A FORMAL TERMINOLOGY FOR THE ANODICALLY PASSIVE STATE

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A new electrochemical approach is formulated for the definition of the concept of the passivated state of a metallic anode and of its changes in the different sectors of the polarization curve. In connection with this, a proposed system of terms and characteristic quantities is discussed.

In the science of the kinetics of electrode reactions, the graphical and analytical means of depicting the function connection between the electrode potential and the current density are completely equivalent and complement each other organically. A description of the anode behavior of a passivated metal is not conceivable without an examination of its polarization curve. Consequently, the use of the corresponding kinetic equations must also be necessary.

In the generalized equation of electrochemical kinetics

$$i = k(\varphi)e^{2,3\varphi/b}, \quad (1)$$

which was proposed in 1956 [1], passivation of the electrode found its formal expression in the averaged (in terms of adsorption processes), varying from interval to interval, exponential function of the effect of the potential on the factor $k(\varphi)$, previously assumed to be constant:

$$k(\varphi)_n = k_n e^{-2,3\varphi/b_1}. \quad (2)$$

Correspondingly, in the interval of potentials in which $b_1 = b$, a value of zero is attained and, in the interval in which $b_1 < b$, also a negative value of the derivative $di/d\varphi$.

In spite of its generalized character, Eq. (1) enabled the formulation and fixation of the existing concepts with respect to the dissolution of a passive metal, both with regard to the electrochemical process and with respect to passivation itself, and with respect to the surface change with increases the overvoltage of this process. Over the years, the electrochemical theory of passivity has been considerably enriched and additional weighty confirmations have been obtained. However, its further development and correct perception has encountered some difficulties of a terminological character, because of the evident lack of agreement between the established meanings of the existing terms, connected semantically with earlier model concepts, and new meanings which must be incorporated into electrochemical theory.

For example, independently of what concrete meaning is incorporated by various authors in the terms: potential of total passivation (see Fig. 1, point e) or the region of total (optimal) passivity (sector ef), semantically these terms themselves can only be connected with the concept of an invariable state of the electrode, attained at point e and retained over the sector ef. At the same time, it follows from (1) that "total passivity" is not yet achieved at the point e, and that the lack of dependence of the stationary current on the potential in the sector ef is due precisely to a change in the degree of passivity and of the accompanying factor $k(\varphi)$ (2), which also compensates for the direct effect of the potential on the rate of the process, approximately expressed by "instantaneous" polarization curves of the Tafel type (for example en).

On the contrary, the left-hand stationary branch, parallel to the branch ab, is assumed to be characterized as "active" or "activated," etc. which, semantically, should be connected with a decrease in the

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passivation of the electrode. In fact, in accordance with (1), the "normal Tafel slope" of a branch, for example fg, means that over its whole extension the electrode retains a constant value of $k(\varphi)$, and means also a constant degree of passivation attained at the point f.

A multitude of similar examples bears witness to the need for developing a consistent system of concepts and terms for the electrochemical theory of the passive state; this system must obviously be based not on an excess of detailed model concepts, which may be considerably altered in the future, but on sufficiently general formal categories of electrochemical kinetics.

STATIONARY PHENOMENA

The definition of passivity proposed by Tomashov [2], which is widely known and which has been adopted in many academic courses, differs from many others, both by the clearness of its electrochemical approach (which permits limiting the circle of phenomena determined to cases favorable to the inhibition of the anode reaction), but also by its open possibility of the introduction of a quantitative characteristic phenomenon, i.e., the degree of passivity π (equal to the ratio of the anode and cathode polarizations, $\pi = v_a/v_c$).

For corrosion systems, functioning only as the result of the electrically conjugated balanced course of anode and cathode reactions (this definition was proposed for just such systems), the above definition may be considered completely satisfactory. However, the broad recent development of electrochemical investigations of passivity, as well as the increasing use of the method of anodic protection, are creating an ever greater number of partial cases, in which the phenomenon of passivity must necessarily be considered in the absence of conjugated cathode processes and in which, consequently, the principle for the quantitative degree of passivity proposed by Tomashov becomes unsuitable.

