BRIEF COMMUNICATIONS

DISSOLUTION OF PLATINUM UNDER THE CONDITIONS OF THE KOLBE ELECTROCHEMICAL CONDENSATION. AQUEOUS SOLUTIONS OF ACETATES

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The Kolbe reaction of anodic condensation

$$2RCOO^- \rightarrow R{-}R + 2CO_2 + 2e$$

is one of the promising methods for synthesizing bifunctional compounds, which are finding wide use. It is known [1-4] that the process occurs most effectively on platinum anodes. However, there are extremely few data on the corrosion resistance of platinum under these conditions, while for potentials more negative than the region of occurrence of reaction (1), there are no such data at all.

The system of smooth platinum – aqueous acetate solutions was selected as a model, since the electrochemical oxidation of acetate ions is less complicated by the formation of side products (in particular, insoluble films), which may influence the corrosion of the anode, while the results of the investigation can be extended to processes of electrochemical oxidation of anions of monoesters of dicarboxylic acids without any special errors [5]. Moreover, the use of water as a solvent makes it possible to conduct electrolysis in a system of relatively high rates of dissolution of the anode, which makes it possible to shorten the experiment time and expand the range of measurements with respect to potentials.

METHOD

The corrosion of a platinum anode was determined under potentiostatic conditions, using radiochemical [6, 7] and gravimetric methods. In calculating the rate of dissolution, expressed in current units, it was assumed that the passage of platinum into solution is accompanied by an elimination of four electrons. The current yield of platinum A_{Pt} was calculated as the ratio of the rate of dissolution i_{Pt} to the summary anodic current i_a, passing through the system $A_{Pt} = (i_{Pt} \cdot 100/i)\%$.

The experiments were conducted in flow-type glass cells at $30 \pm 0.5°$. The electrodes (working surface 0.65-11.3 cm^2) were prepared from Pl. 1 platinum and were etched before the experiment for 10-20 min in concentrated solutions of nitric and hydrochloric acids, washed with double-distilled water, and dried. The method of the radiochemical measurements was practically the same as that described earlier [8]. Weight losses were determined with an accuracy of $\pm 1 \cdot 10^{-5}$ g.

The working solutions were prepared from analytical grade sodium acetate and cp acetic acid. In experiments with radioactive platinum, double-distilled water was used to prepare the solutions while distilled water was used in the remaining experiments.

In the experiments with radioactive platinum, the potential was maintained with the aid of potentiostats from the Central Laboratory of Automation of the P-5611 and P-5827 types, while in the experiments with nonradioactive platinum, it was maintained with the aid of an electromechanical potentiostat at currents up to 10 A (accuracy of regulation ±5 mV). The potentials are cited according to the normal hydrogen electrode (n.h.e.).

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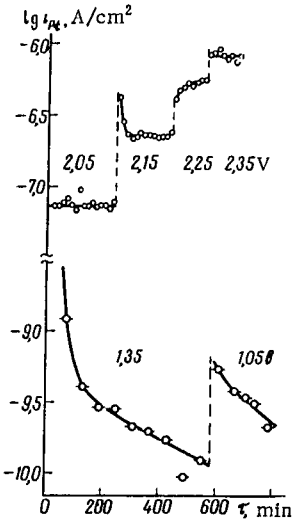

Fig. 1

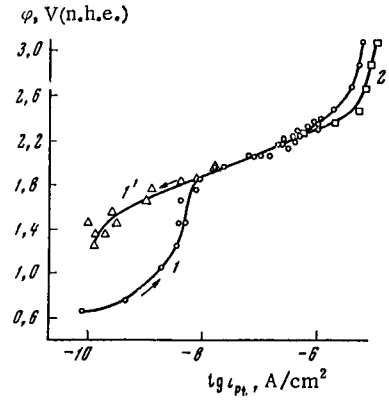

Fig. 2

Fig. 1. Influence of the potential on the rate of establishment of a stationary system of dissolution.

Fig. 2. Dependence of the rate of dissolution of platinum on the potential. 1) Direct recording; 1') reverse recording; 2) curve was constructed according to gravimetric data.

