SURFACE STATE OF A PLATINUM ANODE IN ACIDIC CHLORIDE SOLUTIONS

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In recent years many investigations have been carried out dealing with the surface state of the platinum electrode and with the connection between the presence of oxygen-containing compounds on the Pt surface and the course of anodic reactions (e.g., the work of Veselovskii and co-workers on the synthesis of oxidants [1]). This problem has been reviewed in detail in [2-4]. Of particular interest is the comparison of the state of the Pt surface and the course of anodic reactions in chloride solutions. It is well known that in acidic solution, the presence of chloride inhibits the formation of the oxygen film and lowers the amount of oxygen on the electrode surface [5-11]. It is known, on the other hand, that prior oxidation of the surface promotes a decrease in the adsorption of halide ion [12-17]. However, the available quantitative information about the state of oxidation of Pt in chloride solutions refer either to solutions which are dilute with respect to chloride, or to a narrow potential range.

We set ourselves the task of determining the oxygen coverage of a Pt anode in acid solution at relatively high anodic potentials (from 1.1 to 2.1 V) and over a wide range of chloride concentrations (up to 1.0 N), i.e., under conditions which are of interest from the viewpoint of industrial electrolysis.

For this task we used the potentiodynamic method (application of triangular voltage pulses to the electrode) with a recording of the nonstationary I–t (or I–φ, respectively) curves following the technique described in [18]. The amount of adsorbed oxygen Q_O was determined by integrating the I–t curve in the cathodic half-cycle over the potential range in which the film is reduced, and correcting for the double-layer charging current (the dashed line in Fig. 1).* For the convenience of the discussion, we express oxygen coverage in terms of monolayers of adsorbed oxygen, i.e., in the form $Q_O/2Q_H$ (assuming that the coverage by adsorbed hydrogen corresponds to a monolayer). The data given refer to a potential scan rate of v = 80 mV/sec; at v = 30 mV/sec, Q_O is somewhat higher (by approximately 10%). The potentials are measured and reported relative to the normal hydrogen electrode. The anodic cell compartment was separated from the cathodic compartment. The cell was thermostatted.

A Pt wire of 0.2-mm diameter and an apparent surface area of about 0.02 cm^2 served as the electrode. Since the currents in the region where molecular oxygen and chlorine are evolved, are appreciably higher than the currents for the deposition and stripping of adsorbed oxygen, the selected potential interval was traversed with changing sensitivity of the recorder (PDS-021 two-coordinate potentiometer): the current in the potential range where molecular chlorine and oxygen are evolved and where molecular chlorine is ionized, was recorded with reduced instrumental sensitivity and very intense nitrogen purging. The oxygen coverage was measured in chloride solutions from 10^{-5} to 1 N, with a base electrolyte of 1 N H_2SO_4. The solutions were prepared with doubly distilled water from twice-distilled H_2SO_4; KCl was twice recrystallized. Prior to the experiment, the solutions were subjected simultaneously to electrochemical and adsorptive purification directly in the working cell and under hydrogen atmosphere; this lasted about 20 h.

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*In cases where the potential does not reach values corresponding to the evolution of oxygen or chlorine, one obtains practically coinciding values for the amounts of adsorbed oxygen when integrating the curves for film reduction or for anodic oxygen deposition.

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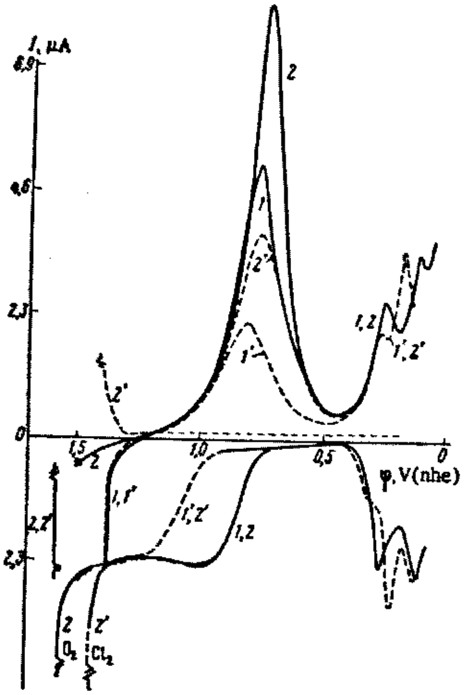