In such cases, any qualitative evaluation of the phenomenon must be based only on those changes which, as a result of passivation, take place in the kinetic characteristics of the process of anode dissolution itself. It is obvious that only such an approach can be considered feasible at the present time, since only independently of cathode processes can the characteristic of the degree of passivation of the electrode be regarded as universal and applicable in equal degree both in the absence and in the presence of conjugated cathode reactions.

Coefficient and Index of Passivation

The decrease in the rate of dissolution or oxidation of a metal, resulting from passivation and taken into account by changes in the factor $k(\varphi)$ in (1), is, in the final analysis, the most universal and from a practical point of view, the most important manifestation of passivity as a whole.* Consequently, it is reasonable to adopt precisely this decrease as the quantitative characteristic of the degree of passivation of the electrode; for this purpose it is necessary above all to select a value of the rate from which it must be calculated.

Since the potential affects the rate of the process, not only through passivation, but also independently of it, the characteristic of passivation cannot be obtained by a direct comparison between rates of the process corresponding to two different potentials. In other words, to obtain this characteristic, the actual rate of the process at a given potential, φ_j, must be related not to some fixed value, but to that value which would be observed at the same potential but in the absence of passivation.

This comparison can most easily and clearly be presented graphically (see Fig. 1), for which it is sufficient to find the points of intersection between the corresponding straight line $\varphi = \varphi_j$ ($j = 1, 2, 3, \ldots$) and the actual polarization curve (points Π_j) and with the continuation of the branch ab (points A_j); we make the plot using the classical equation of electrochemical kinetics:

$$\bar{i} = \bar{k}e^{2,3\varphi/b}, \tag{3}$$

where the constant $\bar{k}$ corresponds to a zero degree of passivation.

The ratio

$$\frac{\bar{i}}{i} = \frac{\bar{k}}{k(\varphi)} = K_\pi \tag{4}$$

*Which, it should be said, in no way contradicts the possibility of evaluating the degree of passivation from the slope of the polarization curve [2].

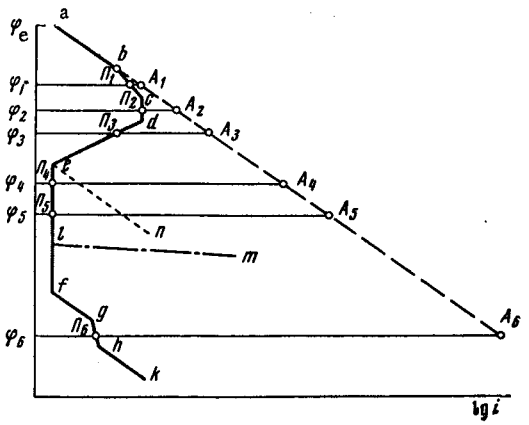

Fig. 1. Schematic illustration of the polarization curve of a metallic anode with variable passivation (legend given in text).

is conveniently used as an independent characteristic of the state of passivation of the electrode, which, in accordance with its completely evident meaning, must be used as the passivation coefficient K_π. With the introduction of the above coefficient, it is useful to rewrite the combination of Eqs. (1) and (3) in the form

$$i = \frac{\bar{i}}{K_\pi} = \frac{\bar{k}}{K_\pi} \cdot e^{2{,}3\varphi/b}. \tag{5}$$

In words this means that, with a given potential the actual current density on a passive electrode may be regarded as that density which would correspond to the potential on an unpassivated electrode, simulated by the passivation coefficient.

If we take account of the widespread use of the logarithmic form of the equations of electrochemical kinetics and the corresponding system of logarithmic coordinates used in plotting the polarization curves, it is easily seen that, instead of the expression for the passivation coefficient in terms of multivalued numbers, it is convenient to use its logarithm which, in accordance with the general principles of physicochemical terminology, may be called the passivation index, $p\pi$.

