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The main aspects of the modern theory of the passive state of metals

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Abstract. The modern theoretical models of the active – passive transition and of the passive state of metals are surveyed. General regularities underlying the functioning mechanisms of passivating oxide layers as well as the adsorption and salt passivation are formulated. The bibliography includes 99 references.

I. Introduction

Despite numerous studies of the passive state of metals conducted over the last few decades and extensive experimental data collected in this field, there is still no consensus on the mechanism of formation [1–19] and functioning [20–25] of passivating (oxide) layers (hereinafter, PL). Passivating systems are thermodynamically non-equilibrium, therefore it is the *in situ* techniques that are the most efficient in their studies. Probably, this is one of the reasons for the frequent succession violations of the theoretical concepts related to the passivity problem, *i.e.*, earlier prevailing concepts are rejected and replaced with new ones. This substantiates a thorough comparative analysis of different passivity models.

The current understanding of the mechanism of the formation of a PL has evolved through several steps. The original concept elaborated by representatives of the German school of electrochemists [26–34] postulated the existence of an equilibrium phase oxide (the so-called phase-film concept). This implied that the passivation is caused by the mechanical shielding of the metal surface (*S*) by a thermodynamically equilibrium oxide layer, the constant passive current being in this case due to the chemical dissolution of the oxide. Gradually, serious contradictions to experiments were found within this concept. In particular, it appeared that the critical potentials observed in polarisation curves, *i.e.*, the activation and passivation potentials, differed from the potentials of formation of the respective oxides. For instance, in the case of iron, the difference is as large as 0.63 V (relative to the standard hydrogen electrode).[26] The experimentally established dependence of the passivation and activation potentials on the electrolyte composition, pretreatment of the metal surface and its properties also contradicted to the phase-film concept. The postulate on the constancy of the passive current, which is equivalent to the rate of the chemical dissolution of the passivating oxide, was disproved by the experimental results, which supported the electrochemical mechanism of transition of the passivated metal into a solution. However, despite the above contradictions, Vetter has proposed [26] an approach rationalising the stability and functioning of a PL. According to the experimental results,[19, 25, 26] the stability is due to the ion exchange between the PL and the electrolyte, which complies with the general conditions of the thermodynamical equilibrium between these two phases.

By the late 1970s, the self-contradictory, in general, phase-film model featured the correct idea that it is the oxide layer that plays a prominent role in the passivation mechanism. These concepts were further developed by other authors who considered the processes of ion transfer through the interfaces and the effects of ion vibrations in the nodes of a crystal lattice.[35–46] The processes of the cluster growth of oxide PL on iron, nickel, copper and other metals were investigated, and semiconducting properties of the PL and the mechanism of breakdown of the passive state were analysed. Popov and Sakha [47] formulated the following systematisation criteria for the models of the passive state.

1. Functioning of a passivating layer is stable provided that the equilibrium between the oxide and the electrolyte is achieved owing to the exchange of oxygen ions. Since the passivated metal undergoes anodic dissolution, the equilibrium with the electrolyte is incomplete and involves only the oxygen sublattice of the PL. Overall, the system oxide – electrolyte is non-equilibrium thermodynamically and thus it should be analysed taking into consideration kinetic factors.

2. The anion composition of a stationary PL remains constant; the anions drift gradually following the shift of the interface metal – oxide (M – O) due to the hopping diffusion. Meanwhile, the composition of the cation (metal) sublattice of the PL is continuously renewed due to transfer of the M_{ox}^{z+} ions into the electrolyte, which is accompanied by cleavage of their bonds with the O_{ox}^{2-} anions migrating in the bulk of the PL. A part of the M_{ox}^{z+} ions that diffuse through the PL from the interface M – O come into the electrolyte independently of the migration of the oxygen anions, which results in continuous disappearance of oxide cells within the PL.

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3. In a stationary mode, new oxide cells are continuously formed at the interface M–O, which compensates for their dissolution in the electrolyte. This provides the stability of the PL. The O_{ox}^{2-} anions are incorporated into the metal phase so that the compensating process of metal conversion into passivating oxide occurs. The volume of the latter typically exceeds the initial volume of the metal.

4. The metal conversion process gives rise to the spatial balance problem due to the difference in the volumes of the initial metal and the derived oxide. The balance is kept due to non-equilibrium cation vacancies at the interface oxide–electrolyte (O–E), which diffuse through the PL towards the interface M–O, where they convert into oxide anion vacancies.[19,25] This is the first role played by the non-equilibrium vacancies.

5. The passivity region has a finite dimension (length), which means that a passivity theory should describe the transpassive transition.[19,23,25] This necessitates accounting for the diffusion in the PL, which gives rise to a dependence of the concentration of non-equilibrium vacancies (*i.e.*, point defectiveness of the PL), which affects the PL length, on the anode potential φ. At low defect concentrations in the PL (*e.g.*, in the cases of Al, Ti, Ta and Zr), the transition potential can be appreciably high. This is the second role played by the non-equilibrium vacancies.

6. A passivity theory should explain from a unified standpoint the mechanisms of the processes that proceed at both interfaces, O–E and M–O, and the ion transfer between them.

The behaviour of metals in electrolyte solutions is characterised by a dependence of the current density of the anode dissolution i_a on the interface potential drop. A polarisation curve typical of such metals as Fe, Ni and Cr is shown schematically in Fig. 1.

The state of a metal surface in an electrolyte is determined by the value of φ. Four major states of a surface are known, *viz.*, active dissolution, active-passive transition, passive state and transpassive transition, to which correspond the following four ranges of the potential values: $\varphi < \varphi_0$, $\varphi_0 < \varphi < \varphi_a$, $\varphi_a < \varphi < \varphi_p$ and $\varphi > \varphi_p$ in Fig. 1. The characteristic points φ_0, φ_a and φ_p depend on the metal and electrolyte properties and on their interaction.

The present review describes the existing theories of the mechanism and kinetics of processes occurring in two most important and complex states, *viz.*, the active-passive transition and the passive state itself.

The multitude of corrosion phenomena cannot be covered within a single theory. The knowledge of the specificity of a system is a prerequisite of any study. For instance, one should determine the statistical scatter in the interatomic distances and bond directions within a PL to account for its incomplete structural ordering (*i.e.*, when it is amorphous). A microscopic-level mechanism of the metal–electrolyte interactions can also be highly specific to the system, *etc.*

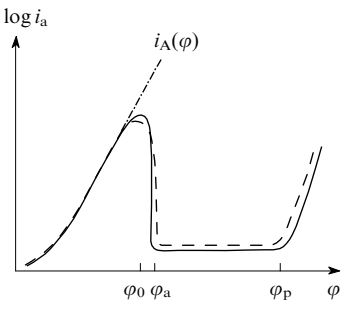


Figure 1. The experimental [26] (solid line) and theoretical [19] (dashed line) dependences of the current densities (i_a) corresponding to dissolution of a metal in an electrolyte on the anode potential;
$i_A(\varphi)$ is the current density in the Tafel region, $(\varphi_0 - \varphi_a)$ is the active-passive transition, $(\varphi_a - \varphi_p)$ is the passivity region.

Meanwhile, shapes of the polarisation curves are essentially identical for many metals: they show the aforementioned regions of the active and passive dissolution as well as of the active-passive and transpassive transitions. This indicates that it is possible (and thus desirable) to develop a unified theoretical model to include maximally simplified processes that govern the shapes of the polarisation curves. These processes include migration of ions through the interfaces PL–metal and PL–electrolyte and within the PL structure itself, an increase in the defectiveness of a PL upon an increase in the potential and the PL crystallisation during the active-passive transition. The kinetics of these processes differ depending on the potential and therefore one process dominates at any specific potential value, which gives rise to the alteration of the four above regions with an increase in the potential. The unified elementary model serves as a base ('framework'), which can be extended or modified to take into account specific factors for consideration of real systems. The author believes that exactly this purpose is pursued by the theory described below, which is open for any extensions and modifications.

II. Formation of a passivating oxide layer upon the active–passive transition ($\varphi_0 < \varphi < \varphi_a$)

According to numerous investigations, the compositions and structures of passivating layers on such metals as Fe, Cr, Ni, Mo and Cu correspond to those of metal oxides M_nO_m (*e.g.*, Fe_2O_3 or Fe_3O_4 in the case of iron). This is evident from both early studies of passivating layers using X-ray diffraction [26] and layer-by-layer etching and more recent methods of scanning tunnelling and optical microscopy.[45,46] Ellipsometry is becoming increasingly popular in studies of PL.[48–52] Especially promising is the ellipsometric topography method,[53,54] which exploits the dependence of the transmission coefficient of a PL on the radiation wavelength.

If an oxide PL possesses a disordered structure (*i.e.*, it is amorphous, as in the case of PL formed on Al, Ti, Ta, Zr and other metals), it can be described by statistical distributions of the interatomic distances and angular directions. However, the passive current density and other parameters can finally be expressed [25] through dispersions in the interatomic distances, angular directions and electric field strengths within the PL. The problem of the independent determination of these parameters is not solved as yet.

In agreement with the concepts formulated above and the general theory of heterogeneous nucleation,[1–18] it was suggested [18–21] that it is the two-dimensional nuclei of an oxide $MO_{z/2}$ that are formed in the initial step of PL formation on the surface of anodically dissolving metal. The formation of nuclei starts at the point φ_0 of the second region in the polarisation curve and is completed at φ_a in the end of this region (see Fig. 1).

In the steady-state mode, the probability I_e of nuclei generation (the number of nuclei per cm^2 per s) is an increasing function of the anode potential φ. Respectively, the steady-state coverage Θ_e of the surface S by nuclei also increases reaching the maximum value $\Theta_e(\varphi_a) \sim 1$ at φ_a.

A further increase in the potential actuates the transition into the passive region in which the thickness of the passivating layer $\delta(\varphi)$ increases with retention of the equilibrium between the oxide and the electrolyte. Indeed, an equilibrium potential φ_{pb} is settled in this range, whereas the surplus potential drop $(\varphi - \varphi_{pb})$ is expended within the thickness $\delta(\varphi)$ of the passivating layer.

This section considers modern models of the kinetics of formation of a PL, functional dependences of I_e, Θ_e and anodic current density i_a on the potential, the energy of the interparticle interactions, energetic heterogeneity of the metal surface and other parameters. These dependences reproduce a nearly vertical decrease (by 5–7 orders of magnitude) in the current upon the active-passive transition, *i.e.*, over a narrow range of potentials $\varphi_0 < \varphi < \varphi_a$ with a width of only 50–70 mV.

1. Kinetics of crystallisation of a passivating layer

Simulations of crystallisation of passivating layers on metal surfaces are based on the molecular-kinetic theory of nucleation. This theory developed in the mid 1970s [1–18] retains its significance to date. According to this theory, nuclei of the passivating layer are generated due to the stepwise attachment of particles to faces of the existing two-dimensional crystals (*i.e.*, prenuclei).

The molecular-kinetic theory [1–18] differs from two other thermodynamical theories by Volmer and Gibbs, which consider generation of nuclei as a mere condensation process without any structure formation. In contrast, the molecular-kinetic theory describes the stepwise attachment of particles to a crystal taking into account its surface structure, influence of neighbours and possible ordering into a crystal lattice. The key steps of these processes can be established [1–14] using simple models that approximate a crystal structure with a lattice of points or array of cubes. These models are based on the nearest-neighbour-interaction approximation, which assumes that the interactions between the real particles rapidly attenuate with an increase in the interparticle distances.