TABLE 1. Influence of pH of the Solution on the Corrosion of Platinum in Acetate Solutions (φ = 2.64 V)

Solution	pH	Rate of dissolution, $\mu A/cm^2$	Current yield of platinum $\cdot 10^{-3}$, %
0.75 N CH_3COOH + 0.75 N CH_3COONa	4.85	24.0	2.1
1.5 N CH_3COONa	8.35	21.8	1.4
1.5 N CH_3COONa + 0.05 N NaOH	12.64	18.0	1.4
1.5 N CH_3COONa + 0.1 N NaOH	13.11	18.7	1.6

RESULTS AND DISCUSSION

The rate of dissolution of smooth platinum was determined radiochemically in a solution of 1.5 N CH_3COOH + 1.5 N CH_3COONa in the potential interval 0.65-3.05 V. The electrode was maintained at each potential for 2-8 h, performing 6-10 measurements of the value of i_{Pt}; then the potential was abruptly displaced to the new value. The time of reaching of a stable rate of dissolution, as in the case of acid electrolytes studied earlier [8], depends substantially on the electrode potential. In the region of potentials of the Kolbe synthesis ($\varphi > 2$V), the value of i_{Pt} is stabilized relatively rapidly; at higher potentials it is stabilized extremely slowly (Fig. 1). Sometimes a stationary system of dissolution was not reached even after 12-15 h polarization of the anode at φ = const. Regardless of whether preliminary polarization of the electrode was performed at a more positive or more negative potential, in the initial period after the shift of the potential, the rate of dissolution was usually higher than the stationary rate. In a number of cases a shift of the potential even in the negative direction was accompanied by an initial increase in i_{Pt} in comparison with its value at the initial, more positive potential (Fig. 1).

Data on the influence of potential on the rate of dissolution, established during the process of prolonged anodic polarization, are presented in Fig. 2. As can be seen, the curves of the direct and reverse pathways show a substantial discrepancy at $\varphi < 1.9$ V. We observed an analogous hysteresis in approximately the same potential region as a number of other authors [9, 10] on the polarization curves characterizing the oxidation of the components of the electrolyte as well. According to the existing concepts, the appearance of

TABLE 2. Influence of the Summary Concentration of the Electrolyte (CH_3COOH + CH_3COONa) on the Corrosion of Platinum (Molar ratio of acid to salt 1:1, φ = 2.84 V)

Summary concentration, M	Rate of dissolution, μA/cm²	Current yield of platinum $\cdot 10^{-3}$, %
0,3	25,6	1,8
1,5	24,0	2,1
3,0	16,0	1,9
5,0	32,4	—

hysteresis may be associated with kinetic hindrances arising during the formation and decomposition of a surface oxygen layer on platinum, or [11] the possibility of the existence of two types of surface oxides, one of which is converted to the other as a result of an irreversible phase transition. Therefore, considering the data of Fig. 2, it may be assumed that the state of oxidation of the electrode has a substantial influence not only on the kinetics of the summary anodic process, but also on the kinetics of the dissolution of platinum.

An attempt was made to investigate hysteresis with the most complete possible exclusion of time effects. For this purpose we selected a potential (1.45 V) in the region of maximum discrepancy of the forward and reverse curves. To verify the reproducibility of the results, and considering the fact that the time of reaching of a stationary system of dissolution, as a rule, was greatly reduced after the electrodes were kept under conditions of intensive dissolution, the measurements were conducted with repeated return to the selected potential from the direction both of more positive and of more negative values according to the scheme: 1.45-2.15-1.45-0.25-1.45-2.15-1.45 V. Such conditioning leads to an almost complete disappearance of the hysteresis. Moreover, in each cycle the stable region of dissolution at φ = 1.45 V proves to be proportional to the anodic current i_a, so that the current yield of platinum (A_{pt}) remains practically constant (~0.08%).

In the region of occurrence of the Kolbe synthesis ($\varphi > 2$ V), the influence of potential on the dissolution of platinum is substantially smaller than in the case of more negative potentials. This is indicated by the results both of radiochemical and of gravimetric measurements (Fig. 2). In this region the corrosion resistance of the anode remains practically constant when the pH of the solution is varied within the interval 4.85-13.11 (Table 1), the summary concentration of the electrolyte within the interval 0.3-5.0 g-eq/liter (Table 2), and molar ratio [CH_3COOH] : [CH_3COONa] in the interval 0.2-5.0. The current yield of platinum in the potential interval 2.4-3.2 V is close to $2 \cdot 10^{-3}$%.

The aggregate of data obtained permits us to conclude that the determining factors in the process of anodic dissolution of platinum in aqueous acetate solutions are the composition and properties of the surface oxygen compounds of the metal, formed at various potentials. The correctness of this conclusion is also indicated by data on the absence of any influence of the anionic composition of the electrolyte on the corrosion behavior of platinum anodes. Actually, at high anodic potentials in aqueous acetate solutions and in solutions of perchloric acid, where oxide films are close in composition [12], the rates of dissolution of platinum and the nature of the dependence of the rate of dissolution on the potential in the interval 1.8-2.8 V are also close (compare the results of this work and [13]).

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