

CORROSION OF PLATINUM CATALYST IN ALKALINE SOLUTIONS

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Summary

The corrosion behavior, as affected by time and potential, of platinum black in alkaline solution at 20 and 70 °C has been studied. It is shown that over the potential range 0.85 - 1.37 V platinum undergoes dissolution, the maximum corrosion rate being observed at $E = 0.93 - 0.95$ V. With time, the corrosion current decreases to $10^{-6} - 10^{-7}$ A/m². When platinum passes into solution the complex ion $[\text{Pt}(\text{OH})_6]^{2-}$ is formed. The influence of platinum pretreatment, leading to removal of surface oxygen compounds, on the rate of corrosion has been investigated. It has been found that Ba^{2+} ions slow down the dissolution process, while Cl^- ions increase its rate. The relationship between the platinum corrosion process and the shift of the oxygen electrode potential from the equilibrium value is discussed. Some conclusions are drawn about the mechanism of platinum corrosion.

1. Introduction

The oxygen electrode is the determining factor in the operation of many power source systems: metal-air, hydrogen-oxygen, etc. In these systems the oxygen electrode works at sufficiently positive potentials by 200 - 300 mV more negative than the equilibrium potential. The most extensively used and efficient catalyst for activation of the oxygen electrode is platinum. In acid and alkaline media, however, platinum catalyst is subject to corrosion. The corrosion behavior and dissolution mechanism of platinum are not clearly understood, which is probably due to experimental difficulties associated with its low rate of dissolution in electrolytes and insufficient sensitivity of the majority of analytical methods of determining the concentration of platinum in solution.

Few studies on platinum dissolution in acid solutions are presently available [1 - 4], the primary attention in those given to corrosion of platinum at high anodic potentials. Corrosion studies on platinum in alkaline solutions at high anodic potentials [5] showed that the dissolution current of platinum in 5N NaOH at its surface oxidation potentials exceeds 10^{-5} A/m². Information on the corrosion behavior of platinum at lower potentials in alkaline solutions became available very recently. The process of platinum dissolution (platinum black and platinized platinum) in KOH solution was studied in refs 6 - 8.

2. Experimental

2.1. Materials

This paper is concerned with the corrosion behavior of platinum in alkaline solutions at 20 and 70 °C. The subject of the studies was platinum black obtained either by chemical reduction with formaldehyde from H_2PtCl_6 solution, or by reducing platinum dioxide suspended in alkaline solution with hydrogen. According to measurements (electrochemical and by the BET method), the specific surface of platinum was ~ 16 and ~ 30 m^2/g , respectively. Experiments were carried out under helium or oxygen atmospheres. If elevated temperatures were used the electrode was immersed in a preheated solution saturated with one of the above mentioned gases. Platinum powder (0.1 g) wrapped in platinum gauze (16 000 holes/ cm^2) served as electrode. The platinum gauze surface constituted an insignificant part of the powder surface and its contribution to the corrosion losses may be neglected. The removal and analysis of dissolution products from the gaps between the platinum black particles into the electrolyte volume provided sufficient accuracy. The amount of dissolved platinum per 1 g after 1 h contact with KOH solution when the weighed portion varied from 50 to 100 mg, was the same.

2.2. Analysis

After contact with platinum the solution was analyzed by the spectrophotometric method. Both the alkaline [9] and the acid solution, obtained by neutralization of the working solution with hydrochloric acid [10], were analyzed. The acid solution was analyzed for platinum complexes using stannous chloride. In both cases the optical density of the solution was measured, corresponding to the maximum light absorption in such solutions (at 224 and 403 nm, respectively), and the platinum concentration was determined by means of a calibration curve prepared from standard solutions. The reproducibility was better in the case of acid solutions using stannous chloride. Standard alkaline solutions of platinum compounds were prepared either from chloroplatinic acid by heating with potassium hydroxide solution [9, 11], or by dissolving platinum metal in *aqua regia*, followed by neutralization of the solution with alkali. The calibration curves determined for the two groups of solutions were similar. Measurement sensitivity was 10^{-6} mol/l. The concentration of dissolved platinum was, as a rule, higher by 1.0 - 1.5 orders of magnitude.

