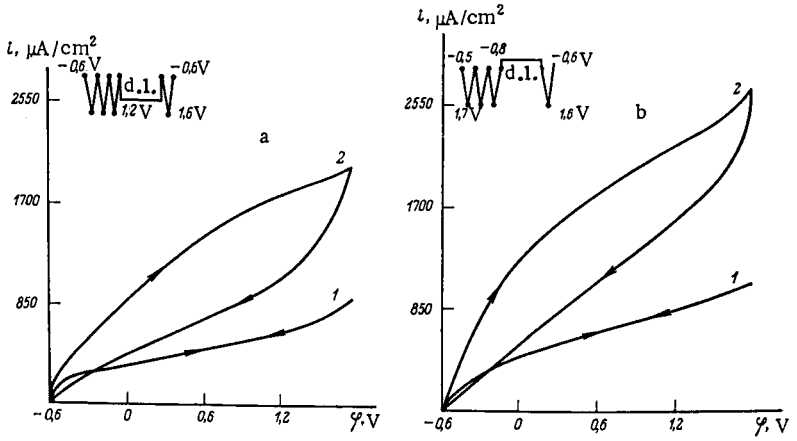

Fig. 3. Polarization program of the electrode (top) and oscillogram of the dark current during linear potential sweep of a p-type SiC-electrode in 0.2 N H_2SO_4: 1) without prior illumination; 2) prior illumination at a potential of: a) 1.2 V, and b) −0.8 V. The direction of the potential sweep is indicated by arrows.

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MEASUREMENT OF THE ELECTRON WORK FUNCTION OF PLATINIZED PLATINUM IN A VACUUM ELECTROCHEMICAL SYSTEM

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For a deeper understanding of the mechanism of the catalytic and electrocatalytic processes on platinum metals it is necessary to study the reaction of these metals with oxygen, hydrogen and water vapor. In such studies in order to ascertain special features of the initial stages of the reaction of the adsorbates just mentioned with the surface it is expedient to use the method of measuring the electron work function (W), which is highly sensitive to the surface state of the metal. Measurements of W for platinum up to the present time have been carried out on a polycrystalline smooth surface, on individual faces of single crystals of platinum and on deposited films. Until now similar measurements on platinized platinum have not been made, probably because of the fact that for precise measurements of W it is necessary to treat the metal in an ultrahigh vacuum at temperatures of the order of ~1000°C which would lead to practically a complete sintering of the surface of the platinized platinum. We have attempted to determine the work function of platinized platinum after treating it under less rigorous conditions than are usually used for such type of measurement. In this case the risk naturally increases of an incomplete purification of the surface from contaminants. However use of a vacuum electrochemical system provides the possibility of additional control of the surface state by means of electrochemical methods. Use of platinized platinum also in principle enables a comparison to be made of the work function and the zero free charge potential [1] of identically treated samples. The need to organize such studies was discussed by A. N. Frumkin in 1976.

Measurement of the work function and the electrochemical measurements were carried out in an apparatus, a diagram of which is shown in Fig. 1.* In order to determine W by the Fowler external photoeffect method [2] in a molybdenum

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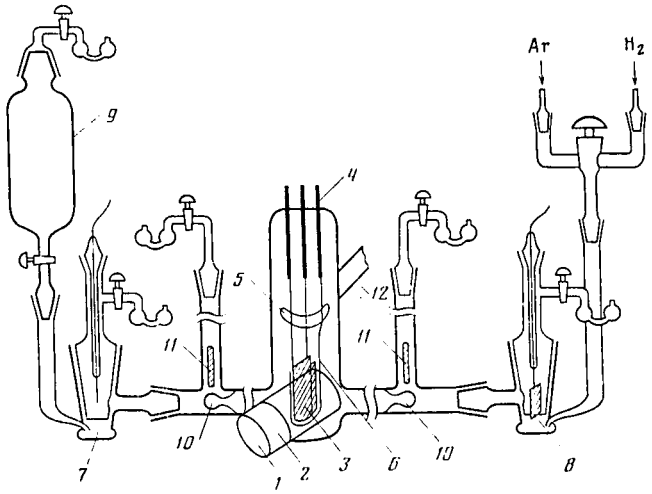

Fig. 1. Diagram of apparatus for vacuum electrochemical measurements on platinized platinum.

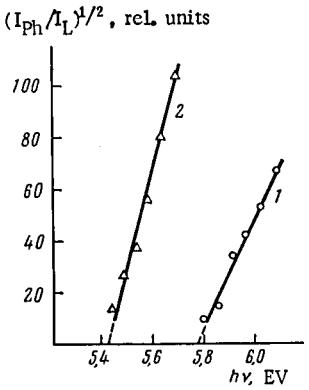

Fig. 2. Fowler plots for platinized platinum: 1) after degassing an aerially oxidized sample at T = 400°C; 2) after reduction in hydrogen and degassing at T = 380°C.

