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Nonequilibrium fluctuation theory on pitting dissolution. I. Derivation of dissolution current equations

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Following the foregoing papers, in this paper, mathematical procedures to describe the time development of the unstable nonequilibrium fluctuations in pitting dissolution are presented: First, general equations depicting the time development of the amplitudes of the fluctuations are deduced, which are the same as those describing nucleation phenomena. Then, with the same definition as nucleation, the average values of the fluctuations are decided, and measurable pitting current is calculated. Actually, some analytical equations are derived for some characteristic parts of the current–time transient. As a result, after applying a constant potential step to the electrode, a slow relaxation current, which follows a double-layer charging current, is decided as the diffusion current of the fluctuations. This current gives the values of passive film coverage and average critical concentration fluctuation on the completely active surface. Moreover, from the minimum current attained by the diffusion current, the ratio of the average critical concentration fluctuation to the autocorrelation distance is determined. Finally, resultant pitting growth current arising from the unstable growth of the fluctuations is deduced as a function of supporting-electrolyte concentration and overpotential, which is attributed to the fact that the instability occurs from the electrostatic interaction of the solution particles in the double layer. © 1997 American Institute of Physics. [S0021-9606(97)51323-7]

I. INTRODUCTION

Pitting dissolution is a typical example of heterogeneous reactions on an electrode surface; in the presence of aggressive ions, passive film is repeatedly rupturing and repairing all over the surface, being accompanied with the local dissolution of the substrate metal.

In spite of the recent development of various surface observation techniques such as scanning tunneling microscope^{1–3} and atomic force microscope,^{4–6} theoretical analysis of this phenomenon does not keep up with such development because of its complex heterogeneity, e.g., we do not completely know what determine the local and overall dissolution rates.

Electrochemistry has a great advantage to measure the reaction rate in the form of electrolytic current. However, such measurement unfortunately does not directly give the microscopic local information of the surface. As shown in Fig. 1, overall data concerning the electrolytic current, which are summed and averaged in a lead wire of the working electrode, are obtained. Therefore, in order to analyze the microscopic processes of heterogeneous reactions like pitting dissolution with electrochemical data, we have to reconstruct the local information, which is once lost during the measurement.

When the electrode potential is shifted from the rest potential to the anodic side of the potential, a new electrostatic equilibrium is quickly formed by the electrical double layer. However, such equilibrium is easily broken by the thermal

motion of solution particles. Especially, in the presence of aggressive ions, as mentioned above, local breakdown and resultant dissolution of substrate follow. Such breakdown, i.e., fluctuation is not at Nernstian equilibrium, is called “nonequilibrium fluctuation.” In foregoing papers,^{7–9} from the viewpoint that the progress of pitting results from the unstable growth of the fluctuation, the mechanism of the instability and its conditions were examined. Then, using the measurement of the critical potential, a new theory to depict the adsorption state of ions on the electrode surface was also developed. Consequently, it was concluded that the specific adsorption of anions is inevitable for the unstable growth of the fluctuation. With these results, microscopic local dissolution current was then computed, and the morphology of the dissolved nickel surface was theoretically determined by using computer graphics.¹⁰

The aim of this paper is, thus, by means of nonequilibrium fluctuation, to derive theoretical equations that describe the macroscopic behavior of the pitting current based on the microscopic information of the pitting surface. The procedure is summarized as follows: As mentioned in a previous paper,⁷ the nonequilibrium fluctuations are composed of asymmetrical and symmetrical ones. In this paper, we take more precise classification. That is, the asymmetrical fluctuations are assorted into two components that remain stable and turn unstable, respectively. All these three components, i.e., stable asymmetrical, unstable asymmetrical, and symmetrical ones, are produced by the nonequilibrium processes. Therefore, they can be further decomposed into reaction and diffusion components, respectively. Consequently, it is concluded that the fluctuations can be eventually classified into six different components.

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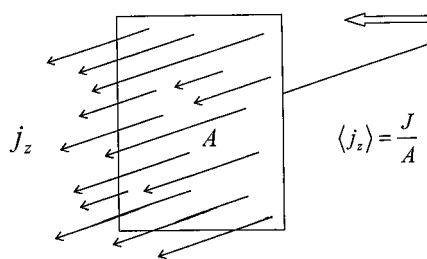


FIG. 1. Transform of electrochemical information. J : total current, $\langle j_z \rangle$: mean current density, and j_z : local current density.

Then, for all the components, general amplitude equations are deduced. At the same time, to determine the initial conditions of the asymmetrical and symmetrical fluctuations, intrinsic fluctuations with Gaussian and white-noise-type spectra are introduced, respectively. Then, some particular amplitude solutions of the asymmetrical fluctuations are obtained. After averaging them over the electrode surface owing to their asymmetrical nature, three current equations are established, i.e., as shown in Fig. 2, the fluctuation–diffusion current, minimum dissolution current, and pit-growth current.

