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It has been shown recently by several researchers [1-4] that the properties of electrolytic deposits of palladium depend on the conditions under which they had formed. In particular, the deposition potential φ_r^{dep} has a strong influence on the adsorption and electrocatalytic properties of electrolytic deposits of Pd [4]. The opinion was expressed that these phenomena are related to structural factors. It was therefore undertaken to study the structure of electrolytic Pd deposits as function of the electrocrystallization conditions since almost no such data are available in the literature.

Pd electrodes, deposited on a polycrystalline Pt support at φ_r^{dep} of 250 and -50 mV, have been studied, since these deposits differ significantly in their adsorption and catalytic properties [4]. The deposits were precipitated from a 1% PdCl₂ solution according to the procedure described in [4]. The structure of the electrolytic deposits was studied by means of scanning microscopy, radiography, the measurement of the thermal EMF and specific resistance in the same way as before, when studying electrolytic Pt deposits [5].

Radiographic investigation gave the following structural parameters of electrolytic Pd deposits:

$\varphi_r^{\text{dep}}, \text{mV}$	$a, \text{\AA}$	$D_{111}, \text{\AA}$	α
250	3,885	700	0,015
-50	3,884	300	-

In both types of electrolytic deposits a significant decrease in the lattice spacing a was observed, as compared with the reference value, which is equal to 3.891 for Pd [6]. The dimensions of the coherent scattering blocks in the direction (111) determined by the method of Fourier differ significantly for these types of sediments. Besides this, a high probability for the appearance of packing defects of the deformation type α was obtained for sediments with $\varphi_r^{\text{dep}} = 250$ mV.

The decrease in lattice spacing in comparison with the reference value can be caused by two main causes: the presence of internal macrostresses and the presence of vacancies in the lattice. According to [7] in the case of Pt the presence of 0.25 atom % of vacancies in the lattice leads to a reduction of a by 0.05 %. When we apply this relationship to Pd, the concentration of vacancies in both types of deposits will be about 0.8 atom %. This value appears to be too high. Consequently, we can assume that the decrease in a is mainly due to the presence of internal macrostresses. Calculation of internal macrostresses for electrolytic Pd deposits that correspond to the observed reduction of the lattice parameter from the equation $(\Delta a/a)(E/\mu) = 2\sigma$ leads to the acceptable value $\sigma = 4 \times 10^4$ N/cm² (E is the Young modulus for Pd and μ is the Poisson coefficient). Similar values can be found in the literature [8].

Additional data on structural defects were obtained by measuring the thermal emf and the specific resistance ρ as function of the annealing temperature. Figure 1 (curves 1 and 2) shows the thermal emf of the pair Pd/Pt-annealed Pt as function of the annealing temperature for deposits with φ_r^{dep} equal to -50 and 250 mV. Since no quantitative data are

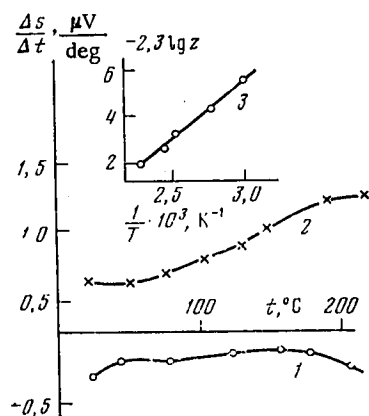


Fig. 1

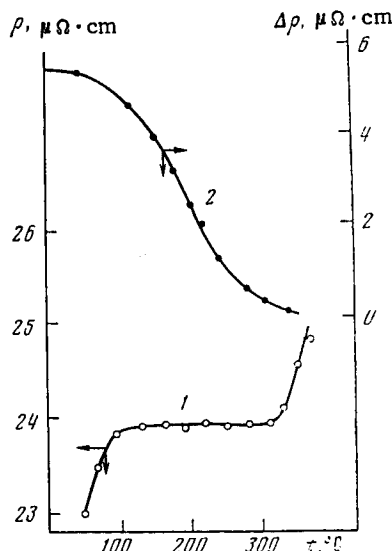


Fig. 2

Fig. 1. Variation of the thermal emf during heating of specimens with 1) $\phi_r^{\text{dep}} = -50$ mV and 2) $\phi_r^{\text{dep}} = 250$ mV, and diagram for the determination of the activation energy of defect movement on the basis of thermal emf data for Pd with $\phi_r^{\text{dep}} = 150$ mV (3).

