One can see from Fig. 2 that the C vs E curves obtained by us at the In_2O_3 electrode satisfy conditions (3). Similar results had previously been obtained at electrodes of ZnO [4] and SnO_2 [5, 6]. In our systems, the average slope of the plot of $1/C^2$ against E is 3.3 $cm^4/\mu F^2$, which corresponds to a carrier concentration of $n_0 = 4.3 \cdot 10^{19}/\varepsilon_s$ particles/cm^3. On the assumption that $\varepsilon_s = 10$ (as for SnO_2 [5]) we have $n_0 = 4.3 \cdot 10^{18}$ particles/cm^3. Similar carrier concentrations had been obtained in [5] for tin oxide. The flat-band potentials varied somewhat between experiments, apparently because of not altogether identical electrode pretreatment. The average value of E_{fb} was about −0.9 V (sce). The differential capacity curves calculated from Eq. (4) while using the values found for n_0 and E_{fb} are in good agreement with the experimental C vs E curves, as can be seen from Fig. 1.

Thus, the differential capacity curves of the In_2O_3 electrode are determined by the carrier distribution in the bulk of the doped, n-type semiconductor, and are practically independent of the composition of the aqueous electrolyte solution.

We express our gratitude to I. V. Shelepin for a discussion of the results.

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ADSORPTION OF OXYGEN AND WATER VAPOR ON PLATINIZED PLATINUM IN AN ELECTROCHEMICAL VACUUM SYSTEM

A. V. Ushmaev, G. F. Voronina,
T. V. Kalish, and O. A. Petrii

UDC 541.183-135.52

Data are available at the present time as to the effect of adsorbed gases on the electron work function (W_e) of smooth polycrystalline platinum [1-4], individual single-crystal faces [5-7], and vapor-deposited platinum films [8, 9]. Similar studies have not been performed with platinized platinum (Pt/Pt) up to now, probably because of the fact that the high-temperature metal treatment usually used to clean the surfaces prior to measuring W_e would cause practically complete sintering of the Pt/Pt surface. We have shown that the work function of platinized platinum can be determined reliably and reproducibly after pretreatment under relatively mild conditions. This treatment consisted in repeated reduction of the sample in hydrogen at 380°C and prolonged, oil-free evacuation at 400°C at $133 \cdot 10^{-8}$ Pa [10].

The effects of adsorbed oxygen and water vapor on the work function of Pt/Pt were studied in an electrochemical vacuum system. Cell design and experimental procedure have been described in [10]. The working electrode was a platinized platinum foil with a thickness of 0.05 mm and an apparent surface area of about 10 cm^2. The true surface area of the test electrodes, which was determined from the hydrogen region of the charging curves, was at least 0.6 to 0.8 ± 0.05 m^2. The work function of Pt/Pt was determined by photoemission following Fowler. The electrochemical behavior of the electrodes was studied by recording potentiodynamic curves. The sweep rate was 1 mV/sec in all measurements. The potentials, E_r, are reported relative to a reversible hydrogen electrode in the same solution.

A typical Fowler plot for platinized platinum is shown in Fig. 1 (curve 1); this is a plot of $(I_{ph}/I_L)^{1/2}$ against $h\nu$, where I_{ph} is the photocurrent coming from the sample, I_L is the light intensity in arbitrary units, and $h\nu$ is the energy of the incident light. Quantity W_e corresponds to the point of intersection of the extrapolated straight-line section of the

Institute of Electrochemistry, Academy of Sciences of the USSR, Moscow. Translated from Élektrokhimiya, Vol. 18, No. 4, pp. 530-534, April, 1982. Original article submitted June 8, 1981.