Let the interatomic distance in the crystal be r_0 and its size $a = nr_0$ changes due to elementary processes of the type $a \to a \pm r_0$, *i.e.*, due to attachment or detachment of a peripheral atomic row, which gives rise to the transformation of the crystal with an edge a to that with an edge $a \pm r_0$. If P and V are, respectively, the probabilities and the rates of the following transitions

$$P_{a \to a \pm r_0},\ P_{a \pm r_0 \to a}, \qquad V_{a \to a \pm r_0},\ V_{a \pm r_0 \to a} \tag{1}$$

n_a is the concentration of crystals with an edge a, then

$$V_{a \to a \pm r_0} = n_a P_{a \to a \pm r_0}, \qquad V_{a \pm r_0 \to a} = n_{a \pm r_0} P_{a \pm r_0 \to a}. \tag{2}$$

Provided that $a \gg r_0$, the following relations can be derived

$$P_{a + r_0 \to a} \simeq P_{a \to a - r_0}, \qquad P_{a \to a + r_0} \simeq P_{a - r_0 \to a}. \tag{3}$$

The resultant rates of the direct and reverse stationary transitions (I) are given by

$$I = V_{a - r_0 \to a} - V_{a \to a - r_0} = V_{a \to a + r_0} - V_{a + r_0 \to a} \tag{4}$$

or further

$$I = V_{a \to a + r_0} - V_{a + r_0 \to a} = n_a (P_{a \to a + r_0} - P_{a \to a - r_0}) - P_{a \to a - r_0}(n_{a + r_0} - n_a). \tag{5}$$

If a reaches the value $a_2 = n_2 r_0$, where n_2 is the number of particles in the edge of the two-dimensional nucleus, then

$$P_{a_2 \to a_2 + r_0} = P_{a_2 \to a_2 - r_0}.$$

Furthermore, for sufficiently large a

$$n_{a + r_0} - n_a \simeq \left(\frac{\mathrm{d}n_a}{\mathrm{d}a}\right) r_0, \qquad a \gg r_0. \tag{6}$$

Taking into account the equation (5), we obtain

$$I_e = \left(P_{a \to a - r_0} \frac{\mathrm{d}n_a}{\mathrm{d}a}\right)_{a = a_2}. \tag{7}$$

The first term in the right part of the equation can be expressed through the work of formation of the peripheral atomic row (W_{a_2})

$$P_{a_2 \to a_2 - r_0} = \mathrm{const}\left[a_2 \exp\left(-\frac{W_{a_2}}{kT}\right)\right]^2. \tag{8}$$

The exponent 2 means that a transition of a square nucleus with an edge a_2 into that with an edge $a_2 + r_0$ requires simultaneous attachment of two rows of particles to two adjoining edges; a_2^2 is the area of the substrate where the nucleus is formed. The second term can be determined from (3) and (4) reformulated as

$$\frac{n_{a + r_0} - n_a}{n_a - n_{a - r_0}} = \frac{P_{a \to a + r_0}}{P_{a \to a - r_0}}, \qquad \frac{P_{a \to a + r_0}}{P_{a \to a - r_0}} = \left[\exp\left(-\frac{W_a - W_a^*}{kT}\right)\right]^2. \tag{9}$$

Here, $(W_a^* - W_a)$ is the difference between the energies of attachment and detachment of a peripheral row of particles.[25] The equations (6), (8) and (9) can be transformed into

$$\ln\left(\frac{\mathrm{d}n_a}{\mathrm{d}a}\right)_{a + r_0} - \ln\left(\frac{\mathrm{d}n_a}{\mathrm{d}a}\right)_a = r_0 \frac{\mathrm{d}}{\mathrm{d}a}\left(\ln\frac{\mathrm{d}n_a}{\mathrm{d}a}\right), \tag{10}$$

$$r_0 \frac{\mathrm{d}}{\mathrm{d}a}\left(\ln\frac{\mathrm{d}n_a}{\mathrm{d}a}\right) = \left[\exp\left(-\frac{W_a - W_a^*}{kT}\right)\right]^2.$$

This according to Stranski *et al.* [2, 5] gives rise to

$$\left(\frac{\mathrm{d}n_a}{\mathrm{d}a}\right)_{a = a_2} = \mathrm{const}\,\exp\left(-\frac{W}{2kT}\right), \tag{11}$$

where $a_2 = n_2 r_0$, $W = 2n_2\Psi$ (Ψ is the interaction energy of two particles arranged at a distance r_0 from each other).

If n_2 is the number of particles in the edge of a square two-dimensional nucleus and $a_2 > a$, then the work of its formation can be represented as a product of the perimeter (L) and specific edge surface of the nucleus (κ)

$$W = L\kappa,$$

where $L = 4a_2$, $\kappa = \Psi/2r_0$. With account of the equations (7), (8) and (11), this gives rise to

$$I_e = \mathrm{const}\left[a_2 \exp\left(-\frac{W_{a_2}}{kT}\right)\right]^2 \exp\left(-\frac{W}{2kT}\right), \tag{12}$$

$$a_2 = n_2 r_0, \qquad W_{a_2} = \left(\Psi - \frac{\Psi}{n_2}\right), \qquad W = 2n_2\Psi.$$

The terms in the right part of the equation (12) account for structuring and condensation, respectively (through values of W_{a_2} and W).

It has been shown [19] that the number of particles in the edge of a nucleus of passivating oxide upon formation of the PL on the surface of an anodically dissolving metal is expressed as

$$n_2(\varphi) = \frac{\Psi}{ze(\varphi - \varphi_{p1}) + \Psi_0 - \Psi},$$

where φ_{p1} is the potential of formation of the passivating oxide $MO_{z/2}$, and Ψ_0 is the interaction energy of particles constituting the oxide nucleus with the metal substrate.

According to the equation (12), the rate of formation of the oxide is

$$I_e(\varphi) \simeq I_0 \exp\left[-\frac{2\Psi^2/kT}{ze(\varphi - \varphi_{p1}) + \Psi_0 - \Psi}\right]. \tag{13}$$

This formula is in agreement with that derived by Pangarov.[11]

2. Coverage of the metal surface with a passivating oxide

The process of coverage of the metal surface with a passivating oxide has been investigated by several authors.[19,26] The oxide nuclei are generated according to the reaction

$$M + \frac{z}{2}H_2O \rightleftharpoons MO_{z/2} + 2H^+ + ze. \tag{14}$$

Two different phases, *viz*., the metal M and an aqueous electrolyte, serve as sources of ions. This is a feature of the PL formation. At the active-passive transition, the nuclei of $MO_{z/2}$ are in equilibrium only with the metal phase. To realise the complete equilibrium, the interphase potential at the interface with the electrolyte should have a specific value, which is not yet reached at $\varphi < \varphi_a$. Therefore, the nuclei dissolve after certain (mean) lifetime.

Indeed, upon the active-passive transition, the transfer of the M^{z+} cations from $MO_{z/2}$ into the electrolyte (*i.e*., dissolution) is continuously compensated for by their transport from the metal substrate. This means that the cationic sublattice of the nucleus remains in a stationary state. From this viewpoint, the critical nucleus of $MO_{z/2}$, as has been said above, is in equilibrium with the metal M, and its size a_2 is determined by the standard equation

$$\sum_i \mu_i v_i = ze\varphi,$$

where μ_i and v_i are the chemical potential and stoichiometric coefficient of the ith reactant in the equation (14), respectively.

The oxygen sublattice of the nucleus of $MO_{z/2}$ is not in a stationary state, since the transfer of the O^{2-} anions into the electrolyte is not compensated for by other processes. This is accompanied by the following reactions

$$MO_{z/2} \longrightarrow M_{ad}^{z+} + \frac{z}{2}O^{2-},$$
$$M_{ad}^{z+} + ze^- \longrightarrow M,$$
$$O^{2-} + 2H^+ \longrightarrow H_2O.$$

The overall process can be formulated as

$$MO_{z/2} + zH^+ + ze \longrightarrow M + \frac{z}{2}H_2O.$$

The current density induced by oxygen removal is

$$I_O(\varphi_b) = \tag{15}$$
$$= i_{ex}\left\{\exp\left[\alpha_O \frac{z_O F}{RT}(\varphi_b - \varphi_{pb})\right] - \exp\left[-\beta_O \frac{z_O F}{RT}(\varphi_b - \varphi_{pb})\right]\right\},$$

where i_{ex} is the exchange current; α_O and β_O are the transfer coefficients ($\alpha_O + \beta_O = 1, z_O = 2$); F is the Faraday number; φ_b is the interface potential; φ_{pb} is the potential of the partial oxygen equilibrium. The equilibrium of the oxide with the electrolyte with respect to oxide ions is achieved only in the end of the transition, *i.e*., at the potential $\varphi \sim \varphi_a$ (see Fig. 1), the equilibrium being characterised by

$$\varphi_b(\varphi) = \varphi_{pb}, \tag{16}$$
$$\varphi = \varphi_a,$$

where φ_{pb} is defined by the condition

$$I_O(\varphi_{pb}) = 0. \tag{17}$$

Therefore, in the end of the active–passive transition, the dissolution of passivating nuclei gradually ceases, the first oxide monolayer becomes continuous, the coverage reaches the value of $\Theta_e(\varphi_a) = 1$, and gradual transition to the passive region occurs.[19,20]

However, this is still an incomplete physical description of the active–passive transition since the reaction (14) competes with the process of active anodic dissolution, which proceeds according to the scheme

$$M + vA^{z_A} \rightleftharpoons (MvA)^{-vz_A+\sigma} + \sigma e, \tag{18}$$
$$(MvA)^{-vz_A+\sigma} \longrightarrow M^{z+} + vA^{z_A-} + (z-\sigma)e, \tag{19}$$

A^{z_A-} are activating anions from the electrolyte and σ is the fraction of the electron charge involved in the chemisorption bonding. The metal surface is covered not only with two-dimensional nuclei [the degree of coverage is $\Theta_e(\varphi)$], but with surface complexes $(MvA)^{-vz_A+\sigma}$ [the degree of coverage is $\Theta_a(\varphi)$] as well. The stationary equations for $\Theta_e(\varphi)$ and $\Theta_a(\varphi)$ can be written as

$$(1 - \Theta_a - \Theta_e)K_a(\varphi) = \Theta_a K_i(\varphi), \tag{20}$$
$$(1 - \Theta_a - \Theta_e)I_e = \Theta_e I_O(\varphi),$$

where $K_a(\varphi)$, $K_i(\varphi)$ are the rates of adsorption of activating anions A^{z_A-} and ionisation of the intermediate complexes $(MvA)^{-vz_A+\sigma}$, respectively,

$$K_a(\varphi) = k_a C_a^v \exp\left[\frac{\alpha_a(z_A - \sigma)F\varphi}{RT}\right],$$
$$K_i(\varphi) = k_i \exp\left[\frac{\alpha_i(z_M - \sigma)F\varphi}{RT}\right].$$

k_a, C_a^v and k_i are preexponential factors; α_a and α_i are the transfer coefficients of anions and ions of the intermediate complexes, respectively.

Therefore,

$$\Theta_e = \frac{I_e}{I_O + (1 + \Theta_a')I_e}(1 - \Theta_a'), \tag{21}$$
$$\Theta_a = (1 - \Theta_e)\Theta_a',$$
$$\Theta_a' = \frac{K_a(\varphi)}{K_a(\varphi) + K_i(\varphi)}. \tag{21a}$$

The anodic currents (rates) $I_e(\varphi)$ and $i_a(\varphi)$ corresponding to the processes (14) and (19) differently depend on the potential φ_0. At low φ, the reactions (19) dominate and the coverage $\Theta_e(\varphi)$ is small. With an increase in φ, the rate $I_e(\varphi)$ increases and $I_e(\varphi_0) \sim i_a(\varphi_0)$ at $\varphi = \varphi_0$ (see Fig. 1). Starting from this moment, two-dimensional nuclei are predominantly generated owing to the strong dependence of I_e on φ, and the current density of anodic dissolution decreases by several orders of magnitude with a change in φ in a narrow range of the order of tens of mV. The total current density $j(\varphi)$ caused by the transfer of the M^{z+} ions into the electrolyte is described by the equation

$$j(\varphi) = \Theta_a(\varphi)K_i(\varphi) + \left[I_O(\varphi_b) + i_O(\varphi_b)\right]\Theta_e(\varphi), \tag{22}$$

where

$$i_O(\varphi_b) = i_0 \exp\left(\frac{\alpha z_M F}{RT}\varphi_b\right),$$

i_0 is the preexponential factor and α is the particle transfer coefficient.

The formula (22) takes into account all mechanisms contributing to the value of $j(\varphi)$. The first term corresponds to the active dissolution; the second one is due to dissolution of the nuclei at a rate $I_O(\varphi_b)$, which results in flaking away of the M_{ox}^{z+} ions; the third term accounts for the metal ion transfer through the nuclei into the solution and their migration through the two-dimensional passivating oxide layer; it predominates for the passive region at $\varphi > \varphi_a$.