II. THEORY

Nonequilibrium fluctuations discussed in the literature^{7–11} are provided with two kinds of irreversible processes, i.e., pitting dissolution and diffusion of dissolved metal ions.

At the initial stage, the reactions of the dissolution following the double-layer charging process produce the nonequilibrium concentration fluctuations with asymmetry, developing a diffusion layer outside the double layer. The asymmetrical fluctuations are generally defined as the differences of the physical quantities from the electrostatic equilibrium state. Therefore, taking the electrode surface as the x – y plane, as shown in Fig. 3, the asymmetrical fluctuation

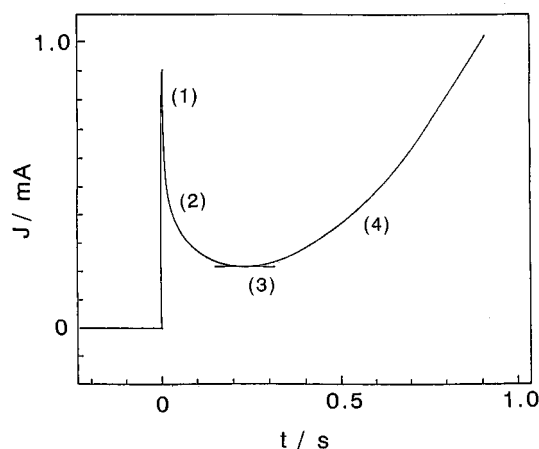


FIG. 2. Current–time variation in nickel pitting dissolution in NaCl solution. (1) double-layer charging current, (2) fluctuation–diffusion current, (3) minimum dissolution current, and (4) pit-growth current.

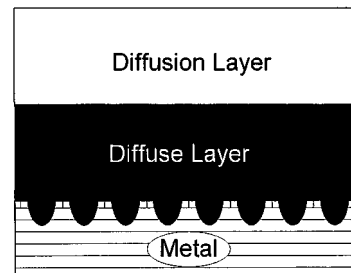
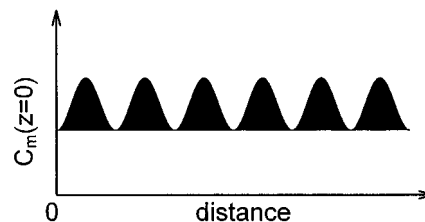


FIG. 3. Schematic depiction of asymmetrical concentration fluctuation. In the case of dissolution, it takes a positive value from the electrostatic equilibrium state (Ref. 7).

of the concentration of the dissolved metal ion is expressed in the following:

$$c_m(x, y, z, t)^a \equiv C_m(x, y, z, t) - C_m^*(z = \infty), \quad (1)$$

where the fluctuation takes a positive value owing to the dissolution of the substrate metal, and superscript a indicates asymmetrical fluctuation. Then, symbol “*” denotes the electrostatic equilibrium, and $C_m(x, y, z, t)$ and $C_m^*(z = \infty)$ are the concentration and the bulk concentration, respectively. Considering the scale of the fluctuation, the thickness of the electric double layer can be neglected, so that the electrostatic value of the concentration is equal to the bulk concentration.

As the diffusion layer extends into the bulk of the solution, the main role for yielding the fluctuations is transferred from the reaction at the electrode surface to the diffusion of dissolved metal ions in the bulk of the solution. Then, another fluctuation, i.e., symmetrical fluctuation, emerges, which is induced by the thermal motion of the solution particles during the mass transfer of the metal ions in the diffusion layer; as shown in Fig. 4, it changes positively and negatively around the average value according to the location,

$$c_m(x, y, z, t)^s \equiv C_m(x, y, z, t) - \langle C_m(x, y, z, t) \rangle, \quad (2)$$

where “ $\langle \rangle$ ” means the averaging in the x and y directions, and superscript s implies symmetrical fluctuation. The electrolytic current, which simultaneously flows, can be predicted by the amplitude equations for the fluctuations, which depict the kinetics of the irreversible processes.

