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APPLIED ELECTROCHEMISTRY AND CORROSION PROTECTION OF METALS

Recovery of Palladium from Spent Solutions for Manufacture of Catalysts

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Abstract—Palladium recovery from $[Pd(NH_3)_4]Cl_2$ solutions (concentration in terms of the metal ~1 g l^{-1}) with flow-through porous electrodes was studied. The conditions of effective electrochemical recovery of Pd were found. Various porous cathodes were compared.

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It is known that platinum-group metals (Pt, Pd, etc.) are widely used for manufacture of catalysts. Because of their high cost and exhaustion of primary sources of raw platinum materials, a considerable attention is being paid to recuperation of platinum metals from catalysts and technological solutions used in their manufacture [1, 2]. For example, a solution of tetraamminepalladium(II) chloride $[Pd(NH_3)_4]Cl_2$ is used in manufacture of glass-fiber catalysts for purification of automobile exhaust gases [3]. The impurities appearing in catalyst deposition make a repeated use of a solution impossible, although its Pd concentration changes only slightly and remains at a level of 1 g l^{-1}. At present, Pd is recovered from these solutions by evaporation, which involves high electric power expenditure and long process duration. A possibly more promising and economically efficient way to recover palladium from these solutions is by electrolysis with flow-through porous electrodes (PEs).

The goal of our study was to find conditions for effective electrochemical recovery of Pd from spent solutions of a complex ammoniate $[Pd(NH_3)_4]Cl_2$ and compare the operation efficiencies of various porous cathodes.

EXPERIMENTAL

We performed experiments on electrochemical recovery of palladium in the potentiostatic mode (ER-20A potentiostat, Poland) at a temperature of 20 ± 1°C on a laboratory installation similar to that described in [4]. As flow-through porous cathodes served fibrous carbon materials KNM and VNG-30 (Russia), Carbopon V-22 (Poland), and metallized Sintepon, i.e., polyester fibers coated with a thin layer of silver [5]. Selected characteristics of these materials are listed in the table [5, 6]. The anode of the electrolyzer was made of graphite. The geometric area of the electrodes was 0.3 dm^2; volume of the circulating solution being processed, 0.5 l; and flow rate, 0.1 $cm^3\ s^{-1}$ across 1 cm^2 of the geometric surface area of the cathode. We used the circulation mode of PE operation, with the solution delivered from the front (facing the anode) part of the cathode.

We identified the cathode processes occurring in the solutions under study by means of parallel measurements of the current and electrode mass at a varying potential, with an IPC-compact potentiostat (Institute of Physical Chemistry, Russian Academy of Sciences, Russia) and QCM-200 quartz microbalance (Stanford Research System, USA). In this case, the role of the working electrode was played by a gold film deposited in the form of a circle with an area S = 1.37 cm^2 onto one side of a thin plate of a quartz single crystal (AT-cut, resonance frequency 5 MHz, mass sensitivity 56.6 Hz μg^{-1}).

The study was carried out on synthetic and real spent solutions of tetraamminepalladium(II) chloride

Physicochemical characteristics of the fibrous porous materials used in the study

Material	Layer thickness L, cm	Fiber diameter d_f, µm	Porosity ε	Electrical conductivity $æ_{eff}$, Ω–1 cm^{-1}
Carbonized unwoven material KNM	0.25	12	0.98	0.009
Carbon felt VNG-30	0.37	11	0.96	0.09
Carbon felt Carbopon V-22	0.30	5	0.94	0.12
Metallized Sintepon	1.20	20	0.99	1.10

$[Pd(NH_3)_4]Cl_2$ with a concentration of about 1 g l^{-1} in terms of the metal. The Pd concentration was determined in the course of electrolysis by voltammetry on a renewable graphite electrode [7] and, at a number of control points, by the atomic-absorption method. The cathode potentials were measured relative to a saturated silver chloride reference electrode. The distribution of palladium across the thickness of a porous electrode was studied by processing of micrographs of a PE cross-section [8]. The micrographs were obtained with a Neophot-21 microscope (Carl Zeiss, Germany) and processed with Photo M software.

