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Electrochemical Oxidation of Formic Acid on the Surface of an Anodically Modified Ag15Pd Alloy

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Abstract

It was shown that the phase transformation of palladium into its own phase during the selective dissolution of the Ag15Pd alloy proceeds in the instantaneous nucleation mode and is limited by the surface diffusion of Pd ad-atoms to the growing three-dimensional nucleus of the new phase. The kinetic regularities of the electrooxidation of formic acid on an Ag15Pd alloy subjected to preliminary selective dissolution were established using transient electrochemical methods. It was found that the process of anodic destruction of HCOOH in an acidic sulphate solution proceeds at a higher rate on the anodically modified Ag15Pd alloy, the surface of which is morphologically developed and enriched with palladium as a result of potentiostatic selective dissolution under overcritical polarization conditions. The process of electrooxidation of HCOOH is non-stationary, proceeds in a mixed-kinetic mode and accelerates with increasing anodic potential. Kinetic currents of anodic oxidation of formic acid were determined by the chronoamperometry. A correlation between the value of the electric charge transferred during preliminary anodic modification of the Ag15Pd alloy and the rate of the kinetic stage of the electrooxidation of HCOOH was revealed.

Keywords: alloy, silver, palladium, selective dissolution, phase transformation, formic acid, electrooxidation.

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1. Introduction

The anodic behaviour of metal alloy is often selective. During the selective dissolution of a binary homogeneous A,B-alloy, the electrochemically negative component A undergoes preferential ionization. This process is a source of defects (including vacancies) in its surface layer [1], which under certain conditions of anodic selective dissolution of the alloy or under the influence of corrosion environment [2–7] is morphologically destabilized and passes into a highly developed, dispersed state. This transition is based on irreversible processes of phase regrouping of an electropositive metal [8–10], which is thermodynamically possible

with overcritical anodic potentials and charges. With subcritical potentials, only the dissolution of the electronegative component occurs, the alloy surface is morphologically stable, and the concentration of the noble component increases when approaching the interphase boundary with the electrolyte. In the overcritical region of potentials and charges along with the ionization of component A in the highly defective surface layer of the alloy, component B recrystallizes from metastable structurally disordered state in its own highly developed phase [11]. As a result, the selective dissolution of alloys in the region of overcritical potentials can be used to obtain electrode materials with a micro- and nanoporous structure. Such materials can be used for the

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manufacture of electrodes in electrochemical power sources in electrochemical energetics. An important advantage of the electrochemical method for producing highly developed electrode materials by selective dissolution of alloys is the possibility of optimization of their morphological and electrocatalytic properties by controlling the process of the preliminary anodic modification of the alloy [12–15].

Considering that palladium effectively accelerates the anodic oxidation of formic acid [16–18], it seems promising to use the process of selective dissolution of homogeneous Ag,Pd-alloys for the synthesis of the electrocatalyst of the anodic process in low-temperature fuel cells operating on the direct oxidation of HCOOH [19]. During anodic polarization in an acidified non-complexing medium solid solutions of the Ag-Pd system based on silver undergo selective dissolution of silver, accompanied by a phase transformation of palladium [7, 11]. It is possible to form an electrode material with various degrees of morphological development of the surface layer and its enrichment with palladium and, as a result, with different electrocatalytic activity with respect to the electrooxidation reaction of formic acid by regulating the conditions of the anodic dissolution of solid solutions, i.e. the electrode potential and the electric charge transferred through the electrode.

The purpose of this study was the identification of the kinetic regularities of electrooxidation of formic acid on the surface of an Ag15Pd alloy (atomic fraction of palladium 15 %) subjected to selective dissolution of silver, and determination of the role of the conditions of preliminary anodic modification of the alloy in the kinetics of anodic destruction of HCOOH.

The objectives of study were as follows:

1. To find conditions and identify the kinetic regime of the process of recrystallization of palladium upon anodic selective dissolution of the Ag15Pd alloy in an acidic nitrate medium.

2. To determine the kinetic regularities of the electrooxidation process of formic acid on the surface of the anodically modified alloy Ag15Pd in an acidic sulphate medium.

