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Citation: *The Journal of Chemical Physics* **103**, 8602 (1995); doi: 10.1063/1.470119

View online: <http://dx.doi.org/10.1063/1.470119>

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Instability of nonequilibrium fluctuation in electrochemical nucleation.

I. Occurrence of instability

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(Received 1 May 1995; accepted 27 July 1995)

From the viewpoint of unstable growth of nonequilibrium fluctuations, nucleation processes were examined. Electrostatic equilibrium produced by the electric double layer is always locally broken by the thermal motion of solution particles. This breakdown, i.e., fluctuation occurs not at the Nernstian equilibrium, so that we call it "nonequilibrium fluctuation." In examining the mechanism of the fluctuation, it was shown that a new type of instability occurs, which takes place in the absence of the intense specific adsorption of ions on the electrode surface. Then, two different modes for the instability are possible, that is, one is the case where from the beginning, there is no specific adsorption, and another the case where the surface is specifically adsorbed by the ions at the initial stage. The former case allows the fluctuation to continuously transfer from the stable state to the unstable nucleus growth whereas in the latter case, immediately after specific adsorption ceases, nucleation starts rapidly. On the contrary, when the specific adsorption occurs at the nonspecifically adsorbed surface, nucleation will be suddenly stopped. Furthermore, the fluctuation of the second type is formed for the mass flux of depositing metal ions in the diffusion layer, which becomes always unstable, accompanied with the unstable growth of the fluctuation of the first type. © 1995 American Institute of Physics.

I. INTRODUCTION

Much attention concerning the recent development of various surface observation techniques has been paid to the nucleation phenomena in electrochemistry. The studies of electrochemical nucleation are roughly classified into three fields; energetics based on the thermodynamics,¹⁻⁴ kinetics coming from the rate process,⁵⁻⁷ and morphological crystallography.^{8,9} In the first case, with the computation of the bonding energies of lattice atoms, the crystal face preferable for growth and then the crystal morphology were obtained. At the same time, deriving the free energy necessary to make embryos, the size of the crystal nucleus, and the activation energy for the nucleation were estimated.^{6,10}

On the other hand, in the next case, for the metal deposition onto the same metal, the surface diffusion of adatoms to the kinks and steps, or the direct discharge of the dehydrated ions was first assumed. Then, using resultant current-potential curve, current-time transient, and potential time variation, the parameters such as the surface diffusion coefficient, and the rate constant of electron transfer were calculated.¹¹ For the metal deposition onto different metal, by the use of Abrami equation,¹² many equations depicting current-time transients which arise from two-dimensional or three-dimensional nucleus formation have been derived and then experimentally examined.^{6,7,13,14} Finally, as to the morphological crystallography, many experimental results have been reported under various electrolysis conditions.^{9,15} However, in spite of so many investigations, we have as before one unsolved problem concerning the factors which determine the initiation of nucleation. In other words, it is still unknown how the critical potential of the nucleation is decided.

Morphological stability analysis, first introduced by

Mullins and Sekerka,¹⁶⁻¹⁹ has been a useful tool to predict the morphological stability of the growing interface, which arises from the mass flux disturbed by the thermal motion of solution particles. Such an interface is considered to be morphologically stable when any infinitesimal perturbation introduced to the electrode surface decays with time. On the other hand, when the perturbation grows with time, the interface is regarded as morphologically unstable. For electrochemical nucleation, the morphological stability have also been precisely studied.²⁰⁻³³ All these theories treat the processes after nucleation starts, so that the critical conditions for nucleus formation cannot be derived. In these mathematical models, the fluctuations induced during mass transfer of metal ion in the diffusion layer are employed, of which average values are thus equal to zero, i.e., such fluctuations have a kind of symmetry.

However, fluctuations of another kind which are controlled by the reaction in the electric double layer are possible; the stability analysis therefore gives the critical condition which determines the commencement of nucleation. They are considered to have asymmetry, that is, their average values are not equal to zero since the reaction proceeds in a specific direction. In this paper, we first examine the stability of an electrode surface nucleated by different metal, then makes it clear that the nucleation arises from the unstable growth of the two kinds of fluctuation. Finally, by inspection of the instability factors, the critical condition for nucleation is presented.

II. THEORY

In an electrode system, two different kinds of thermodynamic equilibria play substantially important roles; one is

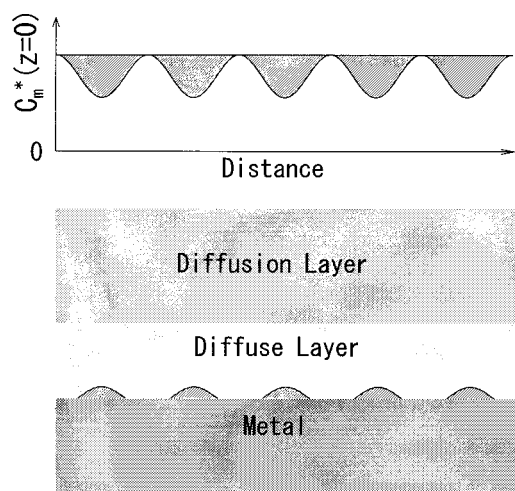


FIG. 1. Schematic depiction of occurrence of asymmetrical concentration fluctuation. In the case of deposition, it takes negative value from the electrostatic equilibrium state.

Nernstian equilibrium in relation to electrode reactions and another is electrostatic equilibrium arising from the formation of the electric double layer.

When the electrode potential initially settled at the rest potential is shifted to cathodic direction, the electrode system starts the transition to a new equilibrium state. At first, the resultant reconstruction of the double layer leads the dielectric relaxation, which yields a new potential difference maintaining electrostatic equilibrium. The equilibrium newly formed is, however, easily and incessantly broken by the thermal motion of solution particles. Since the electrode system is not at Nernstian equilibrium, we call such breakdown “nonequilibrium fluctuation.” The physical quantities related to the nucleation fluctuate on the one side of the electrostatic equilibrium, that is, such fluctuations take place toward one particular direction where the reaction proceeds. For example, as shown in Fig. 1, the concentration fluctuation takes definite negative sign; in this sense, the fluctuations of this kind have asymmetry.

