MECHANISM OF THE DISCHARGING OF $PdCl_4^{=}$ IONS

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The article is devoted to a study of the influence of the concentration of palladium and chlorides on the equilibrium potential and cathodic polarization in the electrodeposition of palladium from ammonium chloride solutions, as well as an investigation of the galvanostatic and potentiostatic turnon oscillograms. The exchange currents were determined as a function of the concentration of chlorides, and the orders of the reaction were calculated for the two Tafel portions of the curve. A double mechanism of the discharging of $PdCl_4^{=}$ ions was demonstrated.

There are two versions of the mechanism of the electrodeposition of palladium from electrolytes with a chloride complex [1-6]: 1) discharging of the ions predominating in solution, $PdCl_4^{=}$, occurs at the cathode [1, 2, 6]; the slow step is the reaction of addition of the first electron [1, 2]; 2) neutral particles of $PdCl_2$, which are formed in the preceding chemical reaction of successive elimination of two ligands, are discharged; the slow step is the elimination of the first Cl^- ion [3-5].

The experimental data are also contradictory. Thus, according to [6], the product $i\tau^{1/2}$ does not depend on the current density, from which it is concluded that the limiting current is of a diffusion nature; according to [5] $i\tau^{1/2}$ decreases with increasing current density, and it is concluded that the preceeding chemical reaction is the slow step.

In this work we determined the orders of the electrochemical reaction according to the Fetter method [7], for which we investigated the dependence of the potential of an unpolarized electrode and the rate of the cathodic reaction on the concentration of the complex former in solution. The measurements were performed in ammonium chloride electrolytes with a Pd concentration 0.025 g-ion/liter and an excess of the chloride ion 0.05, 0.1, 0.15, 0.20, 0.25, and 0.30 M. Constancy of the ionic strength was maintained by the addition of a 1 M solution of Na_2SO_4.

Conclusions drawn on the mechanism of the process were verified, investigating the potential-versus-time and current-versus-time dependences with potentiostatic and galvanostatic turnon.

EXPERIMENTAL METHODS

A thermostatically controlled (± 0.5°) cell with cathodic and anodic spaces separated by a ground joint, in an argon medium, was used. The electrode was the end of a Pt wire with ϕ 1 mm, sealed into glass, coated with a 5-6 μ layer of palladium, electrolytically deposited from an ammonium chloride electrolyte

TABLE 1. Slopes of the Tafel Portions of the Cathodic Polarization Curves

Tafel portion	Chloride ion concentration, M					
	0,05	0,1	0,15	0,20	0,25	0,30
I	78	90	80	74	76	74
II	140	136	126	120	118	118

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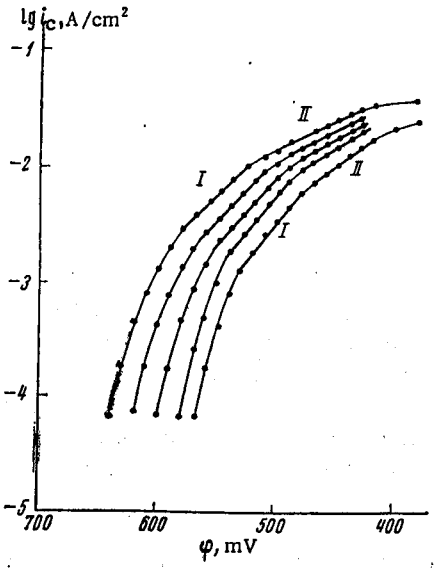

Fig. 1

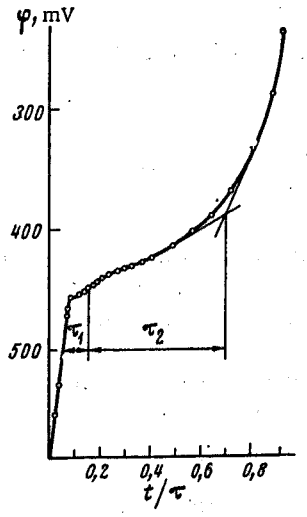

Fig. 2

Fig. 1. Influence of the chloride ion concentration on the cathodic polarization; [Pd] = 0.025 M, [Cl^-]: 1) 0.05; 2) 0.1; 3) 0.15; 4) 0.2; 5) 0.3 M.

