EFFECT OF HEAT TREATMENT ON THE POTENTIAL OF ZERO FREE CHARGE IN PLATINIZED PLATINUM

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The effect of heat treatment in an atmosphere of hydrogen in the range between 20 and 200°C on the potential of zero free charge in platinized platinum was investigated, and the values of the Gibbs adsorption of hydrogen ions (Γ_{H^+}) on the heat-treated electrodes in an atmosphere of oxygen in an acidified solution of sodium sulfate were determined. It was found that the potential of zero free charge (PZFC) is shifted toward the negative side with increase in the heat treatment temperature. Investigations were carried out into the topography of the surfaces of the heat-treated platinized platinum by scanning electron microscopy.

The effect of heat treatment of a platinized platinum electrode (Pt/Pt) in an atmosphere of oxygen and hydrogen on the adsorption of hydrogen and oxygen and on the electrochemical oxidation of methanol was studied in [1, 2].

In the present work attempts were made to determine the potential of zero free charge (PZFC) of platinized platinum which had been heat treated in an atmosphere of hydrogen and also the values of the Gibbs adsorption of hydrogen ions (Γ_{H^+}) on electrodes which had been heat treated in an atmosphere of oxygen.

As working electrode we used a platinized platinum gauze with an apparent surface area of 100 cm^2. The electrode was platinized from 2% H_2PtCl_6 of pure grade at a current density of 2-4 mA/cm^2 by the method described in [3]. After deposition of the platinum the electrodes were subjected to cathodic polarization in 0.1 N sulfuric acid at a current density of 10 mA/cm^2 for 1 h for the desorption of chloride ions.

The working electrode, which had been previously activated by anodic–cathodic treatment and had been thoroughly washed with twice-distilled water, was placed in the measurement cell, through which hydrogen or oxygen was blown. For heating, the bottom part of the cell was immersed in a cylindrical furnace. After the attainment of the required temperature the electrode was held for 1 h. The accuracy with which the temperature was maintained amounted to ±5°C. After heating the electrode was cooled to room temperature and was immediately brought into contact in the measurement cell with a solution of 0.1 N Na_2SO_4 + 0.002 N H_2SO_4, which had previously been blown with hydrogen or oxygen, respectively. After each heat treatment and after the adsorption measurements the true surface area of the Pt/Pt along the length of the hydrogen part of the charging curve in 1 N sulfuric acid was determined [4]. The true surface area of the working electrodes amounted to 2-4 m^2.

For the measurements of the PZFC we determined the variation in the concentration of hydrogen ions in the solution during the formation of the electric double layer (EDL) by titration [5, 6].

The principal results are given in Fig. 1 in the form of the relations between Γ_{H^+} and E_r (E_r denotes the potentials referred to a reversible hydrogen electrode in the same solution) for the heat-treated Pt/Pt electrodes in an atmosphere of hydrogen at 20-200°C for 1 h. From these data it is seen, in particular, that the $|\Gamma_{H^+}|$ values for $E_r = 0$ decrease with increase in the heat-treated temperature, and the section where Γ_{H^+} is independent of E_r becomes smaller with small E_r values.

The point where the Γ_{H^+}, E_r curves intersect the abscissa axis corresponds to the zero free charge potential. Since the PZFC was determined in a solution of 0.1 N Na_2SO_4 + $2 \cdot 10^{-3}$ N H_2SO_4, where specifically adsorbed ions are absent, it can be equated to the zero-charge potential of the double layer [7]. In Fig. 1 it is seen that there is a shift of the PZFC toward

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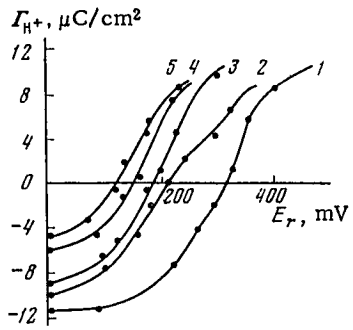

