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Abstract

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DETERMINATION OF THE CAPACITANCE OF A SMOOTH LEAD ELECTRODE BY MEASURING THE POTENTIAL DROP

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The process of cathodic hydrogen evolution on lead has been studied by many authors ($^{1-11,\,15-19}$), but up to the present time there is no unified opinion regarding the mechanism of this process. Soviet electrochemists ($^{1,\,3-5}$) have shown that the hydrogen overvoltage on lead, over a wide interval of current densities, obeys the Tafel equation with constants a = 1.52—1.56 V and b = 0.10—0.12 V. It may be assumed that in this case the overvoltage is due to the slowness of the discharge stage of hydrogen ions ($^{3-5}$). A different point of view is held by Hickling and Salt (^{16,17}), who explain the hydrogen overvoltage on lead at various current densities either by the slowness of recombination of hydrogen atoms or by the slowness of electrochemical desorption of hydrogen. A. N. Frumkin (^{14}) showed that the conclusions of Hickling and Salt are not entirely reliable because of errors made in the treatment of the experimental data and insufficient purity in carrying out the experiments. Recently, works have again appeared (^{18,19}) in which experimental data on the dependence of the hydrogen overvoltage on lead on the current density and on the time after cessation of polarization are explained by slow processes of removal of adsorbed hydrogen. Additional information regarding the mechanism of the hydrogen-evolution process and the participation of electrochemically active adsorbed hydrogen in this process can be obtained by measuring the potential drop of the electrode after switching off the polarizing current (^{13,20}). The presence on the surface of adsorbed hydrogen, in equilibrium with hydrogen ions in the double layer, should lead to a considerable increase in the capacitance of the electrode, calculated from the potential-drop curve, as compared with the capacitance of the electrical double layer.

In the present work, the potential drop of a smooth lead electrode after interruption of polarization was measured in 1 N solutions of HCl and H_2SO_4 in the range of cathodic current densities $3 \cdot 10^{-1}$—$6 \cdot 10^{-5}$ A/cm^2. The drop curves were recorded by means of an oscillographic setup, the principle of operation of which was described in detail earlier (^{21}). The electrode capacitance C was calculated from short sections of the drop curves using the following equation:

$$C = \frac{2.3 i_0 (t_2 - t_1)}{b'} \left(10^{\Delta\eta_2/b'} - 10^{\Delta\eta_1/b'}\right), \tag{1}$$

where $\Delta\eta_1$ and $\Delta\eta_2$ are the values of the overvoltage drop after times t_1 and t_2 after the current was switched off, i_0 is the density of the polarizing current, and b' is the coefficient in the equation for the dependence of overvoltage on $\lg i_0$. Since no assumptions regarding the mechanism of the process were made in deriving (1), the capacitance found is a purely experimental quantity ([14,20]).

The hydrogen overvoltage on smooth lead is very sensitive to minute amounts of impurities in the solution and in the metal ([1,4,5,18]). Therefore, in the present work much attention was devoted to the purification of the reagents used. Water and acids were distilled twice; gaseous hydrogen was purified of traces of oxygen by passing it through three furnaces with a palladium or platinum catalyst (at a temperature of 300—400°). The solutions used were subjected before measurement to cathodic purification on lead in a separate–

part of the cell. The electrode studied was a plate of spectrally pure lead from Hilger. The preparation of the electrode and the treatment of its surface by preliminary polarization (reduction of oxides and smoothing) were carried out according to the method developed by B. N. Kabanov, Z. A. Iofa, and others ([1]). The potential-decay curves were recorded after a steady value of the overvoltage had been established at the given current density.

The dependence of the overvoltage on the current density in the investigated range of polarizations can be expressed by the formulas: $\eta = 1.53 + 0.120 \lg i_0$ for $1\,N$ H_2SO_4 and $\eta = 1.51 + 0.117 \lg i_0$ for $1\,N$ HCl. The values of the constant a in the Tafel equation in our experiments are close to the data of B. N. Kabanov, Z. A. Iofa, and others ([1]) and Ya. M. Kolotyrkin ([7]), but they are higher than the data of a number of other authors ([8,9,11,15,16,18]). Our measurements showed that the use of a less pure metal, as well as deviations in the method of surface preparation, lead to a considerable lowering of the overvoltage.