The corrosion losses were determined after electrode contact with a continuously stirred electrolyte solution for a fixed time. It should be borne in mind that the rate of dissolution of platinum thus found is a quantity characterizing the integral and not the instantaneous process rate.

3. Results and discussion

3.1. Composition of corrosion products

One of the problems of interest for elucidation of the corrosion mechanism of platinum is the nature of the dissolved platinum particles. The pola-

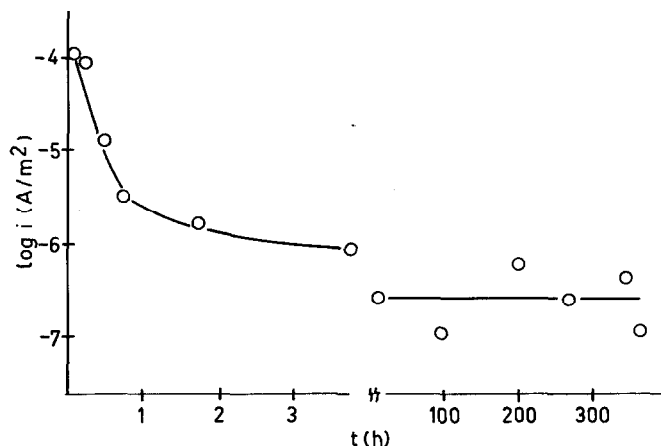


Fig. 1. Dependence of Pt corrosion current in 1N KOH at 20 °C on its contact time with electrolyte at $E = 1.05$ V.

rization curve of the electroreduction of platinum corrosion products in alkaline medium coincides with the reduction curve of the platinum hexahydrocomplex synthesized in refs. 9 and 11. The solution spectra are also similar. This warrants the suggestion that the complex ion $[\text{Pt}(\text{OH})_6]^{2-}$ is mainly formed during corrosion of platinum in alkaline medium.

3.2. Dependence of corrosion current on time

The corrosion rate of platinum decreases with time. Figure 1 shows the dependence of the corrosion rate (in electrical units) of platinum on the time of its contact with alkaline solution at 20 °C and a potential of 1.05 V (the potentials are given against the reversible hydrogen electrode in the same solution). At first, measurements were made every 5 - 10 min, but at the end of the experiments some tens of hours were required for corrosion products to accumulate in sufficient quantity for analysis. Each measurement was performed on a fresh volume of alkaline solution. Similar results were obtained for cases where platinum corrosion was studied in one and the same volume of solution and analytical samples were taken after definite time intervals. Therefore, the decreasing corrosion rate with time is unconnected with accumulation of dissolution products in solution.

The corrosion rate of platinum in the first 5 min of contact was 1.05×10^{-4} A/m² (1 A/m² corresponds to 1.82 g (Pt)/(h m²)); after 1.5 - 2.0 h it dropped by almost two orders and the steady corrosion rate was $(1.1 - 4.4) \times 10^{-7}$ A/m².

3.3. Dependence of corrosion rate on potential

The dependence of corrosion rate on potential was studied in the range 0.85 - 1.37 V at 70 °C in 1N KOH under a helium atmosphere. The corrosion current was measured after an hour's contact with an alkaline solution, each

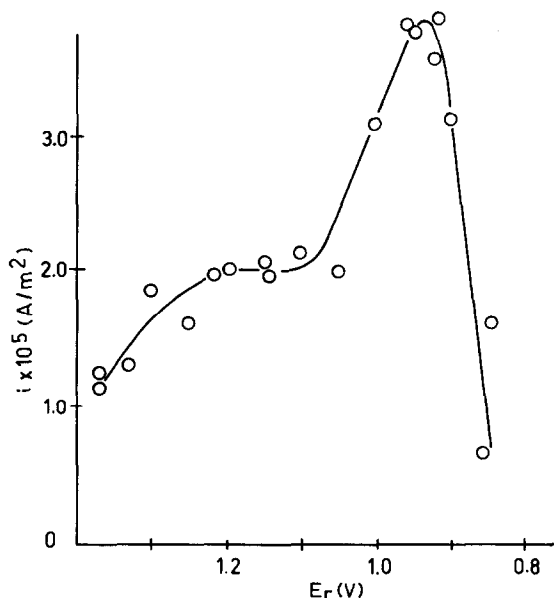


Fig. 2. Dependence of Pt corrosion current in 1N KOH at 70 °C on potential. Atmosphere: helium.