3. To identify the influence of the conditions of the selective dissolution of the Ag15Pd alloy on the electrooxidation rate of formic acid on

the anodically modified surface of the alloy in an acidic sulphate medium.

2. Experimental

The studies were carried out on an alloy of the Ag-Pd system with atomic fraction of palladium 15 %. The alloy was prepared by direct melting in a tungsten induction furnace preliminarily evacuated and filled with argon (1.2 atm.) in A_2O_3 crucibles. The metals were kept in a molten state at 1723 K, then cooled to 1373 K at a rate of 600 K/h, after which they were quench hardened in water. According to the phase diagram and quench hardening mode, the obtained alloy was a statistically disordered solid solution [20].

In order to make the electrode, the alloy was cut, polished, and placed in a frame of polymerized epoxy resin. Standard preparation of the electrode surface included striping on sanding paper with decreasing grain size, polishing on chamois with an aqueous MgO suspension to a mirror finish, washing with distilled water, degreasing with ethyl alcohol, followed by washing with twice distilled water, and drying with filter paper.

Working solutions of 0.1 M $KNO_3 + 10^{-5}$ M $HNO_3 + 10^{-5}$ M $AgNO_3$ and 0.05 M $H_2SO_4 + 1$ M HCOOH were prepared using twice distilled water from analytical grade reagents and sulphuric and nitric acid fixanals. Deaeration of the working solutions with chemically pure argon was carried out directly in the electrochemical cell for at least 2 h. The experiments were conducted in non-mixed solutions.

In studies, a standard three-electrode cell was used, without separation of the spaces of the working and auxiliary electrodes. The auxiliary electrode was platinum. The silver chloride reference electrode was located in a separate vessel and connected to the cell by an electrolytic bridge filled with a saturated solution of ammonium nitrate, with a Luggin capillary. The potentials in the study are presented relative to the standard hydrogen electrode scale.

The change and maintenance of the electrode potential, as well as the registration of polarization curves and curves corresponding to the current decay, were performed using an IPC-Compact universal computerized potentiostatic set. The electrode prepared for the experiment was placed in a cell filled with a deaerated working

solution and kept for some time until the quasi-stationary value of the open-circuit potential was established. For potentiodynamic measurements, the potential scan rate was set $V = dE/dt$ and the polarization of the I, E -curve was recorded. For chronoamperometric measurements the potential $E = \text{const}$ was set and I, t -dependence of the current decay was recorded for some time. Current density i was calculated by dividing the current strength per unit geometric area of the electrode.

3. Results and discussion

Bilogarithmic curves corresponding to the current decay obtained at different anodic potentials are shown in Fig. 1. Linear sections, probably corresponding to the process of selective dissolution in the regime of non-stationary diffusion [11], proceeding with rate $i_{\text{diff}}(t)$ can be distinguished on these curves. When reaching a certain time point t_{cr} the current decay slowed down, and the linearity of the current dependence was impaired. With the increase of the anodic potential, the deviation from linearity increased, and the length of the linear section and t_{cr} parameter noticeably reduced.

The curvature of the bilogarithmic chronoamperograms was probably caused by the acceleration of silver ionization due to the phase regrouping of palladium [7, 11], accompanied by

the displacement of palladium ad-atoms over the alloy surface to the nucleation sites of the new Pd phase. During this process new underlying layers of the alloy, which were in contact with the electrolyte solution, were released and as a result, the total ionization flux increased. Assuming the additivity of the rates of two parallel non-stationary processes, the selective dissolution of silver in the delayed diffusion mass-transfer mode and the phase transformation of palladium in the heterogeneous nucleation mode, the current transient of the nucleation process can be determined using the formula [11]:

$$i_{\text{nucl}}(t) = i_{\text{SD}}(t) - i_{\text{diff}}(t)$$

as the difference of the total (i_{SD}) and diffusion (i_{diff}) currents. Current density transients of phase formation obtained using such calculations and plotted as nucleation current density dependencies i_{nucl} from nucleation time $t_{\text{nucl}} = t - t_{\text{cr}}$ are shown in Fig. 2. It can be seen that with an increase in the potential, the process rate increased, and the current dependences had a curve shape with a maximum or reaching a plateau characteristic for nucleation processes.

