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Abstract

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MEASUREMENTS OF THE POTENTIAL DECAY OF A PLATINUM ANODE AFTER INTERRUPTION OF THE POLARIZING CURRENT

In measurements of anodic polarization curves on platinum in hydrochloric (^{1}) and sulfuric (^{2}, ^{3}) acid, a step-like increase of the potential is observed in a certain range of current density, characteristic of the acid concentration under study and of the chosen method of preparing the electrode. In (^{1}) it was suggested that the potential jump during anodic polarization of platinum is associated with the formation, in the potential interval 2.2–3.0 V, of a new form of surface oxide, accompanied by a decrease in the adsorption energy of O atoms or OH radicals formed upon discharge of water molecules. This leads to an increase in the overvoltage, if it is assumed to be determined by the slowness of the electrochemical formation of adsorbed oxygen. An analogous explanation was proposed by Rüetschi and Delahay (^{4}) to account for the form of the polarization curve observed by Hickling and Hill (^{5}) during oxygen evolution from alkaline solutions on Pd and Au. A study of the dependence of the position and magnitude of the potential jump on the nature and concentration of the acid anion leads to the conclusion that not only oxygen and water, but also acid anions take part in the formation of the chemisorbed layer; moreover, as experiments with ClO_4^- anions labeled with O^{18} have shown, at potentials above the upper boundary of the jump, exchange becomes possible between adsorbed oxygen and oxygen entering into the composition of the ClO_4^- anion (^{6}).

For the investigation of anodically polarized platinum, the method of measuring potential-decay curves after interruption of the current may also be applied (^{5}, ^{7}). In our work, the electrode capacitance was calculated from the decay curves by the formula $C = \frac{i_0 t}{\Delta\varphi}$, where $\Delta\varphi$ is the initial segment of the potential drop over the time t, and i_0 is the polarization current density before interruption of the current (^{8}). This formula is valid under the condition that the self-discharge current in the initial period of potential decay is equal to the polarization current. In calculating the capacitance, the ohmic potential drop, calculated by Kabanov' s formula (^{9}), was discarded. In parallel, capacitance calculations were carried out using points lying on the decay curve, whereby the ohmic drop was eliminated. In this case, instead of i_0, i_0' was substituted into the formula; this was determined from the polarization curve, taking into account the potential decay before the start of the measurement. The position

Fig. 1. Dependence of capacitance on current density in $HClO_4$ solutions: 1—0.6 N, 2—1.35 N, 3—4.3 N, 4—10 N. 1′, 2′, 3′, 4′—polarization curves for the same solutions. The arrows indicate the direction in which the curves were traced. The dashed line shows the polarization curves corrected for the ohmic potential drop.

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of the portion of the curve was chosen so that, on the one hand, it was as close as possible to the interruption potential and, on the other hand, so that the current i_0' fell in a region of the polarization curve not distorted by the ohmic potential drop. The results of both determinations agree with one another within the limits of experimental error.

Measurements of the potential decay were made with an electronic oscilloscope with triggered sweep. The decay curve consisted of a series of points defining the time scale (time marks) at intervals of $5.4 \cdot 10^{-6}$, $1.29 \cdot 10^{-5}$, $2.55 \cdot 10^{-5}$, and $2.02 \cdot 10^{-4}$ sec. During the experiment the current was switched off by an electronic device for 10^{-1}-10^{-3} sec; the decay curve obtained on the oscilloscope screen was recorded with a photographic attachment, after which the polarization was again automatically switched on. Then, after a stable potential had been established, the potential-decay curve corresponding to the next point of the polarization curve was recorded. The current before interruption was maintained for 2 min. The potential decays after inter-

opening the current for a longer time, up to 10 sec, were studied with an MPO-2 loop oscillograph with an electronic amplifier. Visual measurements were also made with a cathode voltmeter and a stopwatch.

