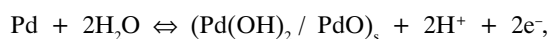

Kinetic regularities of cathodic reduction of palladium (II) oxide surface layer

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This work represents a cyclic voltammetric study of the kinetic regularities of cathodic reduction of the palladium oxide surface layer. Investigations have been performed in 0.5 M H₂SO₄ with two types of Pd electrodes: a bulk palladium electrode and ~ a 0.5 μm thick electroplated palladium coating on Au. The potential range of voltammetric investigations was confined to 0.4–1.4 V in order to avoid a possible interference of hydrogen and oxygen evolution processes. It has been found that cathodic reduction of the stationary Pd(II) hydroxide (oxide) surface layer formed at $E_a = 1.4$ V in 0.5 M H₂SO₄ follows the laws of diffusion kinetics from the beginning of the cathodic process up to the cathodic peak potential E_p , i.e.: $dE/d\ln i = dE_p/d\ln i_p \approx RT/F$ and $dE_p/d\ln v \approx RT/F$, since $i_p = \text{const} \cdot v$, where v is the potential scan rate. It has been presumed that the kinetic parameters established are determined by the following summary electrochemical reaction:



which, in the course of the cathodic process, proceeds reversibly due to an increase in pH at the electrode surface. $(\text{Pd}(\text{OH})_2 / \text{PdO})_s$ represents a surface layer of slightly soluble Pd(OH)₂ or/and PdO phases.

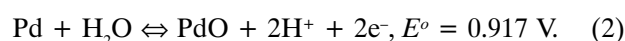
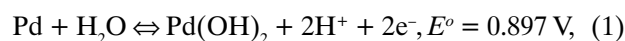
Key words: palladium, surface, Pd(II) oxide layer, reversible cathodic reduction, diffusion kinetics, sulfuric acid

INTRODUCTION

Anodic oxidation of noble metals, formation of surface compounds and their cathodic reduction are the processes, which have been intensively investigated over the last 50 years [1–5]. It is believed that anodic reaction taking place on the surface of Pt group metals and gold prior to the beginning of oxygen evolution, represents electro-/chemisorption of water molecules or, in other words, stepwise underpotential oxidation of water, yielding eventually a monolayer of adsorbed oxygen atoms, where metal and oxygen atoms are in the ratio 1:1. This simple and popular model is still used for the evaluation of the true surface area of noble metal electrodes [6–8]. It is also deemed that the processes of oxygen atoms chemisorption and their reduction are irreversible. The possibility of direct electrochemical oxidation of noble metals in the range of potentials preceding O₂ evolution is not

considered, though thermodynamically such process is entirely possible [9]. Formation of the surface oxides in the potential range indicated is believed to be the result of the chemical oxidation of the metals by atomic oxygen [5].

In the case of palladium, the prevailing opinion is that anodic oxidation of the metal, taking place prior to the beginning of O₂ evolution, yields the layer of chemisorbed oxygen – PdO [10–14]. However, other researchers report the formation of Pd(II) oxide or hydroxide [15, 16]. So what, in fact, is the product of anodic reaction? The literature still fails to answer unequivocally this question. Theoretically, direct electrochemical oxidation of palladium is possible at $E > 0.9$ V under standard conditions [9], and it should lead to formation of a mixed layer of slightly soluble Pd(OH)₂ and PdO phases, since the values of standard potentials of Pd/Pd(OH)₂ and Pd/PdO couples are very close, viz.:



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In a microgravimetric study [17] we have shown that palladium dissolves in 0.5 M H_2SO_4 upon potential cycling in the range from 0.5 V to 1.3 V. The latter fact, in accordance with the results obtained in [15, 16], can be explained presuming that a layer of $\text{Pd}(\text{OH})_2$ and PdO phases, which forms during the anodic process, partly dissolves into the electrolyte.

Thus, the experimental results discussed above [15–17] call into question the assumption that the anodic process represents an irreversible stepwise oxidation of water molecules.

The object of the present work was to analyze theoretically the regularities of reversible reduction of palladium oxide surface layer and to compare them with experimental data obtained for a bulk palladium electrode and electroplated palladium coating on gold in 0.5 M H_2SO_4 .