The determined current transients of the phase formation process were re-plotted in coordinates, criterion for various models of heterogeneous nucleation [21], which allowed revealing the nature of the kinetic limitations of the formation

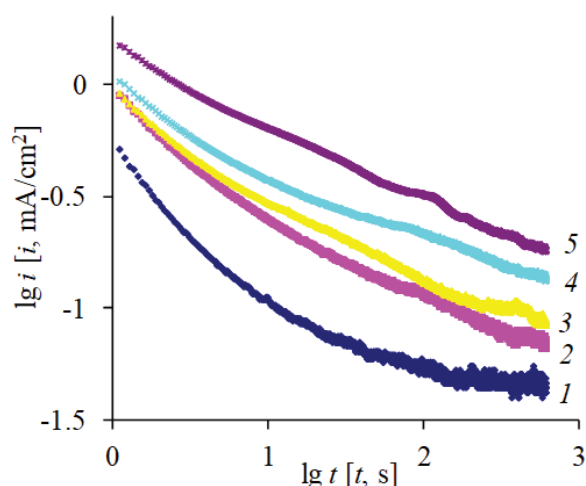


Fig. 1. Anodic chronoamperograms of Ag15Pd alloy in 0.1 M $\text{KNO}_3 + 10^{-3}$ M $\text{HNO}_3 + 10^{-3}$ M AgNO_3 solution at potentials of 835 (1), 840 (2), 850 (3), 860 (4), 870 (5) mV and replotted in logarithmic coordinates

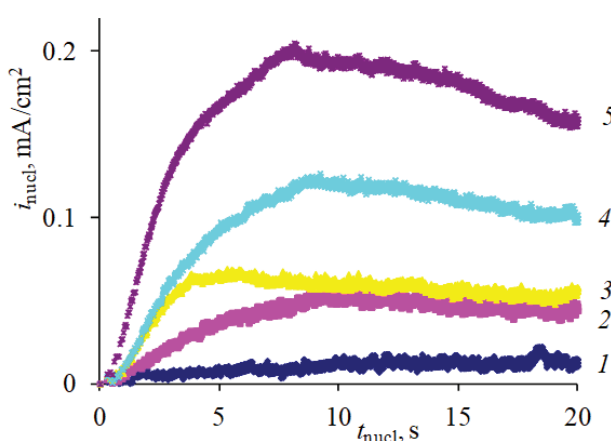


Fig. 2. Current transients of the phase regrouping of palladium upon selective dissolution of the Ag15Pd alloy in 0.1 M $\text{KNO}_3 + 10^{-3}$ M $\text{HNO}_3 + 10^{-3}$ M AgNO_3 solution at potentials of 835 (1), 840 (2), 850 (3), 860 (4), 870 (5) mV

of the palladium phase. Linearisation was possible only in $i_{\text{nucl}}, t_{\text{nucl}}^{1/2}$ -coordinates, criterion for instantaneous nucleation in the diffusion mode of a 3D-nucleus (Fig. 3). An increase in the slope of the linear initial parts of the chronoamperograms during the ennoblement of the electrode potential indicated an increase in the effective rate constant of the formation of the palladium phase $k_{\text{eff}} = di_{\text{nucl}}/dt_{\text{nucl}}^{1/2}$.

Polarization curves of the electrooxidation of formic acid on the surface of an Ag15Pd alloy subjected to anodic modification at various values of the applied electrode potential E_{mod} and transferred electric charge q_{mod} , respectively are shown in Figs. 4 and 5. It can be seen that the rate of electrochemical destruction of the HCOOH increased both with a positive shift of E_{mod} and with an increase in q_{mod} . It turned out that on the surface of the modified alloy, the electrooxidation of formic acid proceeds with a noticeable rate only under the condition $E_{\text{mod}} \geq 830$ mV.