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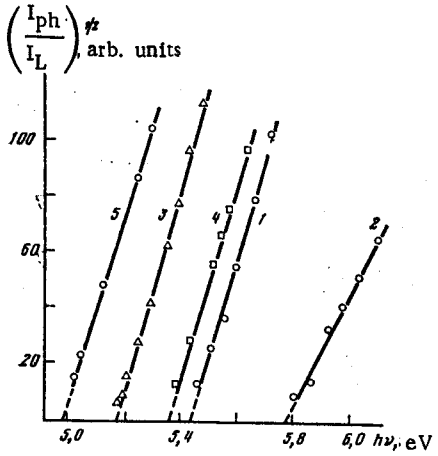

Fig. 1

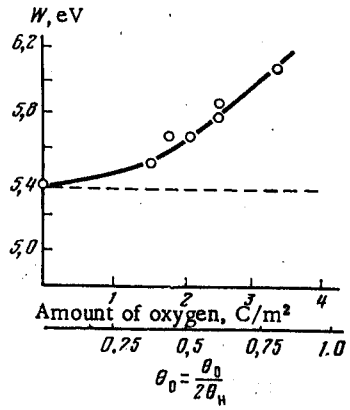

Fig. 2

Fig. 1. Fowler plots of $(I_{ph}/I_L)^{1/2}$ against hν for Pt/Pt: 1) after reduction and degassing at T = 380°C; 2) after oxygen adsorption at room temperature; 3) after adsorption of water vapor ($p_{H_2O} = 133 \cdot 10^{-5}$ Pa); 4) after reduction of Pt/Pt and degassing at room temperature; and 5) after adsorption of water vapor ($p_{H_2O} = 133 \cdot 10^{-5}$ Pa) on Pt/Pt degassed at room temperature.

Fig. 2. The work function of Pt/Pt as a function of the amount of chemisorbed oxygen; Q_o is the amount of chemisorbed oxygen (in coulombs) found from the initial cathodic potentiodynamic curve, Q_H is the amount of adsorbed hydrogen found from the cyclic anodic potentiodynamic curve.

curve with the axis of hν. The work function of Pt/Pt where the surface is free of adsorbed hydrogen, oxygen, as well as of those microimpurities that can be detected in electrochemical measurements is 5.35 to 5.45 ± 0.05 eV, according to [10]. The work function was found to be lower for strongly sintered electrodes having a true surface area of less than 0.1 m^2 (roughness factor below 100). Sintering evidently is attended by a relative increase in the surface concentration of microimpurities, which causes lower W_e. Another possible reason for this change could be the emergence of faces with lower W_e on the Pt/Pt surface during recrystallization.

Oxygen adsorption was studied over the pressure range of $p_{O_2} = 133 \cdot (10^{-3}$ to $10^{-4})$ Pa at room temperature after different times of exposure. The amount of chemisorbed oxygen was calculated by graphical integration of the cathodic potentiodynamic curve measured from the steady-state potential. This was attained after immersing the electrode into 1 N H_2SO_4 that had been carefully purged with argon, and was about 1.02 V. It follows from Fig. 1 (curve 2) that oxygen raises W_e. Figure 2 shows W_e as function of the amount of chemisorbed oxygen. One can see that in the region of intermediate coverages, W_e increases approximately linearly with coverage, and it is over 6.25 eV at $\theta_o \sim 1.0$. Prolonged exposure (17 to 24 h) of the oxidized sample to oxygen atmosphere ($p_{O_2} \sim 133 \cdot 10^{-4}$ Pa) at room temperature reduces the original effect by 0.1 to 0.2 eV. The bond strength of the adsorbed oxygen increases somewhat under these conditions, according to the electrochemical measurements; this is seen as a cathodic displacement of the oxygen desorption peak in the potentiodynamic curve. This result differs from the data obtained at smooth Pt [2], where after oxygen adsorption at $p_{O_2} = 133 \cdot 10^{-5}$ Pa and room temperature, the observed increase in W_e vanished after 4 to 5 h vacuum exposure, and W_e returned to the original value; this was explained in terms of oxygen penetrating into the metal.