A. Derivation of amplitude equations

1. Conservation of fluctuations

The nonequilibrium concentration fluctuations, whether they may be asymmetrical or symmetrical, are eventually formed by the reaction at the interface and the diffusion in

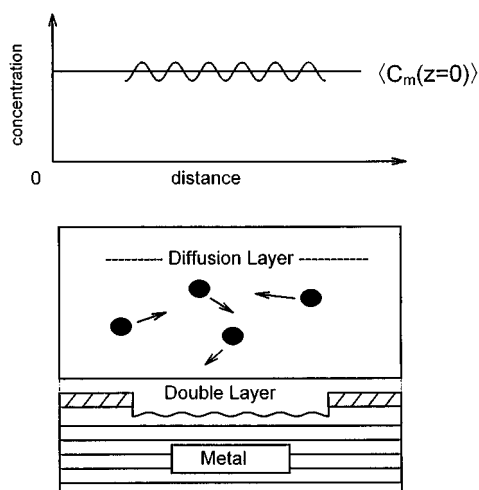


FIG. 4. Schematic depiction of symmetrical concentration fluctuation. It takes positive and negative values around the average value (Ref. 7).

the solution. Namely, they can be expressed by the following conservation laws of the nonequilibrium fluctuations, i.e.,

$$c_m(x, y, z, t)_i^a = c_m(x, y, z, t)_{i,D}^a + c_m(x, y, z, t)_{i,R}^a \quad (i = s \text{ or } u), \quad (3)$$

and

$$c_m(x, y, z, t)^s = c_m(x, y, z, t)_D^s + c_m(x, y, z, t)_R^s, \quad (4)$$

where the subscripts D and R indicate the components generated by the diffusion and reaction, respectively. As will be stated later, the subscript i indicates the stable (s) or unstable (u) component of the asymmetrical fluctuations. All the fluctuations are assorted, as shown in Fig. 5, into six components.

2. Basic equations for diffusion and reaction

The concentration fluctuations arising from the diffusion process in a static solution with a large amount of supporting electrolyte are followed by the equations

$$\left(\nabla^2 - \frac{1}{D_m} \frac{\partial}{\partial t} \right) c_m(x, y, z, t)_{i,D}^a = 0 \quad (5)$$

and

$$\left(\nabla^2 - \frac{1}{D_m} \frac{\partial}{\partial t} \right) c_m(x, y, z, t)_D^s = 0, \quad (6)$$

where $\nabla^2 \equiv \partial^2/\partial x^2 + \partial^2/\partial y^2 + \partial^2/\partial z^2$, and D_m is the diffusion coefficient.

The significance of the adsorption process of aggressive ions in the instability of the pitting dissolution was pointed out in a preceding paper.⁷ Aggressive anions are adsorbed on the surface of the passive metal, forming a complex with the lattice cation.¹¹ This complex is then activated to dissolve the metal ion. Therefore, the dissolution is thought to be controlled by the fluctuation of the complex concentration, which in turn is equal to the fluctuation of the concentration of the dissolved metal ion.

Assuming a first-order reaction, the fluctuations due to reactions are, thus, expressed by the following rate equations at the interface:

$$j_z(x, y, 0, t)_i^a = z_m F k_a c_m(x, y, 0, t)_{i,R}^a \quad (7)$$

and

$$j_z(x, y, 0, t)^s = z_m F k_a c_m(x, y, 0, t)_R^s, \quad (8)$$

where $j_z(x, y, 0, t)_i^a$ and $j_z(x, y, 0, t)^s$ are asymmetrical and symmetrical fluctuations of the reaction current densities, respectively. Then, k_a is the anodic reaction coefficient for pitting dissolution, being exhibited by

$$k_a = k_{cr}^a \exp(B' \langle \Phi_1 \rangle), \quad (9)$$

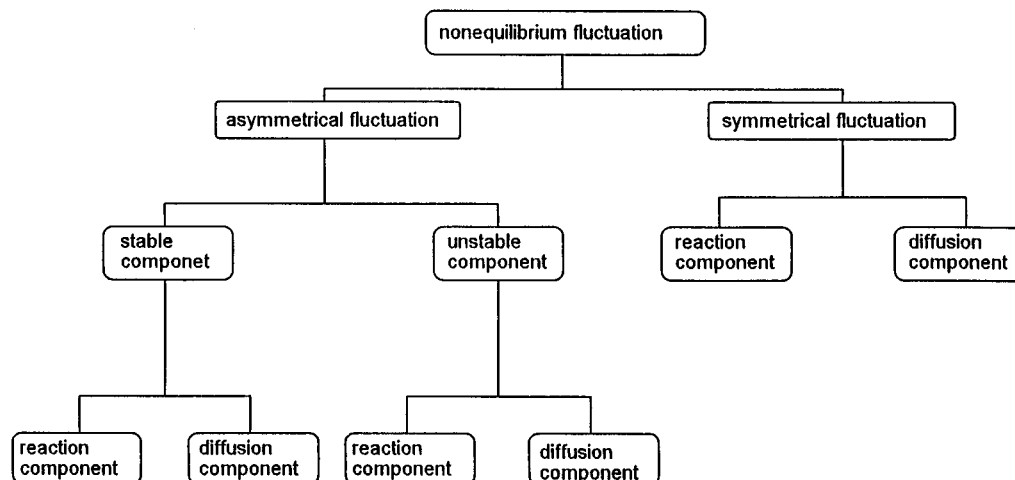


FIG. 5. Classification of nonequilibrium fluctuations.