For the establishment of the kinetic regularities of the anodic destruction of HCOOH on the surface of the anodically modified Ag15Pd alloy, the process was carried out under potentiostatic conditions in the region of the voltammetric maximum, varying the values of the anodic modification potential of the E_{mod} and electric charge q_{mod} transferred through the electrode at the stage of selective dissolution. The analysis showed that chronoamperograms of electrooxidation of formic acid (not provided in the

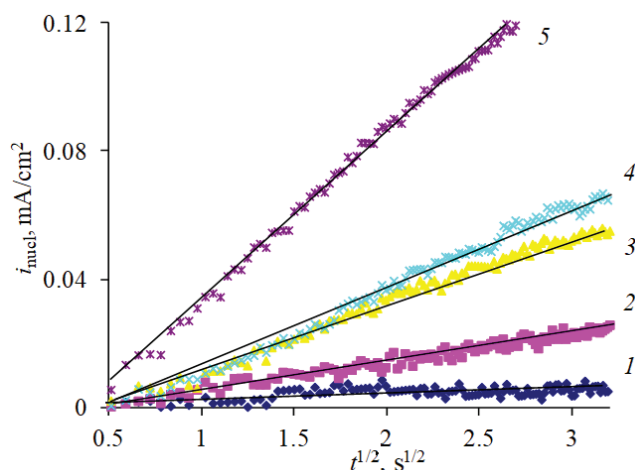


Fig. 3. Chronoamperograms of the formation of the palladium intrinsic phase, replotted in coordinates, criterion for instantaneous nucleation in the diffusion mode of growth of a three-dimensional nucleus on the surface of an Ag15Pd alloy upon its selective dissolution in 0.1 M $\text{KNO}_3 + 10^{-3}$ M $\text{HNO}_3 + 10^{-3}$ M AgNO_3 at potentials of 835 (1), 840 (2), 850 (3), 860 (4), 870 (5) mV

article), regardless of the values E_{mod} and q_{mod} were non-linear in the Cottrell coordinates, criterion for diffusion kinetics, but they were characterized by a smooth current decay to almost zero. Such shape of the curves corresponding to the current decay indicates a non-stationary process and the implementation of mixed-kinetic control, when the diffusion of an electroactive substance to the electrode is accompanied by a kinetic stage. According to [22], we found the partial rate of this

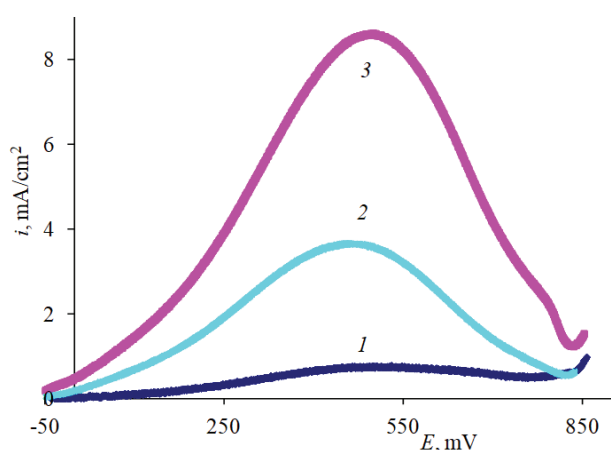


Fig. 4. Voltammograms of electrooxidation of formic acid in 0.05 M $\text{H}_2\text{SO}_4 + 1$ M HCOOH on an anodically modified Ag15Pd alloy subjected to selective dissolution in an acidic nitrate solution for 10 min at potentials of 830 (1), 840 (2), 850 (3) mV