Figure 1 (curve 3) shows data concerning the effect of water vapor ($p_{H_2O} = 133 \cdot 10^{-5}$ Pa) on W_e of platinized platinum that had been prereduced in hydrogen and degassed at 400°C. The procedure used to purify and admit water vapor to the system has been described in [4]. Water vapor reduces the work function of Pt/Pt by 0.2 to 0.3 eV. This effect is much smaller than that observed with smooth platinum, where it was on the order of 1.0 eV [4]. The steady-state potential of an electrode that had been in contact with water vapor is set up in the

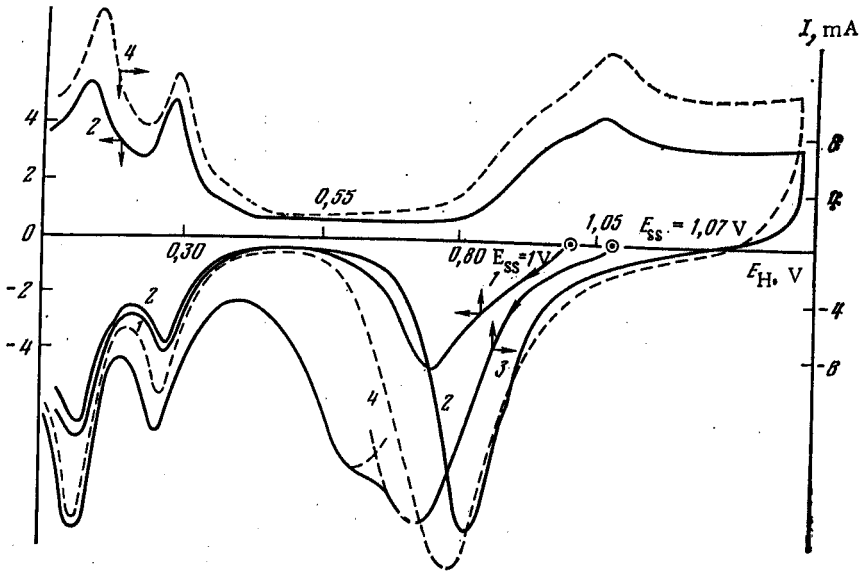

Fig. 3. Potentiodynamic curves of Pt/Pt in 1 N H_2SO_4: 1) and 3) after measuring W_e in the presence of water vapor on a clean surface and on an oxidized surface, respectively 2) and 4) cyclic potentiodynamic curves for the same electrodes.

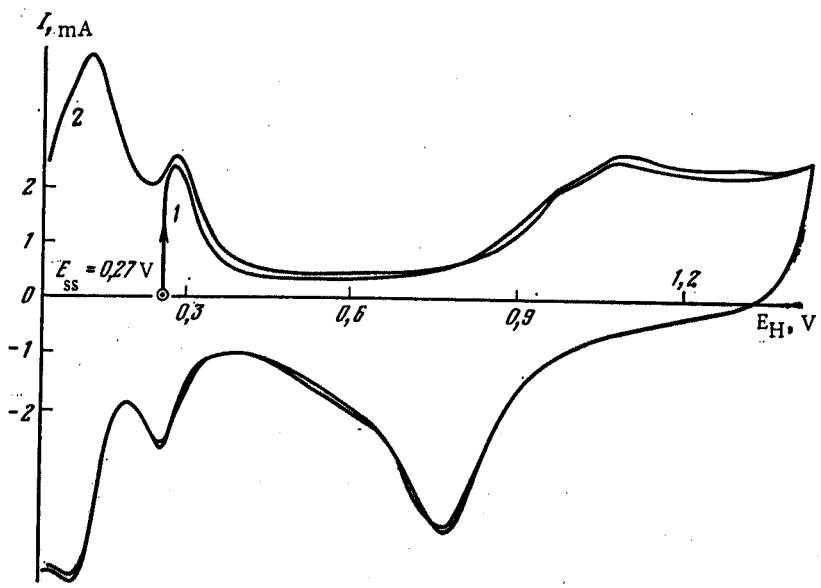

Fig. 4. Potentiodynamic curves of Pt/Pt in 1 N H_2SO_4: 1) after measuring W_e in the presence of water vapor on a reduced and degassed Pt/Pt surface at room temperature; 2) the cyclic potentiodynamic curve.