Fig. 2. 1) Specific resistance and 2) resistance changes caused by the escape of defects as function of annealing temperature.

available in the literature on the influence of point defects on the thermal emf for Pd, an assessment was made on the basis of the data for Pt. According to [9, 10] for Pt $\Delta s/n = 5-10$ $\mu V/deg \cdot \text{at.}\%$ of vacancies, where $\Delta s/n$ is the thermal emf calculated for 1 at.% of vacancies. By assuming that in the case of Pd deposits with $\phi_r^{\text{dep}} = 250$ mV all the thermal emf annealed is due to vacancies, we can assess their concentration to be equal to 0.06-0.12 at.%. However, some doubt has been expressed recently that in these deposits the variation of the thermal emf is due only to the annealing of the defects and that traces of dissolved hydrogen have no effect. The weak relationship between the thermal emf and the annealing temperature for deposits with $\phi_r^{\text{dep}} = -50$ mV is probably due to the occurrence of two parallel processes which have an opposite effect on the thermal emf and compensate each other in the temperature interval studied: the annealing of defects and the removal of sorbed hydrogen.

The curve of thermal emf for Pd deposits with $\phi_r^{\text{dep}} = 250$ mV was used to calculate the activation energy Λ of defect movement. According to [9], the diffusion of defects is described by the equation

$$D = k \left(\frac{c_0 - c_t}{c_t} \right) \cdot \frac{1}{t}$$

regardless whether they move towards the surface or towards internal outlets; t is the annealing time at a given temperature, c_0 is the average concentration of the defects before and c_t the concentration after annealing, D is the diffusion coefficient, and k is a constant for the given sample. In [9] these values are correlated with the thermal emf which can be measured directly:

$$D = k \left(\frac{s_0^i - s_t^i}{s_0^i - s_{\infty}} \right) \cdot \frac{1}{t},$$

where s_0^i and s_t^i are the corresponding values of thermal emf for the i -th isothermal annealing, s_{∞} is the residual thermal emf. The thermal emf after annealing at 210 $^{\circ}C$ was selected

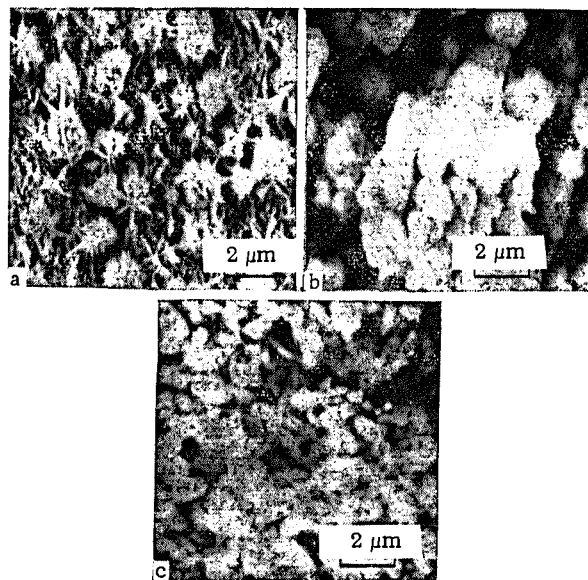


Fig. 3. Microphotographs of the surface of palladium deposits with ϕ_{r}^{dep} equal to a) 250, b) 20, and c) -50 mV.

for this parameter. According to [11], the diffusion coefficient of the defects is an exponential function of the reciprocal annealing temperature:

$$D = D_0 \exp\left(-\frac{A}{BT}\right).$$

The relationship between $\log z = \log \left(\frac{s_0^i - s_t^i}{s_0^i - s_\infty} \right)$ and $1/T$ is shown in Fig. 1 which gave an activation energy $A \approx 0.4$ eV.