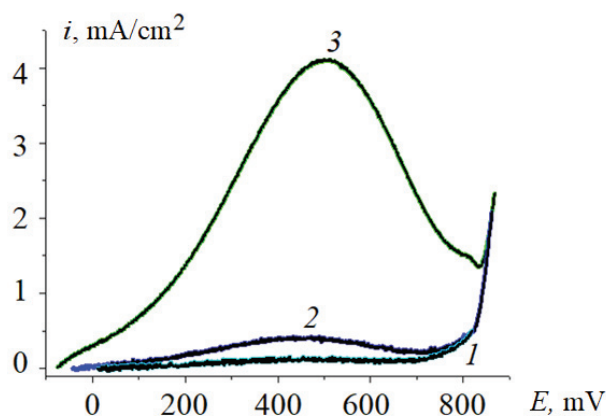


Fig. 5. Voltammograms of electrooxidation of formic acid in 0.05 M $\text{H}_2\text{SO}_4 + 1$ M HCOOH on the surface of an Ag15Pd alloy subjected to anodic modification at $E_{\text{mod}} = 850$ mV and $q_{\text{mod}} = 15$ (a), 25 (b), 46 (c) mC/cm²

stage (“kinetic current”), re-plotting the initial sections of the curve corresponding to the current decay in coordinates $i-t^{1/2}$ (Fig. 6). We took into account that if the electrode process includes successive stages of volume diffusion and some kinetic stage, for example, a stage of charge transfer or a chemical reaction, characterized respectively by a diffusion coefficient D and rate constant k , then i,t -curve corresponding to the current decay in such a mixed-kinetic mode is described by the equation:

$$i(t) = i(0) \cdot \exp(k^2Dt) \cdot \operatorname{erfc}(kD^{1/2}t^{1/2}).$$

Partial rate of the kinetic stage $i(0)$ was determined by extrapolating the linearized part of the chronoamperogram on the ordinate axis at $t \rightarrow 0$, taking into account that for $k^2D \ll 1$ (“kinetic” electrooxidation mode) current transient obeys the ratio:

$$i(t) = i(0) \cdot \left(1 - \frac{2kD^{1/2}t^{1/2}}{\pi^{1/2}}\right).$$

It turned out that not only at the ennoblement of the electrode potential of selective dissolution of the alloy, but also with an increase in the electric charge passed during its anodic modification, the rate of the kinetic stage of the electrooxidation of HCOOH increases (Fig. 7). This can be explained by both the enrichment of the surface of the Ag15Pd alloy with palladium and the probable increase in its electrocatalytic activity due to the formation of a non-equilibrium, energetically metastable, and morphologically more highly developed phase during the recrystallization of Pd at the stage of selective dissolution of the Ag, Pd alloy. The revealed correlation between the parameters of the anodic modification of the silver-palladium alloy and the rate of electrochemical destruction of formic acid can be the basis for the development of optimal technological conditions for the formation of new effective electrode materials for low-temperature fuel cells operating on direct oxidation of HCOOH.

4. Conclusions

The analysis of the partial current transients of the phase regrouping of palladium showed that the process of Pd recrystallization during the selective dissolution of the Ag15Pd alloy includes an instantaneous nucleation stage, while the

nucleus growth mode is diffusion-controlled. It was found that the rate of electrooxidation of formic acid in a sulphate medium on an anodically modified Ag15Pd alloy increases with an increase in the anodic destruction potential of HCOOH. The process is non-stationary and proceeds in a mixed-