where k_{cr}^a is the anodic reaction rate coefficient at the critical potential, and $\langle \Phi_1 \rangle$ and B' are the average overpotential of the Helmholtz layer and the constant expressed below,

$$B' \equiv \frac{\alpha z_m F}{RT}, \quad (10)$$

where F , R , and T have usual meanings, and α means the transfer coefficient for the reaction.

3. General amplitude equations

Using these basic equations, we can derive the general equations controlling the time development of the amplitudes of the concentration fluctuations. These equations, as shown in a preceding paper,¹⁴ can describe not only pitting dissolution, but also nucleation. Especially, at the interface, the equation for asymmetrical fluctuation is

$$c_m^0(0,t)_{i,R}^a + \frac{1}{\sqrt{\pi D_m}} \int_0^t \frac{\exp\{-D_m k^2(t-t')\}}{\sqrt{t-t'}} dt' \\ \times k_a c_m^0(0,t')_{i,R}^a dt' = c_m^0(0,t)_i^a, \quad (11)$$

and for symmetrical fluctuation,

$$c_m^0(0,t)_R^s + \frac{1}{\sqrt{\pi D_m}} \int_0^t \frac{\exp\{-D_m k^2(t-t')\}}{\sqrt{t-t'}} dt' \\ \times k_a c_m^0(0,t')_R^s dt' = c_m^0(0,t)^s. \quad (12)$$

Here, the amplitudes, $c_m^0(0,t)_u^a$ and $c_m^0(0,t)^s$ will develop with time according to the processes discussed in a preceding paper,⁷ respectively. On the other hand, the stable components, $c_m^0(0,t)_s^a$ tend to remain constant according to the intrinsic power spectrum as will be mentioned later.

B. Statistical natures of the fluctuations

1. Average values

As mentioned in the preceding section, the total nonequilibrium fluctuation, $c_m(x,y,z,t)_{\text{non}}$ can be divided into two components; one is the asymmetrical fluctuation with positive value, and another is the symmetrical fluctuation changing with positive and negative values. Since the symmetrical fluctuation becomes positive and negative depending on the location, we can assume that $c_m(x,y,z,t)^s$ averaged in the x and y directions is equal to zero.¹⁴ Thus, the average value of the total nonequilibrium fluctuation is equal to that of the asymmetrical fluctuation, i.e.,

$$\langle c_m(x,y,z,t)_{\text{non}} \rangle = \langle c_m(x,y,z,t)^a \rangle. \quad (13)$$

Namely, the average total nonequilibrium fluctuation is equal to its average asymmetrical component. The area average of the concentration is, therefore, given by

$$\langle C_m(x,y,z,t) \rangle = C_m^*(z=\infty) + \langle c_m(x,y,z,t)^a \rangle. \quad (14)$$

Hence, it is assumed that the average value $\langle c_m(x,y,z,t)^a \rangle$ of the asymmetrical component is replaced by the root-mean-square (rms) value. In particular, for $z=0$, it can be written as

$$\langle c_m(x,y,0,t)^a \rangle = + \langle |c_m(x,y,0,t)^a|^2 \rangle^{1/2}, \quad (15)$$

where the plus sign defined for the rms value corresponds to the case of dissolution where the surface concentration increases. From the Rayleigh theorem,¹⁵ we can derive the following relation:¹⁴

$$\langle |c_m(x,y,0,t)^a|^2 \rangle = \langle |c_m^0(0,t)^a|^2 \rangle. \quad (16)$$

For simplicity,

$$\langle |c_m^0(0,t)^a|^2 \rangle \equiv \frac{1}{XY} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} |c_m^0(0,t)^a|^2 dk_x dk_y,$$

where X and Y imply the x - and y -side lengths of electrode, and k_x and k_y are the x and y components of the spatial wave number of the fluctuation, respectively. Consequently, the average values of the nonequilibrium fluctuations can be calculated in terms of their amplitudes.

Furthermore, since the asymmetrical components of the nonequilibrium fluctuations control the reactions themselves, according to Eq. (7), the averaging procedure mentioned above leads to the following total reaction current J , i.e.,

$$J = z_m F S k_a \langle c_m(x,y,0,t)_R^a \rangle, \quad (17)$$

where z_m is the charge number of dissolved metal ion, S the effective surface area, and $c_m(x,y,0,t)_R^a$ means the total asymmetrical concentration fluctuation participating in the reaction.

