SOLUTION OF SMOOTH PLATINUM DURING POLARIZATION IN ACID SOLUTIONS

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Despite the fact that platinum electrodes are widely used both in theoretical and in applied electrochemistry, very little data exists in the solution kinetics of platinum itself under conditions of electrolysis. This is for the most part explained by the stability of platinum towards corrosion, and the low sensitivity of the majority of the methods employed for the determination of its rate of solution.

We have investigated the influence of potential on the rate of solution of smooth platinum in solutions of a series of inorganic acids. The radio-chemical method employed was that of Mituya and Obayashi [1], improved by Gorodetskii, Dembrovskii, and Losev [2]. The platinum samples (0.01 mm thick foil, 99.999% Pt) having been activated in the reactor (20-80 h; neutron stream $(1.2\text{-}4)\cdot 10^{13}$ n/cm$^2\cdot$sec), were placed, after pretreatment with concentrated nitric acid, in the clamp-cell used for carrying out the electrolysis. The solution being studied was introduced into the cell at a given rate, and the platinum polarized at a constant value of the potential over several hours, generally sufficient to establish the stationary state for the solution process. The rate of passage of the radioactive platinum into the solution was controlled by taking a sample of electrolyte at the cell exit (without interrupting the polarization), and analyzing it with the aid of a multichannel scintillation γ-spectrometer. Measurements at different potentials were as a rule accomplished passing from less positive to more positive values.

The results of the measurements show, that in the initial stage of electrolysis, solution of platinum in acidic electrolytes is observed at all potentials studied, including the region where hydrogen is evolved (1 N H_2SO_4). The rate of solution falls with time, reducing at not too positive potentials, to below the limit of sensitivity of the method (of the order of 10^{-9} A/cm^2†).

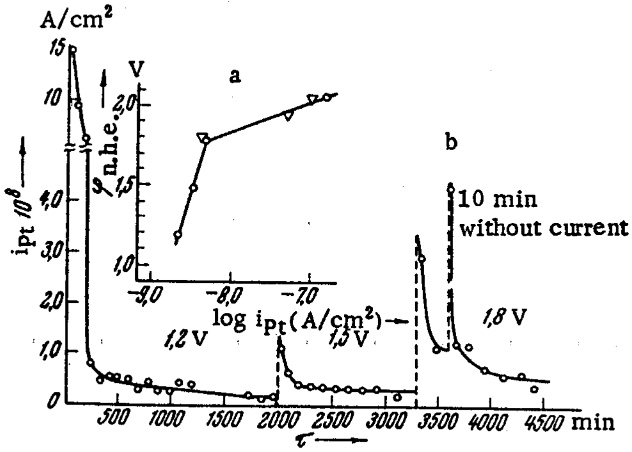

Fig. 1. Influence of potential on rate of solution of platinum in 1 N H_2SO_4. Room temperature a) stationary curve; b) change in rate of solution with time.

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†The rate of solution here and further on is expressed in units of current on the visible surface. For the purpose of calculation it is assumed that it is compounds of 4-valent platinum that pass into solution.

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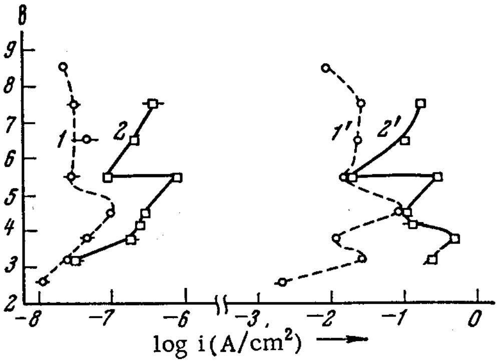

Fig. 2. Influence of potential on rate of solution of platinum (1, 2) and rate of over-all anode process (1', 2') in 20 and 15 N H_2SO_4. Temperature −17°C.

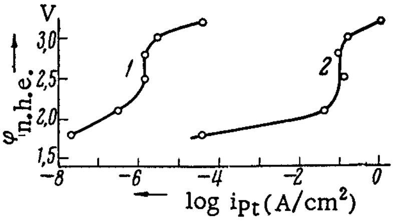

Fig. 3. Influence of potential on rate of solution of platinum (1) and rate of over-all anodic process (2) in 3 N $HClO_4$. Temperature +25°C.

Data concerning the steady rate of dissolution of platinum in 1 N H_2SO_4 are presented in Fig. 1a. The velocity of the process depends slightly on the potential in the range $1.2 < \varphi < 1.8$ V (by n.h.e.) and grows with a further shift of potential in the anode direction.