If the electrode system is stable, the fluctuations are always around the electrostatic equilibrium. Hence, we can regard such electrode as an ideal polarized electrode. On the other hand, if the electrode system is unstable, the fluctuations start to grow with time, diverging from the electrostatic equilibrium. The nucleation current rapidly develops, so that nuclei grow actively. In this case, the nuclei are yielded by the interaction between the electrode surface and ions in the double layer, and therefore, tend to take two-dimensional morphology.

As the reaction progresses, the mass flux induced by the asymmetrical concentration fluctuation forms a diffusion layer outside the double layer, and nonequilibrium fluctuations of another type occur in the diffusion layer, which come from the mass transfer of the metal ions perturbed by thermal motion of solution particles. Therefore, as shown in Fig. 2, the mass flux fluctuates around its average value, i.e., the fluctuations take both signs of plus and minus; in this sense, they have symmetry. The nucleation corresponding to

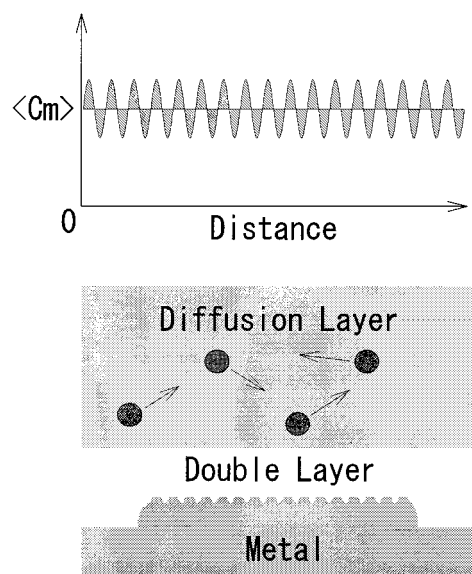


FIG. 2. Schematic depiction of occurrence of symmetrical concentration fluctuation. It takes positive and negative values around the average value.

the fluctuations of this type occurs from the disturbance of the thermal motion of the solution particles in the diffusion layer, and therefore is expected to yield three-dimensional nuclei.

A. Asymmetrical and symmetrical fluctuations

Nonequilibrium fluctuations are defined as the differences from the electrostatic equilibrium. For example, the nonequilibrium fluctuation of the concentration $C_m(x, y, z, t)$ of depositing metal ions is written as

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

where $C_m^*(z, t)$ is the concentration in the electrostatic equilibrium, which is assumed to be unique in the directions parallel to the surface. In the present case, the electrode surface is taken as the x - y plane in Cartesian coordinates. The superscript a indicates the asymmetrical feature of the fluctuations, which change on the one side of the equilibrium, e.g., $c_m(x, y, z, t)^a$ takes negative value due to the depletion of the metal ions.

From Eq. (1), the average concentration is given as

$$\langle C_m(x, y, z, t) \rangle = C_m^*(z, t) + \langle c_m(x, y, z, t)^a \rangle, \quad (2)$$

where $\langle \rangle$ means the average with respect to the electrode surface. As stated in the previous section, in the diffusion layer, there are fluctuations of another kind, i.e., symmetrical type fluctuations, which are defined as the difference from their own average value. The symmetrical concentration fluctuation, is thus written in the form

$$c_m(x, y, z, t)^s \equiv C_m(x, y, z, t) - \langle C_m(x, y, z, t) \rangle, \quad (3)$$

where superscript s indicates the symmetrical feature of the fluctuation varying on the both sides of the average value.

Therefore, the total nonequilibrium fluctuation is given as follows:

$$c_m(x, y, z, t)_{\text{non}} = c_m(x, y, z, t)^a + c_m(x, y, z, t)^s, \quad (4)$$

where subscript non indicates the total nonequilibrium fluctuation.

In the similar way, for the electrostatic potential $\Phi(x, y, z, t)$, we can define the asymmetrical fluctuation, i.e.,

$$\phi(x, y, z, t)^a \equiv \Phi(x, y, z, t) - \Phi^*(z, t). \quad (5)$$

The average potential is

$$\langle \Phi(x, y, z, t) \rangle = \Phi^*(z, t) + \langle \phi(x, y, z, t)^a \rangle. \quad (6)$$

Then, the symmetrical component is defined as

$$\phi(x, y, z, t)^s \equiv \Phi(x, y, z, t) - \langle \Phi(x, y, z, t) \rangle. \quad (7)$$

The total fluctuation is

$$\phi(x, y, z, t)_{\text{non}} = \phi(x, y, z, t)^a + \phi(x, y, z, t)^s. \quad (8)$$

For the electrolytic (faradaic) current density vector $\mathbf{J}(x, y, z, t)$, the asymmetrical component is also written in the similar form to Eq. (5), i.e.,

$$\mathbf{j}(x, y, z, t)^a \equiv \mathbf{J}(x, y, z, t) - \mathbf{J}(t)^*, \quad (9)$$

where $\mathbf{J}(t)^*$ means electrostatic component, being equal to zero after the double layer is charged. The average value is

$$\langle \mathbf{J}(x, y, z, t) \rangle = \mathbf{J}(t)^* + \langle \mathbf{j}(x, y, z, t)^a \rangle. \quad (10)$$

The symmetrical component is

$$\mathbf{j}(x, y, z, t)^s \equiv \mathbf{J}(x, y, z, t) - \langle \mathbf{J}(x, y, z, t) \rangle. \quad (11)$$

Then, the total fluctuation is

$$\mathbf{j}(x, y, z, t)_{\text{non}} = \mathbf{j}(x, y, z, t)^a + \mathbf{j}(x, y, z, t)^s. \quad (12)$$