Fig. 1

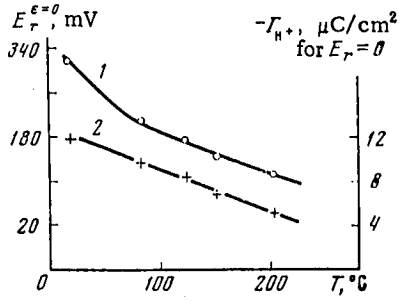

Fig. 2

Fig. 1. Dependence of the adsorption of hydrogen ions Γ_{H+} on E_r in a solution of 1 N $NaSO_4$ + 0.002 N H_2SO_4 for heat-treated Pt/Pt electrodes in an atmosphere of hydrogen at temperatures, °C: 1) 20; 2) 80; 3) 120; 4) 150; 5) 200.

Fig. 2. Dependence of the potential of zero free charge $E_r^{\varepsilon=0}$ (curve 1) and the adsorption of hydrogen ions Γ_{H+} for E_r = 0 (curve 2) on the heat-treatment temperature of Pt/Pt electrodes in an atmosphere of hydrogen.

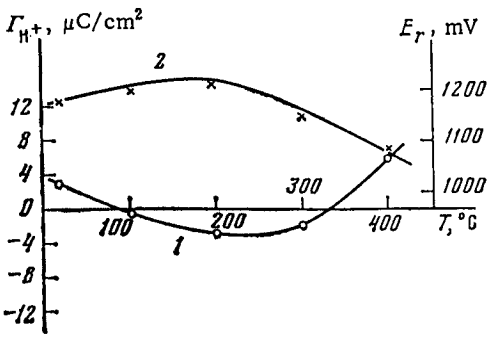

Fig. 3. Dependence of the adsorption of hydrogen ions Γ_{H+} (curve 1) and the steady-state oxygen potential (curve 2) on the heat-treatment temperature of Pt/Pt electrodes in an atmosphere of oxygen.

the negative side with increase in the heat-treatment temperature in an atmosphere of hydrogen, and at 200°C this shift amounts to about 200 mV. Figure 2 shows the dependence of the PZFC and Γ_{H+} for E_r = 0 on the heat-treatment temperature. It is seen that significant variation of the PZFC occurs even during heat treatment at 80°C.

Interesting data were obtained during direct determination of Γ_{H+} at platinized platinum which had been heated in oxygen. The electrode was heated in an atmosphere of oxygen in the range between 20 and 400°C for 1 h and brought into contact with a solution of 0.1 N Na_2SO_4 + $2\cdot10^{-3}$ N H_2SO_4, which had been previously saturated with oxygen. The change in the composition of the solution due to the formation of the electric double layer was determined by titration. The results are given in Fig. 3 (curve 1). The dependence of Γ_{H+} on temperature has a minimum for platinized platinum heated at 250°C, and the curve intersects the abscissa axis twice, i.e., Γ_{H+} changes sign twice. Thus, heating in oxygen at 100-350°C leads to recharging of the surface during subsequent immersion of the electrode in the solution, due probably to the formation of a sufficient quantity of oxygen dipoles turned with the negative end toward the solution, as a result of which the cations are attracted to the surface. The decrease in the surface recharging effect at T > 250°C and its disappearance at higher temperatures are probably explained by a change in the state of the adsorbed oxygen at the elevated temperatures. It is curious that the inverse form of the Γ_{H+}, T-curve shows a temperature dependence of the steady-state oxygen potential of the platinized platinum heated in oxygen, established during contact with a solution of 0.1 N Na_2SO_4 + $2\cdot10^{-3}$ N H_2SO_4 blown with oxygen (Fig. 3, curve 2). The maximum recharging effect on the Pt/Pt surface by the oxygen di-

