INFLUENCE OF CHEMISORBED HYDROGEN ON THE ELECTRON WORK FUNCTION OF PLATINUM

G. F. Voronina, L. A. Larin, and T. V. Kalish

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A large number of papers has been concerned with hydrogen adsorption on platinum. Hydrogen adsorption at the platinum electrolyte solution interface has been examined in detail in the work of A. N. Frumkin. It can be shown by the method of charging curves that two forms of adsorbed hydrogen exist, one being strongly bound, the other weakly bound to the surface [1]. These forms are revealed particularly clearly in the studies of platinum by the potentiodynamic method [2].

Two states of adsorbed hydrogen have also been detected in studies of the platinum vacuum interface. According to the data of [3-7], the change from the strong form of binding of hydrogen to platinum to the weak form occurs at $\theta \leqslant 0.5$, and is attended by a reversal of the sign of surface charge. These studies were conducted chiefly at temperatures below 293°K, and using platinum surfaces of different origin: evaporated films, the tips of field emitters, and individual faces of single crystals. According to [5, 7], it depends on the structure of the platinum surface whether hydrogen adsorption occurs in the strong or weak form. On the basis of quantum mechanical concepts, attempts were made in [8] to explain the existence of different forms of hydrogen bonding to the platinum surface theoretically.

In the present work, the change in the electron work function (W) of polycrystalline platinum was studied while hydrogen adsorbed on it at room temperature. These conditions appear to be closer to those of the electrochemical experiments.

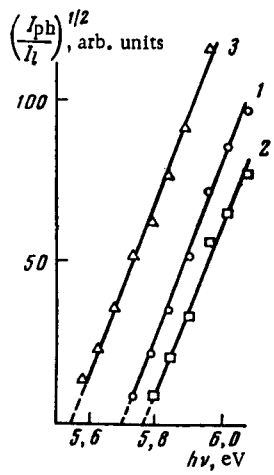

Fig. 1

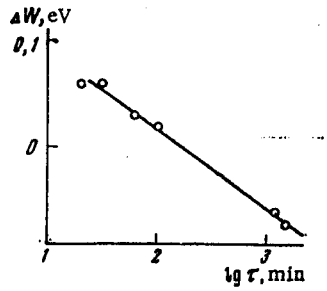

Fig. 2

Fig. 1. Plots of $(I_{ph}/I_l)^{1/2}$ against the energy, hν, of the irradiated light: 1) purified surface, 2 and 3) hydrogen exposure to the extents of 2×10^{-6} and 20×10^{-5} mm Hg·min, respectively.

Fig. 2. The change in the work function of platinum during hydrogen chemisorption ($p_{H_2} = 1.2\times10^{-7}$ mm Hg); τ is the adsorption time in min.

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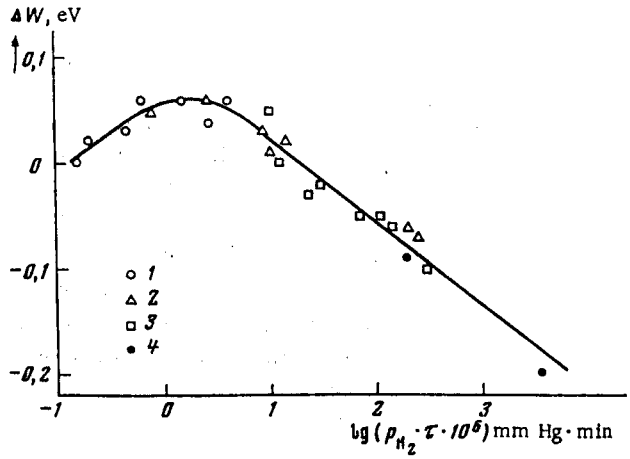

Fig. 3. The change in the work function of platinum as a function of exposure in hydrogen at different p_{H_2}: 1) 10^{-8}, 2) 10^{-7}, 3) 10^{-6}, and 4) 10^{-5} mm Hg.

The work function was determined from the extrinsic photoeffect, and calculated according to Fowler from the relation between the photocurrent of the sample and the energy of the irradiated light. The platinum test sample, which was material of 99.99% measuring $40 \times 5 \times 0.02$ mm^3, was placed into the center of a spherical glass cell of 40-mm radius which had an optical window of quartz. The inner surface of the sphere, which was coated with a layer of evaporated platinum, served as the electron collector. The cell was fused to an ultrahigh-vacuum glass system which had been preevacuated at a special pumping station. Final evacuation and prolonged maintenance of a vacuum of 1 to 2×10^{-10} mm Hg was accomplished with a miniature titanium-diode pump assembled inside a glass frame and powered with batteries.

The composition of the residual gases and the purity of hydrogen were controlled with an RMO-4S omegatron. Hydrogen was admitted to the system via a heated nickel capillary.

The surface of the platinum test sample was purified by thermal treatment in oxygen ($\tau = 30$ min, $p_{O_2} = 1 \times 10^{-5}$ mm Hg, $T = 1400$°K) and prolonged degassing in a vacuum of 1 to 5×10^{-10} mm Hg at $T = 1400$–1600°K.