EXPERIMENTAL

A P-5848 potentiostat with H-307 analogue recorder (Russia) was used for voltammetric investigations. A thermostatically controlled water-jacketed glass cell ($\sim 20 \text{ cm}^3$) with separate working, counter and reference electrode compartments was used. A pure Pd ($>99.99\%$) plate of 1 cm^2 apparent area as well as bright $\sim 0.5 \mu\text{m}$ thick electroplated Pd coating on a pure Au ($>99.99\%$) plate of 2 cm^2 apparent area were used as working electrodes. The gold electrode surface roughness factor, k , evaluated according to the Burshtein method [8], was ~ 2 . Smooth and bright Pd coating was plated from a neutral sulfate electrolyte consisting of $1\text{--}2 \text{ g dm}^{-3}$ Pd, $0.5 \text{ M H}_2\text{SO}_4$, NH_4OH (to attain pH 6–8) and $1\text{--}2 \text{ g dm}^{-3}$ of brightener, at a temperature of $50 \text{ }^\circ\text{C}$ and cathodic current density $i_c = 1 \text{ A dm}^{-2}$. Rh-plated titanium was used as the anode. The pure Pd and Au plates were polished mechanically and subsequently cleaned chemically to remove the remains of polishing paste. The electroplated Pd coating was subjected to voltammetric investigations immediately after the plating, whereas the bulk Pd electrode was cleaned prior to measurements with a fine-grained pulp of $\text{MgO} + \text{CaO}$, washed with hot distilled water and activated in $0.5 \text{ M H}_2\text{SO}_4$ for $\sim 30 \text{ s}$. The reversible hydrogen electrode (RHE) in the working solution was used as the reference. All potentials in the text are referred to SHE. A pure Pt ($>99.99\%$) plate 2.0 cm^2 in the apparent area served as the counter electrode. The solutions were made from ultra pure concentrated sulfuric acid (GOST 14262-78) and bi-distilled water. The solutions were deaerated by bubbling pure argon through them for 20–30 min. Argon was also used to maintain the inert atmosphere over the solutions during the measurements. All experiments were carried out at room temperature ($20 \text{ }^\circ\text{C}$).

RESULTS AND DISCUSSION

Figure 1 shows cyclic voltammograms of two types of Pd electrodes – a bulk palladium electrode (Fig. 1a, curves 1, 7) and an electroplated $\sim 0.5 \mu\text{m}$ thick pure palladium coating on gold (Fig. 1b). The potential range of voltammetric investigations has been confined to the palladium oxide formation/reduction region 0.4–1.4 V in order to avoid the interference of hydrogen and oxygen evolution processes.