The specific resistance of Pd deposits at room temperature (18°C) is higher than the literature value for the compact metal (10.8 $\mu\Omega \cdot \text{cm}$ [12]). For deposits with $\phi_{r}^{\text{dep}} = 250$ mV, $\rho = 20 \mu\Omega \cdot \text{cm}$ and for deposits with $\phi_{r}^{\text{dep}} = -50$ mV ρ is about 70 $\mu\Omega \cdot \text{cm}$. This significant increase in the specific resistance is due mainly to the nonuniformity of the deposits. The presence of cracks was detected under the electron microscope already at low magnifications.

Figure 2 shows the change in the specific resistance of the deposits during heating to 350° at a rate of $\sim 5^\circ/\text{min}$ (curve 1). During heating up to about 100° the resistance increased in accordance with the temperature coefficient of resistance for Pd given in the literature. At temperatures 100–300° a deviation from the normal course of the ρ vs. t curve was observed, due to alignment (ordering) of the crystal lattice. The value of ρ remained practically constant, due to compensation of two effects: the increase in temperature and the removal of defects. A further increase in temperature led to an increase in ρ again, since the escape of defects was terminated. Curve 2 in Fig. 2 represents the value of $\Delta\rho$ due to the escape of defects as function of the annealing temperature. In the same way as it was done for the thermal emf, these data were used to assess the activation energy of the process: $A \approx 0.3$ eV. Although this assessment is coarse, the satisfactory agreement of the values for A and approximately the same range of annealing temperatures used in both methods leads us to the conclusion that the annealing of the same defects has been recorded. On the basis of the relatively low activation energies and temperature intervals it can be concluded that the defects probably represent bivalancies [11].

The quantitative assessment of the defect structure of deposits with $\phi_{r}^{\text{dep}} = -50$ mV is not possible due to methodical difficulties, caused by their high degree of dispersion and low mechanical strength. This has prevented us from establishing correlations between the structure and the electrocatalytic properties of Pd electrodes, deposited at different potentials.

The electron microscope pictures obtained on a scanning microscope show that the deposits obtained at potentials of -50, 20, and 250 mV differ significantly in surface character and particle size (Fig. 3). A dendritic structure can be observed on deposits with $\varphi_r^{\text{dep}} = 250$ mV which contain crystallites similar to snow flakes. The deposits with $\varphi_r^{\text{dep}} = 20$ mV shows spherical concretions, while the deposits with $\varphi_r^{\text{dep}} = -50$ mV show simple round shapes.

Thus, the structural studies have demonstrated that the surface character and the dimension of the blocks of coherent scattering of Pd deposits depend strongly on the deposition potential. On the example of deposits with $\varphi_r^{\text{dep}} = 250$ mV it was established that the lattice of the electrolytic deposit of Pd contains significant amounts of different types of defects.

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THE DIFFERENT NATURE OF THE ELECTROREDUCTION OF AROMATIC CARBONYL COMPOUNDS IN NONAQUEOUS MEDIA AT LOW AND HIGH CONCENTRATIONS OF THE DEPOLARIZER

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In a study of the influence of various components of the medium (proton donors, the nature and concentration of the indifferent electrolyte, composition of the solvent) on the mechanism of the electroreduction of organic compounds in nonaqueous media [1, 2], usually the possibility of a change in the nature of the process, depending on the concentration of the depolarizer, has not been taken into account. Such a change might be due to adsorption phenomena on the electrode. It is known, however, that in the transition from aqueous solutions to organic solvents, the solubility of the organic substances is appreciably increased, and the adsorption of the depolarizer and products of the electrochemical reaction on the electrode surface is thereby reduced, and, consequently, the influence of all the adsorption effects on the electrode processes is decreased [3]. In a consideration of these phenomena, the possibility of chemisorption of the particles intermediately formed on the electrode has not been taken into account. However, in [4] the formation of "activated complexes" between the anion radicals or dianions of organic compounds and mercury, through

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