The experiments were carried out in a cell with separated electrodes; the potential was measured relative to a hydrogen electrode in the same solution. Two electrodes made of platinum wire with areas of 0.01 and 0.15 cm^2 were used as anodes. Special attention was paid to the preparation of the electrodes. Before each experiment the electrodes were washed in dilute nitric acid, then in concentrated sulfuric acid, after which they were anodically polarized for 30 min with a current of $6 \cdot 10^{-4}$ A/cm^2 in 1 N H_2SO_4. Deviations in

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the preparation of the electrodes have a strong effect on the polarization curves, as well as on the results of the capacitance measurements. The experiments were carried out in 0.6, 1.35, 4.3, and 10 N solutions of perchloric acid. The dependence of the electrode capacitance on $\lg i$, as well as the polarization curves, are presented in Fig. 1. At potentials corresponding to the lower branch of the polarization curve, for concentrations of 0.6 and 1.35 N $HClO_4$ (curves 1, 2), capacitance values of about 100 $\mu F/\mathrm{cm}^2$ are observed, and the capacitance increases as the current density approaches that at which the potential jump occurs. In some experiments the potential jump occurred at higher current densities than usual, for example at $8 \cdot 10^{-1}$ A/cm^2 instead of the normal value $6 \cdot 10^{-1}$ A/cm^2. In this case the capacitance increased approximately to 200-250 $\mu F/\mathrm{cm}^2$. The causes of such deviations in the behavior of the electrode are not yet clear. The large observed capacitance values, considerably exceeding the capacitance of the double layer, indicate that the filling of the surface increases with increasing polarization by an electrochemically active, i.e., ionizable, substance. It may be assumed that in this potential region, at least on part of the surface, the slowest stage is not the transfer of electrons from water molecules to the electrode, but the decomposition of surface compounds with the formation of oxygen.

Other results are obtained when the capacitance is determined at potentials lying at the upper boundary of the jump, or exceeding this limit. In this case the value C is $20 \pm 2\,\mu F/\mathrm{cm}^2$, which is characteristic of the capacitance of the dou-

layer. Owing to the insufficient frequency of the time marks and the considerable magnitude of the potential decay $\Delta\varphi$, reaching 1 V in 10^{-4} sec, calculation of the capacitance for the upper branch of the polarization curve is inaccurate. In addition, the large magnitude of the decay in this potential region casts doubt on the fulfillment of the assumption that the self-discharge current is equal to i_0, although the error cannot be very large, since according to measurements carried out by the polarographic method (^{10}), the change in the current in the potential interval under consideration remains within narrow limits. The simplest explanation of the observed phenomena consists in assuming that, as the surface layer is filled with oxygen, the centers present on the surface with a high adsorption energy for O atoms and OH radicals, which are formed as a result of the discharge of water molecules, are gradually switched off.

As a result, the rate of the discharge reaction decreases sharply, and in order to maintain a constant current density it becomes necessary to increase the electrode potential by an amount corresponding to the overvoltage that has arisen for the discharge of water molecules. Thus, it is assumed here that the nature of the jump is connected with a change in the character of the slowest stage of the overall process.

Fig. 2. Potential-decay curves as a function of the time elapsed after interruption of the current in 1.35 N $\mathrm{HClO_4}$.
1 $-i = 10^{-4}$ A/cm^2, 2 -10^{-3} A/cm^2, 3 -10^{-2} A/cm^2, 4 -10^{-1} A/cm^2, 5 $-$ $6 \cdot 10^{-1}$ A/cm^2, 6 $-$potential decay after polarization by a current of $6 \cdot 10^{-1}$

Fig. 2. Potential-decay curves as a function of the time elapsed after interruption of the current in 1.35 N HClO4. 1 –i = 10^-4 A/cm^2, 2 –10^-3 A/cm^2, 3 –10^-2 A/cm^2, 4 –10^-1 A/cm^2, 5 –6 • 10^-1 A/cm^2, 6 – potential decay after polarization by a current of 6 • 10^-1 A/cm^2 for one hour

Figure 2: Fig. 2. Potential-decay curves as a function of the time elapsed after interruption of the current in 1.35 N HClO4. 1 –i = 10^-4 A/cm^2, 2 –10^-3 A/cm^2, 3 –10^-2 A/cm^2, 4 –10^-1 A/cm^2, 5 –6 • 10^-1 A/cm^2, 6 – potential decay after polarization by a current of 6 • 10^-1 A/cm^2 for one hour

A/cm^2 for one hour.