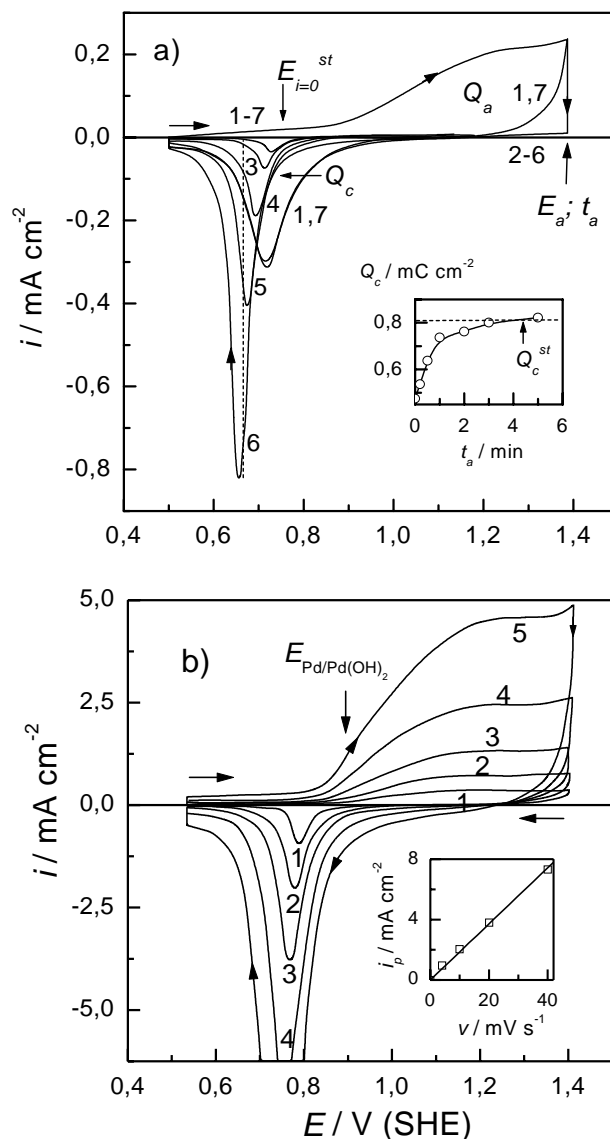


Fig. 1. Cyclic voltammograms of bulk Pd electrode (a) and $\sim 0.5 \mu\text{m}$ thick electroplated pure Pd coating on Au (b) in $0.5 \text{ M H}_2\text{SO}_4$, $20 \text{ }^\circ\text{C}$. a) Curves 1, 7 – $t_a = 0$, $\nu = 80 \text{ mV s}^{-1}$; 2–6 – $t_a = 3 \text{ min}$ at $E_a = 1.4 \text{ V}$, $\nu = 80 \text{ mV s}^{-1}$ for anodic part of the cycle and 4, 10, 20, 40 and 80 mV s^{-1} , respectively, for cathodic part; insertion: $Q_c - t_a$ dependence for $E_a = 1.4 \text{ V}$. b) Curves 1–5 – $\nu = 4, 10, 20, 40$ and 80 mV s^{-1} , respectively; insertion: $i_p - \nu$ dependence. Symbols: $E_{i=0}^{st}$ – stationary value of the open circuit potential of $\text{Pd}|\text{Pd}(\text{OH})_2 / \text{PdO}$ electrode; Q_a and Q_c – anodic and cathodic charges; E_a and t_a – anodization potential and time

The voltammograms in Fig. 1 reveal one anodic and one related cathodic process in the potential range of interest. As one can see from Fig. 1a, when the potential scan is stopped at 1.4 V, the rate of the anodic process decreases significantly down to *ca.* 10 $\mu\text{A cm}^{-2}$ and then stays practically constant. As the duration of anodic polarization, t_a , at 1.4 V increases, so does the Q_c of the cathodic peaks (see insertion in Fig. 1a). However, when $t_a > 3$ min, the increase in Q_c becomes slow. It means that during this period of time an almost stationary amount of Pd compounds is formed on the electrode surface ($Q_c = Q_c^{st} \approx 0.8 \text{ mC cm}^{-2}$). Curves 2–6 (Fig. 1a) reflect the regularities of cathodic reduction of such stationary oxide layer on the bulk Pd electrode at different potential scan rates, ν . One can see that in this case the cathodic peaks are situated so that up to the peak potential, E_p , they coincide and prolong one another to form one integral i - E profile virtually independent of ν , whereas at $E < E_p$ the curves diverge and their segments shift towards more negative E values as ν increases. The peak points E_p and i_p can be regarded as marginal points of the integral i - E profile, starting from which the character of the cathodic process changes. The identity of curves 1 and 7 in Fig. 1a shows that the initial state of the electrode surface, *i.e.* surface roughness and electrochemical activity, have not changed during the measurements. Analogous regularities of the surface oxide layer reduction have been found for the gold electrode in [18].

Comparison of voltammograms presented in Figs. 1a and 1b and reflecting the same electrochemical processes shows that the rates of anodic and cathodic processes in the case of $\sim 0.5 \mu\text{m}$ thick, bright Pd coating on the inert Au substrate are more than 20 times higher as compared to the bulk Pd electrode under the same conditions. In the case of Pd-black coating [19–21] the latter effect may be ascribed to an increase in the electrode real surface area. However, in our case such increase in electrode activity could not be accounted for by the mere increase in surface roughness, since the coating was bright and reproduced the texture of the substrate. Most likely this is caused by the surface structure of the palladium coating being more defective and completely free from hardly reducible oxides [22], the formation of which is impossible within the E range of the coating deposition. A comparison of the cathodic charge values in Figs. 1a and 1b, *viz.* $\sim 0.6 \text{ mC cm}^{-2}$ and $\sim 18 \text{ mC cm}^{-2}$, respectively, suggests that the thickness of the oxide layer formed on the bulk Pd electrode makes just $\sim 3\%$ of the oxide layer thickness in the case of electroplated Pd coating. As one can see from Fig. 1b, voltammograms of Pd coating reveal a region of electrochemical reversibility of the system, *i.e.* there is a rather wide E range, from $\sim 0.8 \text{ V}$ to