Fig. 2. Curves of galvanostatic turnon: Pd) 0.025, [Cl^-]) 0.3 M; i_c = 1.4 mA/cm².

with a concentration of metallic palladium 0.1 M (the potential of deposition was significantly more positive than the potential of the liberation of hydrogen). The homogeneity of the surface obtained was estimated according to the value of the static potential in the same solution.

The current source was a P-5827 potentiostat. The recording instrument was a KSP-4 potentiometer. The reference electrode was a saturated silver chloride electrode; the potentials are cited relative to the normal hydrogen electrode. The salts were cp grade, palladium chloride grade "pure" MRTU-6-09 No. 1964-64. Before the redistillation, potassium permanganate was added to the water to oxidize traces of organic compounds. The mixture was magnetic. Complete removal of diffusion limitations was evidenced by the fact that a decrease in the rate of mixing did not lead to any decrease in the current strength. To prevent the influence of an increase in the surface in the region of potentials where the current exceeded approximately one third of the limiting value, the measurements were performed each time on a newly prepared surface.

In the absence of current the potential satisfies the criteria of the equilibrium potential [7]: 1) it obeys the Nernst equation, 2) mixing of the electrolyte does not affect it, and 3) it does not depend on the state of the electrode.

In the interval of Cl^--ion concentrations 0.1-0.4 M and Pd^{++} 0.01-0.035 M, the indicated potential can be expressed by the equation

$$\varphi=\varphi_0+\frac{RT}{nF}\ln\frac{K[PdCl_4]^{2-}}{4[Cl^-]}$$

where K = 10^{-14} is the instability constant of the complex ion $[PdCl_4]^{2-}$; φ_0 = 983 mV.

This gives a basis for believing that in an ammonium chloride electrolyte for palladium plating the complex $PdCl_4^{=}$ predominates. Nonetheless, the high acidity of such solutions (pH = 1.3-2.5 without the introduction of free hydrochloric acid) permits us to assume the presence of an acid-base equilibrium and the presence of particles in solution with a lower number of ligands, in accord with the equations:

$$PdCl_4^{=}+HOH\rightleftarrows[PdCl_3HOH]^-+Cl^- \quad (1)$$
$$\updownarrow$$
$$[PdCl_3OH]^{=}+H^+$$

$$[PdCl_3OH]^-+HOH\rightleftarrows[PdCl_2(OH)_2]^-+H^++Cl^-. \quad (2)$$

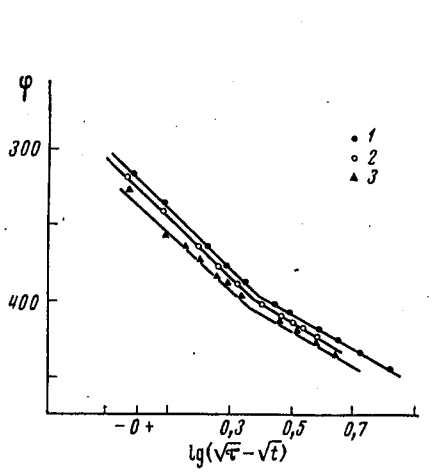

Fig. 3

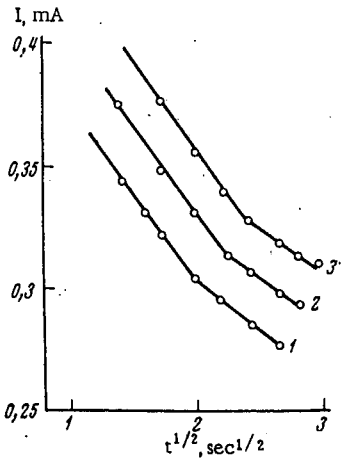

Fig. 4

Fig. 3. Dependence of $\log(\sqrt{\tau}-\sqrt{t})$ on φ at various current densities. Pd 0.025 M, NH_4Cl 0.3 M: 1) 1.4, 2) 1.8, 3) 2.4 mA/cm^2.