Source of the ultraviolet radiation was a production-line DRSh-1000 lamp operated under conditions ($I = 20$ A, $V = 19$ V) which were maintained artificially. A calibrated F-7 photocell was used to measure the light intensity.

A platinum surface purified as described above is characterized by a work function value of 5.70 ± 0.07 eV. At the end of the measurements of W we examined the composition and, roughly, the amount of the gases adsorbed on the platinum surface during the time over which W was measured. It was shown by flash desorption that hydrogen is the chief component in the desorbed gases; the amount of hydrogen is approximately that corresponding to one hundredth of monatomic coverage. The amounts of other gases desorbed (CO_2, CO, N_2, H_2O) were two to three orders of magnitude smaller. No change in the W of platinum after thermodesorption was observed, which confirms the insignificant surface contamination by residual gases.

Data are presented in Fig. 1 for the sample's photocurrents (expressed as $(I_{ph}/I_l)^{1/2}$ where I_{ph} is the photocurrent of the sample and I_l is the intensity of the light, in arbitrary units) as functions of the energy of irradiated light ($h\nu$, in eV), both for cleaned platinum (curve 1) and for platinum carrying different amounts of chemisorbed hydrogen (curves 2 and 3). The hydrogen chemisorbed after an exposure of 2×10^{-6} mm Hg · min increases the work function by 0.06 eV (curve 2). Hydrogen exposure to the extent of 20×10^{-5} mm Hg · min decreases the work function by 0.15 eV (curve 3). There is practically no change in the slope of the Fowler straight lines during hydrogen adsorption.

The change in electron work function of platinum which occurs during hydrogen adsorption at a constant pressure of 1.2×10^{-7} mm Hg is presented in Fig. 2. One can see that the maximum increase in W, by 0.06 eV, occurs within the first 20 min. With the passage of time this effect decreases, and becomes zero after 120 min. Further hydrogen adsorption is accompanied by a decrease in work function. The amount of hydrogen that can be desorbed from the platinum surface at the point of surface charge reversal was determined by flash desorption (heating for 1 sec to 1200°C). It corresponds approximately to the formation of 0.1 of a

monatomic layer. Results of experiments concerning the change in W during hydrogen adsorption in the pressure range from 2×10^{-8} to 1×10^{-5} mm Hg are presented in Fig. 3, and indicate that starting from an exposure of 0.16×10^{-6} mm Hg · min the work function increases with increasing exposure, and attains its maximum value, corresponding to an increase of 0.06 eV, with an exposure of 2×10^{-6} mm Hg · min. Subsequent hydrogen adsorption is attended by a decrease in W, and over a rather wide range of pressures (10^{-7} to 10^{-5} mm Hg), the change in W is a linear function of the logarithm of exposure. Reversal of the sign of surface charge of the platinum occurs at an exposure of 20×10^{-6} mm Hg · min at P_{H_2} between 2×10^{-7} and 2×10^{-6} mm Hg. This sort of change in the W of platinum during hydrogen adsorption can be explained by the formation of two different forms of hydrogen bonding to the platinum [3, 6].

The increase in W found to occur during hydrogen adsorption below $\theta\approx 0.1$ at room temperature does not correspond to the results of [8], but is in harmony with ideas [7] that an electronegative component can be produced at low coverages over the whole temperature range where hydrogen adsorbs. Our data are in qualitative agreement with the results of electrochemical investigations [1, 2] according to which two forms of hydrogen bonding to the platinum exist.

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MACROKINETICS OF THE ELECTROCHEMICAL DISSOLUTION OF ALUMINUM IN A SLIT CELL WITH FLOWING ELECTROLYTE

CHARACTERISTICS OF THE ANODIC DISSOLUTION OF ALUMINUM IN THE KOH + H_2O_2 SYSTEM

N. D. Koshel', A. N. Verba, and O. S. Ksenzhek

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The electrochemical dissolution of aluminum in alkaline solutions is accompanied by a corrosion process with hydrogen depolarization. The mechanism and kinetics of these processes under various conditions have been discussed in the literature and are well known. A considerably more complicated picture arises if there is present in the solution an oxidant which not only changes the potential of the corrosion system by acting as a depolarizer and increasing the rate of dissolution of the metal in the active region [1, 2] but which also is able to act on the kinetics of anodic dissolution, slowing the process in certain circumstances [3-5].

In this work, the kinetics of dissolution of aluminum in the KOH + H_2O_2 system was studied in a continuous flow slit cell [6]. Under stabilized operating conditions at a constant potential, we measured the external polarization current (i_p), the total rate of dissolution of aluminum (i_d) from the weight loss of the sample, and the rate of hydrogen evolution. The experiments were carried out at 30°C with H_2O_2 concentrations from 0 to 0.3 M and solution flow rates from 4.7 to 20 cm/sec. The alkali concentration was 2.0 M.

F. E. Dzerzhinskii Dnepropetrovsk Chemical-Technological Institute. Translated from Élektrokhimiya, Vol. 14, No. 2, pp. 300-303, February, 1978. Original article submitted January 31, 1977.

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