

CORROSION OF PLATINUM IN ALKALINE SOLUTIONS

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Platinum electrodes find wide application in electrochemistry. But the data on the corrosion behaviour of platinum proper are very scarce and virtually its dissolution mechanism is not understood. This seems to be explained by the experimental difficulties associated with the low absolute dissociation rate of platinum in electrolyte solutions and insufficient sensitivity of most methods used in investigating corrosion of smooth electrodes.

Since platinum is used as a catalyst in various electrocatalytic processes it is necessary to have at one's disposal information on the corrosion behaviour of platinum in a wide potential range, both in acid and alkaline electrolytes.

In our investigation we studied the corrosion behaviour of platinum in 1N alkaline solutions at 20° and 70 °C. The experiments were made on platinum black obtained by reduction with hydrogen. We used the electrochemical, spectrophotometric and BET methods. The experiments were carried out in helium or oxygen atmosphere.

A problem of interest in investigating the corrosion mechanism of platinum is the nature of the dissolved platinum species. Data suggest that the main species formed during corrosion of platinum in alkaline medium is the complex ion/ $\text{Pt}(\text{OH})_6^{2-}$. It was established that increase in electrolyte temperature leads to higher platinum concentration in solution. The corrosion rate decreases with time. The mean initial corrosion rate (in the first five minutes of contact) is $19 \times 10^{-8} \text{g/hr/cm}^2$. After contact for 1.5-2 hours with solution it decreases almost by two orders. The steady corrosion rate is $2.8 \times 10^{-11} \text{g/hr/cm}^2$. We examined the dependence of the process rate on the electrode potential. It is shown that this dependence is rather complex. Comparison of the dependence of the corrosion rate on potential with the data on the behaviour of platinum in alkaline solution with respect to oxygen adsorption and desorption processes suggests that the increase in the platinum dissolution rate can be due to the presence of the second form of adsorbed oxygen in alkaline solution.

Thus analysis of the obtained experimental data and comparison of the results of the corrosion and adsorption measurements warrant the conclusion that dissolution of platinum goes through intermediate formation of oxides which can be formed by interaction with the solution components (OH^- , H_2O) and with molecular oxygen.

It is of interest to find which step of this process is the slow one; formation of surface oxides or their subsequent dissolution. We measured the exchange currents of the oxygen adsorption-desorption process on a platinum electrode in the same potential range in which we studied corrosion. This result indicates that the formation of surface oxide layers is not the limiting step in the platinum corrosion process.

It is interesting to compare the corrosion rates for platinum obtained by us with the current value necessary for maintenance of the equilibrium oxygen potential, which is 10^{-10} to 10^{-11} Amp/cm². This value is close to the steady state corrosion of platinum influences significantly the shift from the equilibrium value of the platinum electrode potential in electrolyte solution saturated with oxygen.

Keywords : Corrosion; Platinum; Alkaline Electrolytes; Equilibrium Oxygen Potential