time on a new portion of platinum powder and in fresh electrolyte. As can be seen from Fig. 2, this quantity depends on potential in a very complex manner. At first, when the potential varied from 0.85 to 0.95 V it increased considerably and then dropped sharply, which points to an increased passivation of platinum. In the potential range 1.05 - 1.25 V the corrosion current varied little, and when the potential increased further to 1.37 V it decreased still more. At potentials more negative than 0.85 V, the corrosion current was so small that measuring it presented some difficulties. It should be noted that the character of the change of the corrosion current dependence on potential, measured after contact of platinum with KOH solution for 4 h was similar, though its value was smaller and the maximum much less pronounced.

In alkaline solution saturated with oxygen, the corrosion rate dependence of platinum was similar to that in Fig. 2. However, when experiments were performed with particular care it appeared that in oxygen [$i(O_2)$], the corrosion current was higher than in an inert atmosphere [$i(He)$], the difference between the two current values depending on potential. The change in potential from 0.9 to 1.2 V led to a decrease in the quantity [$i(O_2) - i(He)$]/ $i(O_2)$ (Fig. 3).

According to refs. 1 - 5, platinum dissolution in acid and alkaline solution proceeds *via* formation of metal compounds with oxygen, appearing on the electrode surface during discharge of electrolyte components (H_2O , OH^-). In this connection it is expedient to compare the corrosion rate dependence on potential found by us with the data on oxygen absorption and desorption on platinum in alkaline media. Different forms of adsorbed oxygen are pre-

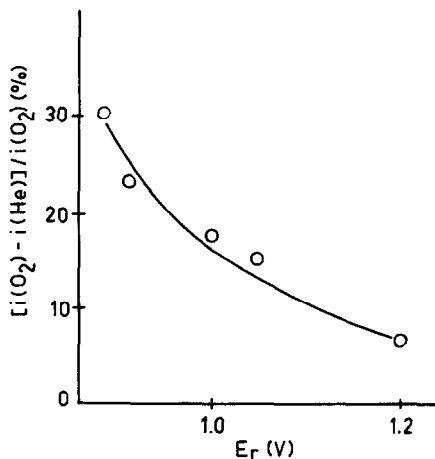


Fig. 3. Dependence $[i(O_2) - i(He)]/i(O_2)$ in 1N KOH at 70 °C on potential.

sent on the platinum surface in alkali [12]. In the range $E_r < 0.8$ V, as the result of OH^- ion discharge, OH groups are formed on the surface, the adsorption of which is to some extent reversible. At more positive potentials oxygen is adsorbed in the atomic form, its removal necessitating a significant overpotential. It is probably the appearance of the second form of adsorbed oxygen that is responsible for the increase of the platinum corrosion rate at $E > 0.85$ V. Its decrease at $E > 0.95$ V seems to be due to strengthening of the oxygen bond with the platinum surface.

3.4. Influence of platinum pretreatment on corrosion current

In order to clarify the role of surface compounds in the corrosion process, a study was made of the influence of platinum reduction on the corrosion rate. At first the corrosion rate was determined after one hour's contact of platinum stored in air with alkaline electrolyte. Then the powder was kept at the same potential in solution until the steady-state current $10^{-6} - 10^{-7}$ A/m² was reached. Subsequently the surface was reduced either by cathodic polarization at $E_r = 0.0$ V, or by hydrogen gas with which the electrolyte solution was saturated. Then the corrosion current was again determined after one hour of contact with a fresh sample of alkali. At all the potentials investigated, reduction of the platinum surface on which the corrosion rate had become steady, led to an activation of the dissolution process. The corrosion current of the reduced sample, however, was somewhat less than for the unreduced sample. The difference seems to correspond to dissolution of the surface layer formed during oxidation in air. If the platinum powder, the corrosion rate of which became steady at a certain fixed potential, is kept dry in air for several hours and then again brought into contact with alkali, the corrosion rate at this potential increases.