2. Intrinsic spectra

a. The case of asymmetrical fluctuations. After changing the electrode potential from the stable side of the critical potential to the unstable side, nonequilibrium fluctuations turn unstable via the critical state. At the same time, the reactions occurring at the interface yield new asymmetrical fluctuations in accordance with the potential difference.

In general, with the normalization of the critical fluctuation, the initial spatial spectrum of the concentration fluctuation corresponding to the wave-number components, k_x and k_y , is given as

$$P_{\text{int}}(k_x, k_y)^a \equiv \frac{1}{XY} \frac{|c_m^0(0,t)_{\text{int}}^a|^2}{c_{cr}^2}, \quad (18)$$

where the subscript “int” implies the intrinsic spectrum component, which decides the initial conditions of the fluctuations, $c_m^0(0,t)_{\text{int}}^a$ is the intrinsic component of the amplitude of the asymmetrical fluctuation at $z=0$, which is initially produced by the electrode reaction, then is slowly modulated by the overall reaction process, and c_{cr} means the rms value, i.e., the average value of the critical concentration fluctuation, which is, according to Eq. (16), equal to the rms value of its amplitude at the critical state. Assuming an isotropic Gaussian distribution with normalization, we have the actual form of the power spectrum as follows:

$$P_{\text{int}}(k_x, k_y)^a \equiv \frac{a^2}{\pi} \exp(-a^2 k^2), \quad (19)$$

where a is the autocorrelation distance, which depends on the electrode conditions, and k is equal to $(k_x^2 + k_y^2)^{1/2}$.

The most important parameters deciding the intrinsic power spectrum or the autocorrelation distance are the total overpotential $\langle \Phi_0 \rangle$ of the double layer, which is measured from the critical potential and the coverage θ of passive film. The increase of the absolute value $|\langle \Phi_0 \rangle|$ of the overpotential activates pit formation, so that a number of minute pits will emerge. On the contrary, the decrease of θ , in other words, the enlargement of the active area of the electrode surface allows pits with larger diameters to grow. Since such pit sizes reflect the value of the autocorrelation distance, it is expected that the autocorrelation distance decreases with $|\langle \Phi_0 \rangle|$ and increases with the coverage $1 - \theta$ of the active area. Though the actual function form of the autocorrelation distance should be determined by the experiments, we conveniently assume

$$a = (1 - \theta) \tilde{a}_{\text{cr}} \exp(-B |\langle \Phi_0 \rangle|^p), \quad (20)$$

where p is the positive constant. The symbol “ \sim ” indicates the value corresponding to the completely active surface without any passive films. According to above discussion and the experimental data in the nickel dissolution,¹³ coefficient B must be positive and would take the following form:

$$B = B_1 + \alpha_0(1 - \theta), \quad (21)$$

where B_1 and α_0 are constants.

On the other hand, since the amplitude is also considered to increase with the coverage of the active area, for the intrinsic amplitude, the following equation,

$$c_m^0(0, t)_{\text{int}}^a = (1 - \theta) \tilde{c}_m^0(0, t)_{\text{int}}^a, \quad (22)$$

is assumed. Corresponding to the above equation, the critical average value of the concentration fluctuation can also be expressed as¹²

$$c_{\text{cr}} = (1 - \theta) \tilde{c}_{\text{cr}}. \quad (23)$$

Then, it can be said that all the initial fluctuations do not grow up with time; some parts of them actually turn unstable, but others still remain stable. Therefore, according to the classification of Fig. 5, the amplitude of the intrinsic asymmetrical fluctuation is also divided into stable and unstable components. Introducing the stability ratio γ_s^a and instability ratio γ_u^a , the stable component is written as

$$|c_m^0(0, t)_{\text{int}, s}^a| = \gamma_s^a |c_m^0(0, t)_{\text{int}}^a|, \quad (24)$$

and the unstable component is

$$|c_m^0(0, t)_{\text{int}, u}^a| = \gamma_u^a |c_m^0(0, t)_{\text{int}}^a|. \quad (25)$$