$\sim 1.2 \text{ V}$, where both anodic and cathodic processes take place. The rates of cathodic and anodic reactions become equal at $E \approx 0.89 \text{ V}$. The latter value corresponds to the reversible potential of the Pd|Pd(OH)₂ electrode in the solution under investigation. Very high values of anodic charges ($Q_a \approx 40 \text{ mC cm}^{-2}$) are totally incompatible with the model of oxygen adsorption [5, 7]. Presuming that the anodic process represents a direct electrochemical oxidation of Pd to Pd(OH)₂, 40 mC cm^{-2} should correspond to oxidation of ~ 90 atomic layers of Pd lattice, since the theoretical charge corresponding to adsorption of a monolayer of O atoms in the case of ideal surface ($k = 1$) is 0.42 mC cm^{-2} [7]. The imbalance between Q_a and Q_c values (Fig. 1b) means that about half of the oxide layer dissolves into electrolyte [17, 23]. The thickness of Pd(OH)₂ (and/or PdO) surface layer with corresponding $Q_c \approx 18 \text{ mC cm}^{-2}$ should be about 50 nm, since Pd(II) compounds with the coordination number 4 are known to have a planar square configuration of the molecules [24] and such molecule can occupy about 5 atomic sites on Pd surface.

A valuable information regarding the nature of electrochemical processes taking place on the palladium electrode may be derived from the data presented in Fig. 2 and that is the pH-dependence of the stationary open-circuit potential $E_{i=0}^{st}$ of the bulk Pd electrode with a surface oxide layer formed anodically in sulfate or phosphate solutions. These results have been reported in [25]. One can see that the dependence is linear, the slope $\Delta E_{i=0}^{st} / \Delta \text{pH}$ is

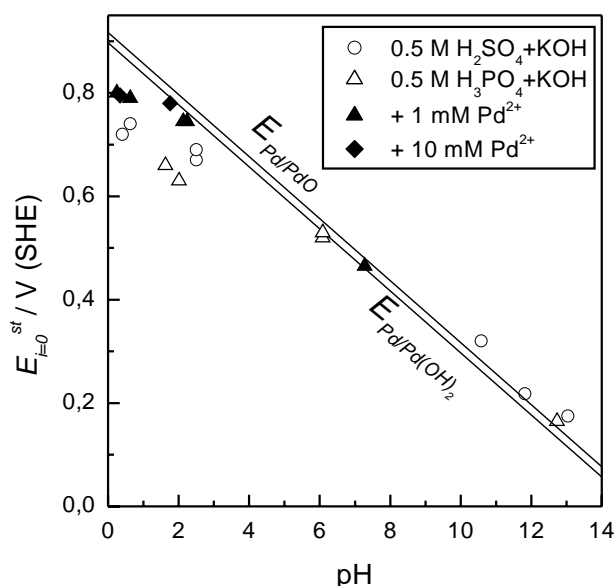


Fig. 2. The pH-dependence of the stationary open-circuit potential $E_{i=0}^{st}$ of Pd electrode with a surface oxide layer in 0.5 M $\text{H}_2\text{SO}_4 + \text{KOH}$ (O), 0.5 M $\text{H}_3\text{PO}_4 + \text{KOH}$ (Δ) and sulfate or phosphate solutions containing 1 mM (\blacktriangle) and 10 mM (\blacklozenge) of Pd^{2+} ions; 20 °C