The values of the coefficient b in the Tafel equation given above correspond to relatively "slowly" measured polarization curves (the duration of measurement of the whole curve was 15-20 min). During this time, processes may take place that change the state of the electrode surface and the dependence of the overvoltage on $\lg i_0$ ([5]). It may be assumed that during measurement of the decay curve (down to 10^{-1} sec) these processes do not have time to exert an influence, and the character of the dependence of the potential on the current density remains the same for the entire curve. This assumption is confirmed by semilogarithmic overvoltage-decay curves, part of which is shown in Fig. 1. The rectilinearity of the η–$\lg t$ curves, beginning from a certain value $t \gg Cb'/2.3 i_0$, indicates that the quantities a, b' and C remain constant on a given curve for all values of η ([5,14]). The slope of the straight line $\partial\eta/\partial \lg t$ is equal, in this range of η values, to the slope b' of the overvoltage curve η_0–$\lg i_0$, recorded on an unchanged surface.

The capacitance of the lead electrode was calculated from equation (1); the value of the coefficient b' was determined from the rectilinear part of the given decay curve η—$\lg t$. The results obtained for different values of the initial current density i_0 are given in Table 1.

Table 1

1 N HCl	1 N HCl	1 N HCl	1N H_2SO_4	1N H_2SO_4	1N H_2SO_4
i_0, A/cm^2	$b' = \dfrac{\partial\eta}{\partial \lg t}$, V	C, μF/cm^2	i_0, A/cm^2	$b' = \dfrac{\partial\eta}{\partial \lg t}$, V	C, μF/cm^2
$3.0 \cdot 10^{-1}$	0.145	15.3	$8.82 \cdot 10^{-2}$	0.146	13.6
$5.66 \cdot 10^{-2}$	0.146	13.3	$1.39 \cdot 10^{-2}$	0.142	13.4
$2.5 \cdot 10^{-2}$	0.136	14.2	$9.1 \cdot 10^{-3}$	0.140	12.8
$5.05 \cdot 10^{-3}$	0.138	13.1	$3.47 \cdot 10^{-3}$	0.132	12.5
$1.01 \cdot 10^{-3}$	0.127	14.7	$1.36 \cdot 10^{-3}$	0.123	16.0
$5.05 \cdot 10^{-4}$	0.122	15.0	$4.17 \cdot 10^{-4}$	0.119	14.2
$1.52 \cdot 10^{-4}$	0.118	12.8			
$6.15 \cdot 10^{-5}$	0.123	13.3			

From the data of Table 1 it is evident that the values of the coefficient b' differ considerably from the usual coefficient b at current densities higher than 10^{-3}–10^{-2} A/cm^2, and reach values of 0.140–0.146 V. The reason for the change in b' remains unexplained within the scope of the present work.

The capacitance of a smooth lead electrode is equal to 12.5–16 μF per 1 cm^2 of visible surface and does not depend either on the potential or on the time t in the considered range of values of η and t. Measurement of the capacitance of a smooth lead cathode with the aid of alternating current gave values close to 15 ([10]) or to 18 μF/cm^2 ([2,12]); on spongy lead, for low current densities in ([19]), capacitance values of 10.5 μF/cm^2 were obtained.

Our data indicate that the decay of the overvoltage after sw-

switching off the external current is caused by discharge of ions of the double electric layer, and on the surface of cathodically polarized lead there is no electrochemically active hydrogen in a concentration accessible to determination by this method. Consequently, in the process of hydrogen evolution on lead, adsorbed hydrogen accumulates in a noticeable amount; in any case its concentration cannot exceed several thousandths of the maximum possible surface concentration ([20]). In light of what has been set forth, an explanation of the overvoltage on lead by theories based on the assumption of equilibrium of adsorbed hydrogen with hydrogen ions in the double layer is unlikely.

Fig. 1. Potential-decay curves of a lead electrode in 1 N HCl.
(1—$i_0 = 3.0 \cdot 10^{-1}$; 2—$i_0 = 3.7 \cdot 10^{-3}$; 3—$i_0 = 7.4 \cdot 10^{-4}$; 4—$i_0 = 6.5 \cdot 10^{-5}$ A/cm^2)

Fig. 1. Potential-decay curves of a lead electrode in 1 N HCl.

Figure 1: Fig. 1. Potential-decay curves of a lead electrode in 1 N HCl.

For the overvoltage-decay curves, a characteristic "crossing" is observed (Fig. 1). Hickling and Salt ([16,17]) explain this phenomenon by a change in the mechanism of the electrode process, while Ya. M. Kolotyrkin ([5]) explains it as the result of a change in the state of the electrode surface depending on the density of the polarizing current. The latter explanation seems to us more probable; in its favor also speaks the slow decrease of the overvoltage during polarization at high current densities ($i_0 > 10^{-3}$ A/cm^2). A detailed clarification of this phenomenon requires the application of other experimental methods of electrochemical kinetics.

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