Taking account of (4) we can write the relationship

$$p\pi = \lg K_\pi = \lg \bar{i} - \lg i, \tag{6}$$

from which it can be clearly seen that, graphically (see Fig. 1), at a given potential, φ_j, the passivation index can be expressed directly by the segment $\Pi_j A_j$.

To find the connection between $p\pi$ and the other kinetic parameters of the process, we take logarithms in (1) and rewrite it in the form

$$\lg i = \frac{\eta - a(\varphi)}{b}, \tag{7}$$

which differs from an ordinary Tafel equation, solved for log i, by the fact that $a(\varphi)$ is a function of the potential.

Comparing (7) with the same solution of the classical Tafel equation, corresponding to Eq. (3) as well as with (6), we find

$$p\pi = \frac{a(\varphi) - a}{b}. \tag{8}$$

Thus, in the expressions establishing the dependence of the current density on the potential, the passivation index may be regarded as the increment of the constant a in the Tafel equation due to passivation, referred to the normal Tafel slope b, established for an active electrode

$$\eta = (a + bp\pi) + b \lg i, \tag{9}$$

$$\lg i = \frac{\eta - (a + bp\pi)}{b}. \tag{9a}$$

Angular Passivation Coefficients

Differentiating Eqs. (9a) and (8) with respect to φ, and taking into account that $\partial\eta/\partial\varphi = (\varphi - \varphi_e) = 1$, we obtain

$$\frac{\partial \lg i}{\partial \varphi} = \frac{1}{b} - \frac{\partial p\pi}{\partial \varphi} \tag{10}$$

or

$$\frac{\partial \lg i}{\partial \varphi} = \frac{1}{b}\left[1 - \frac{\partial a(\varphi)}{\partial \varphi}\right] \tag{10a}$$

In accordance with (10), the actual slope of the stationary polarization curve of a passivated electrode at any given point is equal to the algebraic difference between the tangents of the angles formed with the same axis by the normal Tafel straight line for an active electrode (i.e., 1/b) and the derivative of the passivation index with respect to the potential, which, in the sense of this relationship, may be called the angular passivation coefficient.

With comparison between the equivalent notations (10) and (10a), it may be noted that the derivative $\partial\alpha(\varphi)/\partial\varphi$ represents the same angular passivation coefficient, but referred to the standard slope 1/b. Being proportional to $\partial p\pi/\partial\varphi$, the above derivative is expressed by less cumbersome numbers, which sometimes permits simplifying and following more clearly certain laws governing the change in the passivated electrode. This may be called the reduced angular passivation coefficient.

Characteristic Values of the Angular Passivation Coefficients and Slopes of the Polarization Curves

An analysis of Eqs. (10) and (10a) permits separating out a number of characteristic values and intervals of change in the angular passivation coefficients which, in accordance with the above-mentioned equations, correspond to particular slopes of the polarization curve. Let us consider and briefly characterize these using the example of some hypothetical system (see Fig. 1), assuming that, in addition to changes in the degree of passivation, there are no other factors capable of affecting the slope of the polarization curve acting in this system. We must also bear in mind that the determination of a given sector or branch of the polarization curve must, to an equal degree, correspond also to the respective interval or region of potentials.

1. $\partial p\pi/\partial\varphi = 0$ (or $\partial\alpha(\varphi)/\partial\varphi = 0$, the Sector of Constant Passivation or Isopassivation. Characterized by the ordinary "Tafel" slope $\partial\log i/\partial\varphi = 1/b$ (sectors ab, fg, hk). With the additional condition: $p\pi = 0$ (or $a(\varphi) = a$) there is a partial case of zero passivation (sector ab).

2. $\partial p\pi/\partial\varphi = 1/b$ (or $\partial\alpha(\varphi)/\partial\varphi = 1$), the Sector of Compensating Passivation or Synthetic Passivation. The increments of the potential equalized by the increments of the passivation index, so that the stationary current does not depend on the potential: $\partial\log i/\partial\varphi = 0$ (sectors cd and ef).