A starting spent aqueous solution of $[Pd(NH_3)_4]Cl_2$ has a high resistivity (About 550–600 Ω cm). The depth to which the electrochemical process penetrates into flow-through porous electrodes strongly depends on the conductivities of the liquid and solid phases and markedly decreases as these conductivities become lower [9]. For this reason, it is inappropriate to subject a starting solution to electrolysis without preliminarily raising its conductivity. Therefore, we tested various methods for pretreatment of a solution before electrolysis. Acidification of a solution to raise its conductivity was found to be unacceptable because this leads to precipitation of the poorly soluble dichloroamminepalladium salt $[Pd(NH_3)_2]Cl_2$ [10] and causes a more intense evolution of hydrogen at the porous cathode in the course of electrolysis.

The best method for pretreatment of the solution is its alkalization, because this simultaneously raises the solution conductivity and hinders the side cathodic reaction of hydrogen evolution. Addition of NaOH to the starting solution first leads to a sharp decrease in the solution resistance, but, at alkali concentrations exceeding 5–6 g l^{-1}, the effect rapidly decays. Therefore, we mostly performed further experiments with solutions to which 6 g l^{-1} of NaOH was added, which corresponded to pH 12.7 and a resistivity of about 150 Ω cm.

To choose the working range of PE potentials, it is necessary to preliminarily identify cathode processes in a solution under study. Figure 1 shows parallel measured curves of current and cathode mass variation with the cathode potential in a spent solution. It can be seen that, at potentials in the range from +250 to –1200 mV, the voltammetric curve clearly shows three cathodic peaks with initial potentials of –350, –450, and –1100 mV. Comparison of this curve with that describing the variation of the mass shows that only the second peak is associated with the cathodic deposition of the metal. The rise in the cathodic current at potentials more negative than –350 mV is presumably due to reduction of dissolved O_2 on gold, and its new rise at potentials more negative than –1100 mV, to the onset of H_2 evolution on palladium. Calculation of the electrochemical equivalent of the metal deposit at E = –700 mV gives, with the fraction of current consumed for the oxygen reduction taken into account, a value of about 53 g, which corresponds to metallic Pd. Figure 2 shows cathodic polarization curves measured on

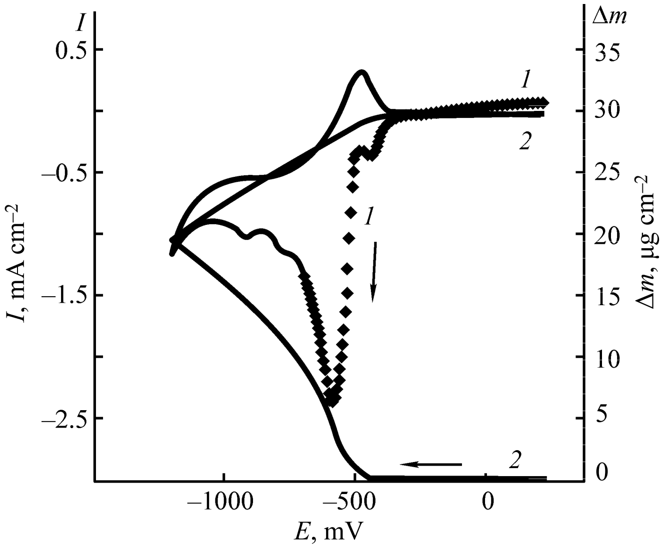

Fig. 1. (*1*) Current *I* and (*2*) change in the cathode mass, Δ*m*, vs. the potential *E*. Palladium concentration in solution 1 g l^{-1}, pH 12.7, potential sweep rate 20 mV s^{-1}.