3. The energetic inhomogeneity of a metal surface

The concepts described above underlie the modern theory of the PL formation. A further step in this approximation consists of consideration of the energetic inhomogeneity of a surface, which implies that different areas of a surface ΔS_i interact with the electrolyte with different strengths and generate different current densities of anodic dissolution. A variable energy Ψ_{0i} can be

attributed to every sufficiently small area and the overall surface will thus be characterised by a sum

$$S = \sum_i \Delta S_i(\Psi_{0i})$$

or integral

$$S = \int_{\varepsilon_{\min}}^{\varepsilon_{\max}} \mathrm{d}s(\Psi_{0i}),$$

the integration limits $\varepsilon_{\max}$ and $\varepsilon_{\min}$ depend on the properties of the metal. The electrode processes can be described using the specially specified autonomous function $f(\Psi_{0i})$ of statistical distribution of energies Ψ_{0i} over the surface, the local current density $j(\varphi, \Psi_{0i})$ and the local coverage $\Theta(\varphi, \Psi_{0i})$. Their integral values are determined by the following equations

$$\int_{\varepsilon_{\min}}^{\varepsilon_{\max}} f(\Psi_{0i})\mathrm{d}\Psi_{0i} = 1, \tag{23}$$

$$i_{\mathrm{a}}(\varphi) = \int_{\varepsilon_{\min}}^{\varepsilon_{\max}} \mathrm{d}\Psi_{0i} f(\Psi_{0i}) j_i(\varphi, \Psi_{0i}),$$

$$\Theta_{\mathrm{e}}(\varphi) = \int_{\varepsilon_{\min}}^{\varepsilon_{\max}} \mathrm{d}\Psi_{0i} f(\Psi_{0i}) \Theta_{\mathrm{e}i}(\varphi, \Psi_{0i}).$$

The energy of interaction of particles constituting a nucleus with the metal Ψ_{0i} is contained in the probability (13) and, consequently, in all other parameters. The local coverages and current densities can be expressed as follows:

$$\Theta_{\mathrm{e}i}(\varphi, \Psi_{0i}) = \frac{I_{\mathrm{e}i}(\varphi, \Psi_{0i})[1 - \Theta'_{\mathrm{a}}(\varphi)]}{I_{\mathrm{O}}(\varphi_{\mathrm{b}}) + [1 - \Theta'_{\mathrm{a}}(\varphi)] I_{\mathrm{e}i}(\varphi, \Psi_{0i})}, \tag{24}$$

$$\Theta_{\mathrm{a}i}(\varphi, \Psi_{0i}) = \big[1 - \Theta_{\mathrm{e}i}(\varphi, \Psi_{0i})\big]\Theta'_{\mathrm{a}}(\varphi),$$

$$I_{\mathrm{e}i}(\varphi, \Psi_{0i}) = I_0 \exp\left[-\frac{2\Psi^2/kT}{ze(\varphi - \varphi_0) + \Psi_{0i} - \Psi}\right],$$

$$j_i(\varphi, \Psi_{0i}) = \Theta_{\mathrm{a}i}(\varphi, \Psi_{0i}) K_{\mathrm{i}}(\varphi) + \big[I_{\mathrm{O}}(\varphi_{\mathrm{b}}) + i_{\mathrm{O}}(\varphi_{\mathrm{b}})\big]\Theta_{\mathrm{e}i}(\varphi, \Psi_{0i}).$$

The formulas (23) and (24) together determine the total coverage $\Theta_{\mathrm{e}}(\varphi)$ of the surface S with the two-dimensional passivating oxide layer and the total anodic current density $i_{\mathrm{a}}(\varphi)$ within the region of the active–passive transition. The system of equations (23), (24) and (21a) gives rise to

$$\Theta_{\mathrm{e}}(\varphi) = \int_{\varepsilon_{\min}}^{\varepsilon_{\max}} \mathrm{d}\Psi_{0i} f(\Psi_{0i}) \Theta_{\mathrm{e}i}(\varphi, \Psi_{0i}),$$

$$i_{\mathrm{a}}(\varphi) = \int_{\varepsilon_{\min}}^{\varepsilon_{\max}} \mathrm{d}\Psi_{0i} f(\Psi_{0i}) j_i(\varphi, \Psi_{0i}),$$

$$i_{\mathrm{A}}(\varphi) = \frac{K_{\mathrm{a}}(\varphi) K_{\mathrm{i}}(\varphi)}{K_{\mathrm{a}}(\varphi) + K_{\mathrm{i}}(\varphi)},$$

$$i_{\mathrm{a}}(\varphi) = i_{\mathrm{A}}(\varphi)\big[1 - \Theta_{\mathrm{e}}(\varphi)\big] + \big[I_{\mathrm{O}}(\varphi_{\mathrm{b}}) + i_{\mathrm{O}}(\varphi_{\mathrm{b}})\big]\Theta_{\mathrm{e}}(\varphi),$$

where $i_{\mathrm{A}}(\varphi)$ corresponds to the current density of the active dissolution of those parts of the metal surface, which are not covered by passivating two-dimensional nuclei.

The latter expression represents the general formula for the calculation of the dissolution current $i_{\mathrm{a}}(\varphi)$ over the whole range of the potential. The calculations using this formula (see the dashed line in Fig. 1) agree with the experimental data.[26]

The functions $i_{\mathrm{A}}(\varphi)$ and $\Theta_{\mathrm{e}}(\varphi)$ play the key role in the prepassive region $\varphi < \varphi_0$. According to calculations, it is the active dissolution that makes the dominant contribution to the total anodic current $i_{\mathrm{a}}(\varphi)$ before the maximum of the polarisation curve (*i.e.*, at $\varphi < \varphi_0$) because $\Theta_{\mathrm{e}}(\varphi)$ is small and $i_{\mathrm{A}}(\varphi)$ becomes more important. After the maximum, *i.e.*, in the region of the active–passive transition, the coverage $\Theta_{\mathrm{e}}(\varphi)$ rapidly increases and the active dissolution is gradually replaced by the formation of two-dimensional nuclei. A continuous monolayer with $\Theta_{\mathrm{e}} \approx 1$ is completed at $\varphi = \varphi_{\mathrm{a}}$ and the passivity region itself starts afterwards ($\varphi > \varphi_{\mathrm{a}}$).

III. Processes in a steady-state passivating oxide layer at $\varphi_{\mathrm{a}} < \varphi < \varphi_{\mathrm{p}}$

The processes proceeding in a passivating layer have been analysed in numerous studies.[19, 22–25, 37–47, 55–59]. According to the concepts developed in these works, the structure of a PL consists of two interpenetrating ionic sublattices (metallic and oxygen). The ions electrodiffuse *via* vacancies in the respective sublattices. Overall, the composition of PL formed on hard metals (Fe, Ni, Cr, Cu, *etc.*), as has been mentioned above, corresponds to oxides $\mathrm{M}_n\mathrm{O}_m$. The ions constituting these oxides are marked with the subscript index 'ox', *i.e.*,

$$\mathrm{M}^{z+} \longrightarrow \mathrm{M}^{z+}_{\mathrm{ox}},$$

$$\mathrm{O}^{2-} \longrightarrow \mathrm{O}^{2-}_{\mathrm{ox}}.$$

Positions of the PL and interfaces M–O and O–E are shown in Fig. 2. To provide stability of the PL, the interphase (crystal–electrolyte) equilibrium conditions should be met at the external interface O–E for both the cation and anion sublattices.[19, 26, 27] For a general case of an ionic crystal $\mathrm{N}_n\mathrm{P}_m$, these conditions are derived from the expressions for the ion current densities i_{N} and i_{P}.

$$i_{\mathrm{N}} = \overrightarrow{k}_{\mathrm{N}} \exp\left(\alpha_{\mathrm{N}} \frac{z_{\mathrm{N}}\mathrm{F}}{RT}\varphi_{\mathrm{b}}\right) - \overleftarrow{k}_{\mathrm{N}} C_{\mathrm{N}} \exp\left(-\beta_{\mathrm{N}} \frac{z_{\mathrm{N}}\mathrm{F}}{RT}\varphi_{\mathrm{b}}\right), \tag{25}$$

$$i_{\mathrm{P}} = \overrightarrow{k}_{\mathrm{P}} C_{\mathrm{P}} \exp\left(\alpha_{\mathrm{P}} \frac{z_{\mathrm{P}}\mathrm{F}}{RT}\varphi_{\mathrm{b}}\right) - \overleftarrow{k}_{\mathrm{P}} \exp\left(-\beta_{\mathrm{P}} \frac{z_{\mathrm{P}}\mathrm{F}}{RT}\varphi_{\mathrm{b}}\right),$$

$$\alpha_{\mathrm{P}} + \beta_{\mathrm{P}} = 1,$$

$$\alpha_{\mathrm{N}} + \beta_{\mathrm{N}} = 1,$$

where $\overrightarrow{k}$ and $\overleftarrow{k}$ are the rate constants of the direct and reverse reactions of the ion transfer into the electrolyte solution; α and β are the transfer coefficients; C_{N}, C_{P}, z_{N} and z_{P} are the concentration and charge numbers, respectively, of ions $\mathrm{N}^{z_{\mathrm{N}}+}$ and $\mathrm{P}^{z_{\mathrm{P}}-}$ that constitute $\mathrm{N}_n\mathrm{P}_m$ crystal; φ_{b} is the interface O–E potential.

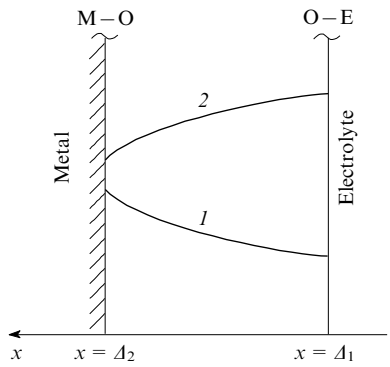


Figure 2. A scheme of ion concentration distributions $N_{\mathrm{M}}(x)$ (*1*) and $N_{\mathrm{O}}(x)$ (*2*) in a passivating layer.
$\delta(\varphi) = \Delta_2 - \Delta_1$.

At the equilibrium, the currents i_N and i_P should be equal to zero, and the potential φ_b should have its equilibrium value φ_{pb}, *i.e.*,

$$i_N = 0,$$
$$i_P = 0,$$
$$\varphi_b = \varphi_{pb}.$$

This gives rise to the following two expressions for φ_{pb}

$$\varphi_{pb} = \frac{RT}{z_N F}\left(\ln \frac{\overleftarrow{k}_N C_N}{\overrightarrow{k}_N}\right), \tag{26}$$

$$\varphi_{pb} = \frac{RT}{z_P F}\left(\ln \frac{\overleftarrow{k}_P}{\overrightarrow{k}_P C_P}\right).$$

They are compatible provided that

$$C_N^n C_P^m = \left(\frac{\overrightarrow{k}_N}{\overleftarrow{k}_N}\right)^n \left(\frac{\overleftarrow{k}_P}{\overrightarrow{k}_P}\right)^m, \tag{27}$$

$$z_N n = z_P m.$$

If these conditions are not met, no equilibrium is possible between the electrolyte and the ionic crystal and the latter disintegrates.

The situation is more complicated in the case of a PL. Indeed, since the anodic current is non-zero in the passivity region $\varphi_a \leqslant \varphi \leqslant \varphi_p$, which means that the passivated metal dissolves at a low rate, the metal sublattice of the PL appears non-equilibrium with respect to the electrode.

Notwithstanding, according to experiments, passivating layers are stable, and the anodic current does not depend on the potential in the range $\varphi_a \leqslant \varphi \leqslant \varphi_p$ (see Fig. 1).

These experimentally established facts are only possible provided that two conditions are met. First, the oxygen sublattice should be in equilibrium with the electrolyte in a steady-state mode, *i.e.*, a partial equilibrium PL–electrolyte should be realised, which means that

$$i_O = 0, \tag{28}$$
$$i_M \equiv i_a \neq 0,$$

where i_O and i_M are the current densities of the O_{ox}^{2-} and M_{ox}^{z+} ions, respectively. Second, the transfer of the M_{ox}^{z+} ions from the PL to the electrolyte should be compensated for by their continuous supply from the bulk of the PL to its border (that is the interface O–E). The interface M–O serves as a source of the M_{ox}^{z+} ions.

Therefore, all the processes proceeding at the interfaces and in the bulk of the PL are self-consistent. Three components can be distinguished in the mechanism of a PL functioning, *viz.*, the interaction of the interface O–E with the electrolyte, which initiates detachment of the M_{ox}^{z+} ions from the PL lattice and their transfer into the electrolyte; the ion transfer through the bulk of PL described above; the processes at the interface M–O where the O_{ox}^{2-} ions diffuse into the metal and form new cells M_nO_m. These three components and the self-consistency between them have been considered elsewhere.[19,23–25]

1. The interaction between metal and electrolyte at the interface oxide–electrolyte

Activating anions A^{z_A-} and water molecules are adsorbed at the metal surface S and form molecular complexes $(MA \cdot v\,H_2O)^{z-z_A+\sigma}$ with the M_{ox}^{z+} ions. This is accompanied by weakening of binding of the surface sites M_{ox}^{z+} with the surface itself, *i.e.*, the energy barrier to their transfer into the electrolyte is decreased. The molecular complexes are characterised by a mean lifetime τ on the metal surface; the M^{z+} ions constituting the complexes detach from the surface and pass into the electrolyte. The mechanism of the surface disintegration (anodic dissolution) can be represented with a two-step scheme

$$M_{ox}^{z+} + vH_2O + A^{z_A-} \rightleftharpoons (MA\,v\,H_2O)_{ad}^{z-z_A+\sigma} + \sigma e, \tag{29}$$
$$(MA\,v\,H_2O)_{ad}^{z-z_A+\sigma} \longrightarrow M^{z+} + v\,H_2O + A^{z_A-} - \sigma e.$$

The A^{z_A-} species and H_2O molecules manifest catalytic activity, and the resultant current density i_a of the M^{z+} ions in the steps (29) (that is the number of the elementary acts of the particle detachment per s per cm^2, *i.e.*, $i_a \sim 1/\tau$) is given by

$$i_a \simeq kN_M[A^{z_A-}] \exp\left[-\frac{\varepsilon - \alpha(z-\sigma)F\varphi_b}{RT}\right], \tag{30}$$

where k is the rate constant of the second step of the reaction (29); $N_M \simeq 10^{16}$ cm^{-2} is the concentration of the M_{ox}^{z+} ions on the surface S; ε is the binding energy of the complexes, which depends on the existence of A^{z_A-}; α is the transfer coefficient describing the asymmetry of the potential drop ($\alpha < 1$). The involvement of the A^{z_A-} anions from the electrolyte in the elementary acts of the anodic dissolution has been established experimentally.

