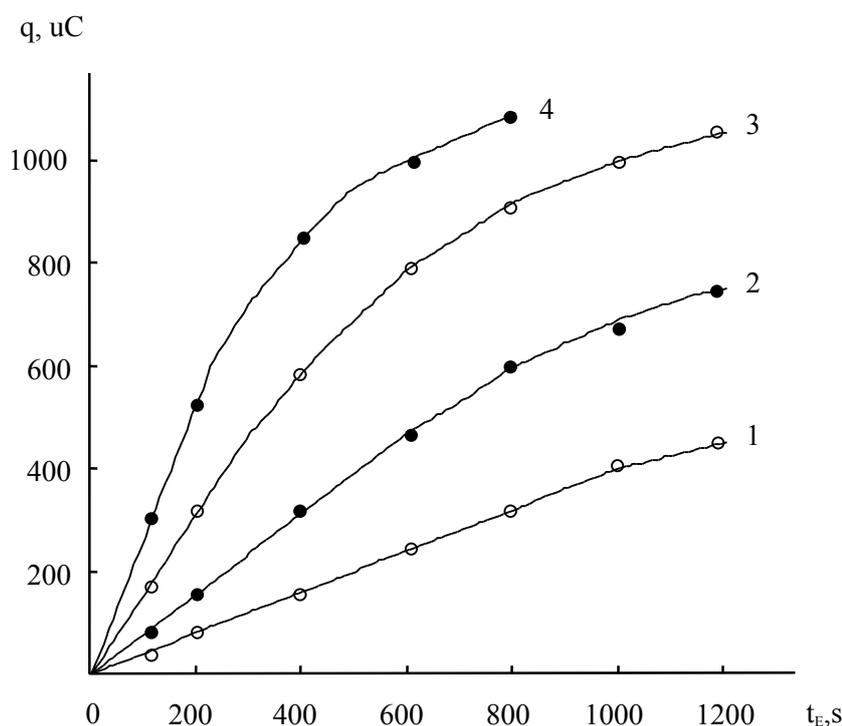


Figure 3: The dependencies of quantity of sediment formed on electrode on time of preliminary electrolysis for different concentration of ions Fe^{2+} in solution 0,02 M $\text{Na}_2\text{B}_4\text{O}_7 + x$ M H_2SO_4 ($\text{pH}=8$). $\varphi_s=0,15$ V; C, M: 1 – $4 \cdot 10^{-5}$; 2 – $8 \cdot 10^{-5}$; 3 – $1,5 \cdot 10^{-4}$; 4 – $3 \cdot 10^{-4}$.

Statistical processing of iron (II) determinations by the method of inversion voltammetry on a graphite electrode in model aqueous solutions showed that the proposed method makes it possible to determine $1 \cdot 10^{-6}$ mol / l of Fe^{2+} in a solution with a relative standard deviation of 0.1.

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