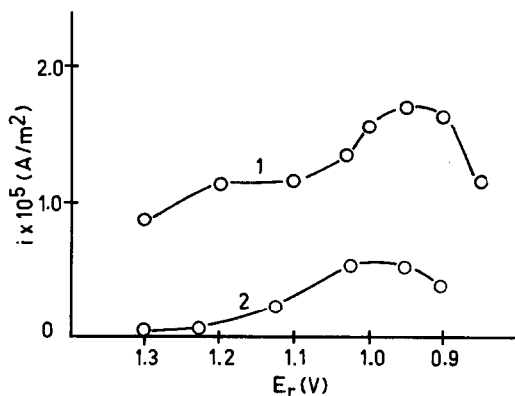


Fig. 4. Dependence of Pt corrosion current on potential in alkaline solution saturated with helium at 70 °C: 1,1N KOH; 2,1N KOH + 1×10^{-3} N Ba²⁺.

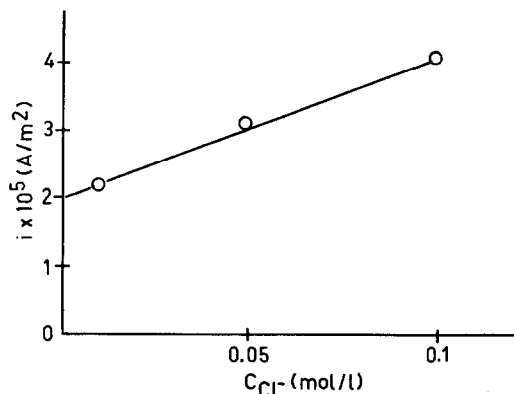


Fig. 5. Dependence of Pt corrosion current in 0.1N KOH at 70 °C and $E = 0.95$ V on Cl⁻ concentration (contact of Pt with solution: 30 min).

3.5. Influence of Ba²⁺ and Cl⁻ on corrosion current of platinum

It is known that Ba²⁺ and Cl⁻ ions are adsorbed on the platinum surface, resulting in a change in the amount of oxygen compounds and in the strength of the oxygen bond with the metal surface [13 - 16]. Figure 4 shows the dependence of the corrosion current under helium atmosphere at 70 °C in a pure KOH solution and in a solution containing 10^{-3} N Ba²⁺ (contact with electrolyte is 1 h). The introduction of a very small amount of Ba²⁺ into KOH solution leads to a marked slowing down of the platinum dissolution process, and with increasing potential, the decrease of the rate of this process becomes greater: if at the potential 0.95 V the amount of dissolved platinum during 1 hour's contact with an alkaline solution decreases 3 times, then in the potential range 1.2 - 1.3 V the corrosion losses drop by 1.0 - 1.5 orders.

Cl⁻ ions produce an opposite effect. In Fig. 5 the dependence of the corrosion current in 0.1N KOH at a potential of 0.95 V on the chlorine ion con-

centration is given. It can be seen that the higher the Cl^- concentration, the greater is the rate of platinum corrosion. A similar dependence was observed in refs. 2 and 17 for acid electrolytes containing halogen ions.

The dissimilar effect of Ba^{2+} and Cl^- ions on the platinum dissolution process in alkaline solution is associated with their influence on oxygen adsorption on platinum. As has been pointed out above, the slowing down of the platinum corrosion process at $E_r > 0.95$ V is due to the formation of a stronger bond of adsorbed oxygen with the platinum surface. Since adsorption of Ba^{2+} ions leads to strengthening of the bond between adsorbed oxygen and platinum [13, 15], the addition of Ba^{2+} to alkaline solution should lower the amount of platinum that has passed into solution, which was found experimentally. Adsorption of halogen ions, on the contrary, hinders the formation of a passivating film of adsorbed oxygen [14], which seems to account for the increase in the corrosion rate of platinum in the presence of Cl^- ions.