The equilibrium exchange of the oxide ions between the PL and the electrolyte, which provides the stability of the PL, is the second stationary process proceeding on the metal surface[26]

$$O^{2-} \rightleftharpoons O_{ox}^{2-}. \tag{31}$$

This exchange realises a partial equilibrium between the electrolyte and the PL. It determines the equilibrium potential $\varphi_{pb} = \varphi_b$ of the passive region, and, consequently, independence of the current corresponding to the anodic dissolution of the passivated metal of the anode potential. Water molecules dissociating upon adsorption on the metal surface serve as a source of ions in the process (31). A more detailed scheme of the oxide ion exchange is given below:

$$(H_2O)_{ad} \rightleftharpoons 2H^+ + O_{ad}^{2-}, \tag{32}$$
$$O_{ad}^{2-} \rightleftharpoons O_{ox}^{2-};$$

the overal process can be represented as

$$(H_2O)_{ad} \rightleftharpoons 2H^+ + O_{ox}^{2-}. \tag{33}$$

The current density corresponding to the reaction (33) is described by the equation

$$i_O = \overrightarrow{k}[H_2O]N_M \exp\left(\frac{\alpha_O z_O F\varphi_b}{RT}\right) - \overleftarrow{k} N_O[H^+]^2 \exp\left(-\frac{\beta_O z_O F\varphi_b}{RT}\right),$$

where N_M and N_O are the surface concentrations of the M_{ox}^{z+} and O_{ox}^{2-} ions, respectively, on the metal surface, $\alpha_O + \beta_O = 1$, $z_O = 2$. If the equilibrium (33) is reached, then

$$i_O = 0, \tag{34}$$
$$\varphi_b = \varphi_{pb}.$$

This gives rise to

$$\varphi_{pb} = \frac{RT}{z_O F}\ln\left(\frac{\overleftarrow{k}}{\overrightarrow{k}}\frac{N_O}{N_M}\frac{[H^+]^2}{[H_2O]}\right). \tag{35}$$

The value of φ_{pb} can be estimated using the following relations:[19]

$$\varphi = \varphi_{pb} + \Delta\varphi, \tag{35a}$$
$$\Delta\varphi = E\delta(\varphi),$$
$$E = \frac{\varphi_p - \varphi_{pb}}{\delta_p},$$

where $\Delta\varphi$ and E are the potential drop and decrease in the electric field strength within the PL; δ_p is the thickness of the PL at $\varphi = \varphi_p$ (see Fig. 1).

The equation (35a) gives rise to

$$\varphi_{pb} = \frac{\varphi_a \delta_p - \varphi_p \delta_a}{\delta_p - \delta_a}, \tag{35b}$$

where δ_a is the thickness of the PL in the beginning of the passive region.

Since the equilibrium interphase potential (35) is constant in the passive region $\varphi_a \leqslant \varphi \leqslant \varphi_p$, the thickness of the PL depends on φ. It can be determined using the Günterschulz formula for the current density of the M^{z+} ions through the interface M–O,

$$i_b = i_{b0} \exp(\beta E), \tag{36}$$

where

$$E = \frac{\varphi - \varphi_{pb}}{\delta(\varphi)},$$

$$\beta = \alpha_b a_M \frac{zF}{RT},$$

α_b is the transfer coefficient at the interface PL–metal, and a_M is the sublattice constant of the PL. In a steady-state mode, flows of the metal ions through the interfaces M–O and O–E are the same, *i.e.*,

$$i_a = i_b. \tag{37}$$

The equations (30), (36) and (37) give rise to

$$\delta(\varphi) = \beta \frac{\varphi - \varphi_{pb}}{\ln(i_a / i_{b0})}. \tag{38}$$

A surplus potential drop $\Delta\varphi = \varphi - \varphi_{pb}$ is realised on a thickness $\delta(\varphi)$.

2. Ion transfer in the bulk of the passivating layer

When an M_{ox}^{z+} metal ion passes from the PL lattice to the electrolyte, its original bonds to the neighbouring O_{ox}^{2-} counterions are broken, and thus the oxide unit cell is destroyed. This gives rise to a gradual drift of the interface O–E towards metal in a steady-state mode. Simultaneously, the dynamical equilibrium (31) is realised and consequently the anion composition of the PL remains constant.

At the inner interface M–O, the O_{ox}^{2-} ions constantly diffuse into the metal structure forming new PL cells and compensating for their disappearance from the outer interface O–E. The diffusion rate is determined by the formula for the current density i_b of the M^{z+} ions [see formula (36)]. The emerging oxide cells replace the metal M, which means that the metal is converted layer-by-layer into oxide. A part of the M^{z+} metal ions located near the interface M–O are transferred through it to the PL and converted into the M_{ox}^{z+} ions, which further migrate *via* vacancies of the metal sublattice towards the electrolyte. As a result, the near-interface area of the metal is enriched with vacancies, which are required for diffusion of the O_{ox}^{2-} ions into the metal lattice.

These processes result in a drift of the interface M–O towards the metal. If a metal layer with a thickness of Δx disappears for a time Δt, the interface M–O also drifts by Δx at a velocity of

$$\upsilon = \frac{\Delta x}{\Delta t} = \frac{i_b}{z_M F} \frac{\mu}{\rho_0}, \tag{39}$$

where μ and ρ_0 are the amount (in moles) and density of the metal, respectively. The whole anionic composition of the PL, *i.e.*, its oxygen sublattice, drifts together with the interface.

Thus the M_{ox}^{z+} and O_{ox}^{2-} ions move in the bulk of the PL in the opposite directions. This provides self-consistency in the kinetic and structural interrelations between the interfaces O–E and M–O.[37–43] The ratio of the electrodiffusion flows of these ions is determined by the strengths of their interactions with the electrolyte and the metal.

Thus, the mutually compensating processes of the PL formation and disintegration proceed at the interfaces O–E and M–O in the steady-state mode. The thickness of the PL remains constant at a level sufficient to make a surplus potential drop $\Delta\varphi = \varphi - \varphi_{pb}$, where φ_{pb} is the potential of the interface O–E, which remains constant over the whole passive region. As a result, the current density i_a corresponding to the transfer of the M_{ox}^{z+} ions into the electrolyte is independent of the anode potential. The ion transfer through the bulk of the PL proceeds by the mechanism of electrodiffusion in a strong electric field (in strong electric fields, the Ohm law is violated), this results in a specific concentration distribution of the M_{ox}^{z+} and O_{ox}^{2-} ions and non-equilibrium vacancies over the PL lattice. The ions move *via* vacancies of their own sublattices, their occurrence in foreign sublattices can be considered as fluctuations, since the own sublattices provide sufficient amount of free sites. In this context, the anion and cation sublattices can be regarded as closed subsystems.

a. Electric field in the passivating layer

Let us introduce the following notations $N_M(x)$, $N_O(x)$, $N_{Mv}(x)$ and $N_{Ov}(x)$ for the concentrations of the M_{ox}^{z+} and O_{ox}^{2-} ions and the non-equilibrium vacancies of the metal $V_M(x)$ and oxygen $V_O(x)$ in the respective sublattices of the PL, respectively, *i.e.*,

$$N_M = [M_{ox}^{z+}], \tag{40}$$

$$N_O = [O_{ox}^{2-}],$$

$$C_M(x) = \frac{N_{Mv}}{N_{Mg}}, \tag{40a}$$

$$C_O(x) = \frac{N_{Ov}}{N_{Og}},$$

where N_{Mg} and N_{Og} are the densities of the total number of sites in the cation and anion sublattices

$$N_{Mg} = N_M(x) + N_{Mv}(x), \tag{41}$$

$$N_{Og} = N_O(x) + N_{Ov}(x).$$

The bulk charge density $\rho(x)$ in the PL can be represented as a sum of the ion and electron terms [55–57]

$$\rho(x) = \rho_i(x) + \rho_e(x),$$

where

$$\rho_i(x) = e\left[z_M N_M(x) - z_O N_O(x)\right],$$

$$\rho_e(x) = -eC_e(x),$$

$C_e(x)$ is the electron concentration in the PL. The electric field potential in a layer $\varphi_l(x)$ is given by the Poisson equation

$$\frac{d^2\varphi_l(x)}{dx^2} = -\frac{4\pi}{\varepsilon_l}\rho(x),$$

$$\varphi_l(\Delta_1) = \varphi_{pb},$$

$$\varphi_l(\Delta_2) = \varphi,$$

$$\Delta_1 \leqslant x \leqslant \Delta_2(\varphi),$$

ε_l is the dielectric constant of the PL, Δ_1 and Δ_2 are coordinates of the interfaces O–E and M–O, respectively (see Fig. 2). A solution of the Poisson equation can be written as

$$\varphi_l(Z) = \varphi_{pb} + (\varphi - \varphi_{pb})Z + \Phi_0 Q_0(Z), \tag{41a}$$

where

$$Z = \frac{x - \Delta_1}{\delta(\varphi)},$$

$$\delta(\varphi) = \Delta_2(\varphi) - \Delta_1,$$

$$0 \leqslant Z \leqslant 1,$$

$$\Phi_0 = \frac{4\pi F z_M}{\varepsilon_l}\left(\frac{N_{Mg}}{N_A}\right)\delta^2(\varphi),$$

(N_A is the Avogadro number),

$$Q_0(Z) = \int_0^Z \mathrm{d}\eta \int_0^\eta \mathrm{d}\xi \bar{\rho}(\xi) - Z \int_0^1 \mathrm{d}\eta \int_0^\eta \mathrm{d}\xi \bar{\rho}(\xi), \tag{41b}$$

$$\bar{\rho}(Z) = n_{\mathrm{M}}(Z) - n_{\mathrm{O}}(Z) - n_{\mathrm{e}}(Z),$$

$$n_{\mathrm{M}}(Z) = \frac{N_{\mathrm{M}}(Z)}{N_{\mathrm{Mg}}},$$

$$n_{\mathrm{O}}(Z) = \frac{N_{\mathrm{O}}(Z)}{N_{\mathrm{Og}}},$$

$$n_{\mathrm{e}}(Z) = \frac{C_{\mathrm{e}}(Z)}{z_{\mathrm{M}} N_{\mathrm{Mg}}}.$$

The parameter $\Phi_0 \sim \delta^2(\varphi)$ is small and thus the last term in the equation (41a) can be neglected. In the physical sense, this is due to the fact that the field of the bulk charge in the PL is small as compared to the field induced by the interphase potential drop. Taking this into account, the electric field strength in the PL can be rewritten as

$$\vec{E} = -\vec{k_0}\left[-\frac{\partial\varphi_{\mathrm{l}}(Z)}{\partial x}\right],$$

and

$$\frac{\partial\varphi_{\mathrm{l}}(Z)}{\partial x} \simeq \frac{\varphi - \varphi_{\mathrm{pb}}}{\delta(\varphi)},$$

which is in agreement with the expressions (36) and (38).

b. Electrodiffusion of ions of the passivating layer in a strong electric field

The ion transfer in a PL is determined [37, 55–59] by the kinetics of the M_{ox}^{z+} ions transfer into the electrolyte and diffusion of the O_{ox}^{2-} ions into the metal. Owing to the transfer, specific concentration distributions of the $N_{\mathrm{M}}(x,t)$ and $N_{\mathrm{O}}(x,t)$ ions (see Fig. 2) and $N_{\mathrm{Mv}}(x,t)$ and $N_{\mathrm{Ov}}(x,t)$ vacancies are settled, which depend on the anode potential φ. They characterise the concentration of point defects in the PL, *i.e.*, C_{M} and C_{O} [see relations (40a)].