Here, there is the following relationship between γ_s^a and γ_u^a , i.e.,

$$\gamma_s^{a2} + \gamma_u^{a2} = 1. \quad (26)$$

b. The case of symmetrical fluctuations. The intrinsic power spectrum of the symmetrical concentration fluctuation accompanied with the asymmetrical fluctuations is depicted as

$$P_{\text{int}}(k_x, k_y)^s \equiv \frac{1}{XY} \frac{|c_m^0(0, t)_{\text{int}}^s|^2}{c_{\text{cr}}^2}, \quad (27)$$

where $c_m^0(0, t)_{\text{int}}^s$ means the amplitude of the intrinsic symmetrical fluctuation. Since this kind of fluctuation is characterized by the disturbances imposed to the mass transfer in the diffusion layer owing to the thermal motion, the autocorrelation distance is negligibly small compared with that of the asymmetrical fluctuation, and the fluctuation, in this case, does not receive the modulation from the reaction process. It is, thus, approximately assumed that the power spectrum has a time-independent white-noise-type distribution. Hence, the introduction of the white-noise coefficient γ^s leads to

$$P_{\text{int}}(k_x, k_y)^s = \gamma^s{}^2. \quad (28)$$

C. Current equations after a constant potential step is applied

1. Double-layer charging current

After the electrode potential is changed from the passive potential region to the active region beyond the critical potential, the reorganization of the electrical double layer first takes place, and the electrode system transfers to a new electrostatic equilibrium; a charging current simultaneously flows. Since this process occurs much faster than the change of the fluctuations, we can treat it separately from other processes of the fluctuations. Supposing that a working electrode is initially held at the rest potential, of which overpotential V_0 is measured from the critical potential, and then a constant potential step with the overpotential V is imposed to it, the same as in the nucleation case,¹⁴ we can obtain the following equation:

$$J(t) = S(V - V_0)/R_s \exp(-t/R_s C_0), \quad (29)$$

where R_s is the specific area resistance of the solution, and C_0 is the overall capacity of the double-layer per unit area, as shown in a preceding paper⁷ in the form

$$\frac{1}{C_0} = \frac{1}{C_H} + \frac{1}{C_D \{(\partial Q_1^*/\partial Q_2^*)_\mu + 1\}}, \quad (30)$$

where C_H and C_D are the capacities per unit area of the Helmholtz layer and the diffuse layer, respectively. $(\partial Q_1^*/\partial Q_2^*)_\mu$ denotes the electric charge coefficient discussed in a preceding paper.⁸

2. Fluctuation-diffusion current

To calculate the average current density, the contribution of the symmetrical fluctuations may be neglected because, as mentioned before, their average values are assumed equal to zero. We will, thus, use the general amplitude equation, Eq. (11), for the asymmetric components. Immediately after the double-layer charging is completed, the diffusion layer still hardly develops, i.e., the thickness of the diffusion layer is much smaller than the autocorrelation distance of the asymmetrical fluctuation. Here, the diffusion layer thickness and autocorrelation distance can be estimated as $\sqrt{D_m t}$ and $1/k$, respectively. So, the following condition holds

$$t \ll 1/(D_m k^2). \quad (31)$$

Then, assuming that the reaction is much faster than the diffusion, i.e.,

$$t \gg D_m/k_a^2, \quad (32)$$

and using the same calculation as the nucleation case,¹⁴ we can derive the following expression of the fluctuation–diffusion current similar to the Cottrell equation:

$$J = z_m F D_m S (1 - \theta) \tilde{c}_{cr} \sqrt{\frac{1}{\pi D_m t}}. \quad (33)$$

3. Minimum dissolution current

As the reaction proceeds, the diffusion layer develops into the bulk of the solution outside the double layer. When the diffusion layer thickness increases much more than the autocorrelation distance of the asymmetrical nonequilibrium fluctuations, a steady state emerges. Contrary to Eq. (31), in this case, the following condition holds,

$$t \gg 1/(D_m k^2). \quad (34)$$

Then, it is assumed that the reaction rate coefficient is large, so that

$$k_a/(D_m k) \gg 1. \quad (35)$$

Therefore, in the same way as in the nucleation case,¹⁴ the minimum current observed after the fluctuation–diffusion current can be derived as

$$J_{\min} = J_{cr} \exp(B|V|^p), \quad (36)$$

where the critical pitting current J_{cr} is given by

$$J_{cr} = z_m F D_m S \alpha_{cr}. \quad (37)$$

α_{cr} is the critical concentration gradient at $V=0$, defined as

$$\alpha_{cr} = \frac{c_{cr}}{a_{cr}} = \frac{\tilde{c}_{cr}}{\tilde{a}_{cr}}, \quad (38)$$

which is independent of θ , and takes a constant value.

