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Abstract

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ON THE STRUCTURE OF THE DOUBLE ELECTRIC LAYER ON PLATINUM

(Presented by Academician A. N. Frumkin, 3 II 1960)

To elucidate the structure of the double layer it is necessary to know the potential of zero charge. By adsorption methods it was shown that on reduced Pt the potential of zero charge φ is, in a Na_2SO_4 solution, about 0.11–0.15 V (^{1,2}), in a NaCl solution 0.05 V, and in a NaBr solution 0.02 V (^{1}) relative to the normal hydrogen electrode. By the less accurate method of the edge angle of gas bubbles, a value of φ equal to 0.27 V was obtained in an H_2SO_4 solution (^{3}). Recently, by a new crossed-thread method, a value of φ equal to 0.2 V was found (^{4}).

However, by the method of measuring capacitance with alternating current, a number of works have obtained more positive values for φ, equal to 0.6–1.1 V (^{5,6}). A strong dependence of the latter on the pH of the solution was discovered: φ changes from +0.5 to −0.35 V as the pH changes from 1 to 12 (^{7}). Calculation from the work function gives the value $\varphi = 0.6–0.7$ V (^{6}). It should be noted that adsorption measurements imply that on oxidized platinum $\varphi = 0.7–0.9$ V (^{1,2}). In view of the contradictory data on the potential of zero charge on platinum, we considered it necessary to investigate in greater detail the capacitance of the double layer on platinum.

In the present work the capacitance of a smooth platinum electrode was measured in sulfuric-acid solutions of various concentrations at different frequencies of alternating current. The method for measuring capacitance was described in our preceding work (^{8}). The equivalent circuit of the electrode is represented as a series connection of the capacitance C_1 and the resistance R_2.

The dependence of the capacitance of a platinum electrode, measured in this way, on the potential at different frequencies in solutions of $0.01\,N$ H_2SO_4 and $1N$ $Na_2SO_4 + 0.01N$ H_2SO_4 is presented in Figs. 1 and 2, from which it is evident that the capacitance curves at low frequencies, independently of the

Fig. 1 and Fig. 2 graphs

Figure 1: Fig. 1 and Fig. 2 graphs

concentration of the solutions, pass through a rather sharp minimum at a potential close to 0.5 V. However, with increasing frequency of the alternating current the form of the capacitance curve changes, and at a frequency of 200 kHz the left-hand rise on the capacitance curve disappears entirely*. Such a strong dependence of the magnitude of the capacitance and of the form of the curve on frequency, as well as the magnitude of the phase shift, indicate that at low frequencies a pseudocapacitance is being measured (9), which disappears completely only at high frequencies. On smooth platinum, owing to the presence of adsorbed atoms, even in the "double-layer" region a small pseudocapacitance is observed at low frequencies (10,8), and the capacitance curve passes through a minimum corresponding, apparently, to the potential of the least adsorption of atoms on Pt. Thus, the minimum on the capacitance curves of a platinum electrode at low frequencies is the result of the intersection of two adsorption-capacitance curves corresponding to two processes: the process of discharge of ions and ionization of adsorbed hydrogen atoms on the one hand (9,8), and the process of deposition and removal of adsorbed—of oxygen—on the other hand (11-13). Apparently, the capacitance minimum at a potential of 1.07 V, which Robertson (5) observed on Pt in 1 N HCl, can be explained in a similar way. As a result of the shift of the platinum oxidation potential (14) and of the region of hydrogen adsorption toward more negative potentials, the minimum in the capacitance curves obtained by us at low frequencies is shifted (Fig. 3). As can be seen from a comparison of Fig. 3 with the data of (7), the position of this capacitance minimum with respect to potential coincides with the values of the potentials of zero charge given in the article by V. L. Kheifets and B. S. Krasikov, obtained at identical pH. These authors, without investigating the change in the shape of the capacitance curve with the frequency of the alternating current and measuring the capacitance at low frequency (50 Hz), concluded that the minimum corresponds

Fig. 1. Curves of the dependence of capacitance on potential in a solution of 0.01 N H_2SO_4 at various frequencies: 1 –0.2 kHz; 2 –1 kHz; 3 –5 kHz; 4 –10 kHz

Fig. 2. Curves of the dependence of capacitance on potential in a solution of 1 N Na_2SO_4 + 0.01 N H_2SO_4 at various frequencies: 1 –1 kHz; 2 –20 kHz; 3 –100 kHz; 4 –200 kHz

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* In the first of these solutions it was not possible to carry the measurements to such high frequencies as in the second, because of the greater specific resistance of the first solution.

to the point of maximum diffuseness of the double layer, i.e., to the potential of zero charge, which, evidently, cannot be agreed with.

In order to be able to measure, with sufficient accuracy, the capacitance of the double layer on reduced platinum in the region of the zero potential in dilute solutions, it is necessary to eliminate the adsorption capacitance due to hydrogen. By increasing the frequency of the alternating current, one can reach the point where only the capacitance of the double layer will be measured (which we have at pH 2, apparently, at a frequency of 200 kHz (Fig. 2)). Meanwhile, in dilute solutions, because of the high resistance of the solution, at such frequencies the sensitivity of the bridge to capacitance is low; therefore, in the case of 0.01 N solutions we limited ourselves to measurements at a frequency of 10 kHz and proceeded by further decreasing the concentration of hydrogen ions in the solution, in order to shift the region of hydrogen adsorption away from the zero point toward more negative potentials (9). Figure 4 presents the curves of the change in capacitance with potential at a frequency of 10 kHz in 0.01 N Na_2SO_4 solutions with different concentrations of hydrogen ions. In a solution with pH 5, at this frequency and at potentials more positive than 0.05 V, the pseudocapacitance is almost absent (Fig. 4, 3) and the capacitance of the double layer is measured (the phase-shift angle here is 90°). However, as is seen in Fig. 4, there is no capacitance minimum at the zero point.