close to $2.3RT / F$ and the standard potential is very close to $E^{\circ}_{Pd/Pd(OH)_2}$ given in the literature [9]. These findings suggest that the Pd electrode with a layer of anodically formed surface oxide behaves like a metal–oxide electrode of the second kind in a range of pH from ~ 3.0 to ~ 12.0 . In the case when the solution phase is saturated with $Pd(OH)_2$, the E –pH dependence of the metal–oxide electrode is observed starting from $pH \approx 2.0$. It is noteworthy that similar results have been obtained by other researchers [26, 27] in the case of thermally prepared Pd|PdO electrodes. Grubb et al. [26] have shown that such electrodes behave like metal–oxide electrodes in the range of pH values from ~ 2.0 to ~ 12.0 and the standard potential E° is close to the theoretic value [9]. Kinoshita et al. [27] have reported that Pd|PdO electrodes prepared by the thermal method show an almost theoretical $\Delta E / \Delta pH$ slope in the pH range from 2.5 to 8. If the Pd electrode with a layer of anodically formed surface compounds represents a reversible metal–oxide electrode, hence it follows that the anodic process is an electrochemical oxidation of palladium resulting in the formation of slightly soluble phases of $Pd(OH)_2$ and PdO on the electrode surface.

In the case of reversible reduction of the oxide layer of the metal–oxide electrode, the electrode potential and the surface concentration of OH^- ions, c_s , are given by the Nernst equation [28]:

$$E = E^{\circ} - \frac{RT}{F} \ln c_s, \quad (3)$$

or

$$c_s = \exp\left(\frac{F(E^{\circ} - E)}{RT}\right). \quad (4)$$

There are two essentially different cases of reversible reduction of the oxide layer of the metal–oxide electrode:

- 1) OH^- ions produced in the cathodic process remain on the electrode surface;
- 2) OH^- ions freely diffuse away from the electrode surface into solution bulk.

Let us assume now that there is no diffusion of the cathodic reaction product, *i.e.* OH^- ions, into the bulk of the solution and they remain on the electrode surface. Such situation is possible only if the oxide layer is continuous and thick enough to block the diffusion of OH^- ions into the solution for some time after the cathodic process has started. The oxide layer can serve as a barrier for OH^- diffusion until about half of it is reduced, *i.e.* up to the potential E_p of the cathodic current peak, as may be judged from Fig. 1b. In such a case the amount of OH^- ions produced on the electrode surface in a unit of time should be equal to the change in their surface concentration, *viz.*:

$$i/F = dc/dt. \quad (5)$$

Differentiation of Eq. (4) with respect to time and insertion of the expression obtained into Eq. (5) gives:

$$i = \frac{F^2 v}{RT} \exp\left(\frac{F(E^{\circ} - E)}{RT}\right) = \frac{F^2 v c_s}{RT}, \quad (6)$$

where $v = dE/dt$. It follows from Eq. (6) that in the case of reversible reduction of the surface oxide layer, when the resulting OH^- ions cannot diffuse away from the electrode surface, i should depend on the potential in the same way as c_s does, *i.e.* exponentially according to Eq. (6), and should be directly proportional to v . As one may see from Fig. 1b and the insertion therein, the current up to the peak point i_p increases linearly with the potential scan rate. An analogous v -dependence of i is also observed for the anodic process. However, at $E > E_{Pd/Pd(OH)_2}$ the anodic process becomes irreversible as a result of anodic passivation of the electrode.

Another case of the reversible reduction of the surface oxide layer is when OH^- ions produced in the cathodic reaction can freely diffuse away from the electrode surface into the bulk of the solution. Experimentally such situation may be observed provided that the oxide layer is rather thin or not continuous. In the solution under investigation, *i.e.* 0.5 M H_2SO_4 , OH^- ions should be neutralized by H^+ ions, however, if Q_c is just ~ 1 mC cm^{-2} , the reserve of the OH^- ions accumulated on Pd electrode surface in the form of oxide layer is up to 100 times higher than the surface concentration of H^+ ions. Thus, the influence of neutralization reaction should be insignificant. In the latter case of reversible reduction of the surface oxide layer, one of the main equations of diffusion kinetics [28],