4. Pit-growth current

As the unstable growth of the fluctuations is promoted, the minimum current starts to grow up. According to a preceding paper,⁷ the unstable component of the asymmetrical concentration fluctuation is provided by the amplitude equation

$$c_m^0(0,t)_u^a = c_m^0(0,t)_{\text{int},u}^a \exp\left\{\int_0^t f(t) dt\right\}, \quad (39)$$

where the initial value $c_m^0(0,0)_u^a$ in a preceding paper is replaced by $c_m^0(0,t)_{\text{int},u}^a$ in consideration of the modulation by the reaction, and $f(t)$ is a positive function defined as

$$f(t) = -\frac{\Omega D_m c_{cr} k}{RT} \left\{ z_m F \left(\frac{\partial \langle \Phi_1 \rangle}{\partial \langle \Phi_2 \rangle} \right)_\mu L_\phi + \Omega \gamma^* k^2 \right\} - \frac{\Omega^2 \gamma^* D_{ad} C_{ad}^*}{RT} k^4, \quad (40)$$

and Ω is the molar volume of metal, $(\partial \langle \Phi_1 \rangle / \partial \langle \Phi_2 \rangle)_\mu$ is the double-layer potential coefficient, and L_ϕ is the potential gradient at the outer Helmholtz plane. Then, γ^* is the isotropic surface energy, D_{ad} is the surface diffusion coefficient, and C_{ad}^* is the surface concentration of adatoms.

Since the conditions fulfilled by Eqs. (34) and (35) are still maintained, in the same way as in the nucleation case,¹⁴ the growth current is obtained as follows:

$$J = J_0 \exp(l_G t^2), \quad (41)$$

where J_0 means the current component, which becomes unstable at the minimum state, that is,

$$J_0 = \gamma_u^a J_{\min}, \quad (42)$$

then, l_G is expressed as

$$l_G = \frac{1}{2} A_0^2 \alpha_{cr}^2 C_s^*(z=\infty) |V|^2 \exp(2B|V|^p), \quad (43)$$

where in the present case, the supporting electrolyte is assumed to be a simple 1:1 salt like NaCl, so that A_0 is simply expressed in the form [Eq. (A17) in the appendix, of Ref. 14]

$$A_0 = z_m |z_s| F^2 \sqrt{\frac{2}{\epsilon (RT)^3}} \Omega D_m, \quad (44)$$

where z_s is charge number of either of the supporting electrolytes including sign, and ϵ is dielectric constant.

According to Eq. (41), the dissolution current increases with time, which is, however, gradually suppressed by the subsequent decrease of the double-layer overpotential, as follows: the overpotential V applied to the electrode has the relationship

$$V = \langle \Phi_0 \rangle + R_s J/S + \langle H \rangle, \quad (45)$$

where $\langle \Phi_0 \rangle$ is the average total double-layer overpotential, $R_s J/S$ is the average Ohmic drop, and $\langle H \rangle$ is the average concentration overpotential.

At constant V , $\langle \Phi_0 \rangle$ decreases with increasing $R_s J/S$, so that the diffuse layer overpotential $\langle \Phi_2 \rangle$ approaches zero, i.e., the critical condition of the instability. Therefore, J finally becomes equal to $(V - \langle H \rangle)S/R_s$. In the present case, with the assumption that $\langle H \rangle$ is kept small, it is predicted that J gradually approaches VS/R_s .

III. CONCLUSION

When a constant anodic potential step is applied, after double-layer charging, nonequilibrium fluctuations start to grow. The fluctuations vary along the electrode surface, which reflects the heterogeneity of the pitting dissolution. To calculate the observed current, therefore, they must be mathematically averaged over the electrode surface, and then equalized to the rms values of the amplitudes of the fluctuations.

Here, amplitude equations for asymmetrical concentration fluctuations are required to compute the dissolution current in consideration of the reaction at the electrode surface and diffusion in the stationary solution. Actually, the current equations are analytically derived by means of the amplitude

equations for the following four stages: (1) After double-layer charging, the initial diffusion current flows, which decreases with time, in a similar manner to the Cottrell equation. (2) After decreasing with time, the current attains a minimum value, which is a function of the critical current and the overpotential. (3) Then, as pitting progresses, the fluctuations turn unstable. Initially, the current increases in proportion to the exponential function of the second order of time. (4) As the pitting dissolution more progressively develops, the growth rate of the current is gradually suppressed because of the Ohmic drop of the solution.

