ANODIC DISSOLUTION OF PLATINIZED PLATINUM IN ALKALINE SOLUTIONS

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The corrosion behavior of smooth platinum in acid solutions has been studied in detail [1, 2]. Where the acids contain no complexing anion the dissolution of a platinum anode was shown to begin after reaching the oxygen adsorption potential. Steady-state dissolution currents for smooth platinum were observed in alkaline solutions only at oxygen evolution potentials. A number of side experimental results, however, indicated that platinum dissolves at lower anodic potentials [4, 5]. The corrosion behavior of platinum black in alkaline solutions at elevated temperatures has been studied [6, 7]. The corrosion resistance of platinized platinum in electrolyte solutions has not yet been examined.

The purpose of the present work is to study the corrosion behavior of platinized platinum in 7.5 M KOH at 80°C. The Pt/Pt electrodes were prepared in the conventional manner by galvanostatic deposition from 2% H_2PtCl_6 onto a platinum gauze with an apparent surface area of ∿120 cm^2. The true electrode surface was measured after each experiment through a charge curve in 1 N H_2SO_4 and found to be ∿10 m^2. Before starting an experiment the electrode was anodically and then cathodically polarized in 1 N H_2SO_4 at a current density of ∿5 mA/cm^2 of apparent surface. The electrode was thoroughly rinsed with double distilled water and placed into a cell containing a hot alkaline solution. After the above treatment the potential of the immersed electrode did not exceed an E_r of 0.06 to 0.08 V (E_r is the potential relative to that of a reversible hydrogen electrode in the same solution). The studies were carried out in a three-electrode Teflon cell [8] placed in an air thermostat. The electrode potential was brought to a selected value (E_r) by means of a P-5827 potentiostat. An hour thereafter the alkali solution was removed for analysis and replaced by fresh, hot alkali from an auxiliary vessel. Oxygen-free nitrogen was passed through the solution continuously.

The solutions were analyzed for platinum content by the Ayres and Meyer method [9], modified for alkaline solutions. A 5-ml portion of the test solution was transferred to a 25-ml volumetric flask, 6 ml of concentrated HCl and 5 ml of 1 M $SnCl_2$ in 3.5 M HCl were added, and the solution brought to the mark with double distilled water. Absorbances were measured against a blank in 5-cm cuvettes using an SF-16 spectrophotometer at a wave length of 403 nm. The platinum ion concentrations were determined from a linear calibration curve which we plotted for a range of $2\cdot10^{-6}$ to $2\cdot10^{-4}$ M Pt(IV). The method's lower detection limit was 10^{-6} M Pt(IV) although the dissolved platinum concentration usually exceeded 10^{-5} M. The measurement accuracy was ±20%.

Spectra of alkaline solutions after contact with a Pt/Pt electrode were measured with the aid of a Specord spectrophotometer. The maximum absorption was at 224 nm, which is similar to that of the Pt(IV) hexahydroxo complex [10]. This indicates that platinum passes into solution as $[Pt(OH)_6]^{2-}$. The average dissolution rate for the time interval selected (i, A/cm^2) was calculated from

$$i=4FcV/St,$$

where c is the Pt(IV) concentration, mole/ml; V is the volume of the solution, ml; S is the true electrode surface area, cm^2; t is the time, sec; and F is the Faraday number, C/mole.

The method yielded dependencies of time on the platinum dissolution rate in 7.5 M KOH at 80°C for a number of potentials (Fig. 1). At $E_r < 0.92$ V (curves 1-3) the dissolution rate was found to be practically constant with time (the first measurement was made an hour after the potential was set). At $E_r \geqslant 0.93$ V (curves 4 and 5) the dissolution rate dropped during the first 4-5 h and then remained constant (within the limits of analytical accuracy).

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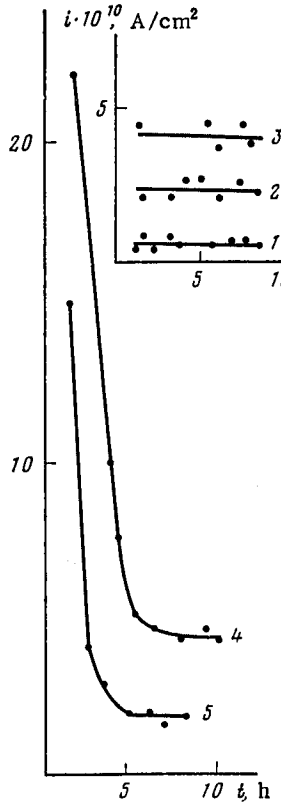

Fig. 1

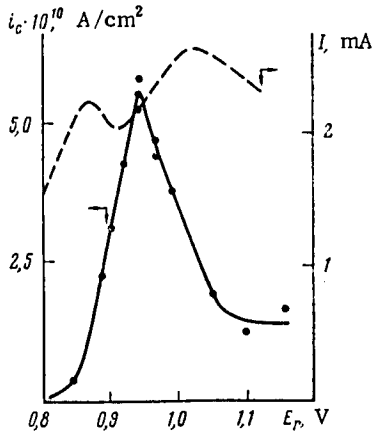

Fig. 2

Fig. 1. The dissolution rate of a Pt/Pt electrode as a function of time at potentials (V) of E_r = 0.84 (1); 0.88 (2); 0.90 (3); 0.95 (4); and 1.15 (5).

Fig. 2. The steady-state dissolution rate as a function of potential and the potentiodynamic curve for a Pt/Pt electrode in 7.5 M KOH at 80°C.

Henceforth this rate will be arbitrarily called the steady-state average platinum dissolution rate (i_c).