Fig. 4. Dependence of the current density on the time in the case of potentiostatic turnon. Pd 0.025 M, NH_4Cl 0.125 M: 1) φ = 450 mV; 2) 400 mV; 3) 350 mV.

From Fig. 1 it is evident that an increase in the chloride-ion concentration at the same potential leads to a decrease in the cathodic current density. On these curves two Tafel regions (I and II) are distinguished. The slopes of these portions are cited in Table 1.

The values of the transport coefficients calculated according to the average slopes are 0.631 for Tafel region I and 0.782 for II, while the logarithms of the current density of exchange found by their extrapolation are close to 3.5 (which agrees with the data of [3, 5]) and 3, respectively, and have a very small tendency to increase with increasing chloride concentration.

Calculation according to Fetter gives the following value of the orders of the reaction with respect to the chloride ion:

on Tafel region I

$$L_{B^{I}Cl^-}=\left(\frac{\partial}{\partial \lg}\frac{\lg i_0}{[Cl^-]}\right)^{I}-\alpha\nu_{Cl^-}\frac{L}{n}=-0.55-0.631(-4)=1.974;$$

$$L_{B^{I}Cl^-}=\left[2.303\frac{RT}{LF}\left(\frac{\partial \lg i_0}{\partial \lg[Cl^-]}\right)^{I}\left(\frac{\partial \lg[Cl^-]}{\partial\varphi_p}\right)-\alpha^{I}\right]\nu_{Cl^-}\frac{L}{n}$$

$$=\frac{(-4)(-0.55)\cdot 29.5}{-118}-0.631(-4)=1.974;$$

on Tafel region II

$$L_{B^{II}Cl}=\left(\frac{\partial \lg i_0}{\partial \lg[Cl^-]}\right)^{II}-\alpha^{II}\nu_{Cl^-}\frac{L}{n}=-0.19-0.782(-4)=2.938\approx 3;$$

$$L_{B^{II}Cl}=\left[2.303\frac{RT}{LF}\left(\frac{\partial \lg i_0}{\partial \lg[Cl^-]}\right)^{II}\left(\frac{\partial \lg[Cl^-]}{\partial\varphi_p}\right)-\alpha^{II}\right]\nu_{Cl^-}\frac{L}{n}=$$

$$=\frac{(-4)(-19)\cdot 29.5}{-118}-0.782(-4)=2.938\approx 3.$$

In these equations: α is the transport coefficient; ν is the stoichiometric coefficient; L is the valence of the transition; n is the valence of the electrode reaction; the remaining notationas are as usual.

Thus, on the basis of a determination of the orders of the reaction with respect to the chloride ion in cathodic polarization, we can suggest the following mechanism for the discharging of complex ions of palladium in acid chloride electrolytes. At low overvoltages:

1) $PdCl_4^{=}\rightleftarrows PdCl_2+2Cl^-$; 2) $PdCl_2+2e\rightleftarrows Pd+2Cl^-$.

At high overvoltages:

$$1)\ PdCl_4^{=} \rightleftarrows PdCl_3^{-} + Cl^{-}; \quad 2)\ PdCl_3^{-} + 2e \rightleftarrows Pd + 3Cl^{-}.$$

The data obtained on the mechanism of discharging at a low cathodic polarization agree with the data of Kravtsov and Zelenskii [3, 5].