The thickness of the Helmholtz layer is the order of the diameter of water molecule³⁴ whereas the scale of the fluctuation is considered to be the order of the nucleus diameter. Therefore, neglecting the thickness of the Helmholtz layer in comparison with the scale of the fluctuations, we can obtain the fluctuation of the surface form $Z(x, y, t)$, as follows:

$$\zeta(x, y, t)^a \equiv Z(x, y, t) - Z^*(x, y), \quad (13)$$

where the value of $\zeta(x, y, t)^a$ is defined positive because of deposition. Thus average height of the surface is

$$\langle Z(x, y, t) \rangle = Z^*(x, y) + \langle \zeta(x, y, t)^a \rangle. \quad (14)$$

The symmetrical fluctuation is

$$\zeta(x, y, t)^s \equiv Z(x, y, t) - \langle Z(x, y, t) \rangle, \quad (15)$$

where $\zeta(x, y, t)^s$ takes, owing to the symmetrical nature, both positive and negative values. Then, the total fluctuation is given as

$$\zeta(x, y, t)_{\text{non}} \equiv \zeta(x, y, t)^a + \zeta(x, y, t)^s. \quad (16)$$

B. Basic equations

1. Diffusion equation

In the presence of large amount of supporting electrolyte, the depositing metal ions transfer in a static solution without any convection according to the diffusion equation

$$\left(\nabla^2 - \frac{1}{D_m} \frac{\partial}{\partial t} \right) C_m(x, y, z, t) = 0, \quad (17)$$

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 of the active species. Substituting Eqs. (1) and (3) into Eq. (17), the following equation for the asymmetrical and symmetrical fluctuations is derived, i.e.,

$$\left(\nabla^2 - \frac{1}{D_m} \frac{\partial}{\partial t} \right) c_m(x, y, z, t) = 0, \quad (18)$$

where $c_m(x, y, z, t)$ means $c_m(x, y, z, t)^a$ or $c_m(x, y, z, t)^s$. Henceforth, for simplicity, we adopt the following notation: In the equations applicable to the fluctuations of both kinds, they are denoted as one quantity without the superscript a or s .

2. Current density

When there is large amount of supporting electrolyte in a solution, the conductivity is determined by the activities of the electrolyte. In reckoning the value, as mentioned above, we can neglect the thickness of the double layer because it is negligibly small in comparison with the scale of the fluctuations. Thus using the concentrations of ions j 's instead of the activities, the conductivity is expressed as

$$\sigma^* = \sum_{j \neq m} \frac{z_j^2 F^2}{RT} D_j C_j^*(z = \infty), \quad (19)$$

where $j \neq m$ means the exclusion of the metal ion from the summation which is possible because the electric charges in the solution are mainly carried by the majority carriers, i.e., the supporting electrolyte ions, and z_j the charge including sign of the ion j of the supporting electrolyte, D_j the diffusion coefficient, and $C_j^*(z = \infty)$ is the bulk concentration, F , R , and T have their usual meanings, i.e., Faraday constant, gas constant and absolute temperature, respectively. Neglecting the diffusion potential,³⁵ the current density fluctuation is expressed by the electrostatic potential fluctuation, that is,

$$\mathbf{j}(x, y, z, t) = -\sigma^* \nabla \phi(x, y, z, t). \quad (20)$$

Then, the conservation of electricity gives

$$\nabla \cdot \mathbf{j}(x, y, z, t) = 0. \quad (21)$$

Furthermore, as a boundary condition, there is a well-known relationship between the current density and the concentration gradient of the active species at the interface, i.e.,

$$\mathbf{n} \cdot \mathbf{j}(x, y, z, t) = -z_m F D_m \{ \mathbf{n} \cdot \nabla c_m(x, y, z, t) \}, \quad (22)$$

where \mathbf{n} means the unit normal vector of the electrode surface.

3. Surface diffusion of adatoms

After dehydrating, active species of ions receive electrons at the interface, being adsorbed on it as adatoms. Then, the adatoms diffuse along the electrode surface according to the local difference of their chemical potential. Finally, after traveling to unstable sites, they are incorporated into the substrate as lattice atoms. As shown in Fig. 3, the mass balance of adatoms comes from the mass flux \mathbf{j}_{flux} of the metal ions

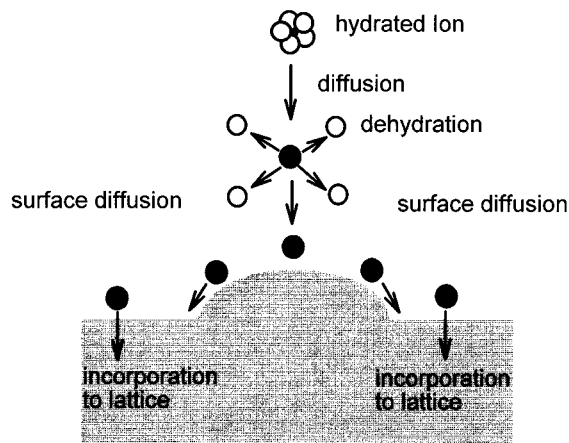


FIG. 3. Schematic diagram for the mass balance near the electrode surface; both the surface diffusion and deposition simultaneously occur. It is assumed that the adatoms are kept in equilibrium with the lattice atoms.

from solution phase to the interface, the mass flux \mathbf{j}_{surf} of adatoms by the surface diffusion, and the mass flux \mathbf{j}_{inc} of the adatoms by the incorporation to crystal lattice, that is,

$$\frac{\partial}{\partial t} c_{\text{ad}}(x, y, t) + \nabla_{\perp} \cdot \mathbf{j}_{\text{surf}} = \mathbf{n} \cdot \mathbf{j}_{\text{flux}} - \mathbf{n} \cdot \mathbf{j}_{\text{inc}}, \quad (23)$$

where $c_{\text{ad}}(x, y, t)$ is the fluctuation of the adatom concentration, and $\nabla_{\perp} \equiv (\partial/\partial x, \partial/\partial y)$.