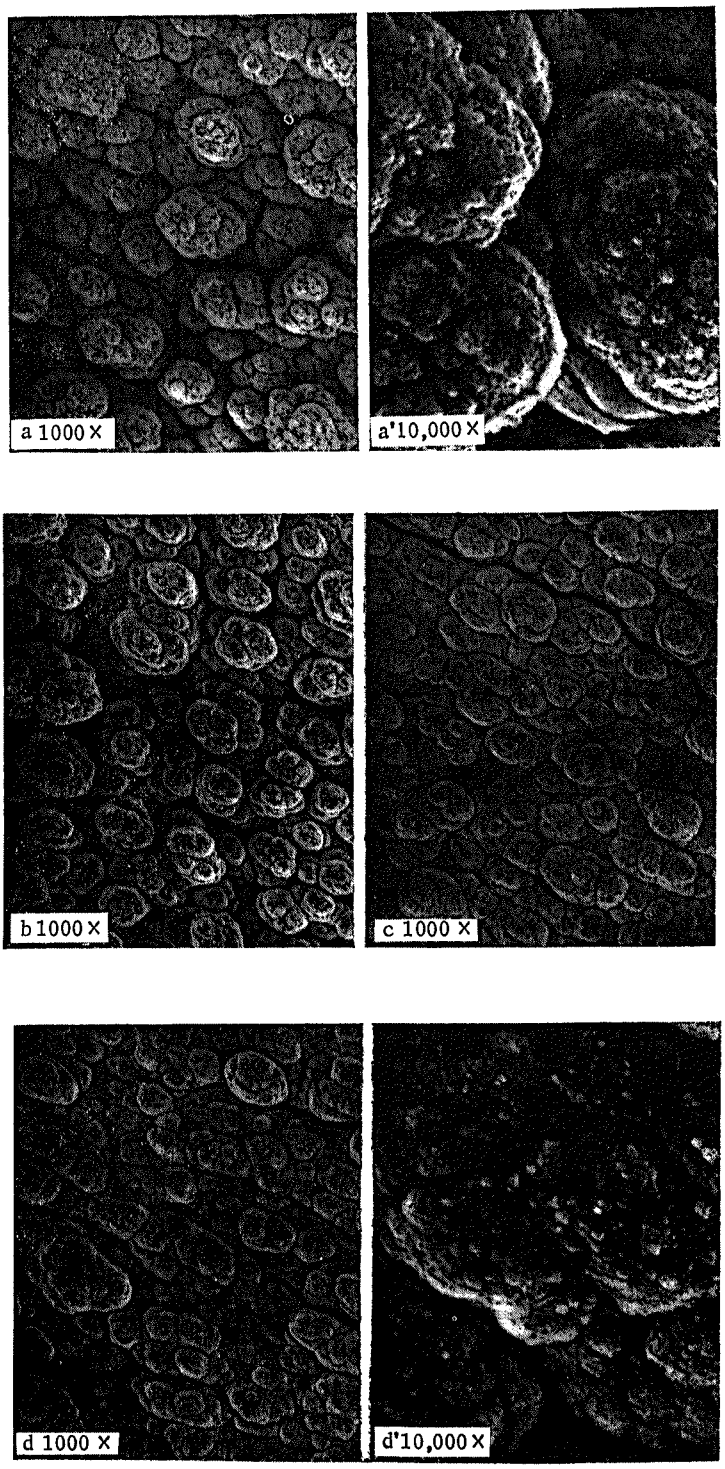

Fig. 4. Electron photomicrographs of samples of Pt/Pt heat-treated under various conditions. a) and a') Freshly prepared Pt/Pt; b) heat treatment in oxygen at T = 220°C, t = 1 h; c) heat treatment in hydrogen at T = 100°C, t = 1 h; d) and d') heat treatment in hydrogen at T = 300°C, t = 1 h.

poles occurs at an oxidation temperature of 200-250°C. The maximum steady-state oxygen potential, which amounts to ~1.21 V, is established under these conditions.

An investigation was carried out into the topography of the surfaces of heat-treated Pt/Pt electrodes by scanning electron microscopy. The surface of the samples was photographed in secondary electrons on an ISM-50A electron microscope with an accelerating potential of 35 kV.