Fig. 1. I−φ curves for the Pt electrode: 1, 2) 1 N H_2SO_4 solution; 1', 2') 1 N H_2SO_4 + 10^{-2} N KCl solution. 1, 1') end potential 1.4 V; 2, 2') end potential 1.6 V. Anodic currents are plotted downwards on the ordinate, cathodic currents are plotted upwards. The temperature was 20°C.

Figure 1 shows, as examples, typical curves for pure H_2SO_4 solution (curves 1 and 2) and for an H_2SO_4 solution containing chloride (curves 1' and 2'). They have the usual form with peaks (or plateaus) for the adsorption and desorption of hydrogen and oxygen. Curves 2 and 2' in the figure are cut off in the region where molecular chlorine and oxygen are evolved, and where molecular chlorine is ionized, because at more positive potentials, the sensitivity with respect to current was strongly decreased. First of all it can be seen from Fig. 1 that the oxygen coverage of the anode increases when in solutions of like composition, be it in the absence or presence of chloride, the anodic end potential is raised. As the anodic potential increases, there is also a shift in the potential φ_n (corresponding to maximum current of film reduction) to the cathodic side (compare curves 1 and 2 with 1' and 2'), indicating an increase in the bond strength between oxygen and the Pt surface. This strenthening of the Pt−O bond with potential has previously been noted for pure H_2SO_4 solution [19-21].

It must be noted that we have not made any special attempts to determine the stoichiometry of the surface coverage. It appears, however, that under our conditions, even in acidic chloride solutions of appreciable concentration, the surface film on the Pt anode − for whose removal the current is expended − consists of oxygen, i.e., is of the form Pt−O rather than Pt−Cl_2 (in [8] it is assumed that in 1 N chloride at pH 0-2, the film has the composition Pt−Cl_2). It can be seen from Fig. 1 that the nonstationary I−φ curves at potentials between the reversible hydrogen value and oxygen evolution (in H_2SO_4) or chlorine evolution (with chloride addition) are of the same character: up to the region where the current changes drastically, and where Cl_2 is evolved or reduced, there appear in the chloride solutions, neither on the anodic nor the cathodic curve any new maxima or plateaus of current, or any deformations in the shape of existing peaks which would point to the formation or reduction of a new surface compound in this potential range.* It can thus be assumed that at potentials negative to the equilibrium chlorine potential, the surface film which is formed consists of adsorbed oxygen atoms and specifically adsorbed Cl^- ions. At more positive potentials, it is very likely that chlorine is present in the surface film, either in the form of strongly adsorbed Cl^- ions with partial charge transfer (as proposed in [12] for the adsorption of Br^-) or in the form of adsorbed chlorine atoms, but it is not possible with the present method to find them at potentials where molecular chlorine is evolved.

Marked oxygen deposition on the Pt surface, which in the absence of chlorine begins at about 0.8 V (curves 1 and 2), is inhibited in the presence of chloride and occurs only at higher potentials (curves 1' and 2'), this inhibition being stronger the higher the chloride concentration. In the presence of chloride, the oxygen surface film diminishes as compared to that in pure H_2SO_4, and becomes less strong (one observes a small shift of φ_n to the anodic side).

Figure 2 shows the oxygen coverage of the Pt anode as a function of oxidation potential in solutions of different composition. It can be seen that in H_2SO_4 solution, the coverage increases approximately linearly with potential up to 2.0–2.1 V (with some bending at ~1.6 V): monolayer coverage of the electrode occurs at a potential of ~1.5 V; coverage with two monolayers at ~1.9-2.0 V. In the presence of chloride, the oxygen coverage is less than that in pure H_2SO_4, but in a solution of given composition containing chloride, the oxygen coverage increases with potential. At high potentials, the curves in the absence and presence of chloride approach each other; only in 1 N chloride there remains a significant difference in oxygen coverage relative to pure H_2SO_4 even at high potentials. It can thus be seen that at low potentials,

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*If these processes do occur, their contribution to the total current is small.