Here, it is assumed that the exchange rate between the adatoms and lattice atoms is so high that an equilibrium can be expected between them. If the activity of lattice atom is kept constant all over the crystal surface, the concentration of the adatoms becomes independent of the location. The concentration fluctuation of the adatoms thus can be neglected. Consequently, it is concluded that the fluctuation of the chemical potential of the adatoms does not result from the variation in the activity of the adatoms, but from the surface deformation due to nucleation.

According to above discussion, with surface diffusion coefficient, D_{ad} and surface concentration, C_{ad}^* of the adatoms, the mass flux of the adatoms along the surface is given as

$$\mathbf{j}_{\text{surf}} = -\frac{D_{\text{ad}}}{RT} C_{\text{ad}}^* \nabla_{\perp} \psi(x, y, t), \quad (24)$$

where $\psi(x, y, t)$ expresses the fluctuation of the chemical potential of the adatoms by the change of surface form, i.e.,

$$\psi(x, y, t) = -\Omega \gamma^* \nabla_{\perp}^2 \zeta(x, y, t), \quad (25)$$

where $\nabla_{\perp}^2 \equiv \partial^2/\partial x^2 + \partial^2/\partial y^2$, Ω the molar volume of depositing metal, and γ^* is the isotropic surface free energy. Then, in terms of the mass flux of active species, Eq. (22) is rewritten as

$$\mathbf{n} \cdot \mathbf{j}_{\text{flux}} = D_m \{ \mathbf{n} \cdot \nabla c_m(x, y, z, t) \}. \quad (26)$$

Sign of the flux is defined plus in the case of deposition. Finally, the surface deformation rate is decided by the deposition rate and mass flux of the adatoms, as follows:

$$\frac{\partial}{\partial t} \zeta(x, y, t) = \Omega \left\{ \frac{\partial}{\partial t} c_{\text{ad}}(x, y, t) + \mathbf{n} \cdot \mathbf{j}_{\text{inc}} \right\}. \quad (27)$$

By substituting Eqs. (24) to (27) into Eq. (23), the following equation is obtained:

$$\frac{1}{\Omega} \frac{\partial}{\partial t} \zeta(x, y, t) = -\Omega \gamma^* \frac{D_{\text{ad}}}{RT} C_{\text{ad}}^* \nabla_{\perp}^4 \zeta(x, y, t) + D_m \{ \mathbf{n} \cdot \nabla c_m(x, y, z, t) \}, \quad (28)$$

where $\nabla_{\perp}^4 \equiv \partial^4/\partial x^4 + \partial^4/\partial y^4$.

C. Electrochemical potential fluctuation of depositing metal ions

If the electron transfer between the metal ions and the adatoms is much faster than the diffusion of the metal ions, an equilibrium between them can be approximately assumed. In general, this charge-transfer reaction may be represented by the following formal reaction, i.e.,



where $M(\text{ad})$ adatom, M^{z_m+} active metal ion and e is electron. From Eq. (29), the chemical potential of adatoms has the relationship, i.e.,

$$\mu_{\text{ad}}(x, y, t) = \bar{\mu}_m(x, y, \zeta, t) + z_m \bar{\mu}_e(x, y, t), \quad (30)$$

where ζ denotes the surface deformation $\zeta(x, y, t)$ by the nucleation, and $\bar{\mu}_m$ denotes the electrochemical potential of the metal ions at the outer Helmholtz plane and $\bar{\mu}_e$ is the electrochemical potential of free electrons in the metal phase. The spatial fluctuation of the electrons can be neglected due to their large mobilities. Thus the fluctuation of the chemical potential of the adatoms becomes equal to that of the electrochemical potential of the metal ions, that is,

$$\delta \mu_{\text{ad}}(x, y, t) = \delta \bar{\mu}_m(x, y, \zeta, t), \quad (31)$$

where $\delta \mu_{\text{ad}}$ and $\delta \bar{\mu}_m$ indicate the fluctuations of the chemical potential and electrochemical potential, respectively. Moreover, as discussed for Eq. (25), the fluctuation of the chemical potential of the adatoms is, in turn, equal to the fluctuation, $\psi(x, y, t)$, i.e.,

$$\delta \mu_{\text{ad}}(x, y, t) = \psi(x, y, t). \quad (32)$$

Then, the fluctuation of the electrochemical potential of the metal ions in the Helmholtz layer can be described from Eqs. (25), (31), and (32), as follows:

$$\delta \bar{\mu}_m(x, y, \zeta, t) = -\Omega \gamma^* \nabla_{\perp}^2 \zeta(x, y, t). \quad (33)$$

For the purpose of deriving the boundary conditions, we must take different procedures depending on the types of fluctuations, i.e., asymmetrical and symmetrical fluctuations.

1. Boundary condition of asymmetrical fluctuations

In order to define the electrochemical potential of the metal ions in the diffuse layer, i.e., the outer region of the electric double layer, we can imagine an idealized electrode which is reversible to the ions. In the present case, we mean a small electrode composed of the same metal as the deposited metal, through which only a negligible current is passed

and which has no potential variations in the diffuse layer not to alter conditions from those prevailing in its absence.³⁶

Frequently, the electrochemical potential of an ionic species is split into an electrical term and a chemical term, which are determined by the following two cases: In the absence of concentration variations, such probe electrode will measure the electric potential differences in the diffuse layer adjacent to the deposited metal surface against the potential in the bulk of the solution. This is equivalent to measuring the electrochemical potential $\bar{\mu}_m$ of the metal ions without concentration difference in the diffuse layer.