The dual mechanism of discharging is confirmed by the presence of two limiting current plateaus on the chronopotentiogram in a plot of φ versus t/τ (Fig. 2).

In the case of a sufficiently large polarization, when the rate of the reverse electrochemical reaction under conditions of semiinfinite linear diffusion can be neglected, the value of σ_c is described by the equation [8]:

$$\varphi_c = -\frac{RT}{\alpha nF}\ln\frac{i_c}{i_0} + \frac{RT}{nF}\ln(\tau^{1/2} - t^{1/2}), \tag{3}$$

where τ is the transit time; t is the time of change of the potential.

According to this equation, the dependence of φ on $\ln(\tau^{1/2} - t^{1/2})$ at various current densities should be linear. Figure 3 presents the relationship between the potential and the logarithmic term of Eq. (3), obtained in the case of galvanostatic turnon in an ammonium chloride electrolyte. On the curves cited, two linear portions with different slopes are clearly distinguished. The values of the transport coefficients calculated from the reciprocal of the slopes of these portions are equal to 0.68 and 0.81, respectively, which is in sufficiently good agreement with the values obtained from the polarization measurements (0.631 and 0.78, respectively).

Using the method of potentiostatic turnon, the dependence of the current density on the time under conditions of semiinfinite diffusion is expressed by the formula [9]

$$i_c = i_0\left\{\exp\left[-\frac{\alpha nF(\varphi-\varphi_p)}{RT}\right]\exp\left[\frac{(1-\alpha)nF(\varphi-\varphi_p)}{RT}\right]\right\}\xi(Q\sqrt{t}),$$

where $\xi(Q\sqrt{t})$ is the time function derived for the conditions described above; t is the time during which a change in the current strength is observed after the circuit is opened. The dependence of i_c on $\sqrt{t}$ should be linear according to this equation. Actually, on the curves of potentiostatic turnon in an ammonium chloride electrolyte in a plot of i_c versus $\sqrt{t}$ (Fig. 4) there are two linear portions with different slopes, which indicates the occurrence of two different electrode reactions and confirms the data of the polarization measurements and galvanostatic turnon.

Thus, in the region of overvoltages up to 120-150 mV, the electrodeposition of palladium occurs from a neutral particle, formed as a result of the elimination of $2Cl^-$ ions from the complex particle $PdCl_4^{=}$, which predominates in solution. In the region of higher overvoltages, discharging occurs from the complex particle $PdCl_3^-$, formed by the elimination of 1 Cl^- ion from $PdCl_4^{=}$. The change in the mechanism is accompanied by a change in the Tafel slope and by the appearance of a point of inflection on the i_c-versus-φ curve.

LITERATURE CITED

1. I. B. Panova, K. S. Ramm, and B. S. Krasikov, in: Protective Metallic and Oxide Coatings. Corrosion of Metals and Investigations in the Field of Electrochemistry [in Russian], Nauka, Moscow (1965), p. 82.
2. W. Watt, J. Amer. Chem. Soc., 10, 716 (1963).
3. V. I. Kravtsov and M. I. Zelenskii, Vestnik LGU, 4, No. 22, 128-139 (1966).
4. T. N. Heumann and A. C. Schürmann, J. Electrochemie, 67, 601 (1963).
5. M. I. Zelenskii, Author's Abstract of Candidate's Dissertation [in Russian], Leningrad State University (1969).
6. S. P. Pilite, R. M. Vishomirskii, and A. M. Molchadskii, Tr. Akad. Nauk LitSSR, Ser. B., 1, (44), 25 (1966).
7. K. Fetter, Electrochemical Kinetics [Russian translation], Khimiya, Moscow (1967).
8. P. P. Delahay, New Instruments and Methods in Electrochemistry [Russian translation], Izd-vo Inostr. Lit., Moscow (1957), p. 223.
9. B. S. Damaskin, Principles of Modern Methods of the Study of Electrochemical Reactions [in Russian], MGU (1965), p. 15.