Measurements of the capacitance from the potential decay, carried out in more concentrated solutions (curves 3, 4), give, in general, a similar picture of the dependence of the capacitance on $\lg i$, i.e., its decrease to a value of about $20\,\mu$F/cm^2 when the potential is raised to the upper branch of the polarization curve. In the present case, however, the change in capacitance is expressed considerably less sharply, and the capacitance in the lower portion of the polarization curve does not exceed $70\,\mu$F/cm^2, gradually decreasing as the slope of the polarization curve increases. When polarization curves are recorded from high current densities, corresponding to the upper branch of the polarization curve, toward lower ones, hysteresis is observed. The capacitance in this case increases only to values not exceeding $50\,\mu$F/cm^2. This result indicates that the process of change of the electrode surface after the jump is irreversible.

Figure 2 presents complete potential-decay curves in $1.35\,N$ $HClO_4$ after interruption of the current, in the form of a dependence on the logarithm of time. As is seen from Fig. 2, the decay curves beginning from potentials corresponding to the lower branch of the polarization curve at initial current densities from 10^{-4} to 10^{-1} A/cm^2 (curves 1-4) fall on one straight line. Its slope is 0.1 V, which approximately coincides with the slope of the polarization curve in the same interval of current densities. This result indicates that in the potential interval 1.6–2.2 V oxygen evolution proceeds by an unchanged mechanism and, consequently, that one and the same character of the surface is preserved.

In the decay from a potential of 3.2 V (curve 5), at the beginning of the decay curve there is a section with a rapid fall of potential, then a section with a slope equal to the slope of the lower branch of the polarization curve, and at the end of the decay an increase in the slope is observed. The latter phenomenon, the causes of which are unclear and requires additional investigation. It should be noted that the decay starting from potentials corresponding to the upper branch of the polarization curve proceeds to lower potentials than the decay from potentials of the lower branch, i.e., an intersection of the potential-decay curves is observed. This phenomenon is especially clearly manifested at high anodic potentials (the upper portion of the polarization curve, see Fig. 3). One possible explanation

Figure 3

Figure 3: Figure 3

of this intersection is that, after the surface has been filled with oxides, strengthening of the surface compound occurs when a greater polarization is imposed, i.e., a process of interaction between surface groups, which could be called two-dimensional crystallization and which leads to a decrease in the electrochemical activity of the polarized electrode.

Fig. 3. Curves of potential decay after interruption of the current:
1 $-i = 5.2 \cdot 10^{-1}$ A/cm^2; 2 $-6.4 \cdot 10^{-1}$ A/cm^2;
3 -1.3 A/cm^2; 4 -2.6 A/cm^2; 5 -5.2 A/cm^2

In works (11), strengthening of the oxide film with time was noted at lower anodic potentials than those considered here. We also observed a dependence of the behavior of the platinum electrode on the duration of current passage at higher potentials. With prolonged passage of a current of $4 \cdot 10^{-1}$ A/cm^2 at an initial potential of 2.2 V, a gradual increase in potential occurs; within an hour it rises by 0.1-0.2 V, while the capacitance over the same time decreases from 80-90 μF/cm^2 to 25-30 μF/cm^2. Thus, the filling of adsorption centers with oxygen increases with time, and as a result the jump to the upper branch of the polarization curve occurs at lower current densities. Prolonged polarization of the electrode by a current of $6 \cdot 10^{-1}$ A/cm^2 in 1.35 N $HClO_4$ at a potential of 3.2 V on the upper branch of the polarization curve also affects the rate of decay. As can be seen from Fig. 2 (curves 5, 6), the potential decay after polarization for one hour occurs faster than after polarization for 2 min. The decay rate in the time interval from 10^{-5} to 10^{-4} s after interruption increases from $1.4 \cdot 10^4$ V/s to $2.1 \cdot 10^4$ V/s. These results can also be associated with strengthening of the surface oxides with time.

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