For the fluctuation of the electrical part of the electrochemical potential, it follows that

$$\begin{aligned}(\Phi_1)_{\text{rev}} &= \frac{1}{z_m F} \delta \bar{\mu}_m(x, y, z, t)^a \\ &= \phi_2(x, y, z, t)^a,\end{aligned}\quad (34)$$

where $(\Phi_1)_{\text{rev}}$ is the potential value measured by the probe electrode, which detects the electrochemical potential as an electric potential difference of the Helmholtz layer, and ϕ_2^a is the potential fluctuation in the diffuse layer.

In the presence of concentration variations, on the contrary, it is convenient to conceive of the diffuse layer without any differences of the electrical conditions corresponding to the critical state which is discussed later, so that the concentration fluctuation must be measured from the critical state. Such condition can be realized by imposing to the probe electrode a Helmholtz layer potential of which the absolute value is equal to the potential difference in the diffuse layer but the sign is opposite.

According to Eq. (A8) in Appendix A, therefore, the probe electrode must have the following potential:

$$\begin{aligned}(\Phi_1)_{\text{rev}} &= \frac{1}{z_m F} \delta \bar{\mu}_m(x, y, z, t)^a \\ &= \frac{RT}{z_m F c_{\text{cr}}} c_m(x, y, z, t)^a,\end{aligned}\quad (35)$$

where c_{cr} means the average critical concentration fluctuation, being defined on the flat surface as [see Eqs. (1) and (A9) in Appendix A]

$$c_{\text{cr}} = |\langle C_m(x, y, 0, t)_{\text{cr}} \rangle - C_m^*(z = \infty)|, \quad (36)$$

where subscript cr means the critical value.

Using the definition of the concentration fluctuation mentioned above, as discussed in Eq. (A7) in Appendix A, instead of Eq. (1), $c_m(x, y, z, t)^a$ is redefined as the concentration fluctuation measured from the critical state, that is,

$$c_m(x, y, z, t)^a + c_{\text{cr}} \rightarrow c_m(x, y, z, t)^a. \quad (37)$$

Here, it should be noted that this redefinition of $c_m(x, y, z, t)^a$ does not yield any kind of change in the calculation of the fluctuations since the introduction of constant c_{cr} does not affect the variable portions of the fluctuations. Therefore, $c_m(x, y, z, t)^a$ is actually expressed as Eq. (53) only by the spatially variable portion.

In general, the fluctuation of the electrochemical potential can be expressed as a linear combination of Eqs. (34) and (35),

$$\delta \bar{\mu}_m(x, y, z, t)^a = z_m F \phi_2(x, y, z, t)^a + \frac{RT}{c_{\text{cr}}} c_m(x, y, z, t)^a. \quad (38)$$

However, at the boundary of the diffuse layer and the Helmholtz layer called the outer Helmholtz plane, such fluctuations will also affect the electric potential in the Helmholtz layer; we newly add a potential function $\phi_1(x, y, t)^a$ of the Helmholtz layer to Eq. (38)

$$\begin{aligned}\delta \bar{\mu}_m(x, y, \zeta^a, t)^a &= z_m F \{ \phi_1(x, y, t)^a + \phi_2(x, y, \zeta^a, t)^a \} \\ &\quad + \frac{RT}{c_{\text{cr}}} c_m(x, y, \zeta^a, t)^a,\end{aligned}\quad (39)$$

where ζ^a implies the outer Helmholtz plane deformed by deposition, $\zeta(x, y, z, t)^a$.

Then, ϕ_1^a and ϕ_2^a are related to each other, as follows:

$$\phi_1(x, y, t)^a = \left(\frac{\partial \langle \Phi_1 \rangle}{\partial \langle \Phi_2 \rangle} \right)_\mu \phi_2(x, y, \zeta^a, t)^a, \quad (40)$$

where $\langle \Phi_1 \rangle$ and $\langle \Phi_2 \rangle$ are the area-averaged potential differences of the Helmholtz layer and the diffuse layer, respectively. Subscript μ suggests that chemical potentials (activities) of all the components are kept constant.

Therefore, substituting Eq. (40) into Eq. (39), it follows that

$$\begin{aligned}\delta \bar{\mu}_m(x, y, \zeta^a, t)^a &= z_m F \left\{ \left(\frac{\partial \langle \Phi_1 \rangle}{\partial \langle \Phi_2 \rangle} \right)_\mu + 1 \right\} \phi_2(x, y, \zeta^a, t)^a \\ &\quad + \frac{RT}{c_{\text{cr}}} c_m(x, y, \zeta^a, t)^a.\end{aligned}\quad (41)$$

Finally, we can obtain the boundary condition for the asymmetrical components by using Eqs. (33) and (41), i.e.,

$$\begin{aligned}z_m F \left\{ \left(\frac{\partial \langle \Phi_1 \rangle}{\partial \langle \Phi_2 \rangle} \right)_\mu + 1 \right\} \phi_2(x, y, \zeta^a, t)^a \\ + \frac{RT}{c_{\text{cr}}} c_m(x, y, \zeta^a, t)^a + \Omega \gamma^* \nabla_\perp^2 \zeta(x, y, t)^a = 0.\end{aligned}\quad (42)$$

The effect of surface deformation in the Helmholtz layer should be involved in this equation; that is, the c_m^a and ϕ_2^a should change in location on the electrode surface. Such effect can be expressed by the first order expansions of the c_m^a and ϕ_2^a at the curved outer Helmholtz plane ($z = \zeta^a$) against the flat Helmholtz plane ($z = 0$), i.e.,

$$c_m(x, y, \zeta^a, t)^a = c_m(x, y, 0, t)^a \pm L_m \zeta(x, y, t)^a, \quad (43)$$

$$\phi_2(x, y, \zeta^a, t)^a = \phi_2(x, y, 0, t)^a \pm L_\phi \zeta(x, y, t)^a, \quad (44)$$

where L_m and L_ϕ are the averaged concentration fluctuation gradient and the averaged potential gradient at the flat outer Helmholtz plane, respectively, i.e.,

$$L_m \equiv \left\{ \frac{\partial \langle c_m(x, y, z, t)^a \rangle}{\partial y} \right\}_{z=0}, \quad (45)$$

$$L_\phi \equiv \left\{ \frac{\partial \langle \Phi(x, y, z, t) \rangle}{\partial y} \right\}_{z=0}. \quad (46)$$