To try to explain this, one should consider the peculiarities of the double layer on platinum and other similar metals. On many solid metals there is a considerable dispersion of capacitance with frequency and, what is especially important, the magnitude of the capacitance at sufficiently high frequencies has a small value even at high solution concentrations (15–17, 5, 6, 8).

For example, according to our data, at a frequency of 20 kc in an acidified 1 *N* solution of Na_2SO_4 the capacitance is 16, and at a frequency of 200 kc it is 11 μF per 1 cm^2 of visible surface; moreover, in the region of the zero-charge potential there is no rise characterizing, in the case of mercury or lead electrodes, deformation of anions (Fig. 2). If it is assumed that at a frequency of 200 kc the measured surface is practically equal to the visible one, then the capacitance in the near-cathodic region proves to be one and a half times, and in the anodic region (i.e., more positive than the zero point) 3–4 times lower than in the case of mercury. Dispersion not associated with adsorption pseudocapacitance can be explained by the geometrical heterogeneity of the solid surface (microcracks and pores). The reason for the low general value of the capacitance over a broad range of potentials at all frequencies at which adsorption pseudocapacitance is not manifested is unclear. It is possible that it consists in the reduced electron density in the metal near the surface, owing to the presence of chemisorption of oxygen and hydrogen atoms* or in the separation of the plates of the double electric layer upon formation of an atomic adsorption layer on at least part of the surface ([18]). Slight chemisorption is present even within the "double-layer" region of potentials. In contrast to the decrease in electron density observed in the case of germanium ([19]), the effect of lowering the electron density in the case

Fig. 3

Figure 2: Fig. 3

Fig. 4

Figure 3: Fig. 4

of metals should not be closely associated with the zero point, but should be observed over the entire range of potentials in which adsorption of atoms occurs and, consequently, a decrease in the density of charges of the double layer.

Fig. 3. Curves of the dependence of capacitance on potential ($\nu = 1$ kc) in various solutions:
1 –1 N H_2SO_4; 2 –0.01 N H_2SO_4; 3 –0.01 N Na_2SO_4 + 0.0001 N H_2SO_4; 4 –0.01 N Na_2SO_4 + 0.00002 N H_2SO_4

A decrease in the surface charge due to the diffuseness of the electronic plate of the double layer should lead, at the same potential, to an increase in the diffuseness of the ionic plate, i.e., to an additional lowering of the capacitance and to a broadening of the range of potentials in which the influence of the zero point on the capacitance is manifested (the width of the minimum). Additional "smearing" of the minimum may occur because of the physical and chemical heterogeneity of the polycrystalline surface, since different crystal faces, probably, may differ in the zero-charge potential by tens and hundreds of millivolts, while chemically different regions (because of adsorption of atoms) may differ by hundreds of millivolts. As a result of the diffuseness of the electronic plate, the effect from anion deformation should be sharply reduced. Nevertheless, apparently, taking all these factors into account, one might have expected at least small changes of capacitance with potential, exceeding the experimental error, which we did not observe experimentally.

Fig. 4. Curves of the change in capacitance with potential ($\nu = 10$ kc) in a 0.01 N Na_2SO_4 solution with different pH values: 1 –pH 2; 2 –pH 3; 3 –pH 5

The capacitance measured at high frequencies increases only at strongly positive potentials (Fig. 2). Macdonald and Hackerman ([6]),

* An analogous supposition is made in work ([17]).

it is believed that this rise is associated with deformation of anions on the clean surface of platinum and, on this basis, $\varphi_{\mathrm{n}} = 0.8 \pm 0.2$ V is adopted. However, judging from the reduced phase shift, this increase in capacitance is associated with a pseudocapacitance determined by the rate of the reaction of deposition and removal of oxygen from platinum ([12,13]). Only in part can the increase of capacitance with potential be associated with deformation of anions on platinum, but evidently on platinum covered with adsorbed oxygen ([1,2]), since it is highly probable that the value given is the potential of zero charge of oxidized, and not clean, platinum.

From all that has been set forth it follows that the method of measuring the capacitance of the double layer by alternating current in dilute and concentrated solutions, in the case of a platinum electrode, does not make it possible to determine the position of the potential of zero charge. The values of the potentials of zero charge of platinum obtained by this method ($^{5-7}$) are incorrect. The accuracy of the result of calculating φ_n from the electron work function is open to doubt (^{6}), since it is not clear to what extent, in measuring the work function, identity of the surface states of such different metals as Pt and Hg was achieved. Consideration of the data available in the literature on the experimental determination of the zero points of platinum makes it possible to conclude that the most correct are the data obtained by adsorption methods (in particular, 0.15 V in a $1N$ solution of Na_2SO_4).

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Note: Figure translations are in progress. See original paper for figures.