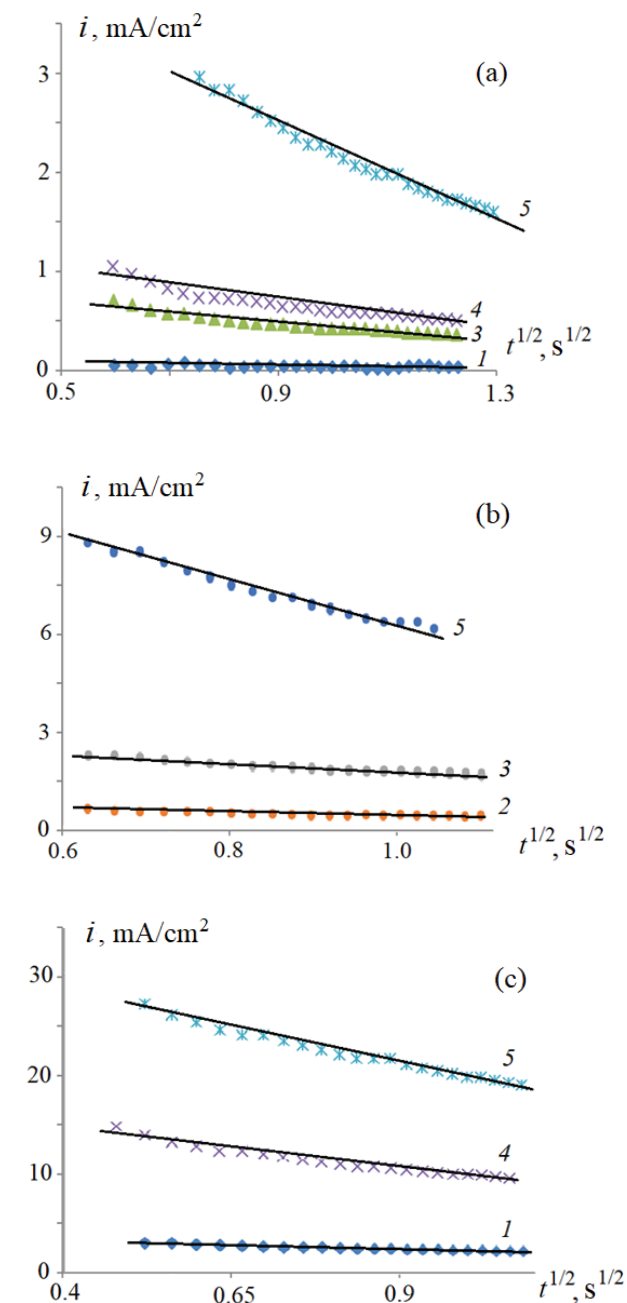


Fig. 6. Criterion $i,t^{1/2}$ -dependence of the process of electrooxidation of formic acid in $0.05 \text{ M H}_2\text{SO}_4 + 1 \text{ M HCOOH}$ at potentials of 300 (1), 400 (2), 500 (3), 600 (4), 700 (5) mV on the surface of an Ag15Pd alloy subjected to anodic modification at $E_{\text{mod}} = 850 \text{ mV}$ and $q_{\text{mod}} = 15$ (a), 25 (b), 46 (c) mC/cm^2

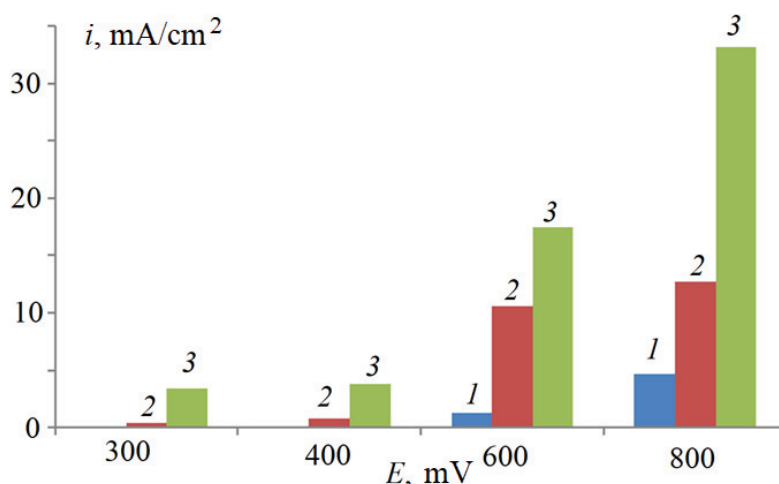


Fig. 7. Kinetic currents of electrooxidation of HCOOH on the surface of an Ag15Pd alloy subjected to anodic modification at $E_{\text{mod}} = 850$ mV and $q_{\text{mod}} = 15$ (1), 25 (2), 46 (3) mC/cm²

kinetic mode. The kinetic currents of the process were determined based on the chronoamperometry of the anodic oxidation of HCOOH in an acidic sulphate solution. It was shown that the rate of kinetic stage increases with an increase in both the electrode potential of selective dissolution and the electric charge transferred during anodic modification of the alloy.

Conflict of interests

The authors declare that they have no known competing financial interests or personal relationships that could have influenced the work reported in this paper.

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