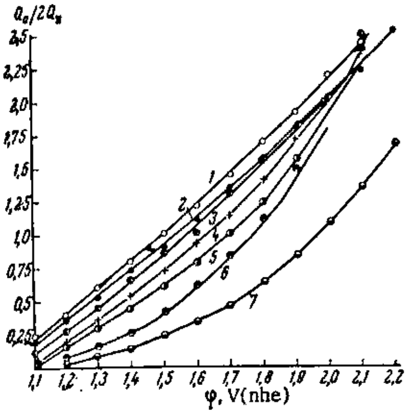

Fig. 2

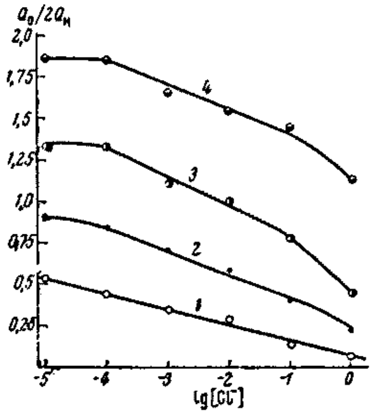

Fig. 3

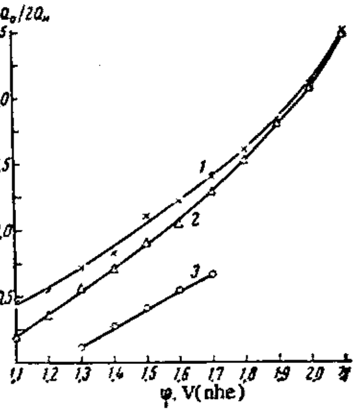

Fig. 4

Fig. 2. Oxygen coverage of a Pt anode as a function of oxidation potential: 1) 1 N H_2SO_4 solution; 2) 1 N H_2SO_4 with the addition of KCl (10^{-5} N); 3) 10^{-4} N KCl; 4) 10^{-3} N KCl; 5) 10^{-2} N KCl; 6) 10^{-1} N KCl; 7) 1 N KCl. The temperature was 20°C.

Fig. 3. Oxygen coverage of platinum as a function of chloride concentration at the potentials: 1) 1.3; 2) 1.5; 3) 1.7; 4) 1.9 V. The temperature was 20°C.

Fig. 4. Oxygen coverage of a Pt anode as a function of oxidation potential: 1) 1 N H_2SO_4 solution; 2) the same, with KCl addition (10^{-2} N); 3) with 1 N KCl. The temperature was 70°C.

chloride expels oxygen from the surface; in 0.1 N and 1 N chloride, the surface is practically free from adsorbed oxygen up to 1.1-1.15 V. Conversely, at high potentials chloride is expelled by oxygen from the surface film.

It can also be seen from Fig. 2 that at constant anode potential, oxygen coverage diminishes with increasing chloride concentration. Figure 3 shows the oxygen coverage as a function of chloride concentration in solution at four potentials. At intermediate chloride concentrations (10^{-4}-10^{-1} N), the oxygen coverage decreases approximately linearly with the logarithm of chloride concentration.

We have also measured oxygen coverage on Pt in the same solutions at 70°C. It must be said that the accuracy of the measurements using our method is lower at elevated temperature; however, the change of coverage with potential and with chloride concentration remains equal in character to that at room temperature (Fig. 4). The effect of temperature is felt in the chloride solutions in a certain increase of the amount of oxygen on the surface relative to that of room temperature, as well as in some strengthening of the bond between oxygen and Pt (which is revealed in a larger shift of φ_n to the cathodic side with increasing oxidation potential than at room temperature).

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