The defectiveness determines the stability of the PL structure. If the critical value C_{c} is exceeded, the structure disintegrates. This is achieved at a potential φ_{p}, which corresponds to the transpassive transition (see Fig. 1). Theoretical estimation of the values of φ_{p} and φ_{a} is one of the most important problems.[60–72]

The expressions for the electrodiffusion flows j_{M} and j_{O} of the M_{ox}^{z+} and O_{ox}^{2-} ions through the PL lattice assume a strong electric field E. The ions move *via* vacancies of their own sublattices. The sum of flows of ions $j_{\mathrm{M}}(x)$ and $j_{\mathrm{O}}(x)$ and non-equilibrium vacancies $j_{\mathrm{Mv}}(x)$ and $j_{\mathrm{Ov}}(x)$ is equal to zero

$$j_{\mathrm{M}}(x) + j_{\mathrm{Mv}}(x) = 0, \tag{42}$$
$$j_{\mathrm{O}}(x) + j_{\mathrm{Ov}}(x) = 0.$$

A microscopic-level scheme of ion hopping between the neighbouring atomic planes separated by interatomic distances a_{M} and a_{O} can be applied [19, 37] to determine $j_{\mathrm{M}}(x)$ and $j_{\mathrm{O}}(x)$. Typically, three consecutive atomic planes I, II and III with coordinates x and $x \pm a$ (Fig. 3) are considered within a PL lattice. The probabilities of direct and reverse ion jumps between them are proportional to the concentrations $N_{\mathrm{M}}(x)$ or $N_{\mathrm{O}}(x)$, to the number of unoccupied sites in the respective planes [*i.e.*, concentrations $C_{\mathrm{M}}(x)$ and $C_{\mathrm{O}}(x)$] and to the activation energy of the jumps W_0. An electric field E decreases the activation energy W_0 by $\pm\alpha z \mathrm{F} a \mathrm{e} E$ (or, on the contrary, increases, if an ion moves against the field direction).[37] Taking this into account, the required flows of cations $j_{\mathrm{M}}(x)$ and anions $j_{\mathrm{O}}(x)$ can be represented as sums of the flows corresponding to direct and reverse jumps

$$j_{\mathrm{M}}(x) = j^{\mathrm{M}}_{\mathrm{II}\to\mathrm{III}} - j^{\mathrm{M}}_{\mathrm{III}\to\mathrm{II}}, \tag{43}$$

$$j_{\mathrm{O}}(x) = j^{\mathrm{O}}_{\mathrm{I}\to\mathrm{II}} - j^{\mathrm{O}}_{\mathrm{II}\to\mathrm{I}}.$$

The equations for j_{M} and j_{O} can be rewritten explicitly

$$j_{\mathrm{M}} = a_{\mathrm{M}} v \left[N_{\mathrm{M}}(x) C_{\mathrm{M}}(x + a_{\mathrm{M}}) \exp\left(-\frac{W_{\mathrm{M0}} + \Delta W_{\mathrm{M}}}{kT}\right) - \right. \tag{44}$$
$$\left. - N_{\mathrm{M}}(x + a_{\mathrm{M}}) C_{\mathrm{M}}(x) \exp\left(-\frac{W_{\mathrm{M0}} - \Delta W_{\mathrm{M}}}{kT}\right)\right],$$

$$j_{\mathrm{O}} = a_{\mathrm{O}} v \left[N_{\mathrm{O}}(x - a_{\mathrm{O}}) C_{\mathrm{O}}(x) \exp\left(-\frac{W_{\mathrm{O0}} + \Delta W_{\mathrm{O}}}{kT}\right) - \right. \tag{44a}$$
$$\left. - N_{\mathrm{O}}(x) C_{\mathrm{O}}(x - a_{\mathrm{O}}) \exp\left(-\frac{W_{\mathrm{O0}} - \Delta W_{\mathrm{O}}}{kT}\right)\right],$$

where v is the number of vibrational periods of ions in occupied sites; ΔW_{M} and ΔW_{O} are the changes in the energy barriers for ion hopping between the planes I–III (see Fig. 3) when the electric field with a strength E is applied.

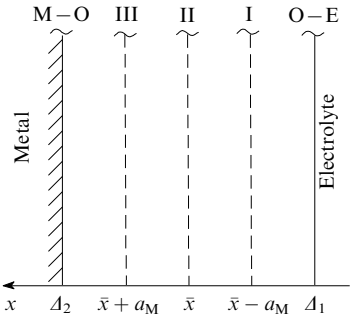


Figure 3. An arrangement of the atomic planes I–III in a passivating layer;
a_{M} is the interatomic distance within the metallic sublattice (a_{O} is the respective distance within the oxygen sublattice).

By expanding the functions $N_{\mathrm{M}}(x \pm a_{\mathrm{M}})$, $C_{\mathrm{M}}(x \pm a_{\mathrm{M}})$, $N_{\mathrm{O}}(x \pm a_{\mathrm{O}})$ and $C_{\mathrm{O}}(x \pm a_{\mathrm{O}})$ into series and taking only linear terms, the following final expressions for j_{M}, j_{O}, diffusion coefficients (D_{M} and D_{O}), ΔW_{M} and ΔW_{O} can be obtained

$$j_{\mathrm{M}} \simeq -\frac{D_{\mathrm{M}}}{a_{\mathrm{M}}} C_{\mathrm{M}} N_{\mathrm{M}} - D_{\mathrm{M}} C_{\mathrm{M}} \frac{\partial N_{\mathrm{M}}}{\partial x}, \quad \frac{\partial N_{\mathrm{M}}}{\partial x} > 0, \tag{45}$$

$$j_{\mathrm{O}} \simeq \frac{D_{\mathrm{O}}}{a_{\mathrm{O}}} C_{\mathrm{O}} N_{rmO} - D_{\mathrm{O}} C_{\mathrm{O}} \frac{\partial N_{\mathrm{O}}}{\partial x}, \quad \frac{\partial N_{\mathrm{O}}}{\partial x} < 0, \tag{45a}$$

$$D_{\mathrm{M}} = a_{\mathrm{M}}^2 v \exp\left(-\frac{W_{\mathrm{M0}} - \Delta W_{\mathrm{M}}}{kT}\right),$$

$$D_{\mathrm{O}} = a_{\mathrm{O}}^2 v \exp\left(-\frac{W_{\mathrm{O0}} - \Delta W_{\mathrm{O}}}{kT}\right),$$

$$\Delta W_{\mathrm{M}} = \alpha_{\mathrm{M}} z_{\mathrm{M}} a_{\mathrm{M}} \mathrm{e} E,$$

$$\Delta W_{\mathrm{O}} = \alpha_{\mathrm{O}} z_{\mathrm{O}} a_{\mathrm{O}} \mathrm{e} E,$$

$$z_{\mathrm{O}} = 2.$$

The flows of non-equilibrium vacancies can be determined using these equations together with the condition (42).

The concentrations $N_{\mathrm{M}}(x,t)$ and $N_{\mathrm{O}}(x,t)$ of the M_{ox}^{z+} and O_{ox}^{2-} ions contained in the formulas (45) are determined by equations of their hopping migration

$$\frac{\partial N_{\mathrm{M}}}{\partial t} = -\frac{\partial j_{\mathrm{M}}}{\partial x}, \tag{46}$$

$$\frac{\partial N_O}{\partial t} = -\frac{\partial j_O}{\partial x},$$

$$\Delta_1(t) \leqslant x \leqslant \Delta_2(t),$$

$$\Delta_2(t,\varphi) - \Delta_1(t) = \delta(t,\varphi).$$

The concentrations of the M_{ox}^{z+} and O_{ox}^{2-} ions at the interfaces M−O and O−E are equal to $N_{M2} \equiv N_M(\delta)$ and $N_{O1} \equiv N_O(0)$, respectively, whereas the concentrations of their vacancies N_{Mv2} and N_{Ov1} at the same interfaces are interrelated through the following expressions

$$N_{M2} = N_{M0} - N_{Mv2},$$

$$N_{O1} = N_{O0} - N_{Ov1}.$$

The interface M−O serves as a source of the M_{ox}^{z+} ions and a sink of the cation vacancies. Similarly, the interface O−E serves as a source of the O_{ox}^{2-} ions and a sink of the anion vacancies. Therefore,

$$N_{Mv2} \ll N_{M2} \simeq N_{M0},$$

$$N_{Ov1} \ll N_{O1} \simeq N_{O0}.$$

For a steady-state mode, the system of equations (44)–(46) can be reduced to two equations for concentrations of non-equilibrium cation and anion vacancies $C_M(x)$ and $C_O(x)$ within the respective sublattices of the PL $[0 \leqslant x \leqslant \delta(\varphi)]$[19]

$$\frac{D_M}{a_M} C_M(1 - C_M) - D_M C_M \frac{dC_M}{dx} + \upsilon(1 - C_M) = \upsilon \frac{N_{met}}{N_{M0}}, \quad (47)$$

$$-\frac{D_O}{a_O} C_O(1 - C_O) - D_O C_O \frac{dC_O}{dx} + \upsilon(1 - C_O) = 0,$$

$$C_M(0) \equiv C_{M1},\ C_M(\delta) \equiv C_{M2} \sim 0,$$

$$C_O(0) \equiv C_{O1} \simeq 0,\ C_O(\delta) \equiv C_{O2},$$

where υ is the velocity of the interface M−O drift, N_{met} is the concentration of occupied sites in the metal lattice.

These vacancies induce an electrical charge and strains in the PL structure and determine its point defectiveness, which in turn determines the dimension of the passive region, *i.e.*, the value of the anode potential $\varphi = \varphi_p$.

Actually, the point defectiveness of a PL cannot exceed a certain threshold depending on the strength of the PL ionic structure. Thus, there is a critical, *i.e.*, the maximum possible value $C_c = (C_M)_{max}$ of the concentration $C_M(x)$. When the critical concentration is exceeded, the dependence of the thickness of the passivating layer on the anode potential [see equation (38)] is violated, which actuates the transpassive transition (transpassivation) observed at $\varphi = \varphi_p$. The theoretical prediction of φ_p as a function of the characteristic parameters of a passivating system is a key challenge to a passivation theory.

The critical defectiveness is reached at $\varphi = \varphi_p$ at the interface O−E since it serves as a source of vacancies of the cation sublattice. In order to find φ_p, one can determine the functions $C_M(x)$ and $C_O(x)$ from the equation (47) and then set $C_{M1} = C_M(0)$. Additionally, it should be taken into account that $C_M(x) \ll 1$, $C_O(x) \ll 1$. In this case,

$$\int_0^\delta C_M(x)dx + \frac{a_M}{2} C_{M1}^2 \simeq \upsilon \frac{a_M \delta}{D_M}\left(\frac{N_{met}}{N_{M0}} - 1\right), \quad (48)$$

$$\int_0^\delta C_O(x)dx + \frac{a_O}{2} C_{O2}^2 \simeq \upsilon \frac{a_O \delta}{D_O}.$$

An approximate solution of the first equation gives

$$2C_{M1} + C_{M1}^2 - 2q\delta = 0,$$

where

$$q = \frac{\upsilon}{D_M}\left(\frac{N_{met}}{N_{M0}} - 1\right).$$

For instance, in the case of a system Fe in 1 M H_2SO_4 (see Refs 73 and 74), which is characterised by the following parameters $D_M \simeq 0.5 \times 10^{-16}$ cm^2 s^{-1}, $z_M \simeq 3$, $\alpha_M \simeq 0.5$, $i_b \simeq 10^{-6}$ A cm^{-2} s^{-1}, $\delta \sim 10^{-7}$ cm, the equation is transformed into

$$C_{M1} = q\delta(\varphi). \quad (49)$$

c. Transpassive transition

The equation (49) implies that the maximum possible defectiveness C_c corresponds to the ultimate thickness of the passivating layer δ_p exactly at the potential of the transpassive transition φ_p

$$\delta_p = \frac{C_c}{q}. \quad (50)$$

A study of the stability of a lattice with respect to its point defectiveness for the case of a cubic packing of black and white balls has established that $C_c \simeq 0.2$, since the long-range order disappears at $C > 0.2$.[75]

An expression for the required φ_p can be obtained from the equations (50), (36) and (38). Indeed, the value of the anode potential corresponding to the oxygen equilibrium φ_{pb}, which is contained in the equation (38), can be estimated using the equation (35b). This gives rise to

$$\varphi_p = \varphi_{pb} + \frac{\delta_p}{\beta}\ln\left(\frac{i_a}{i_{b0}}\right), \quad (51)$$

$$\beta = \alpha_b a_M \frac{zF}{RT},$$

δ_a is the thickness of the PL in the beginning of the passive region ($\varphi = \varphi_a$), where the PL can be regarded as a monolayer.