An analysis of the experimental and literature data enables the assumption to be made, that the kinetics of solution of platinum in 1 N H_2SO_4, in the range of potentials studied, is governed by the rate of passage into solution of the surface metal oxides. On immersion of the oxidized electrode in the solution and displacement of its potential into the field of thermodynamic instability of the surface oxides, the latter are in part reduced, and in part dissolved [3]. It is not excluded that oxygen, having penetrated into the surface layer of the metal and diffusing to the metal – electrolyte boundary, participates in the process [4]. In that case, the more the surface layers of the platinum become poorer in oxygen, the more must the rate of solution decrease, approaching zero asymptotically. The establishment of a stationary process-rate, different from zero, becomes possible at oxidation potentials of the platinum surface under such conditions that surface oxides are formed, at the expense of discharge of the water. The character of the plot of solution current against duration of electrolysis (Fig. 1b) testifies to the fact that the degree of oxidation of the platinum assists acceleration of the solution process, whereas stabilization of the oxygen layer in time leads to its retardation. Short-term interruption of the electrolysis produces activation of the electrode. The substantial increase in the solution rate at potentials $\varphi > 1.8$ V is evidently connected with a change in composition and properties of the oxide film [5].

At high anode potentials a characteristic feature of the solution process for platinum in sulfuric or perchloric acid is the weak dependence of the yield of platinum (by current) on the potential. Figure 2 gives results of measurements of the stable solution-rate of platinum in 15 and 20 N H_2SO_4 at −17° (refrigerated anode) over a wide range of potentials. On the same figure are noted the polarization curves for the oxidation of the components of the electrolyte, measured by current, in the same experiments. As shown in [6], every section of the over-all polarization curve is characterized by its own composition in final products of electrolysis, which testifies to a change in the mechanism of the anodic process in passing from one range of potentials to another. The diagram shows that there is a definite link between the rate of solution and the total current. At all potentials the yield by current of platinum is close to $1 \cdot 10^{-6}$. In the region of formation of a substantially new surface state – at a potential $\varphi = 5.5$ V – in the experiment with 15 N H_2SO_4, a prolonged fluctuation of current was observed, testifying to the occurrence of activation and passivation processes on the electrode (a "jump" from one branch of the curve to the other). At the same time there was observed an analogous fluctuation of the solution-current of the platinum, while in both cases the changes in the rate of the processes were approximately of the same order.

Analogous results were obtained for solutions of perchloric acid. As will be seen from Fig. 3, on passing from potentials of oxygen evolution (lower branch of the polarization curve) to potentials at which ozone-oxygen mixtures are formed (upper branch) there is a symbathy (coincidence) between the way in which the total polarization curve [7] and the partial solution curve for platinum in 3 N $HClO_4$ go.

The presence of a clear link between the kinetics of two formally independent processes – oxidative electrolysis of the components of the electrolyte and solution of the metal – makes extremely probable the assumption that the solution process proceeds via the same electrochemical stages of formation of intermediate complexes – products of the discharge of solution components postulated [8] for the over-all process.

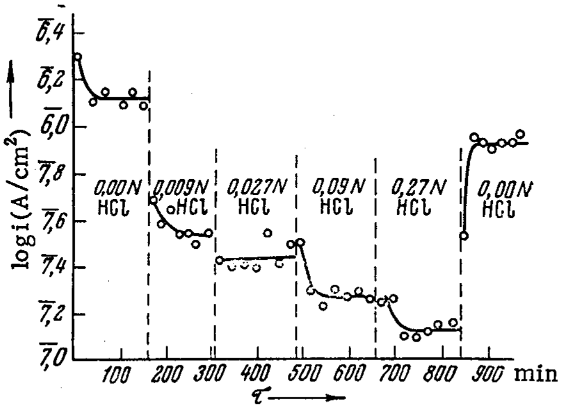

Fig. 4. Dependence of solution rate of platinum in $HClO_4$ at a potential of 2.8 V on the HCl content. Temperature + 25°. Total concentration of acid 3 g-equiv/liter.

In perchloric acid, at least up to potentials of the order of 3 V, the rate of solution of platinum is determined, evidently, by the rate at which the higher oxides of the metal on the surface pass into solution. This supposition enables the double effect, shown by chlorine ions in the solution process, to be explained. It is known [9, 10], that in the active range ($\varphi < 1.1$-1.2 V), chlorine ions accelerate the solution process. Oxidation of the electrode surface leads to retardation of the process. Data regarding the influence of chlorine ions on the solution of platinum in 3 N $HClO_4$ at a potential $\varphi = 2.8$ V, i.e., under conditions where higher oxygen compounds of chlorine are formed [11], are given in Fig. 4. The experiment was carried out in such a fashion, that the change in composition of the electrolyte passing through the cell was accomplished without interrupting the polarization of the electrode. As can be seen from the figure, small additions of hydrochloric acid lower the rate of solution of platinum in 3 N $HClO_4$. With sufficiently small concentrations of chlorine ions, the over-all anodic current is lowered at the same time, which testifies to a reduction in the rate of oxygen evolution [see [12]). It is likely that the effects shown are connected with a reduction in the concentration of active surface oxygen (surface oxides) used in the oxidation of chlorine ions.

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