Hence, in Eqs. (43) and (44), which sign, plus or minus, should be chosen depends on the adsorption state of ionic species in the Helmholtz layer; if any kind of specific adsorption is neglected or such adsorption is not so intense, plus sign can be adopted because there is no inversion of the sign of the electric potential $(\Phi_1)_{\text{rev}}$ measured by the probe electrode depicted in Eqs. (34) and (35). This means that the sign of the potential difference in the Helmholtz layer is the same as that of the potential in the diffuse layer, i.e., $(\partial \langle \Phi_1 \rangle / \partial \langle \Phi_2 \rangle)_\mu > 0$. In this case, as discussed later, the asymmetrical fluctuations associated with nucleation turn unstable.

However, in the case of intense specific adsorption, as will be mentioned in the anodic dissolution of nickel,³⁷ such inversion will be expected. In this case, the minus sign should be taken, so that $(\partial \langle \Phi_1 \rangle / \partial \langle \Phi_2 \rangle)_\mu < 0$ holds.

2. Boundary condition of symmetrical fluctuations

As the reaction proceeds at the electrode, diffusion layer is gradually formed outside the double layer by the asymmetrical concentration fluctuation, being accompanied with the mass transfer of the metal ions. The mass transfer is also disturbed by the thermal motion of solution particles, so that fluctuations of another type, i.e., symmetrical fluctuations take place. Since the thickness of the double layer can be neglected as mentioned before, we can take the flat substrate surface as $z=0$. For the purpose of the definition of the electrochemical potential of the metal ions in the diffusion layer, we can again use the idealized probe electrode which is reversible to the ionic species.

This electrode imagined as a small one does not disturb the conditions in the diffusion layer which is dominant in its absence. Thus, the symmetrical fluctuation of the electrochemical potential of the metal ions is given in the form,

$$\delta \bar{\mu}_m(x, y, \zeta^s, t)^s = z_m F \phi(x, y, \zeta^s, t)^s + RT \delta \{ \ln C_m(x, y, \zeta^s, t) \}^s, \quad (47)$$

where $\phi(x, y, \zeta^s, t)^s$ is potential fluctuation arising from the ohmic drop in the solution. The ζ^s implies the surface deformation by the symmetrical fluctuations, $\zeta(x, y, z, t)^s$.

Using the assumption that

$$|c_m(x, y, \zeta^s, t)^s| \ll \langle C_m(x, y, 0, t) \rangle \quad (48)$$

with Eq. (3), the concentration term in Eq. (47) can be rewritten in the following:

$$RT \delta \{ \ln C_m(x, y, \zeta^s, t) \}^s = \frac{RT}{\langle C_m(x, y, 0, t) \rangle} c_m(x, y, \zeta^s, t)^s. \quad (49)$$

Substituting Eqs. (47) and (49) into Eq. (33), the boundary condition of the symmetrical fluctuations is derived as

$$z_m F \phi(x, y, \zeta^s, t)^s + \frac{RT}{\langle C_m(x, y, 0, t) \rangle} c_m(x, y, \zeta^s, t)^s + \Omega \gamma^* \nabla_\perp^2 \zeta(x, y, t)^s = 0. \quad (50)$$

Here, as the surface morphology changes with nucleation, the concentration distribution in the diffusion layer also changes.

This influence is exhibited by the first order expansion outside the double layer, i.e.,

$$c_m(x, y, \zeta^s, t)^s = c_m(x, y, 0, t)^s + L \zeta(x, y, t)^s, \quad (51)$$

where L implies the averaged concentration gradient in the diffusion layer, which is formed by the asymmetrical fluctuations accompanied with nucleation.

The actual expression is

$$L \equiv \left\{ \frac{\partial \langle c_m(x, y, z, t) \rangle_D^a}{\partial z} \right\}_{z=0}, \quad (52)$$

where $c_m(x, y, z, t)_D^a$ indicates the asymmetric concentration fluctuation arising from the diffusion of the metal ions.³⁸

D. Derivation of amplitude factor

1. Solution of basic equation

Nonequilibrium fluctuation can be described by the two-dimensional waves with various wave numbers, in the present case, composed of x and y components. As discussed in Eq. (37), the most important point to calculate the fluctuation is the extraction of the portion which varies with location. For example, the spatially variable portion of the concentration fluctuation corresponding to a wave number vector (k_x, k_y) is given in the complex notation,

$$c_m(x, y, z, t) = c_m^0(z, t) \exp[i(k_x x + k_y y)], \quad (53)$$

where for simplicity, as mentioned before, the fluctuation is written without the superscript a or s . The $c_m^0(z, t)$ is the amplitude of the wave, which is a function of the absolute value $k[\equiv (k_x^2 + k_y^2)^{1/2}]$ of the wave number vector, location z and time t . The behavior is known from the amplitude equation, which is deduced from the two-dimensional Fourier transform of Eq. (18) in x and y directions, i.e.,

$$\left(\frac{\partial^2}{\partial z^2} - k^2 - \frac{1}{D_m} \frac{\partial}{\partial t} \right) c_m^0(z, t) = 0. \quad (54)$$

Here, provided that the time dependence of the amplitude is much smaller than the space dependence, then Eq. (54) is rewritten as

$$\left(\frac{\partial^2}{\partial z^2} - k^2 \right) c_m^0(z, t) = 0. \quad (55)$$

A boundary condition that in the bulk the fluctuation disappears is given in the following:

$$c_m^0(z, t) \rightarrow 0 \quad \text{as } z \rightarrow \infty. \quad (56)$$

From Eqs. (55) and (56), we can obtain the solution

$$c_m^0(z, t) = c_m^0(0, t) e^{-kz}. \quad (57)$$

With respect to the potential fluctuation in the diffuse layer or diffusion layer, substitution of Eq. (20) into Eq. (21) yields

$$\nabla^2 \phi(x, y, z, t) = 0. \quad (58)$$

We can derive the same kind of the amplitude equation as Eq. (55),

$$\left(\frac{\partial^2}{\partial z^2} - k^2\right)\phi^0(z, t) = 0, \quad (59)$$

where $\phi^0(z, t)$ is the amplitude of the $\phi(x, y, z, t)$.