oxygen region in 1 N H_2SO_4 solution, and has a value of about 1.0 V (Fig. 3). In the cathodic potentiodynamic curve measured by starting from this potential, one sees an oxygen desorption peak (curve 1) which is 50 to 60 mV more cathodic than that in the cyclic potentiodynamic curve (curve 2). The data obtained indicate that oxygen produced by interaction of water vapor from the gas phase is more strongly bonded to the Pt/Pt surface than the oxygen porduced during anodic polarization.

It seems that the adsorbed water vapor dissociates on the surface of platinized platinum, as it does on smooth platinum [4]. However, on Pt/Pt this process is faster, and is accompanied by substantial surface oxidation. Hence the decrease of W_e which occurs on the Pt/Pt surface in the presence of water vapor is much smaller than that which occurs on smooth

platinum. Differences, both in the surface structure and in the degree of surface cleanliness can be responsible [10].

Of interest in this respect are experiments performed with Pt/Pt samples which after the usual prereduction in hydrogen at 380°C had subsequently been degassed at room temperature. The work function of such samples was 5.30 to 5.40 eV (Fig. 1, curve 4), not much different from the W_e of samples that had been degassed at 400°C. The very small difference in W_e-values found for samples which, after prior high-temperature reduction, had been degassed at room temperature and at 400°C, respectively, can be attributed to hydrogen strongly bound to the Pt/Pt surface; this is not desorbed when evacuation is conducted at room temperature. When brought in contact with 1 N H_2SO_4 solution the electrode acquired a steady-state potential of 0.6 to 0.7 V in the double-layer region. After water vapor adsorption ($p_{H_2O} = 133 \cdot 10^{-5}$ Pa), the W_e of such samples decreased by 0.4 to 0.5 eV (Fig. 1, curve 5). It seems that the hydrogen present on the surface retards dissociation of water molecules, possibly altering the mechanism by which this occurs. In this case the steady-state potential assumed by the electrode after immersion into electrolyte solution was in the region of hydrogen adsorption (Fig. 4, curve 1), and the anodic potentiodynamic curve recorded while starting from this potential displayed a hydrogen desorption peak.

Interesting results were obtained when studying water vapor adsorption on a preoxidized Pt/Pt surface. Prior oxygen adsorption was allowed to occur at $p_{O_2} = 532 \cdot 10^{-3}$ Pa and 200°C; additional oxygen adsorption was allowed to occur just prior to measuring W_e, at the same oxygen pressure and room temperature. Under these conditions the work function was 5.7 to 6.0 eV, depending on the time of exposure to oxygen. Water vapor adsorption at $p_{H_2O} = 133 \cdot 10^{-5}$ Pa on a Pt/Pt surface with preadsorbed oxygen practically did not alter the value of W_e, even with long exposure times. Figure 3 shows the potentiodynamic curves recorded in 1 N H_2SO_4 in such an experiment. Here oxygen chemisorption ($p_{O_2} = 133 \cdot 10^{-3}$ Pa) caused an increase in W_e to 5.8 eV; after water vapor adsorption $W_e = 5.76$ eV. Upon contact with electrolyte, the electrode assumed a potential of 1.07 V, i.e., more positive than without chemisorbed water vapor. Here the shape of the cathodic potentiodynamic curve had changed remarkably (Fig. 3, curve 3): the oxygen desorption peak was displaced cathodically, the amount of adsorbed oxygen was higher than one monolayer ($\theta_o = 1.25$), and the shape of the peak was greatly different. A cyclic potentiodynamic curve for this sample is shown for comparison in the same figure (curve 4). It appears that water vapor adsorption on an oxidized surface is attended by decomposition of water molecules and subsequent strengthening of the bonding between the oxygen-containing species and the Pt/Pt surface; this effect is much stronger than that observed when a clean Pt/Pt surface is brought in contact with water vapor.

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