APPLICATION OF THE DOLIN – ÉRSHLER SCHEME TO THE PLATINUM ELECTRODE IN SULFURIC ACID SOLUTIONS

V. A. Safonov, V. D. Dishel',
and O. A. Petrii

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Dolin and Érshler showed [1] that the behavior of a platinum electrode with hydrogen adsorbed on its surface, using an alternating sinusoidal current and fast surface diffusion of hydrogen atoms, can be modeled by an equivalent scheme consisting of the double-layer capacity C_1 connected in parallel with the adsorption capacity C_2 and the hydrogen discharge–ionization reaction resistance r (Fig. 1). The scheme is intended for potentials $\varphi_r > 0.05$ V (where φ_r is the potential against the reversible hydrogen electrode in the same solution), at which the diffusion impedance due to dissolved hydrogen can be neglected. In practice, however, a relationship was observed between the elements of the equivalent scheme and the frequency of the alternating current in the region of low and medium frequencies, indicating slow surface diffusion of hydrogen atoms [1]. The application of the Dolin–Érshler scheme to the platinum electrode has been discussed in [2-4], but without reaching significant results.

The most objective analysis is evidently carried out by computer. We developed therefore an analog program for the BÉSM-6 computer [5] and calculated the elements of the equivalent scheme for a solid platinum electrode in 1 N H_2SO_4 in the potential range 0.05-0.5 V. The calculations were based on data for C_i and R_i at eleven different frequencies ν_i between 60 Hz and 100 kHz, measured in series by means of an ac bridge, described in [6]. The preparation of solutions, electrode activation, and other experimental details were the same as those given in [7].

The parameters C_1, C_2, r, and the resistance of the solution R_S were selected by regression analysis as described in [5]. For this purpose the following function was used:

$$F = \sum_{\nu_i} \left[\left(\frac{C_T - C_i}{C_i} \right)^2 + \left(\frac{R_T - R_i}{R_i} \right)^2 \right], \quad (1)$$

where C_T is the capacity and R_T the resistance at a given frequency, calculated from arbitrary initial values of C_1, C_2, r, and R_S, using well-known equations for the transition from the scheme in Fig. 1 to the scheme with capacity and resistance connected in series; C_i and R_i are experimental values of capacity and resistance at the same frequency, measured in series. The calculations gave the values of C_1, C_2, r, and R_S at which the function F was at a minimum; thus, no assumptions were made regarding the value of C_1.

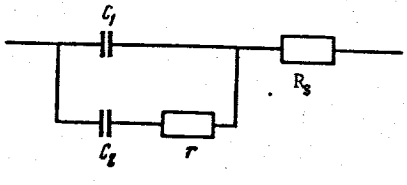

Fig. 1. The Dolin–Érshler scheme: C_1) double-layer capacity; C_2) adsorption capacity; r) reaction resistance; R_S) solution resistance.

The calculations showed that in the potential φ_r interval from 0.1 to 0.5 V, the value of R_S was constant with a deviation of ±3% and practically coincided with the resistance determined experimentally at a frequency of 100 kHz at 0.3-0.5 V. The values of C_1, C_2, and $1/r$ obtained are shown in Figs. 2 and 3 as functions of electrode potential. The sums of squares of relative deviations of experimental and calculated capacities and resistances at all frequencies (the values of function F at different potentials) are given below.

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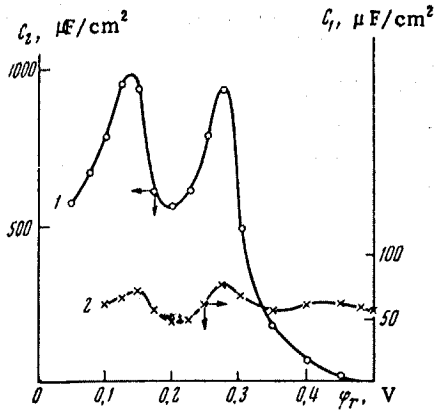

Fig. 2

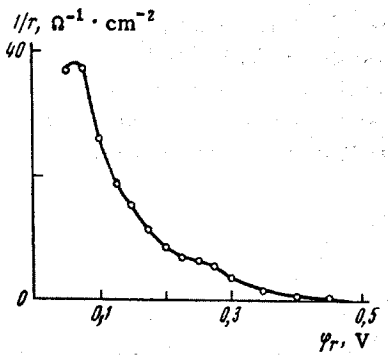

Fig. 3

Fig. 2. Adsorption capacity 1 and double-layer capacity 2 as functions of potential, calculated by computer for the solid platinum electrode in 1 N H_2SO_4 solution.

Fig. 3. Conductivity of the hydrogen discharge–ionization reaction on platinum in 1 N H_2SO_4 solution as function of potential, calculated by computer.

φ_r, mV	100	125	150	175	200	225	250	300	350	400	500
F	0.365	0.224	0.207	0.299	0.269	0.236	0.167	0.191	0.222	0.399	0.695

The data show that the maximum value of F in the interval φ_r = 0.15–0.35 V is about 0.3. This means that deviations in the behavior of the platinum electrode from the Dolin–Érshler scheme are in the region of ±10–15%. When $\varphi_r \leq 0.1$ V, F increased sharply, indicating that the scheme was not applicable. Possibly, the Warburg impedance should be introduced already at 0.1 V. The increase of F when φ_r = 0.4 and 0.5 V is evidently related to the fact that at these potentials the accuracy of determining C_2 and $1/r$ is unsatisfactory since these values are very small.

The analysis shows that the terms $[(R_T - R_i)/R_i]^2$ are the main contributors to the value of F; this is particularly true at the lowest frequencies. Thus, the sum of squares of the relative deviations of R at frequencies 60 and 110 Hz constitute more than half the value of F. The experimental resistance values are higher than those calculated at these frequencies. It is possible that such a resistance behavior is related to some asymmetry in the position of the working and reference electrodes. Ukshe [8] has shown that in the case of an ideally polarized electrode an asymmetrical arrangement of the electrodes causes an increase in the resistance measured with decreasing ac current frequency, while the capacity remains practically constant.

The C_1 vs φ_r curves calculated in the present article are close to those measured in the interval φ_r = 0.15–0.5 V at 100 kHz, at which frequency the pseudocapacity of the adsorbed hydrogen practically disappears. The shape of the C_2 vs φ_r curve is similar to that measured at 60 Hz and to the potentiodynamic curve of the platinum electrode. The shape and values of the $1/r$ vs φ_r curves are similar to those obtained in [7].

We have evaluated an equivalent scheme in which an impedance of the form $A/\sqrt{i\omega}$ was included in series with the capacity C_2 and resistance r, where A is the parameter varied, i is the simulated value, and $\omega = 2\pi\nu$. In this case F decreases by a factor of 10; however, the physical significance of such an impedance is not clear.

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