With the boundary condition the same as Eq. (56), i.e.,

$$\phi^0(z, t) \rightarrow 0 \quad \text{as } z \rightarrow \infty, \quad (60)$$

the following solution is obtained:

$$\phi^0(z, t) = \phi^0(0, t)e^{-kz}. \quad (61)$$

These two solutions have the following relationship; substituting Eq. (20) into Eq. (22), the resultant equation is changed into an amplitude equation by the Fourier transform,

$$\sigma^* \left(\frac{\partial \phi^0(z, t)}{\partial z} \right)_{z=0} = z_m F D_m \left(\frac{\partial c_m^0(z, t)}{\partial z} \right)_{z=0}. \quad (62)$$

Then, substitution of Eqs. (57) and (61) into Eq. (62) leads to the equation

$$\phi^0(0, t) = \frac{z_m F D_m}{\sigma^*} c_m^0(0, t). \quad (63)$$

Moreover, after Fourier transform, the surface diffusion equation Eq. (28) can be rewritten as

$$\frac{1}{\Omega} \frac{\partial}{\partial t} \zeta^0(t) + \Omega \gamma^* \frac{D_{ad}}{RT} C_{ad}^* k^4 \zeta^0(t) = D_m \left(\frac{\partial c_m^0(z, t)}{\partial z} \right)_{z=0}. \quad (64)$$

Substituting Eq. (57) into Eq. (64), it follows that

$$\frac{1}{\Omega} \frac{\partial}{\partial t} \zeta^0(t) + \Omega \gamma^* \frac{D_{ad}}{RT} C_{ad}^* k^4 \zeta^0(t) = -D_m k c_m^0(0, t). \quad (65)$$

This equation will be solved, using the intrinsic boundary conditions of the asymmetrical and symmetrical fluctuations which have already obtained.

2. Amplitude factor of asymmetrical fluctuation

The intrinsic boundary condition for the asymmetrical fluctuations Eq. (42) is, after Fourier transform, given in the following:

$$z_m F \left\{ \left(\frac{\partial \langle \Phi_1 \rangle}{\partial \langle \Phi_2 \rangle} \right)_\mu + 1 \right\} \phi_2^0(\zeta^a, t)^a + \frac{RT}{c_{cr}} c_m^0(\zeta^a, t)^a - \Omega \gamma^* k^2 \zeta^0(t)^a = 0, \quad (66)$$

where $\phi_2^0(z, t)^a$, $\zeta^0(t)^a$, and $c_m^0(z, t)^a$ imply the amplitudes of $\phi_2(x, y, z, t)^a$, $\zeta(x, y, z, t)^a$, and $c_m(x, y, z, t)^a$, respectively.

Taking the Fourier transforms of Eqs. (43) and (44), we can get

$$c_m^0(\zeta^a, t)^a = c_m^0(0, t)^a \pm L_m \zeta^0(t)^a, \quad (67)$$

$$\phi_2^0(\zeta^a, t)^a = \phi_2^0(0, t)^a \pm L_\phi \zeta^0(t)^a. \quad (68)$$

Substituting Eqs. (67) and (68) into Eq. (66), the following equation is obtained:

$$z_m F \left\{ \left(\frac{\partial \langle \Phi_1 \rangle}{\partial \langle \Phi_2 \rangle} \right)_\mu + 1 \right\} \phi_2^0(0, t)^a + \frac{RT}{c_{cr}} c_m^0(0, t)^a + \left\{ \pm z_m F \left(\frac{\partial \langle \Phi_1 \rangle}{\partial \langle \Phi_2 \rangle} \right)_\mu L_\phi - \Omega \gamma^* k^2 \right\} \zeta^0(t)^a = 0, \quad (69)$$

where to derive Eq. (69), we used Eq. (A17) in Appendix A.

Substitution of Eqs. (63) and (69) into Eq. (65) gives the equation

$$\frac{\partial \zeta^0(t)^a}{\partial t} = \left[\frac{\sigma^* \Omega D_m c_{cr} k \left\{ \pm z_m F \left(\frac{\partial \langle \Phi_1 \rangle}{\partial \langle \Phi_2 \rangle} \right)_\mu L_\phi - \Omega \gamma^* k^2 \right\}}{(z_m F)^2 D_m \left\{ \left(\frac{\partial \langle \Phi_1 \rangle}{\partial \langle \Phi_2 \rangle} \right)_\mu + 1 \right\} c_{cr} + \sigma^* RT} - \frac{\Omega^2 \gamma^* D_{ad} C_{ad}^* k^4}{RT} \right] \zeta^0(t)^a. \quad (70)$$

Therefore, the following function can be defined, i.e.,

$$f(t) \equiv \frac{\sigma^* \Omega D_m c_{cr} k \left\{ \pm z_m F \left(\frac{\partial \langle \Phi_1 \rangle}{\partial \langle \Phi_2 \rangle} \right)_\mu L_\phi - \Omega \gamma^* k^2 \right\}}{(z_m F)^2 D_m \left\{ \left(\frac{\partial \langle \Phi_1 \rangle}{\partial \langle \Phi_2 \rangle} \right)_\mu + 1 \right\} c_{cr} + \sigma^* RT} - \frac{\Omega^2 \gamma^* D_{ad} C_{ad}^* k^4}{RT}. \quad (71)$$