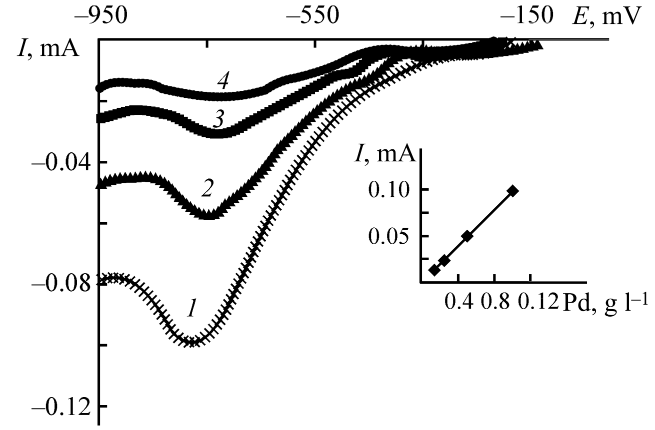

Fig. 2. Cathodic polarization curves measured on a renewable graphite electrode (S = 0.03 cm^2, potential sweep rate 20 mV s^{-1}) in alkaline solutions. (*I*) Current and (*E*) potential. Palladium concentration (g l^{-1}): (*1*) 0.125, (*2*) 0.25, (*3*) 0.5, and (*4*) 1. Inset: dependence of the peak current *I* on the palladium concentration Pd.

a mechanically renewed graphite electrode in solutions with various palladium concentrations. It can be seen that the dependence of the peak height at a potential of about –750 mV on the metal concentration is linear and can be used for fast monitoring of the Pd concentration in the course of electrolysis.

It also follows from an analysis of the reverse run of the curve describing the variation of the cathode mass with the potential (Fig. 1, curve *2*) that Pd deposited from this solution is not anodically dissolved (at least up to E = 250 mV). This makes unnecessary separation of electrode spaces in electrochemical recovery of palladium onto a porous electrode, and the small anodic current observed in the reverse run at E –500 mV can be attributed to a possible oxidation of O_2 reduction products accumulated in the near-electrode layer.

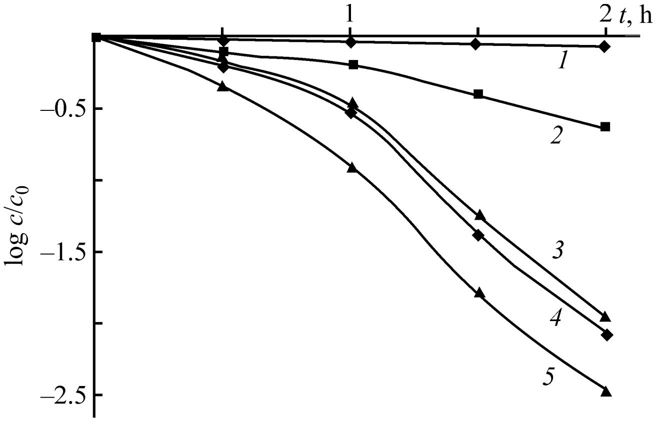

Fig. 3. Dynamics of palladium recovery from a solution under study (*1*) without an alkali and (*2–5*) with addition of 6 g l^{-1} of NaOH on flow-through porous cathodes made of various materials. (c, c_0) Initial and running palladium concentrations and (t) time; the same for Fig. 4. Material: (*1, 2*) KNM, (*3*) Carbopon V-22, (*4*) VNG-30, and (*5*) Sintepon. For the rest of electrolysis conditions, see text.

Taking into account the revealed nature of the cathodic processes, we chose the optimal potential for potentiostatic deposition of Pd on the porous cathode on the basis of the following considerations. On the one hand, it is desirable that, for the metal deposition process to penetrate deeper into a PE, that the difference between the potential set on the front side of the PE and the equilibrium potential of Pd should be as large as possible [11]. On the other hand, a side process of hydrogen evolution begins at potentials more negative than –1100 mV, with the hydrogen-related current rapidly increasing with the cathodic polarization. The intense occurrence of this side reaction is undesirable not only because of the apparent decrease in the current efficiency, but also due to a possible deterioration of the PE operation efficiency. The latter is associated with the rise in the ohmic loss of voltage at increased current densities [12] and also with an increase in the gas content of the solution [13]. Therefore, the maximum value of the PE potential in deposition of Pd from this solution was chosen to be –1300 mV.