Figure 4 shows photomicrographs of samples of platinized platinum heat treated under various conditions. As seen from Fig. 4a, the freshly prepared surface of the Pt/Pt consists of coarse spherical conglomerates, which form a porous structure, and corresponds (according to [8]) to the surface of the electrode prepared at positive deposition potentials. Sintering in an atmosphere of oxygen does not lead to significant changes in the surface (Fig. 4b), and this indicates some stabilizing action from the adsorbed oxygen on the surface of the platinum, which prevents sintering. Heat treatment in an atmosphere of hydrogen leads to significant sintering of the surface, and this takes place more intensively at elevated temperatures (Fig. 4c, d). During sintering the volume porous structure is transformed into a planar structure (the number of pores is considerably reduced), although the linear dimensions and the form of the conglomerates remain practically unchanged. There is also cracking on the surface on account of the shrinkage during sintering.

The roughness factor here decreases sharply. Thus, it must be supposed that the high specific surface area of the freshly prepared platinized platinum is due largely to micropores, and the accessibility of all the micropores (in the volume of the deposit) is due to the high porosity (macroporosity), which is consistent with published data [8].

By comparison of the photographs of the surface of the Pt/Pt with larger magnifications (Fig. 4a', d') it can be concluded that the dimensions and form of the "primary" particles, which are still resolved by the microscope, are practically identical for all the samples. Thus, electron microscopy does not provide an answer to the question of the reasons for the effect of heat treatment on the potential of zero free charge in Pt/Pt. For this purpose it is necessary to use methods which give information directly on the structure and on the composition of the electrode surface itself.

The adsorption capacity with respect to hydrogen and oxygen in 1 N sulfuric acid was investigated for platinized platinum which had been heat treated under conditions of high vacuum and then in an atmosphere of hydrogen at 450° ± 10°C for 1.5 h by means of the vacuum–electrochemical method [9]. The cell and the method used for the measurements were described in [9]. The results from this investigation are given in Fig. 5 in the form of potentiodynamic curves recorded from E_r = 50 mV. (This potential was established after contact between the Pt/Pt electrode heat treated in hydrogen and the solution of 1 N sulfuric acid blown with argon.) The potentiodynamic curve, measured directly after heat treatment (Fig. 1, curve 1), and the cyclic curve (Fig. 2, curve 2) practically coincide. Thus, heat treatment of the electrode under vacuum and then in an atmosphere of hydrogen at 450°C does not change its ad-

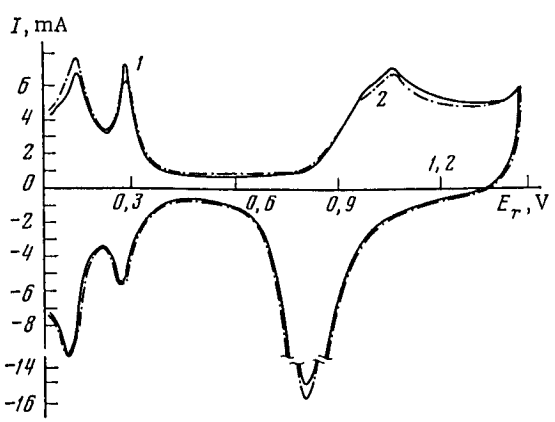

Fig. 5. Potentiodynamic curves for Pt/Pt heat treated in an atmosphere of hydrogen at 450°C for 1.5 h. 1) Immediately after heat treatment; 2) cyclic curve. Indifferent electrolyte 1 N sulfuric acid; potential sweep rate 1 mV/sec.

sorption behavior with respect to hydrogen and oxygen. In the present work we were able to extend the conclusions [2] to higher heat-treatment temperatures, since heat treatment was realized not with external heating of the cell but by passing an electric current through the investigated electrode, which took the form of a platinized platinum foil 0.05 mm thick. Oil-free pumping and the use of hydrogen which had been purified by passing through a nickel capillary guaranteed a high degree of cleanliness in the experiment and ruled out poisoning of the electrode by various uncontrolled impurities, which occurred in [2] during the heating of the cell to temperatures higher than 350-400°C.

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