Figure 2 shows i_c as a function of potential between 0.8 and 1.15 V (at Er < 0.8 V no Pt was found to dissolve, within the accuracy of the analytical method). The curve is seen to pass through a maximum at E_r = 0.93 V. An analogous relation had been obtained earlier for platinum black [6, 7]. The steady-state maximum dissolution rate for platinized platinum at 80°C was $5.6 \cdot 10^{-10}$ A/cm². The rate dropped by an order of magnitude on lowering the temperature to 20°C. The value of i_c decreased ∿3 fold upon replacing the 7.5 N KOH with 1 N KOH. It should be noted that the amount of platinum dissolved during an experiment was only ∿0.1-0.2 monolayers so that the true electrode surface remained practically constant.

The following experiments were carried out to determine how the cathodic and anodic electrode polarization affects the dissolution rate. In one series of experiments the steady-state dissolution rate was found at E_r = 0.93 V. The electrode potential was then shifted to 0.16 V and kept there for an hour. Next the alkaline solution was renewed, the potential again set to E_r = 0.93 V, and the dissolution rate determined. The results are shown in Fig. 3. The cathodic polarization is seen to increase the dissolution rate to the value obtained an hour after the Pt/Pt electrode was immersed in the alkali and then to drop to its steady-state value. In another group of experiments the Pt/Pt was immersed in the alkaline solution, the potential set at E_r = 1.4 V, and the electrode kept at this potential for 0.5 h. The alkaline solution was then renewed, the potential shifted to a selected value, and the i_c determined. In these experiments the initial Pt/Pt electrode dissolution rate was also initially higher than i_c and with time approached the i_c shown in Fig. 2. Thus the steady-state dissoluton rate is independent of the electrode pretreatment.

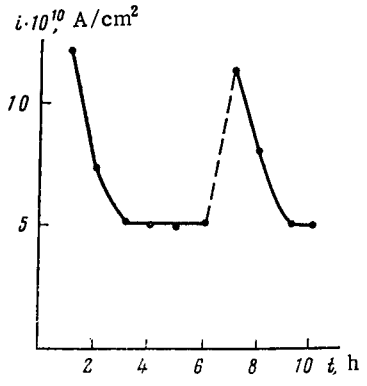

Fig. 3

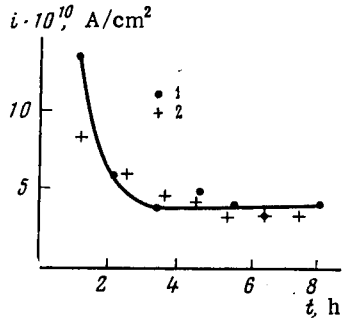

Fig. 4

Fig. 3. The effect of cathodic polarization on the dissolution rate of a Pt/Pt electrode at E_r = 0.93 V.

Fig. 4. The dissolution rate of a Pt/Pt electrode as a function of time at E_r = 0.92 V, in 7.5 M KOH saturated with nitrogen (1) and oxygen (2).

Figure 4 shows the effect of time on the dissolution rate in alkali saturated with oxygen and nitrogen. The coincidence of the curves (within experimental error) shows that dissolved molecular oxygen has no substantial effect on the steady-state dissolution of platinized platinum. On the other hand platinum black has been found to exhibit a higher dissolution rate in oxygen-saturated than in nonoxygenated alkali solution by factors of 1.1 to 1.4 in [7] and 5 to 7 in [6].

Based on the results obtained it may be concluded that the Pt/Pt electrode dissolution of palladium in an alkaline solution [11].

According to [1, 3] smooth platinum dissolves in acid and alkaline solutions through the formation of oxygenated surface compounds. Consequently the complex relation we obtained for the Pt/Pt dissolution rate as a function of potential may probably be due to a change in the state of the adsorbed oxygen. It was shown in [12, 13] that the initial step in the adsorption of oxygen on platinum immersed in alkali is a reversible electrochemical surface reaction with the formation of OH_{ads} species. The formation of a Pt—OH bond weakens that between the Pt atoms in the lattice and creates conditions conducive to the dissolution of platinum. The dissolution rate increases with a rise in surface coverage by OH_{ads} and does not change with time at a constant potential. The adsorbed oxygen adheres more tightly at E_r values greater than the maximum potential shown by the i_c vs. E_r curve [14], possibly due to conversion of the Pt—OH to the HO—Pt bond [15]. The dissolution process is thereby suppressed. The bond becomes stronger with time and is accompanied by a rise in surface coverage by oxygen at a constant E_r, causing a time-dependent dissolution current at $E_r \geqslant 0.93$ V. Platinum dissolves in the passive state at $E_r \approx 1.1$ V.

Figure 2 compares the i_c vs. E_r curve with the potentiodynamic I vs. E_r curve, both for a platinized platinum electrode in an alkaline solution. The I vs. E_r curve is seen to have two maxima within the potential range studied, probably due to two different forms of adsorbed oxygen [15]. Possibly the maximum platinum dissolution current reflects a limiting surface coverage by that form of adsorbed oxygen which corresponds to the left maximum on the I vs. E_r curve. A more detailed comparison is, however, hampered by difficulties in separating the different forms of adsorbed oxygen and by the fact that the I vs. E_r and i_c vs. E_r curves were taken at substantially different applied potential rates.

We attempted using ellipsometry [16] to discover any changes in surfaces properties of a smooth Pt electrode upon shifting from E_r = 0.9 V to E_r = 1.1 V. Positive results were not, however, obtained due to insufficient sensitivity.

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