$$i/i_d = 1 - c_s/c, \quad (7)$$

may be transformed into

$$i/i_d = c_s/c \quad (8)$$

$$\text{and } i = \text{const } c_s, \quad (9)$$

since $c_s/c \gg 1$ in the case of cathodic process, whereas i and i_d are opposite in signs. The i_d here represents the anodic limiting current of OH^- diffusion, whereas c is the concentration of OH^- ions in the solution bulk. In 0.5 M H_2SO_4 the values of i_d and c are extremely low, however, from the theoretic point of view, they represent finite quantities. It is evident from Eq. (9) that in the case under investigation the current of the cathodic reduction of the surface oxide layer is directly proportional to

the surface concentration of OH⁻ ions, c_s , and independent of the potential scan rate. Insertion of Eq. (9) into Eq. (3) gives a Tafel-type expression well known from diffusion kinetics [28]:

$$E = \text{const} + \frac{RT}{F} \ln i. \quad (10)$$

The latter equation in fact represents the Nernst equation (Eq. 3 or 4), since $i \sim c_s$. Consequently, in the latter case of oxide layer reduction E -dependence of $\ln i$ should be linear with the slope RT/F . This was observed experimentally in the case of cathodic reduction of the stationary Pd oxide layer formed on bulk Pd electrode (Fig. 1a). The integral i - E profile described above represents an exponential with the slope $dE/d\ln i$ is close to RT/F , as shown in Fig. 3. The same slope is also observed in $\ln i_p - E_p$ plot, since the peak points (E_p, i_p) may be regarded as the points of the same exponential. The fact that experimental values of the slopes $dE/d\ln i$ and $dE_p/d\ln i_p$ are slightly less than RT/F could be attributed to the influence of neutralization reaction.

Taking into account that $E = E_{i=0} - vt$, Eq. (10) can be rewritten in the case of cathodic current as follows:

$$i = i_o \exp(Fvt / RT), \quad (11)$$

where i_o is an exchange current density of the metal-oxide electrode. In the case under investigation i_o is

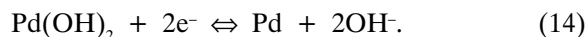
very low, with the order of magnitude characteristic of quasi-equilibrium processes. Since the charge under the integral i - E profile makes the $1/n$ part of the total Q_c (dashed line drawn for curve 6 in Fig. 1a), Q_c can be expressed as

$$Q_c \approx n \int_{i=0}^{i_p} i_o \exp\left(\frac{Fvt}{RT}\right) dE, \text{ where } dE = d(vt). \quad (12)$$

Integration of Eq. (12) gives

$$i_p = Q_c Fv/nRT. \quad (13)$$

As the insert in Fig. 3 shows, the experimental dependence $i_p - v$ is linear and coincides with the one calculated according to Eq. (13), assuming that $n = 2.5$, i.e. that the charge under the integral i - E profile makes up 40% of the total Q_c , which is consistent with the experimental results. Given that $dE/d\ln i = dE_p/d\ln i_p = RT/F$ (Fig. 3) and $d\ln i_p = d\ln v$, which follows from Eq. (13), it turns out that $dE_p/d\ln v = RT/F$. Thus in this case E_p depends on v . This, has been confirmed experimentally for Pd (Fig. 1a) and also in the case of gold [18]. These results indicate that cathodic reduction of the stationary Pd(OH)₂/PdO surface layer follows the laws of diffusion kinetics and that the Pd electrode with the surface layer of Pd(OH)₂/PdO phase behaves like an reversible metal-oxide electrode. The reversibility of the cathodic process in our case is only possible in the E range of about 200 mV, i.e. from the beginning of the cathodic process up to the peak potential E_p (Fig. 1a), till about 40% of the total amount of Pd(OH)₂ is reduced on the electrode surface. The main reason behind it should be the increase of pH at the electrode surface, occurring as a result of surface reaction:



The increase in surface pH by about 3 units within the E range indicated should be sufficient for the transient realization of nearly equilibrium conditions under which the reversible metal-oxide electrode may exist (Fig. 2).

Thus the results obtained call into question the opinion that anodic and cathodic processes proceed irreversibly [7, 10–13]. The reversibility of these processes has been demonstrated for Pd electrode with a layer of anodically formed surface oxide under open-circuit conditions (Fig. 2) and it also has been shown to realize under non-stationary conditions in the course of the cathodic process (Figs. 1 a,b and 3). Chemisorption of water molecules during the anodic process may be understood as hydrolysis of the Pd²⁺ ions, leading eventually to the formation of a surface layer of slightly soluble phases of Pd(OH)₂ and/or PdO [9].

