ON THE CAUSE OF THE CHANGE IN THE ELECTROCHEMICAL PROPERTIES OF PLATINUM IN THE REGION OF ANODIC POTENTIALS

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In a number of studies [1-4] it has been shown that at potentials above 1.5 V in solutions of sulfuric acid there is a change in the properties of the platinum anode, which has been attributed to a change in the state of the platinum surface. However, the mechanism of this phenomenon has remained obscure. In view of this, we undertook this work, in which we recorded the polarization curves, curves of the dependence of the differential capacitance on the potential, and curves of the dependence of the adsorption of SO_4^{-2} anions on the potential in an acidified 0.1 N solution of Na_2SO_4.

The preliminary treatment of the electrode for recording the polarization and capacitance curves and the experimental procedure was the same as in [5]. To prepare the electrode for adsorption measurements, polishing was replaced by calcination in the oxidizing flame of a gas burner with air purging. The adsorption measurements were performed in the following way: the electrode was polarized in a 0.1 N solution of labeled $Na_2S^*O_4$ (S^{35}) for 15 min at a given potential. Special experiments established that the limiting value of the adsorption corresponding to a given potential is reached in a time of about 5 min. Further exposure of the electrodes at the given potential up to one hour does not lead to any appreciable increase in the value of the adsorption. After polarization, the smooth platinum electrodes were removed from the solution, washed in three portions of double-distilled water for 15 sec each, and dried with filter paper. The radioactivity was measured on a 4π-counter.

The results of the electrochemical and adsorption measurements are cited in Figs. 1 and 2. As can be seen from Fig. 1, at a potential of 1.6 V with respect to the saturated calomel electrode, there is a change in the slope of the polarization curve. It should be mentioned that the change in the slope of the polarization curve in sodium sulfate cannot be caused by concentration polarization, since the i versus φ curve taken on a rotating disc electrode has the same form.

The increase in the slope of the polarization curve (coefficient b of the Tafel equation) shows that after 1.6 V, there is a change in the rate of the surface that hinders discharging of water molecules in comparison with charging at less positive potentials. The same conclusion should be drawn from the capacitance data, since a pseudocapacitance peak is observed on the C versus φ curve at this potential (Fig. 2).

From Fig. 2 it is also evident that at a potential close to 1.5 V, the adsorption of the anion SO_4^{-2} begins to increase; the adsorption increases sharply at a potential of 1.6 V. This permits us to conclude that the cause of the change in the slope of the polarization curve and decreases in the pseudocapacitance is a change in the state of the platinum surface, caused by the adsorption of SO_4^{-2} anions.

Such an effect might be expected in the presence of strongly adsorbed SO_4^{-2} anions, contained in platinum oxides. In this case the SO_4^{-2} anions, partially displacing the adsorbed oxygen or being adsorbed on oxygen previously adsorbed on platinum, will decrease its electrochemical activity, in other words, increase its bond strength.

As is shown by the experiment, the adsorption of SO_4^{-2} anions in the region of potentials above 1.5 V is actually very strong. In the case of washing with water, alkali, or acid in air for long periods, the activity of the electrode decreases negligibly, which indicates the incorporation of SO_4^{-2} anions into the composition of the oxide film. Such an explanation is supported by their rapid total desorption after brief (1 min) cathodic polarization at the potential of hydrogen evolution.

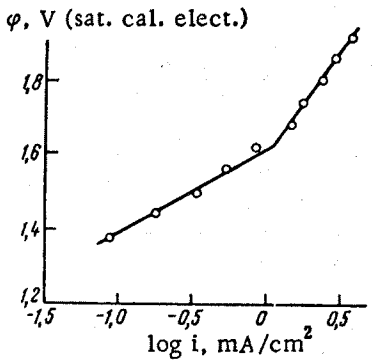


Fig. 1.

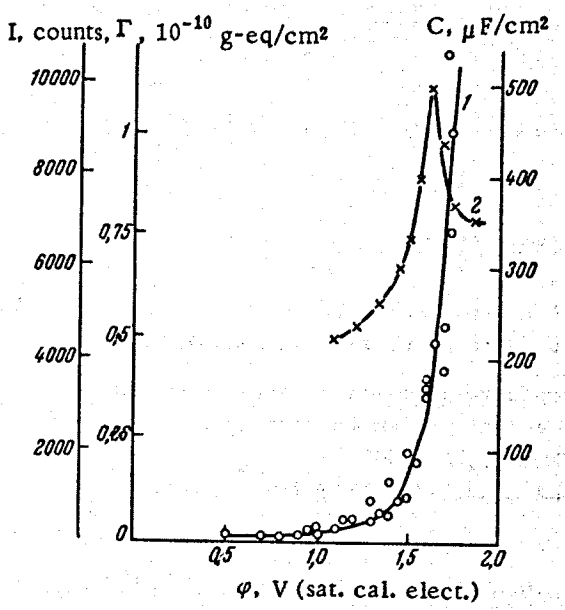


Fig. 2.

Fig. 1. Polarization curve on a smooth platinum electrode in an acidified 0.1 N solution of Na_2SO_4.

Fig. 2. Dependence on the potential in a 0.1 N Na_2SO_4 solution of the adsorption of the anion SO_4^{-2} (Curve 1) at the pseudocapacitance of a platinum electrode, measured at a frequency of 400 cps according to parallel scheme of substitution (Curve 2).

Thus, the results of this work show that the change in the electrochemical properties of a platinum electrode in a sodium sulfate solution is associated with a change in the state of the surface under the influence of adsorption of anions. Such a conclusion confirms the hypothesis advanced earlier [6] on the participation of anions of acid in the process of evolution of oxygen on a platinum electrode.

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All abbreviations of periodicals in the above bibliography are letter-by-letter transliterations of the abbreviations as given in the original Russian journal. *Some or all of this periodical literature may well be available in English translation.* A complete list of the cover-to-cover English translations appears at the back of the first issue of this year.