CORROSION OF PLATINUM IN ALKALINE SOLUTIONS

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Platinum electrodes are widely used in electrochemistry. However, the corrosion behavior and solution mechanism of this metal have scarcely been studied at all, owing to the inadequate sensitivity of most methods of studying the corrosion of smooth electrodes.

Since platinum is used in various electrocatalytic processes (for activation of electrodes in current sources, in electrosynthesis at high anodic potentials, etc.), data are needed on the corrosion behavior of platinum over a wide range of potentials in both acid and alkaline electrolytes.

In acid solutions attention has been chiefly paid to the corrosion of platinum at high anodic potentials. In 5 N NaOH solution at the potentials of surface oxidation of platinum, its solution current exceeds 10^{-9} A/cm^2 [5]; there are practically no data on its behavior at lower potentials, if we except the fact that the potential dependence of its solution rate has been found to have an extremum [6].

We have investigated the behavior of platinum black in alkaline solutions at 20 and 70°C. The platinum black was obtained by reducing platinum dioxide, suspended in an alkaline solution, with hydrogen at 70°C. Its specific surface area, measured electrochemically and by the BET method, was about 30 m^2/g. The investigations were made in an atmosphere of helium or oxygen. The electrode, at elevated temperature, was placed in a preheated solution saturated with the gas. The electrode was of powder (0.1 g) wrapped in a platinum gauze (16,000 holes/cm^2). Since the surface area of the platinum gauze was a negligible fraction of that of the powder, we could neglect the contribution made by the gauze to the corrosion losses. Removal of the solution products from the gaps between the particles of platinum black into the analyzed volume of electrolyte was fairly complete. The amounts of dissolved platinum after 1 h of contact with KOH solution were the same for samples weighing 50-100 mg.

After contact with the platinum the solution was analyzed spectrophotometrically; we analyzed both the alkaline solution itself [7] and an acid solution obtained by neutralizing the working solution with hydrochloric acid [8]. The latter was analyzed in the form of complexes of platinum with stannous chloride. In both cases we measured the optical density of the solution corresponding to the maximum light absorption in these solutions (at 224 and 403 nm, respectively), and from the linear calibration graph for standard solutions determined the concentration of platinum. The reproducibility was better in the analysis of the acid solutions with stannous chloride. Standard alkaline solutions of platinum compounds were prepared from chloroplatinic acid by heating with caustic potash solution, following [7, 9], or by dissolving metallic platinum in aqua regia and neutralizing the solution with alkali. The calibration curves determined for these two groups of solutions were similar. The sensitivity of the measurements was 10^{-6} mole/liter. As a rule, the concentration of dissolved platinum was 1-1.5 orders of magnitude higher.

The corrosion losses were determined after contact between the electrode and a continuously stirred electrolyte for a known time. The quantities thus found characterize the integral, not the instantaneous rate of the process.

To elucidate the corrosion mechanism it is necessary to know the nature of the dissolved particles. The polarization curve of electroreduction of the corrosion product of platinum in an alkaline medium coincides with the curve for reduction of the hexahydro-complex of platinum synthesized in [7, 9]. The spectra of the solutions are also similar. This suggests that corrosion of platinum in an alkaline medium forms mainly the complex ion $[Pt(OH)_6]^{2-}$.

The corrosion rate decreases with time (Fig. 1). At first, measurements were made every 5-10 min, but at the end of the experiment several tens of hours was required to accumulate enough products for analysis

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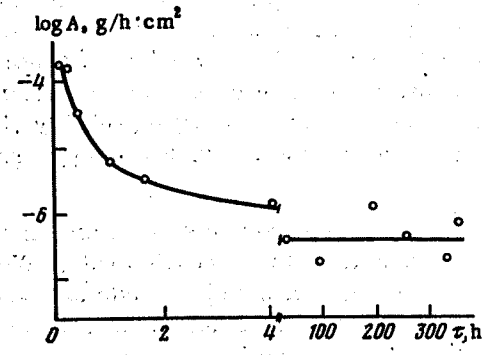

Fig. 1

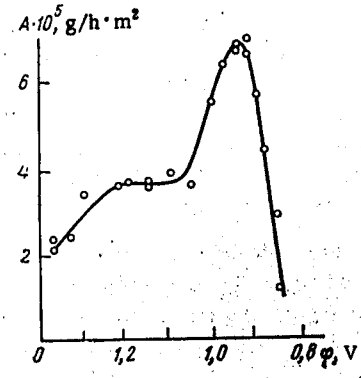

Fig. 2

Fig. 1. Corrosion losses of Pt in 1 N KOH at 20°C vs time of contact of Pt with electrolyte at $\varphi = 1.05$ V.

Fig. 2. Corrosion loss of Pt in 1 N KOH at 70°C vs potential. Atmosphere, helium.