APPENDIX: LIST OF SYMBOLS

a	Autocorrelation distance, m .
A_0	Coefficient defined by Eq. (44).
B	Coefficient defined in Eq. (20), $V^{-1/2}$.
B_1	Coefficient defined in Eq. (21), $V^{-1/2}$.
B'	$\equiv \alpha z_m F/RT$ defined by Eq. (10), V^{-1} .
$C_m(x, y, z, t)$	Concentration of dissolved metal ion, mol m^{-3} .
$c_m(x, y, z, t)$	Fluctuation of $C_m(x, y, z, t)$, mol m^{-3} .
$C_m^*(z = \infty)$	Bulk concentration of dissolved metal ion, mol m^{-3} .
$C_s^*(z = \infty)$	Bulk concentration of supporting electrolyte, mol m^{-3} .
C_{ad}^*	Surface concentration of adatoms, mol m^{-2} .
c_{cr}	Average critical concentration fluctuation, mol m^{-3} .
$c_m^0(z, t)$	Amplitude of $c_m(x, y, z, t)$, mol m^{-3} .
C_H	Differential capacity per unit area of the Helmholtz layer, Fm^{-2} .
C_D	Differential capacity per unit area of the diffuse layer, Fm^{-2} .
C_0	Total capacity per unit area of the double layer, Fm^{-2} .
D_m	Diffusion coefficient of dissolved metal ion, $\text{m}^2 \text{s}^{-1}$.
D_{ad}	Surface diffusion coefficient, $\text{m}^2 \text{s}^{-1}$.
$f(t)$	Function defined by Eq. (40), s^{-1} .
F	Faraday's constant, $96\,487 \text{ mol equiv.}^{-1}$.
J_{\min}	Minimum dissolution current, A.
J_{cr}	Critical pitting current, A.
J_0	Unstable component of J_{\min} , A.
J	Total current, A.
$j_z(x, y, z, t)$	z component of the fluctuation of current density vector, Am^{-2} .
k_x, k_y	x and y components of wave-number vector, m^{-1} .
k	$\equiv (k_x^2 + k_y^2)^{1/2}$, m^{-1} .
k_a	Anodic reaction coefficient, m s^{-1} .
k_{cr}^a	Anodic reaction coefficient at the critical potential, m s^{-1} .
L_ϕ	Average potential gradient at the outer Helmholtz plane, V m^{-1} .
l_G	Growth factor defined in Eq. (43), s^{-2} .
$P_{\text{int}}(k_x, k_y)$	Intrinsic spectrum.
p	Positive constant introduced by Eq. (20).

$\left(\frac{\partial Q_1^*}{\partial Q_2^*}\right)$	Electric charge coefficient of the double layer.
R	Universal gas constant, $8.3143 \text{ J mol}^{-1} \text{ deg}^{-1}$.
R_s	Specific area resistance, $\Omega \text{ m}^2$.
S	Effective surface area, m^2 .
t	Time, s.
T	Absolute temperature, K.
V	Externally applied overpotential, V.
V_0	Initial overpotential, V.
x, y, z	Variables in Cartesian-coordinate system, m.
X, Y	x - and y -side lengths of the electrode, m.
z_m	Charge number of the dissolved metal ion, including sign.
z_s	Charge number of either ion of the supporting electrolyte of 1:1 salt including sign.
α	Transfer coefficient for the reaction.
α_{cr}	Critical concentration gradient, mol m^{-4} .
α_0	Coefficient defined by Eq. (21), $V^{-1/2}$.
γ_s^a	Stability ratio of asymmetrical concentration fluctuation.
γ_u^a	Instability ratio of asymmetrical concentration fluctuation.
γ^s	White-noise coefficient, m.
γ^*	Isotropic surface free energy, J m^{-2} .
ϵ	Dielectric constant, F m^{-1} .
H	Concentration overpotential, V.
θ	Coverage of passive film.
λ	Debye's length, m.
Φ_0	Total overpotential of the double layer, V.
Φ_1	Potential difference of the Helmholtz layer, V.
Φ_2	Potential difference of the diffuse layer, V.
$\left(\frac{\partial \langle \Phi_1 \rangle}{\partial \langle \Phi_2 \rangle}\right)_\mu$	Double layer potential coefficient.
Ω	Molar volume of the dissolving metal, $\text{m}^3 \text{mol}^{-1}$.
\sim	Symbol denoting the quantity on the completely active surface.
$\langle \rangle$	Symbol denoting average in x and y directions.
∇^2	$\equiv \partial^2/\partial x^2 + \partial^2/\partial y^2 + \partial^2/\partial z^2$.
superscripts	
*	Superscript denoting electrostatic equilibrium.
a	Superscript denoting asymmetrical feature of fluctuation.
s	Superscript denoting symmetrical feature of fluctuation.
subscripts	
cr	Subscript denoting the quantity at the critical state.
int	Subscript denoting the intrinsic fluctuation.
non	Subscript denoting total nonequilibrium fluctuation.
s	Subscript denoting the stable component.
u	Subscript denoting the unstable component.

D	Subscript indicating the component generated by diffusion.
R	Subscript indicating the component generated by reaction.
μ	Subscript indicating that the chemical potentials of all the components are kept constant.

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