Thus, the equations (51), (35b) and (50) comprise a system of three equations with three unknowns, *viz.*, φ_p, φ_{pb} and δ_p. Solving this system, for instance, for M = Fe, yields: $\varphi_{pb} \simeq 0.4$ V, $\varphi_p \simeq 1.6$ V, $\delta_p \simeq 2 \times 10^{-7}$ cm, which is in agreement with the experimental data.[26]

3. The interface metal – oxide

a. Interphase reactions

As has been shown above, the incorporation of near-boundary O_{ox}^{2-} ions belonging to the anion sublattice of the PL into the metal is the main process proceeding at the interface M−O. The anions react with the M^{z+} cations forming new unit cells of the passivating oxide M_nO_m and giving rise to a drift of the interface M−O at a velocity υ [see equation (39)].

To form a new cell, an O_{ox}^{2-} ion should pass an interatomic distance a_O typical of the anion sublattice structure and cross the interface M−O, so that a potential drop $\Delta\varphi = a_O E$ is overcome. The electric field E decreases the transition barrier by $\Delta U = \alpha_O z_O a_O eE$.

The probability of oxygen incorporation is proportional to the number of unoccupied sites in the near-boundary layer of the metal ΔM, which is equivalent to the concentration C_{met} of vacancies in the lattice ΔM. The respective current density of incorporation i_{bO} is $(m/n = z/2)$

$$i_{bO} = i_{bO}^0 C_{met}^{z/2} \frac{N_{O2}}{N_{Og}} f(U) \exp(\beta_O E), \quad (52)$$

$$\beta_O = \alpha_O z_O a_O \frac{F}{RT},$$

$$E = \frac{\varphi - \varphi_{pb}}{\delta(\varphi)},$$

$$C_{\text{met}} = \frac{N_{\text{v met}}}{N_{\text{g}}},$$

$$N_{\text{g}} = N_{\text{met}} + N_{\text{v met}},$$

where, as before, N_{O2} is the concentration of the O_{ox}^{2-} ions at the interface M–O; N_{met}, $N_{\text{v met}}$ and N_{g} are the concentrations of occupied and vacant sites in the metal lattice and their sum, respectively. The transfer coefficient α_{O} characterises the asymmetry of the energy barrier ΔU; $f(U)$ is the term describing the ordering process within ΔM.

Due to conversion of the metal into the oxide, an oxide layer with a thickness Δ_{ox} and a number of the M_{ox}^{z+} cations ΔN_1 appears in place of the starting boundary layer ΔM with a number of metal atoms ΔN. In general, thicknesses of the layers ΔM and Δ_{ox} are different. As has been mentioned above, the spatial balance is kept due to the subsystem of vacancies.[19]

Evidently, $\Delta N_1 < \Delta N$. Consequently, only a part of ions from ΔN is involved in the formation of oxide in the layer Δ_{ox}. The remaining part $\Delta N_2 = \Delta N - \Delta N_1$ is surplus and should move away through the interface M–O into the PL and further to the electrolyte. This is the only way to keep the spatial balance in the layer ΔM. Meanwhile, the continuous transfer of the M_{ox}^{z+} ions should proceed in the PL by the mechanism of hopping migration in a strong electric field, as discussed above.

Consequently, the total current i_{b} of the metal disintegration (or anode dissolution) specified in the formula (36) can be subdivided into the current of the M_{ox}^{z+} ion transfer through the PL i_{bM} and the current i_{ω} corresponding to the formation of oxide cells within the layer ΔM. The latter is determined by the number of bonds between the M^{z+} ions and incorporated oxide ions formed per second in the layer ΔM, which generate ω new cells in each unit volume, *i.e.*,

$$\Delta N_1 + \Delta N_2 = \Delta N, \tag{53}$$

$$i_{\text{bM}} + i_{\omega} = i_{\text{b}},$$

for meaning of i_{b}, see the formula (36).

The formation mechanism of new cells M_nO_m based on the vacancy model of the interphase processes has been considered elsewhere.[19, 37] To form a cell, $m\,O_{\text{ox}}^{2-}$ ions should diffuse from the PL to the layer ΔM leaving m anion vacancies in the PL layer. This requires availability of m vacant sites V_{M} within the lattice ΔM, which can be generated only as a result of preceding transition of m out of ΔN_2 ions M^{z+} into the PL. These incoming ions occupy m cation vacancies within the cation sublattice of the PL (which are in turn transferred from the interface O–E by the flow of vacancies) and move towards the electrolyte. The flows of vacancies j_{Mv} and j_{Ov} are generated due to the hopping migration of the M_{ox}^{z+} and O_{ox}^{2-} ions in the opposite directions within the PL.

Thus, the formation of an oxide cell M_nO_m is described by a scheme involving several steps. In the first step, $m\,M^{z+}$ ions pass from the metal lattice to the PL being converted into M_{ox}^{z+} ions and leaving m vacancies V_{M} in originally occupied sites, which can be written as

$$m\text{M} + mV_{\text{M0}} \longrightarrow m\text{M}_{\text{ox}}^{z+} + mV_{\text{M}} + mz\text{e}. \tag{54}$$

The vacancies V_{M0} appear at the interface M–O owing to their hopping migration from the source, *viz.*, the external interface O–E. New M_{ox}^{z+} ions migrate in the opposite directions, *i.e.*, towards the interface O–E, which serves as their sink.

In the second step, $m\,O_{\text{ox}}^{2-}$ ions are incorporated into the metal, occupy vacancies V_{M} and are converted into the $(O_{\text{ox}}^{2-})_{\text{M}}$ ions of the transition layer ΔM, which can be represented as

$$m\,O_{\text{ox}}^{2-} + m\,V_{\text{M}} \longrightarrow (m\,O_{\text{ox}}^{2-})_{\text{M}} + m\,V_{\text{O0}}. \tag{55}$$

Vacancies V_{O0} are generated in the formerly occupied sites and then migrate towards the interface O–E.

In the third step, the ions within ΔM undergo structural ordering, which results in the formation of an oxide cell M_nO_m, *i.e.*,

$$(m\,O_{\text{ox}}^{2-})_{\text{M}} + n\,\text{M} \longrightarrow \text{M}_n\text{O}_m + nz\text{e}. \tag{56}$$

This process is quantified by the term $f(U)$ in the equation (52). The overall process including the steps (54) and (56) can be written as

$$(m+n)\text{M} + mO_{\text{ox}}^{2-} + mV_{\text{M0}} \longrightarrow$$
$$\longrightarrow \text{M}_n\text{O}_m + m\text{M}_{\text{ox}}^{z+} + mV_{\text{O0}} + (m+n)z\text{e}.$$

The above scheme implies that the conversion of vacancies and of their flows occurs at the interface M–O (Fig. 4), *viz.*,

$$V_{\text{M0}} \longrightarrow V_{\text{M}} \longrightarrow V_{\text{O0}},$$
$$j_{\text{Mv}} \longrightarrow j_{\text{Ov}},$$

so that the vacancies V_{M} act as mediators combining the processes (54) and (56).

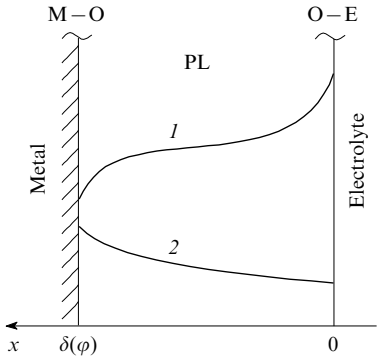


Figure 4. A scheme of concentration distributions of non-equilibrium vacancies in the cationic (*1*) and anionic (*2*) sublattices of a passivating layer.

b. Current densities

According to the equation (52), the total current density of the metal anode dissolution can be represented as a sum of two terms. The first term is the current density i_{bM} corresponding to the transition of the M^{z+} ions from ΔM to the PL, which gives rise to the generation of vacancies V_{M} within the layer ΔM with the concentration C_{met}. The second term is the current density i_{ω} corresponding to the formation of cells of M_nO_m in the layer ΔM owing to the incorporation of the O_{ox}^{2-} ions at a velocity i_{bO}.

The parameters i_{b}, i_{bM}, i_{bO} and i_{ω} are linked through a self-consistent relation[19–25] imposed by the reactions (54) and (55). Indeed, currents of these reactions are equal, since they represent currents of the formation of the vacancies V_{M} and simultaneously of their filling with the O_{ox}^{2-} ions, therefore, in a steady-state mode,

$$i_{\text{bM}} = i_{\text{bO}}. \tag{57}$$

If ω oxide cells M_nO_m are formed in the unit volume of ΔM per second, this consumes $n\omega$ M^{z+} and $m\omega$ O^{2-} ions, which means that

$$i_{\omega} = n\omega z\text{e}, \tag{58}$$
$$z \equiv z_{\text{M}},$$
$$i_{\text{bO}} = m\omega 2\text{e}.$$

The required relation can now be derived from the equations (53), (57) and (58)

$$i_\omega = \frac{n}{\gamma m} i_{bO},$$

$$i_{bO} = i_{bM},$$

$$i_b = i_\omega + i_{bM} = \left(\frac{\gamma m + n}{\gamma m}\right) i_{bO},$$

$$\gamma = \frac{2}{z},$$

$$i_{bO} = i^0_{bO} C^{z/2}_{met} \frac{N_{O2}}{N_{O0}} f(U) \exp(\beta_O E),$$

$$C_{met} = \left\{ \frac{i_{b0} \exp[(\beta - \beta_O)E]}{i^0_{bO}[(\gamma m + n)/\gamma m](N_{O2}/N_{O0}) f(U)} \right\}^{2/z}.$$

This makes it possible to calculate the number of oxide cells M_nO_m appearing per second per cm^2 of the interface M – O

$$\omega = \frac{i_\omega}{nze} = \frac{i_b}{(n + \gamma m)ze}.$$

For an oxide M_2O_3, $n = 2$ and $m = 3$.

The above mathematical approach is applicable to such metals as Fe, Ni, Cr, Mo, Cu, *etc*. Passivating layers on their surfaces are crystalline. In the case of the so-called valve metals (Ta, Ti, Al, Sn, Sb, *etc*.), the PL are characterised by amorphous structures. To allow for this, a statistical scatter in the interatomic distances and angular directions has to be taken into consideration. In such a case, coefficients in the transfer equations will be random quantities and the equations themselves will be stochastic.

The ion transfer also referred to as electrodiffusion, or hopping migration, plays an important role in the functioning mechanism of an oxide PL. It can be formulated as follows.

1. Ion flows provide kinetic and structural interrelations between the interfaces and enable occurrence of electrochemical reactions on them. This retains the ionic sublattices of the PL and ensures its stability.

2. Ion flows govern the growth of the layer $\delta(\varphi)$ thickness. At any potential φ, a specific surplus potential $\varphi - \varphi_{pb}$ is consumed so that the partial interphase equilibrium metal – electrolyte is maintained.

3. The concentration of vacancies increases with an increase in the thickness $\delta(\varphi)$ and reaches its critical value C_c inducing the transpassive transition at $\varphi = \varphi_p$. Therefore, the ion transfer determines the extension of the passive region.

4. Ion transfer generates a subsystem of non-equilibrium vacancies, which maintains the spatial balance at the interface M – O.

In the case of metal alloys, which are the main engineering materials, the passivation process is more complicated. First, a border layer of the alloy appears, which is characterised by modified physical properties. Second, passivating oxide layer formed on the alloy surface contains at least three (in the case of a simple binary A – B alloy) rather than two components. An attempt to develop a theory for such a system has been undertaken [19] but the goal is still far from reach.

Unfortunately, outdated concepts are still employed in the studies devoted to the mechanisms of the electrode processes. The electrode surface is represented as an array of distributed microelectrodes forming galvanic pairs anode – cathode. Within this approach, fictitious electric circuits composed of a small group of atoms are considered and characterised with parameters applicable to macrocircuits, such as resistivity, current and so on.

IV. Other models of the passive state of metals

The mathematical model of passivating layers outlined above is based on the general thermodynamical principle stating that a stable passive state of a metal surface is only possible provided that conditions of the interphase equilibrium between the passivating layer and the electrolyte are met. According to extensive investigations accomplished by the electrochemists of the German school,[26–34] this equilibrium is established due to the reaction

$$H_2O \rightleftharpoons O^{2-}_{ox} + 2H^+, \tag{59}$$

i.e., due to the exchange of the oxide ions (that are formed upon dissociative adsorption of water) between water and the oxide sublattice of the PL. Transfer of the M^{z+}_{ox} ions from the metal sublattice is continuously compensated for by their supply from the metal substrate. The self-consistency of all the processes is determined by the value of the equilibrium interphase potential φ_{pb}. The following two equations

$$\overrightarrow{k}[H_2O] \exp\left(\alpha_O z_{rmO} F \frac{\varphi_{pb}}{kT}\right) - \overleftarrow{k}[H^+]^2 \exp\left(-\beta_O z_O F \frac{\varphi_{pb}}{kT}\right) = 0,$$

$$\alpha_O + \beta_O = 1$$

express the equality of the total numbers of the direct and reverse reaction events (59) occurring at a unit surface for 1 s. The self-consistency of the processes can be explained by the stability of anodically dissolvable (*i.e*., thermodynamically non-equilibrium, in overall) oxide.