3. $0 < \partial p\pi/\partial\varphi < 1/b$ (or $0 < \partial\alpha(\varphi)/\partial\varphi < 1$), the Sector of Uncompensating Passivation or Hypopassivation. The increments of the passivation index are only partially compensated by the direct effect of the potential on the current density, and the slope of the polarization curve with respect to the axis of the potentials is found to have an intermediate value between 1/b and zero, retaining, however, a positive value: $1/b > \partial\log i\ \partial\varphi > 0$ (branches bc and gh).

4. $\partial p\pi/\partial\varphi > 1/b$ (or $\partial\alpha(\varphi)/\partial\varphi > 1$), the Sector of Overcompensating Passivation or Hyperpassivation. The effect of the potential on the passivation index predominates over its direct effect on the current density, and the slope of the stationary curve becomes negative: $\partial\log i/\partial\varphi < 0$. With the partial value: $\partial p\pi/\partial\varphi = 2/b$ (or $\partial\alpha(\varphi)/\partial\varphi = 2$), the slope $\partial\log i/\partial\varphi = -1/b$ (branch de).

5. $\partial p\pi/\partial\varphi < 0$ (or $\partial\alpha(\varphi)/\partial\varphi < 0$), the Sector of Negative Passivation or Dispassivation. The slope with respect to the axis of the potentials $\partial\log i/\partial\varphi > 1/b$ (branch of rupture or pitting, *l*m).

Characteristic Points of the Polarization Curve. These points are the intersections or the conjugations of branches with different passivation slopes; they may be automatically numbered with respect to the branch for which, with an increase of the anode potential, the given point serves as the origin. Then, on Fig. 1, the potential of point d, for example, will be called the hyperpassivation potential, φ_{hp}; the points e are the points of the second synthetic passivation, φ_s''; the points f are the points of the second isopassivation, φ_i'', etc. In the superscripts, as is evident from the examples given, the respective prefixes are abbreviated: iso = i; syn = s; dis = d; hyper = hp; hypo = h.

Arbitrary Scale of Passivating Indices

Accurate numerical plotting of the polarization curve, corresponding to a zero degree of passivation of the metal in the region of potentials where in actual fact the metal is passive is, at the present time unattainable for a majority of corrosion systems. Therefore, in the general case, the passivation index like many other physicochemical quantities, may in practice only be calculated starting from some arbitrary zero line, for example, from the straight line

$$\lg \bar{i} = \frac{\varphi - \varphi_e}{0.12}, \tag{11}$$

which, for a metal with an equilibrium potential φ_e symbolizes the hypothetical dissolution kinetics, obeying an idealized Tafel equation with the constants $a = 0$ and $b = 0.12$.

In this arbitrary scale

$$p\bar{\pi} = \frac{\varphi - \varphi_e}{0.12} - \lg i, \tag{12}$$

and the logarithm of the ratio of the corrosion rates of two different metals M_1 and M_2 at exactly the same potential

$$\lg \frac{i'}{i''} = \frac{\varphi_e'' - \varphi_e'}{0.12} - (p\bar{\pi}' - p\bar{\pi}''), \tag{13}$$

where the primes and double primes denote, respectively, the characteristics of the first and second metal, and the dash above $p\pi$ denotes that it was determined on the assumed arbitrary scale.

NONSTATIONARY PHENOMENA

It is well known from experiment that, immediately after a sudden increase of the potential a passive metal may dissolve considerably more rapidly, and after a sudden decrease, considerably more slowly than in a stationary passive state [3-6]. This is explained by the lag of the changes in the passivation index which, in the first case increases, and in the second case decreases, but which does not immediately reach the stationary value which it should assume at the given final potential. Since such nonstationary periods may sometimes last up to an hour or more, the behavior of the passivated metal, and the states corresponding to it become of interest, not only theoretically but also in practice, and it is expedient to define these states terminologically.