Figure 3 shows for the chosen electrolysis conditions how the concentration of palladium depends on the duration of deposition in solutions with different initial conductivities (curves *1* and *2*) and for various porous cathode materials and a fixed pH value of the solution (curves *2–5*). At a constant volume and flow rate of the circulating solution, the slope of the curves in Fig. 3 is proportional to the effective working surface area of the PE and to the rate of the mass-transfer-limited recovery process of the metal. It can be seen from these data that, in almost all cases, the recovery rate of palladium noticeably grows in the course of time. This is due to a decrease in the concentration of the metal in solution, increase in the slope of the polarization curve (dE/dI), and the corresponding improvement of the uniformity of the current distribution within the PE.

The increase in the working surface area of the PE in the course of metal recovery is a characteristic feature of PEs, and the data in Fig. 3 demonstratively confirm the conclusion that PEs are most effectively used for processing of just diluted solutions [11]. Comparison of curves *1* and *2* in Fig. 3 clearly shows the importance of the preliminary treatment of a solution. Alkalization of the starting solution to pH 12.7 makes it possible to raise, under the same electrolysis conditions, the recovery of palladium from 14 to 77% in 2 h. It also follows from the data in Fig. 3 that the recovery rate strongly depends on the properties of a porous material and, on passing from KNM to metallized Sintepon, grows by approximately a factor of 4. Comparison of curves *2–5* in Fig. 3 with the data in the table suggests that the order in which the materials can be arrange in order of increasing palladium recover rate is for the most part determined by their conductivity. The noticeable advantage of metallized Sintepon over Carbopon V-22 can be attributed to its substantially larger porosity.

It should be specially emphasized that the above-discussed operation efficiency parameters of various porous materials are related to their original state and initial stage of their filling with the metal. Upon deposition of palladium, characteristics of the porous matrices (effective conductivity of threads, their diameter, porosity) naturally change, which may also affect the operation efficiency of the corresponding PEs. These changes are comparatively small for PEs with high initial conductivity and are more pronounced for materials with low initial conductivity, e.g., KNM. Taking into account that this material is now nearly the only industrially manufactured carbon felt, we studied the variation dynamics of its operation efficiency in the course of palladium recovery from successively processed solution portions with the same volumes and initial Pd concentrations. In the conditions of potentiostatic electrolysis with predominance of the target process of palladium deposition, the variation of its rate can be characterized by time dependences of both the palladium concentration in solution and the overall current. Figure 4 shows as an example data on the dynamics of palladium recovery in successive processing of the first three portions of the solution, and Fig. 5, curves describing the variation of the overall current from the beginning of electrolysis until palladium fills the critical cross-section of the PE and the solution ceases to flow.

It can been from the curves in Fig. 4 that, in the initial stage of palladium deposition onto KNM, the metal recovery rate and the PE operation efficiency noticeably grow. For example, the recovery rate becomes 1.7 times higher already for the second portion of the solution, and 1.4 times more for the third portion to become almost the same as that of the most electrically conducting Sintepon. Further, the rise in the recovery rate is noticeably decelerated. Comparison of the data in Fig. 4 with the current variation curves in Fig. 5 shows that the main contribution to the rise in the working surface area and in the recovery rate of palladium comes from the increase in the conductivity of the porous matrix. This is evidenced both by a sharp rise in the initial current for the first 3–4 portions of the solution and by a change in the shape of *I–t* curves. For example, in the first stage of deposition, the electrolysis current first steeply grows (from 40 to 220 mA), despite the

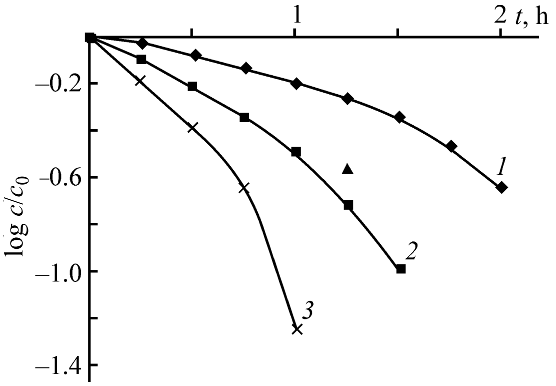

Fig. 4. Dynamics of palladium recovery from $[Pd(NH_3)_4]Cl_2$ solutions on a porous KNM cathode in successive processing of the first three 0.5-l portions of a solution with an initial Pd concentration of 1 g l^{-1}.