glass cell a quartz window (1) of optical glass was provided which was sealed into the apparatus via a quartz–molybdenum junction (2). The studied electrode (3) – a platinized platinum foil of 0.05 mm thickness – was soldered to a platinum wire of 1 mm diameter, and the latter to a molybdenum lead of diameter 2 mm (4), which served as conductor of current when heating up the electrode. The place of combination of the platinum wires with the molybdenum wires was protected from the action of the electrolyte by a glass guard in the form of a small cup (5). The platinized electrode was prepared by the method normally applied [3]. The central part of the apparatus with the studied electrode (3) and photoelectron collector (6) in the form of a loop of platinum wire, which encircled the studied electrode, was separated from the other parts of the apparatus [the auxiliary electrode (7), reference electrode (8), and reservoir for the electrolyte (9)] by small glass bulbs (10). This part of the apparatus was joined to the vacuum system via a branch tube (12) and evacuated to a pressure of 10^{-7}-10^{-8} torr. An oilless evacuation was accomplished by zeolites and Ferranti magnetic discharge pumps inserted in series. The cell was isolated from the pump by an overlapping glass–metal sealing device filled with an In–Sn alloy, after which the electron work function was measured. Then the cell was connected by means of ground glass joints to those parts of the apparatus (7, 8, 9) which permitted the electrochemical measurements to be made. A solution of 1 N H_2SO_4, which served as the electrolyte was previously freed from dissolved gases by purging with spectrally pure argon (with an oxygen content not greater than 0.0005%) in the vessel (9). After carefully purging with argon the connecting parts of the apparatus, the glass bulbs were broken by means of the strikers (11) and the cell filled with the electrolyte.

Initially a series of experiments were carried out on platinized platinum which after contact with the laboratory atmosphere had been degassed in a vacuum of the order of 10^{-8} torr at 400°C for 3 h. A typical Fowler relationship was obtained within the coordinates $(I_{Ph}/I_L)^{1/2}$, $h\nu$, where I_{Ph} is the photocurrent from the sample, I_L is the light intensity in relative units, and $h\nu$ is the energy of the irradiating light, which is shown in Fig. 2. The value of W corresponds to the

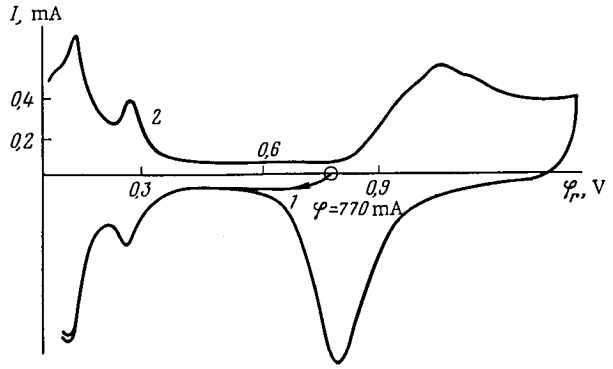

Fig. 3. Potentiodynamic curve for platinized platinum in 1 N H_2SO_4: 1) After repeated reduction in hydrogen and degassing at T = 380°C; 2) after anodic–cathodic polarization (rate of potential sweep 1 mV/sec).

point of intersection of the linear part of the curve with the abscissa. The measured values of the work function of platinum fell within the limits 5.70-5.80 ± 0.05 eV (Fig. 2, curve 1). When in contact with the electrolyte the electrode acquired a potential $\varphi_r \approx 1.02$ V (with respect to a reversible hydrogen electrode in the same solution). From the length of the arrest on the cathodic curve measured from $\varphi_r = 1.02$ V it was established that the amount of oxygen on the electrode surface corresponded to 2.5 ± 0.1 C/m², i.e., the degree of coverage of the surface with oxygen was $\theta = 0.6$. After recording the cathodic charging curve the anodic–cathodic curves were measured over the range $\varphi_r = 0.05$-1.4 V. These curves corresponded in form to the potentiodynamic curves of the normal platinized platinum. Thus heat treatment in vacuum of the aerially oxidized electrode does not alter its adsorption behavior with respect to hydrogen and oxygen.

In order to obtain the platinized platinum surface free from chemisorbed oxygen, the electrode was subjected to repeated (5 to 6 portions) reduction with hydrogen ($P_{H_2} = 10^{-2}$-10^{-3} torr) at 380°C, and was subsequently degassed at the same temperature. After this treatment the work function of the platinized platinum was 5.35-5.45 eV (Fig. 2, curve 2). This value is substantially above that for polycrystalline samples which was determined after reduction of the sample in hydrogen and degassing at 1200°C under oil-pump evacuation conditions at 10^{-6}-10^{-7} torr [4]. Apparently platinization of the surface in the absence of hydrocarbons in the residual gases facilitates the production of a surface of quite high purity. The work function of platinized platinum under the conditions with which we carried out our experiments was ~0.30 eV below the value of W measured for a polycrystalline smooth sample under ultrahigh vacuum (2×10^{-10} torr) after prior baking-out of the oxidizable impurities (C, S, etc.) with oxygen [2] and degassing at 1200°C. Possibly the crystallographic characteristics of platinized platinum, heated to 400°C, and a smooth sample the purification of which is carried out under more rigorous conditions, differ, which also causes a difference in the work function of the platinum samples. The possibility should also be taken into account of the presence on the platinized platinum surface of traces of microimpurities which have an effect on the results of the measurement of W, but are not detected electrochemically.

Where the electrode is in contact with 1 N H_2SO_4 it acquires a potential of 0.7-0.9 V at the boundary of the double layer and oxygen regions. In Fig. 3 is shown the cathodic potentiodynamic curve of the sample with W = 5.40 eV, taken from the potential, which it acquires after contact with the electrolyte. The absence of a peak for the desorption of oxygen on the curve indicates that the surface of the platinized platinum is free from chemisorbed oxygen and the correspondence of the shape of the curve in the hydrogen region with the shape of the anodic–cathodic cyclic potentiodynamic curves indicates a high degree of purity of the platinum surface after treating it with hydrogen and degassing.

The results of the studies which have been made has demonstrated the possibility of sufficiently reliable and reproducible determination of the work function of platinized platinum under comparatively mild conditions of pretreatment.

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