On the basis of the experimental data given above, it can be concluded that platinum dissolution in alkaline medium proceeds in two steps: the formation of surface oxides, both as a result of the discharge of water molecules (or OH^- ions) and due to interaction with molecular oxygen, and their subsequent dissolution. According to our data, the exchange current of the oxygen adsorption-desorption process on platinum black exceeds the corrosion current. Consequently, these steps are not the limiting ones. Such a step can be the passing of the oxygen-containing compounds into solution.

3.6. Corrosion of platinum and equilibrium oxygen potential

The data on the corrosion behavior of platinum in alkaline solutions at potentials near the steady-state potential are of considerable interest in connection with the problem of the equilibrium oxygen potential on the platinum electrode. The corrosion current can play an important role, especially in cases where the exchange current of the electrochemical process occurring on the electrode is sufficiently small and comparable with the corrosion current.

The equilibrium potential of the system $\text{O}_2/\text{H}_2\text{O}$ calculated from thermodynamic data at 25°C and $P_{\text{O}_2} = 1$ atm is 1.229 V. The open-circuit potential, however, on platinum in oxygen-saturated solutions lies, as a rule, in the range 1.0 - 1.1 V. At present the generally accepted view is that the steady-state potential established on platinum in aqueous solution is a mixed one. Bockris *et al.* [18 - 20] believe that the anodic process resulting in a shift of the electrode potential from the equilibrium value actually represents oxidation of micro-impurities in solution. The oxygen reaction becomes sensitive to impurities at a concentration in solution of 10^{-5} mol/l. We showed [21] that the addition of 10^{-5} - 10^{-6} mol/l of methyl alcohol does not affect the rate of cathodic and anodic processes on the platinum electrode. According to refs. 22 and 23, thorough removal of impurities from solution does not ensure establishment of the equilibrium potential.

The mixed potential theory [24] is more likely, according to this, the four-electron process of oxygen reduction is coupled with the anodic reaction

of the formation of surface oxides on the electrode. Using this interpretation of the nature of the steady-state potential, some additional assumptions are necessary concerning the mechanism of removal of oxides from the surface, since the surface coverage with chemisorbed oxygen has a finite value. According to Hoar [25], adsorbed oxygen removal proceeds by its desorption and dissolution in the metal bulk. Another possibility of surface layer removal exists — its dissolution in electrolyte.

It is interesting to compare the corrosion current of platinum with the current value necessary for maintenance of the oxygen potential equilibrium $E = 1.23$ V. According to refs. 26 and 27, the oxygen reduction exchange current on smooth electrodes in alkaline medium is $(10^{-6} - 10^{-7})$ A/m². In the case of highly dispersed platinum on carbon over a wide pH range, this value can be less $(0.2 \times 10^{-7} - 1.0 \times 10^{-6})$ A/m² [28]. The steady-state corrosion current, equal to $(1.1 - 4.4) \times 10^{-7}$ A/m² (see Fig. 1) is comparable with the exchange current of oxygen electroreduction at a potential of 1.23 V. In addition, according to our data [21] obtained on platinized platinum, the current necessary to maintain the steady-state potential of the platinum electrode under oxygen (~ 1.06 V) is $(3 - 4) \times 10^{-4}$ A/m². This value is much larger than the one corresponding to the steady rate of corrosion and is close to the initial rate of platinum corrosion (1.0×10^{-4}) A/m² at the potential indicated (see Fig. 1).

In all cases, when a reversible oxygen potential was experimentally achieved, the platinum electrode had been subjected to oxidation (thermal oxidation, anodic polarization, treatment in concentrated nitric acid). In these cases, as a result of increased surface coverage with oxygen-containing particles, the steady-state potential of the platinum electrode shifts in the positive direction [29]. As follows from the data given above, as the platinized platinum electrode potential increases, especially at $E > 1.23$ V, the corrosion current of platinum in oxygen-saturated alkaline solutions decreases.

The results obtained warrant the conclusion that platinum corrosion exerts considerable influence on the shift of the platinum–oxygen electrode potential from the equilibrium value.

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