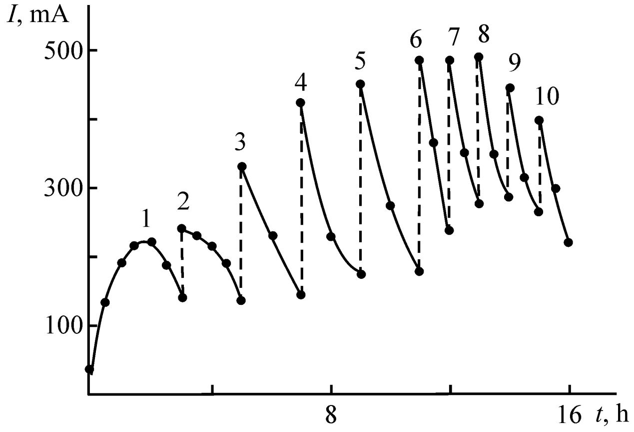

Fig. 5. Variation dynamics of the current *I* in successive recovery of palladium from ten 0.5-l portions of a solution with an initial Pd concentration of 1 g l^{-1} until full clogging of pores in the KNM cathode. (*t*) Time. Figures at curves, portion numbers of the solution being processed.

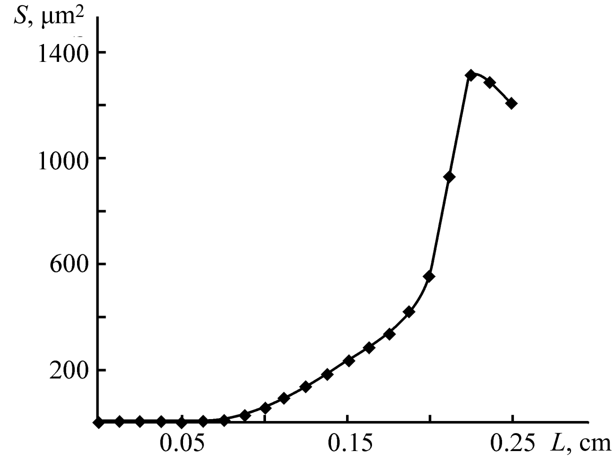

Fig.6. Final palladium distribution across the thickness L of the porous KNM cathode. (S) Average area of a metal ring around a fiber.t

steady decrease in the palladium concentration (Fig. 5), passes through a maximum, and starts to decrease only at the end of the stage (i.e., already at a high degree of solution depletion. The increase in the conductivity of the cathode also noticeably affects the shape of the *I–t* curve for the second cycle. And only beginning from the third portion of the solution being processed, the time dependences of the current take on the steadily decaying shape characteristic of the equipotential PE. The slight rise in the initial currents, observed up to the 6th–8th stage, is presumably due to an increase in the working surface area because of thread thickening, and their subsequent decline, to a decrease in porosity in the most palladium-filled cross-section of the PE.

The final distribution of palladium across the thickness of a flow-through porous KNM cathode is shown in Fig. 6. It can be seen that palladium is distributed within the PE rather nonuniformly and mostly fills the frontal, closest to the anode, part of the electrode. The maximum relative mass of deposited palladium for the KNM cathode is small: about 5 g per gram of the starting porous material. To improve the uniformity of the final distribution of the metal and raise its limiting mass, it is necessary to use thinner, more electrically conducting, and more porous cathode material. The average electric energy expenditure for Pd recovery onto a KNM PE were 0.52 W h per gram of the metal, and the average recovery rate of the metal, 0.83 g h^{-1} per 1 dm^3 of the geometric surface area of the electrode at a recovery of no less than 99%.

CONCLUSIONS

(1) It was shown that electrolysis with flow-through porous cathode is promising for recovery of palladium from spent catalyst production solutions.

(2) It was found that preliminary alkalization of the solutions prior to electrolysis is necessary and the optimal modes of the process were determined.

(3) It was demonstrated that porous materials with high conductivity and porosity are the most effective for cathodic recovery of metals from dilute solutions.

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