Attempts have been undertaken [60–67] to rationalise functioning of a PL in a different way assuming no interphase equilibrium. A few of them are briefly considered below. A mathematical model referred to as 'self-adjusting dissolution of a passivated metal' [63] assumes simultaneous consistent changes in the anode potential φ, dissolution current density i and thickness of the passivating layer $\delta(\varphi)$.

The model is supposed to explain the independence of the stationary current density of the anode potential. It postulates that a PL and a double electrical layer (DEL) can be considered as series capacitors. In that case, the potential drops in the layer and DEL are inversely proportional to their capacities C_f and C_d, respectively,

$$\frac{\varphi - \varphi_b - \varphi_{12}}{\varphi_b} = \frac{C_d}{C_f}. \tag{60}$$

Here, φ_b is the DEL potential and φ_{12} is a suggested potential drop at the interface with the metal. The postulated inverse proportionality substitutes the condition of Vetter's partial oxygen equilibrium (59). Another assumption is that the PL is dissolved according to the equation

$$MO_{z/2} + z\,H^+ \longrightarrow Mn+ + \frac{z}{2} H_2O + (n - z)e \tag{61}$$

and is formed at the opposite interface

$$M_{z/2}O^{2-} \longrightarrow MO_{z/2} + ze. \tag{62}$$

The rates of these reactions are described by the following expressions

$$i_1 = K_1 \exp\left[\frac{\alpha_1 (n - z) F}{RT} \varphi_b\right], \tag{63}$$

$$i_2 = K_2 \exp\left(\frac{\alpha_O z_O F}{RT} aE\right),$$

where subscripts 1 and 2 denote the interfaces PL – electrolyte and PL – metal, respectively; a is the interatomic distance. It is also assumed that the reactions

$$H_2O_{ad} \rightleftharpoons O^{2-}_{ox} + 2\,H^+,$$

$$M^{z+}_{ox} \longrightarrow M^{z+}_{ad}$$

are compatible provided that the exchange current of the first reaction exceeds substantially that of the second one.

This condition can be considered as unrealisable since the corrosion potential of a passivated metal sometimes manifests

sensitivity to the currents at levels comparable to the rate of corrosion and it is the equilibrium that adjusts itself to the potential φ_b rather than *vice versa*.[63] It is also presumed that

$$C_f = \frac{\varepsilon_f}{\delta(\varphi)},$$

$$C_d = \frac{\varepsilon_d}{\delta_d},$$

where ε_f, ε_d, $\delta(\varphi)$ and δ_d are dielectric constants and thicknesses of the PL and DEL, respectively. Taking into account the above assumptions, the equation (60) is transformed into

$$\frac{\varphi - \varphi_b - \varphi_{12}}{\varphi_b} = \frac{\varepsilon_f}{\varepsilon_d}\,\frac{\delta(\varphi)}{\delta_d}, \tag{64}$$

and the following equation is postulated for the film thickness

$$\delta(\varphi) = \frac{\varphi - \varphi_{12} - \varphi_b}{E}.$$

The system composed of the last two equations contains three unknowns, *viz*., $\delta(\varphi)$, E and φ_b at a fixed φ_{12}. The equality of the steady-state rates of dissolution [see equation (63)] and formation of the passivating layer [see (61) and (62)] can be used as the third equation, *i.e*.,

$$i_1 = K_1 \exp\left[\frac{\alpha_1(n-z)F}{RT}\varphi_b\right] = K_2 \exp\left(\frac{\alpha_O z_O F}{RT} aE\right) = i_2.$$

This gives rise to

$$\varphi_b = \frac{RT}{\alpha_1(n-z)F}\ln\left(\frac{K_2}{K_1}\right) + \frac{\alpha_O z_O}{\alpha_1(n-z)} aE. \tag{65}$$

The system (60)–(65) is now closed with respect to the unknowns φ_b, E and $\delta(\varphi)$ provided that the value of φ_{12} is known. After a few simplifying assumptions, these equations can be transformed into

$$\varphi_b = \frac{RT}{F\alpha_O z_O}\ln\left(\frac{K_2}{K_1}\right)\left[\frac{\varepsilon_d a}{\varepsilon_f \delta_d} - \frac{\alpha_2(n-z)}{\alpha_O z_O}\right]^{-1},$$

$$E = \frac{RT}{F\alpha_O z_O}\ln\left(\frac{K_2}{K_1}\right)\left\{\frac{\varepsilon_d}{\varepsilon_f}\delta_d\left[\frac{\varepsilon_d a}{\varepsilon_f \delta_d} - \frac{\alpha_2(n-z)}{\alpha_O z_O}\right]^{-1}\right\}.$$

The last two formulas are final since they are no more dependent on the potential drop φ_{12}. Also note that the following expressions can be written instead of the equation (64)

$$\frac{\varphi_p}{\varphi_d} = \frac{Q_s}{Q_d}\,\frac{c_d}{c_p},$$

$$Q_s \neq Q_d,$$

$$Q_s + Q_d + Q_M = 0,$$

where φ_d is the DEL potential, Q_s is the solution charge, Q_d is the DEL charge, c_d is the DEL capacity, c_p is the PL capacity, Q_M is the metal charge.

Other models do not require fulfilment of the condition of the interphase equilibrium between the passivated metal and water molecules of a solvent as regards oxygen ions. In the model proposed by Alekseev and Kolotyrkin,[66] no diffusion is considered and the current is assumed to be due to the migration of ions in a constant electric field. Respectively, the concentrations of ionic components in sublattices of the PL are independent of coordinates and identical at both interfaces. The neglect of diffusion decreases the order of the ion transfer equations; interfaces and the transpassive transition are described by the integration limits.

The above considerations support Vetter's suggestion[26] that the stability of a passivating layer is caused by the equilibrium exchange of oxygen ions between the PL anionic sublattice and the electrolyte. The existence of the metal sublattice of the PL is provided by a steady-state supply of the M^{z+} ions from the metal through the PL to the interface with the electrolyte. This compensates for continuous transfer of the M^{z+} ions into the electrolyte. Thus, the cation composition of a PL is continuously renewed, whereas the anion composition remains constant but constantly drifts following the dissolving metal surface. The oxygen equilibrium according to Vetter (32) coincides with the condition of the thermodynamical phase equilibrium.[70–72]

Admitting the fundamental character of studies performed by representatives of the German school of electrochemists, it however was noted that their suggestions on the chemical mechanism of dissolution of a passivated metal are erroneous. Actually, the mechanism is electrochemical in character, as has been demonstrated by Novakovsky and Likachev.[68,69] Therefore, it might be concluded that the experimental fundamentals of the passivity theory are laid by the combination of the two works cited above.[26,68]

V. The adsorption and phase-film theories of passivity

The current understanding of the passive state of metals has been evolving over the entire time of its investigation. Originally, the adsorption and phase-film theories of passivity were widely adopted. Their experimental backgrounds have been summarised elsewhere.[73–76] The major postulates of the theories can be formulated as follows.

A general assumption that the passivation is caused by the interaction of the surface metal atoms with the oxygen of the adsorbed water molecules underlies the adsorption theory. This is based on the experimental data from polarisation measurements combined with dedicated studies of adsorption phenomena. It has been established that the current density of the anodic dissolution decreases manyfold when a small amount of oxygen ions forming only a fraction of an oxygen submonolayer is adsorbed.

The following adsorption schemes were considered in order to rationalise this experimental fact

$$(1-\Theta)K_{ad} = \Theta K_i, \tag{66}$$

where

$$K_{ad} \sim \exp(\alpha_a \sigma \varepsilon),$$

$$K_i \sim \left[\beta_i(z_M - \sigma)\varepsilon\right],$$

$$\varepsilon = \frac{F\varphi}{RT},$$

$$i_a = \Theta K_i,$$

Θ is the coverage of the metal surface with adsorption complexes formed as a result of the interaction between the surface metal atoms and the oxygen atoms of water molecules; K_{ad} is the rate of formation of these complexes; K_i is the rate of transfer of the complexes to the solution; ε is a dimensionless potential; σ is the fraction of partially transferred charge; i_a is the transition current density. The equation (66) gives rise to

$$i_a = \frac{K_{ad}K_i}{K_{ad} + K_i}. \tag{67}$$

This equation clearly shows that the equation (66) cannot reproduce the shape of the polarisation curve shown in Fig. 1 for any possible combination of K_{ad} and K_i. Indeed, only three cases are possible.

1. $K_{ad} \sim K_i$; the rates of formation and dissolution of the complexes are similar; consequently, $i_a \approx K_i$ or $i_{ad} \approx K_{ad}$; the dissolution current increases exponentially with an increase in

the potential so that no active – passive and passive transitions can be identified in the polarisation curve.

2. $K_{ad} \gg K_i$; the dissolution step is rate-limiting. In this case, the dependence of the dissolution current on the potential is the same as above.

3. $K_{ad} \ll K_i$; the adsorption step is rate-limiting and $i_a \sim K_{ad}$; the situation remains the same: no passivity region can be identified.

The conclusion on the impossibility of identification of an extended passivity region in the polarisation curve based on the equation (66) directly follows from the equation (67). Since the passivity region is characterised by $i_a = \text{const}$, the equation (67) can be represented in an algebraic form with respect to the potential φ

$$\frac{K_{ad}(\varphi)K_i(\varphi)}{K_{ad}(\varphi) + K_i(\varphi)} = \text{const}, \tag{68}$$

the equality condition is met only for one or a few values of φ, which correspond to the roots of the equation. In other words, no extended passivity region is possible.

Sukhotin suggested [76] a modification of the passivity theory by complicating the adsorption scheme through inclusion of several interaction steps of metal atoms with water molecules. Each step gives rise to its own coverage Θ_k of the surface with oxygen-containing complexes, such as $[MOH]_{ad}$, $[M(OH)_2]_{ad}$, $[M(OH)_3]_{ad}$ and $[MO]_{ad}$. Consequently, the partial currents corresponding to individual steps are $i_k = \Theta_k K_{i,k}$, the total coverage Θ and the total dissolution current i_a can be represented as

$$\Theta = \sum_k \Theta_k ,$$

$$i_a = \sum_k \Theta_k K_{i,k} .$$

The kinetics of each kth steps is determined by its parameters α_k, β_k, $K_{ad,k}$ and $K_{i,k}$. The total number of such steps is large. The theoretical results are to be reconciled with the experimental data by a proper selection of the steps. Nevertheless, despite the use of numerous free variables, discrepancies remain significant,[76] which indicates inadequacy of the adsorption model of passivity. Probably, the substantial deceleration of anodic dissolution by a small amount of preadsorbed oxygen relates to the repulsive interactions between the adsorbed ions. Their mutual influence impedes adsorption on the adjucent neighbouring sites giving rise to a specific dead zone around each adsorbed ion. Taking this into account, [19]

$$K_{ad} \sim \exp(-f_a\Theta)\exp(\alpha_a\sigma\varepsilon),$$

$$K_i \sim \exp(f_i\Theta)\exp\left[\beta_i(z_M - \sigma)\varepsilon\right],$$

where f_a and f_i are constants. These expressions also describe blockage of the active sites on an energetically heterogeneous metal surface, which is a reason for deceleration of the anodic dissolution.

No doubt, the adsorption from solution always represents the first step of formation of an passivating oxygen layer on a metal surface. However, as has been mentioned above, the presence of an oxygen ad-layer is not sufficient to explain all the regions observed in polarisation curves (in particular, the transpassive transition and a finite dimension of the passive region, which is characterised by the independence of the current of a passivated metal dissolution on the potential). Therefore, additional steps of the mechanism of formation of a passivating system have to be considered. The fact of formation of oxide layers with finite thicknesses, which corresponds to the equilibrium oxide – electrolyte, also support the above requirement.

The evolution of concepts concerning oxygen-induced passivation has resulted in the emergence of a phase-film theory of oxide passivity. This theory postulates [26, 76] the existence of a thermodynamically stable oxide layer (unlike that described above) on the surface of hard metals, which is observed at anode potentials $\varphi > \varphi_a$. This layer is referred to as a 'film'. Its structure corresponds to stoichiometry M_nO_m. In the case of valve metals, the film is structurally disordered and can be substantially thicker. Within this theory, the passivation is explained by a mechanical shielding of the metal surface by the phase oxide. The independence of the passive current of the anode potential seems to be attributed to the chemical dissolution of the oxide layer. The potential corresponding to the beginning of the passive region φ_a (see Fig. 1) is interpreted as a potential of formation of the equilibrium oxide.