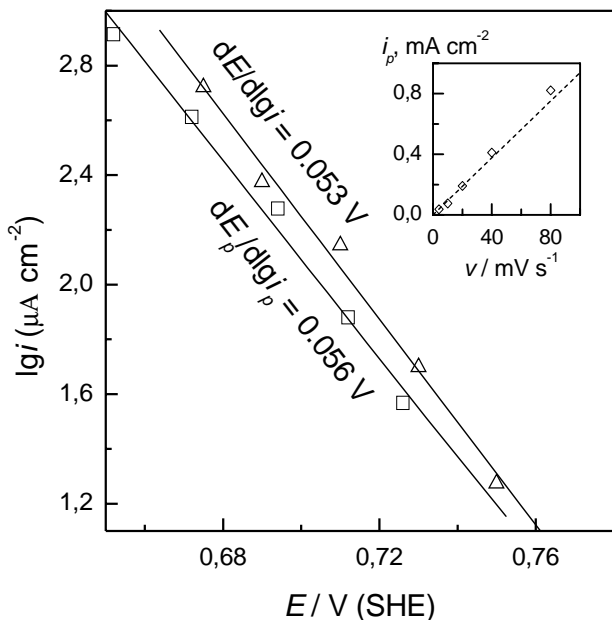
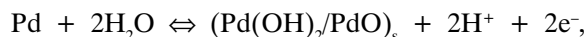


Fig. 3. Dependences $\lg i - E$ (Δ), $\lg i_p - E_p$ (\square) and $i_p - v$ (insert) in the case of cathodic reduction of the stationary Pd oxide surface layer ($Q_c^s = 0.8 \text{ mC cm}^{-2}$). Insert: \diamond – experimental points; straight line calculated according to eq. (13). The data are taken from Fig. 1a

CONCLUSIONS

1. It has been found that cathodic reduction of a stationary Pd(II) hydroxide (oxide) surface layer formed at $E_a = 1.4$ V in 0.5 M H_2SO_4 follows the laws of diffusion kinetics from the beginning of the process up to the cathodic peak potential E_p , i.e.: $dE/d\ln i = dE_p/d\ln i_p \approx RT/F$ and $dE_p/d\ln v \approx RT/F$, since $i_p = \text{const} \cdot v$.

2. It has been presumed that the kinetic parameters established are determined by the following summary electrochemical reaction:



which, in the course of the cathodic process, proceeds reversibly due to increase in pH at the electrode surface. $(Pd(OH)_2/PdO)_s$ represents a surface layer of slightly soluble $Pd(OH)_2$ or/and PdO phases.

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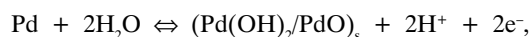
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**Pd(II) OKSIDINIO PAVIRŠINIO SLUOKSNIO
KATODINĖS REDUKCIJOS KINETINIAI
DĖSNINGUMAI**

S a n t r a u k a

Darbe ciklinės voltamperometrijos metodu tirti Pd(II) paviršinio oksidinio sluoksnio katodinės redukcijos dėsningumai 0,5 M H_2SO_4 tirpale. Nustatyta, kad stacionaraus oksidinio sluoksnio, suformuoto esant $E_a = 1,4$ V, redukcijos procesui nuo jo pradžios iki srovės maksimumo (i_p) potencialo, E_p , galioja difuzinės kinetikos dėsningumai: $dE/d\ln i = dE_p/d\ln i_p \approx RT/F$ bei $dE_p/d\ln v \approx RT/F$; čia v – potencialo skleidimo greitis. Šiuos dėsningumus sąlygoja suminė elektrocheminė reakcija



kuri katodinio proceso metu vyksta grįžtamai dėl prielektrodinio sluoksnio pašarmėjimo. $(Pd(OH)_2/PdO)_s$ yra mažai tirpių $Pd(OH)_2$ ir/ar PdO fazių paviršinis sluoksnis.