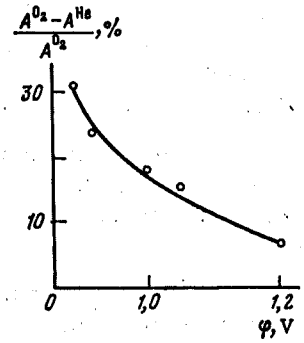

Fig. 3. $(A^{O_2} - A^{He})/A^{O_2}$ in 1 N KOH at 70°C vs potential.

(each measurement was made on a fresh portion of alkaline solution). Similar results were observed when the corrosion of platinum was investigated in the same solution but analysis samples were taken at fixed times. Consequently, the progressive slowing down of the corrosion rate is not due to accumulation of corrosion products in the solution.

From Fig. 1 we see that the mean corrosion rate in the first 5 min of contact is $1.9 \cdot 10^{-4}$ g/h·m²; after 1.5-2 h it falls by nearly two orders of magnitude, and the steady corrosion rate is $2\text{-}8 \cdot 10^{-7}$ g/h·m².

We studied the dependence of the process rate on the electrode potential at 0.85-1.37 V at a temperature of 70°C in 1 N KOH in an atmosphere of helium. The rate of solution was determined after one hour of contact with alkali solution, each time on a new portion of platinum powder and in a fresh electrolyte. As we see from Fig. 2, this rate (in g/h·m² true surface) depends on potential in a rather complicated way. Between 0.85 and 0.92-0.95 V it rises, then sharply falls, probably on account of passivation of the platinum. At 1.05-1.25 V the corrosion rate hardly alters, but with further rise in potential to 1.37 V it again decreases. At potentials more negative than 0.85 V the corrosion rate is so low that it is difficult to measure. We note that the law of variation of the corrosion rate with potential measured after the platinum had been in contact with the KOH solution for 4 h was similar, though the rate of solution was lower and the maximum was much less marked.

According to Chemodanov et al. [1, 5], solution of platinum in acid or alkaline solutions involves the formation of oxygen compounds of the metal at the electrode surface during discharge of the electrolyte components (H_2O, OH^-). In this connection it is helpful to compare the potential dependence found by us for the

corrosion rate with data on the adsorption and desorption of oxygen on platinum in alkaline media. Various forms of adsorbed oxygen [10] are found on the surface of platinum in alkali. At $\varphi < 0.8$ V, OH^- groups are formed on the surface by discharge of OH^- ions, and are adsorbed fairly reversibly. At more positive potentials, water molecules are discharged and oxygen is adsorbed in an atomic form which requires a marked overvoltage to remove it. The appearance of the second form of adsorbed oxygen probably also causes an increase in the corrosion rate of platinum at $\varphi > 0.85$ V. The decrease at $\varphi > 0.95$ V is apparently due, as remarked above, to passivation processes.

To elucidate the role of surface oxygen compounds in the corrosion process we also investigated the influence of pretreatment, in particular reduction of the platinum, on the corrosion rate. We first determined the corrosion losses (A^0) during one hour of contact with an alkaline electrolyte at a known potential φ of platinum kept in air. The powder was then kept at this potential in the solution until the corrosion rate was close to the stationary value A^{stat} (10^{-6}–10^{-7} g/h·m^2). After this the surface was reduced either by cathodic polarization at $\varphi = 0.0$ V or by gaseous hydrogen with which the electrolyte solution was saturated. We then established the electrode potential φ and again determined the corrosion rate for 1 h of contact with a fresh portion of alkali (A'). At all the investigated potentials, reduction of the platinum surface on which the stationary corrosion rate (10^{-6}–10^{-7} g/h·m^2) was established led to activation of the solution process (e.g., $A' = 0.3 \cdot 10^{-5}$ at $\varphi = 0.85$ V, $A' = 2.5 \cdot 10^{-5}$ g/h·m^2 at $\varphi = 1.0$ V).

We also found that the corrosion losses (A^0) of an unreduced specimen are greater than those (A') of a reduced one at each investigated potential from $\varphi = 0.85$ to 1.3 V (see Fig. 2). The difference between A^0 and A' apparently corresponds to solution of the surface layer formed during oxidation in air. If platinum powder with the corrosion rate established at some fixed potential is kept in dry form in air for several hours and then again brought into contact with alkali, the corrosion rate at the same potential increases.

In an oxygen-saturated alkali solution the potential dependence of the corrosion rate of platinum was the same as in Fig. 2. However, when we performed the experiment very carefully we observed that the corrosion rate A^{O_2} in oxygen is higher than that in an inert atmosphere A^{He}; the difference decreases as the potential varies from 0.9 to 1.2 V (Fig. 3).

Thus, the solution of platinum appears to involve the intermediate formation of surface oxides either by discharge of water molecules or by interaction with molecular oxygen. However, it is not clear which is the slow stage – formation of surface oxides or their subsequent solution.

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