The postulate on the chemical mechanism of dissolution of the passivating oxide adopted in the phase-film theory is not supported by experimental data.[68] Typically, the potential of the beginning of the passive region φ_a differs from the potential of formation of the equilibrium oxide. For instance, this discrepancy is as large as 0.63 V in the case of iron.[26, 76] Neither the experimentally observed dependences of φ_a on the surface properties of the metal (*e.g.*, its cleanliness [70]), nor the solution composition and other factors can be explained within this theory.

The passivity theories that were developed later still relied on the assumption that the passivation was achieved due to the interaction of the metal surface with oxygen produced by dissociation of adsorbed water molecules. Presumably, the O^{2-} ions interact with the surface metal atoms forming the topmost ordered monolayer of oxide M_nO_m. This assumption is in agreement with the general theory of heterogeneous formation of a crystal phase through the generation of its two-dimensional nuclei or their stacks. Evidently, kinetics of such a process differs from that of a simple adsorption. In particular, the probability of generation of a two-dimensional nucleus manifests a stronger dependence on the interphase potential drop [see formula (13)].

In the course of growth, further oxide layers are formed atop the first structured monolayer. The increase in the thickness of the layer is caused, first, by too high an electrodiffusion current of the metal ions through the oxide layer to the interface O – E and, second, by too low a surplus potential expended for the current passage through the interface

$$\Delta\varphi = \varphi - \varphi_b .$$

Therefore, the dissociation of water molecules (the donor of the O^{2-} ions) is too intense. Due to an excess of the reactants, *i.e.*, O^{2-} and M^{z+} ions, new oxide cells are formed, the thickness of the layer increases and, respectively, the potential φ_b decreases.

This process ceases when the potential φ_b decreases to the level corresponding to the equilibrium between the PL and the electrolyte due to thickening of the PL. This means that a steady-state mode of the anodic dissolution of passivated metal is settled. Since then, new cells of oxide M_nO_m are formed only on the inner interface, where the oxide ions are incorporated into the metal. This process compensates for the disappearance of cells at the interface O – E. Only anionic sublattice of oxide M_nO_m is in equilibrium with the electrolyte. Between the two interfaces, oppositely directed electrodiffusion flows of the metal and oxide ions are established. Therefore, a stationary passivating layer, overall, is non-equilibrium. The interphase potential drop is

$$\Delta\varphi = \varphi - \varphi_{pb} ,$$

$$\varphi_b = \varphi_{pb} ,$$

$$\delta = \delta(\varphi),$$

where φ_{pb} corresponds to the Vetter potential [26, 27] and $\delta(\varphi)$ is the stationary thickness of the PL dependent on φ. Due to changes in $\delta(\varphi)$, the structure of the PL and processes proceeding in it adjust themselves to conditions of the thermodynamical equilibrium with the electrolyte at every value of φ. In contrast to this, the adsorption theory of oxygen passivation assumes that the oxide coverage remains monolayer at all values of φ and only the dependence of φ on the adsorption coverage of the metal surface

with oxide ions is considered. In other words, growth of the passivating layer is admitted only along this surface.

The oxygen-adsorption and phase-film theories can be considered as particular cases of the formation and functioning of an passivating oxide system (see Sections II and III of the present review).

It is known that a metal can be protected by inhibition of its surface with certain chemicals. The initial stage of this process also includes adsorption from solution, which plays the major role in the mechanism of formation of inhibiting coatings.[77–79] Several authors suggested [80–84] that the inhibition mechanism relates to a change in the rate of the electrode reactions involving organic compounds. This can be due to redistribution of charges over the double electric layer.

The development of mixtures of adsorption inhibitors that provide more efficient protection than any of their components becomes increasingly important. The non-additive action of such mixtures was attributed [85–88] to a change in the charge of the DEL due to the adsorption of anions, which adds a partial negative charge to the intrinsically positive metal surface. An analysis of possible reasons for the non-additive protective action of inhibitor mixtures and, particularly, their mutual intensification (*i.e.*, synergism) has been performed by Kuznetsov *et al.* [89,90]

Finally, it should be noted that not only the initial stage but further steps as well can be of significance in explaining the inhibition mechanism. These steps can either have the adsorption character (*i.e.*, polymolecular adsorption) or the mechanism involved is similar to that of salt passivation considered below.

VI. The salt passivation theory

At a potential $\varphi < \varphi_a$ preceeding the oxide passivation, salt layers (SL) also possessing protective properties can appear on a metal surface.[76] The formation of such layers is referred to as salt passivation (SP) (sometimes, primary salt passivation).

The SP is observed in aqueous solutions of H_2SO_4, $HClO_4$, HNO_3 and other acids in the presence of metal ions capable of forming poorly soluble salts with the respective A^{n-} anions. Two different mechanisms of the SL formation can be envisaged, depending on the solution composition and the nature of the ions.

The first mechanism is realised if salt-forming metal ions are the components of the acidic solution and the SL emerges due to salt precipitation on the metal surface. The formation of an SL according to this mechanism is determined by the saturation of the solution with reactants, the surface solubility product and general regularities of the heterogeneous nucleation.

The second mechanism is realised if the salt-forming M^{z+} metal ions are not present in the starting solution but are produced due to the interaction of the metal surface with the A^{n-} anions yielding salt molecules, *i.e.*, the SP is accompanied by the metal ionisation

$$M \longrightarrow M^{z+} + ze^{-}$$

and the anions are involved in the elementary events of the anodic process.

In this mechanism, the strength of the interparticle binding between the SP molecules and between an SP molecule and the metal substrate are of primary importance. This strength depends on the metal nature and solution composition. On the other hand, it determines the coverage of the surface with the salt layer and the rate of SL dissolution in the electrolyte. There are two possible mechanisms of the formation of an SL structure involving the A^{n-} anions and M^{z+} surface ions in the elementary acts.

According to the first variant, the bonds are sufficiently strong and thus the entire metal surface is covered with the SL, which means that $\Theta = 1$. Thus, a continuous salt layer with a thickness $\delta(\varphi)$ is formed as a result. Its protective properties are determined by the strength of the bonds at the interface with the electrolyte, which prevents transfer of the M^{z+} ions to the electrolyte. Such an SL can possess a crystalline or amorphous structure. An amorphous structure within this approach to the SP problem can be regarded as a lattice that is characterised by a statistical scatter in the interatomic distances and angular directions.

A continuous SL is analogous in properties to a passivating oxide layer with the only difference that both the interparticle M–O bonds in the oxide and binding of the oxide to the metal substrate are stronger. Therefore, the protective properties of an oxide PL surpass those of an SL by several orders of magnitude. This was the first possible mechanism of formation of an SL corresponding to the complete coverage of the metal with salt. The theory of its emergence is fully analogous to the theory of oxide PL outlined in Sections II and III.

The second variant implies that the bonds formed between the SL and the metal are less strong (probably, due to the influence of the energetical inhomogeneity of the metal surface, which gives rise to continuous variations in the activity of different surface areas in the course of dissolution). For this reason, only a part of the surface appears covered, *i.e.*, $\Theta < 1$, and the SL cannot be continuous. The value of Θ is determined by a balance of the direct and reverse processes of surface coverage. This mechanism of functioning of an SL has been considered by Sidorenko *et al.*[91,93,95] and by Popov *et al.*[92,94–96]. Its basic aspects can be formulated as follows.

The structure of an SL cannot be static since it is discontinuous and contains the M^{z+} ions of a metal that is dissolved. This follows from the general regularities of nucleation (of the SL, in this case), which starts with the adsorption step and generation of two-dimensional salt nuclei on the metal surface (at a coordinate $x = 0$). The process further continues to the region $x > 0$, where the nuclei grow on the related, *i.e.*, their own, substrate. This should lead to the formation of a system of pores filled with the electrolyte within the salt structure. The pores constitute a connected space Ω with an interface Σ. The existence of pores is necessitated by the fact that metal undergoes anodic dissolution only from uncovered parts of its surface put in contact with the electrolyte that is a mandatory participant of elementary events. Furthermore, the electrolyte solution is an ion-conducting medium, which is required for the withdrawal of the dissolved M^{z+} ions.

Popov *et al.*[95,96] demonstrated that a solution cannot be either oversaturated or unsaturated or simply saturated in all pores simultaneously. In other words, none of the three following relations

$$C_M^n C_a^m > C_H,$$

$$C_M^n C_a^m < C_H,$$

$$C_M^n C_a^m = C_H,$$

where $C_M = [M^{z+}]$ and $C_a = [A^{n-}]$ are the concentrations of the M^{z+} cations and A^{n-} counteranions, respectively, and C_H is the solubility product of the passivating salt M_nA_m, can be valid for all pores simultaneously. Indeed, in the first case, the pores would disappear owing to constant precipitation (crystallisation) of the salt on the pore walls so that the surface S would appear completely shielded and the metal dissolution would stop. In the second case, the pore walls would dissolve and the SL would disappear. In the third case, the concentration gradients of ionic components would become zero. This means that all pores at any moment t can be subdivided into two classes. In the first type of pores, the solution is oversaturated and the salt crystallises on the pore walls filling them. In the second type of pores, the solution is unsaturated and the salt is dissolved. The pores are continuously redistributed over the two classes. In other words, any elementary volume of an SL at any moment t represents either a solution-filled pore or solid phase. The steady-state porosity $g(x)$, which provides stable functioning of the SL, depends on the mean ratio of times, for which an elementary volume exists in these two states. The interface Σ does not remain static but rather continuously fluctuates. The porosity $g(x)$ is a function of coordinate due to the

non-zero concentration gradients $c_M(x)$ and $c_A(x)$. The reported data [91–96] are fully consistent with the experimental results.[26, 97] Froment *et al.*[97] filmed an SL *in situ* using an accelerated-motion camera at a high magnification (~3500 times) and discovered a phenomenon referred to as 'crystal swarming', which is consistent with the above theory.[91–96] The apparent current density of the metal dissolution passing through an SL is given by the formula

$$i = g_s f(\varphi),$$

$$g_s = g(x)|_{x=0} = 0,$$

$$f(\varphi) = zF\frac{K_{ad}(\varphi)}{1+\beta},$$

$$\beta = \frac{K_{ad}(\varphi)}{K_i(\varphi)},$$

where $f(\varphi)$ is the actual current density at an uncovered part of the metal surface; $K_{ad}(\varphi)$ and $K_i(\varphi)$ are the rates of anion adsorption and metal ionisation in the elementary events of anodic dissolution (transfer of the M^{z+} ions into the electrolyte), respectively. The ion transfer processes proceeding in the pore space of an SL including reactions at the pore walls (*i.e.*, precipitation of the salt on them or dissolution) have been considered elsewhere.[25, 96, 98, 99]

VII. Conclusion

The investigations into the regularities of the interphase phenomena in non-equilibrium systems metal–electrolyte and into the passivation mechanism, in particular, are interdisciplinary in their nature combining physics of metals, solutions and electrolytes and interface processes. Such studies should take into account numerous factors and parameters, which affect the corrosion kinetics and determine the complex shape of polarisation curves (see Fig. 1). With this respect, the present review capitalises on the unified model principle, which assumes that all the phenomena proceeding on the surface of a dissolving metal as well as a sequence of the surface states are governed by a few key processes. The kinetics of these processes differs depending on the anode potential φ and therefore one process dominates at any specific potential value, which gives rise to the alteration of the surface states (with an increase in the potential φ) corresponding to kinks of the polarisation curve and characteristic potentials φ_0, φ_a and φ_p. The dissolution mechanism is changed at these points.

Adherence to the above principle imposes restrictions upon arbitrary assumptions in theoretical speculations with plentiful unknown parameters. The validity of this approach is also justified by the fact that the shapes of polarisation curves are virtually identical for the majority of metals (*e.g.*, Fe, Cr, Ni, Mo, *etc.*).

In the case of an anodically dissolvable metal, the unified model only includes such processes as the M^{z+}, M_{ox}^{z+} and O_{ox}^{2-} ion transfer through the interfaces M–O and O–E; hopping migration of the ions within the PL lattice; PL crystallisation by the mechanism of two-dimensional nucleation. This model is sufficient to reproduce the entire polarisation curve.

Specific features of real systems can be addressed by including respective supplementary factors. The problems of the electrochemical metal passivation under applied voltage and of the elementary event of the anodic dissolution are of special interest. They also can be treated within the approach described.

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