The temporary state, following a preceding residence time at a more positive potential, and characterized by a higher passivation index than the stationary for a given potential, may be called superpassivating.

The opposite state of a passivation potential lower than the given potential, following a preceding residence time at a less positive potential, may correspondingly be called interpassivating.

GENERAL REMARKS

In an evaluation of the proposed set of concepts and terms the following must be taken into account.

a) All the terms and concepts described above are introduced with application to a method for the formal description of the corrosion properties of a system from a direct polarization curve, borrowed from electrochemical kinetics. They are given in full accordance with the quantities entering into the generalized equation of electrochemical kinetics and, in distinction from previous systems, include no quantities or concepts which are foreign to the above equation.

b) The terminology is formal. It is based only on the external characteristics of a phenomenon, and is free of elements connected with any kind of detailed assumptions with respect to the mechanism of the phenomenon or the nature of the passivating particles or surface compounds. This renders it sufficiently independent and universal.

c) The naturally classified characteristics, from which in the proposed system different individual regions of the potential or branches of the polarization curve may be distinguished, constitute a passivation index, as well as the value and sign of its derivative with respect to the potential. With the standard system of the electrode potential, this sign does not depend on the direction in which the polarization curve is recorded.* There is thus eliminated the possibility of confusion which has frequently arisen in the past, when the same investigator has taken exactly the same branch of the polarization curve as both passivated and active, depending from what direction it was considered.

* Even if the corresponding branch of the curve, with a change of the direction in which it is recorded, shifts due to hysteresis phenomena.

d) With the formal description of the phenomena connected with passivation and with changes in the slope of the polarization curve, the terms introduced do not exclude the possibility of the use of additional determinations, characterizing qualitatively the region of values in which, in the given case, the passivation index varies. Thus, also the region of constant passivation, as well as the regions of all three types of passivation (uncompensating, compensating, and overcompensating) can be completely characterized by such postulations as shallow, deep, or moderate. With the presence on the curve of several distinct sectors, they may be distinguished, respectively, by the order of their arrangement along the axis of potentials, for example, as the first, second, or third sector of constant passivation, etc.

At the present time it is hardly possible to limit the scope of such definitions, or to establish rigidly the limits of their application. Nevertheless, it can be asserted that synonyms or antonyms for the same proposed terms, originating from other roots or concepts are unnecessary. This in particular, applies to the term activation, which would be freed for designating special cases of an increase in the rate of dissolution of a metal (for example, nickel) in the region of the potentials of its active state, where there is no basis for speaking of a lowering of the passivation [7-8]. Such terms as overpassivation or transpassivation may also become superfluous, since the cases they designate of the effect of the potential on the rate of dissolution of a passivated metal, can all be more accurately differentiated by the cases of hypopassivation, isopassivation, or dispassivation. (Of course, this does not mean that the above terms can or should be expelled from engineering practice, where they are ordinarily employed to designate an acceleration of corrosion beyond the limits of compensating passivation.)

e) One of the essential conditions in the development of the proposed terminology was to exclude from use terms which have already acquired some other meaning, or which sound too much like them. In many cases, this determined the final choice.

For example, the coefficient and index of passivation could be called the coefficient of passivity and index of passivity, if this did not make them sound too much like the concept of the degree of passivity, introduced by N. D. Tomashov, which is different in principle. In a couple with a superpassivated state it would be more correct, from a semantic point of view, to speak of a subpassive state, but this term has already been used in another sense by V. A. Kistyakovskii. The branches of hyper- and hypopassivation, in full accord with the meaning of these concepts, could be called under- and overpassivating; however, this would also prevent the wide use of the term overpassivating in its modern meaning.

The proposed terms obviously do not always combine in the best manner such advantages as simplicity, accessibility, semantic rigor, and a good sound; however, at the expense of this they exclude as far as possible the mixed mutual confusion of different concepts.

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