The solution of Eq. (70) is

$$\zeta^0(t)^a = \zeta^0(0)^a \exp \left\{ \int_0^t f(t) dt \right\}. \quad (72)$$

In Eq. (71), there is no function of time except for L_ϕ and c_{cr} , so that the amplitude factor of Eq. (72) is easily obtained, i.e.,

$$\int_0^t f(t) dt = \frac{\Omega D_m k}{RT} \left\{ \pm z_m F \left(\frac{\partial \langle \Phi_1 \rangle}{\partial \langle \Phi_2 \rangle} \right)_\mu \int_0^t c_{cr} L_\phi dt - \Omega \gamma^* k^2 \int_0^t c_{cr} dt \right\} - \frac{\Omega^2 \gamma^* D_{ad} C_{ad}^* k^4}{RT}, \quad (73)$$

where for simplicity,

$$\sigma^* RT \gg \left| (z_m F)^2 D_m \left\{ \left(\frac{\partial \langle \Phi_1 \rangle}{\partial \langle \Phi_2 \rangle} \right)_\mu + 1 \right\} c_{cr} \right| \quad (74)$$

is assumed. Owing to the large critical autocorrelation distance of the fluctuations, the second and third terms on the right side of Eq. (73) can be neglected as will be mentioned in the following paper.³⁸

According to Eqs. (65) and (70), we can also derive the solution of $c_m^0(0, t)^a$. Here, with an assumption that time dependence of the parameters other than those in the exponential part is negligibly small, the following equation similar to Eq. (72) is obtained:

$$c_m^0(0,t)^a = c_m^0(0,0)^a \exp \left\{ \int_0^t f(t) dt \right\}. \quad (75)$$

3. Amplitude factor of symmetrical fluctuation

Fourier transform of Eq. (50) yields the following equation of the amplitudes, that is,

$$z_m F \phi^0(\zeta^s, t)^s + \frac{RT}{\langle C_m(x, y, 0, t) \rangle} c_m^0(\zeta^s, t)^s - \Omega \gamma^* k^2 \zeta^0(t)^s = 0, \quad (76)$$

where $\phi^0(z, t)^s$, $c_m^0(z, t)^s$, and $\zeta^0(t)^s$ indicate the amplitudes of $\phi(x, y, z, t)^s$, $c_m(x, y, 0, t)^s$, and $\zeta(x, y, t)^s$, respectively.

On the other hand, Eq. (51) is rewritten, after Fourier transform, as follows:

$$c_m^0(\zeta^s, t)^s = c_m^0(0, t)^s + L \zeta^0(t)^s. \quad (77)$$

Substituting Eq. (77) into Eq. (76), then

$$z_m F \phi^0(0, t)^s + \frac{RT}{\langle C_m(x, y, 0, t) \rangle} c_m^0(0, t)^s + \left\{ \frac{RTL}{\langle C_m(x, y, 0, t) \rangle} - \Omega \gamma^* k^2 \right\} \zeta^0(t)^s = 0. \quad (78)$$

Substitution of Eqs. (63) and (78) into Eq. (65) leads to the derivation of the equation, as follows:

$$\frac{\partial}{\partial t} \zeta^0(t)^s = \left[\frac{\sigma^* \Omega D_m k \{RTL - \Omega \gamma^* \langle C_m(x, y, 0, t) \rangle k^2\}}{(z_m F)^2 D_m \langle C_m(x, y, 0, t) \rangle + \sigma^* RT} - \frac{\Omega^2 \gamma^* D_{ad} C_{ad}^*}{RT} k^4 \right] \zeta^0(t)^s. \quad (79)$$

Therefore, the same kind of function as Eq. (71) can be obtained, i.e.,

$$g(t) \equiv \frac{\sigma^* \Omega D_m k \{RTL - \Omega \gamma^* \langle C_m(x, y, 0, t) \rangle k^2\}}{(z_m F)^2 D_m \langle C_m(x, y, 0, t) \rangle + \sigma^* RT} - \frac{\Omega^2 \gamma^* D_{ad} C_{ad}^*}{RT} k^4, \quad (80)$$

so that Eq. (79) is solved as

$$\zeta^0(t)^s = \zeta^0(0)^s \exp \left\{ \int_0^t g(t) dt \right\}. \quad (81)$$

For simplicity,

$$(z_m F)^2 D_m \langle C_m(x, y, 0, t) \rangle \ll \sigma^* RT \quad (82)$$

is assumed; thus Eq. (80) is rewritten as

$$g(t) = \Omega D_m k \left\{ L - \frac{\Omega \gamma^*}{RT} \langle C_m(x, y, 0, t) \rangle k^2 \right\} - \frac{\Omega^2 \gamma^* D_{ad} C_{ad}^*}{RT} k^4. \quad (83)$$

So, we eventually obtain the amplitude factor,

$$\int_0^t g(t) dt = \Omega D_m k \left\{ \int_0^t L dt - \frac{\Omega \gamma^* k^2}{RT} \times \int_0^t \langle C_m(x, y, 0, t) \rangle dt \right\} - \frac{\Omega^2 \gamma^* D_{ad} C_{ad}^*}{RT} k^4 t. \quad (84)$$

According to the assumption for Eq. (75), we can derive the solution of $c_m^0(0, t)^s$, as follows:

$$c_m^0(0, t)^s = c_m^0(0, 0)^s \exp \left\{ \int_0^t g(t) dt \right\}. \quad (85)$$

E. Criterion of instability

For an unstable electrode system, the asymmetrical fluctuations first turn unstable, then the transition to the unstable state of the symmetrical fluctuations, if possible, will occur. As shown in Eqs. (72) and (81), when the amplification factors become positive for certain wave numbers, the fluctuations become unstable, and the nuclei start to grow. On the contrary, when the amplification factors take negative values without exception for all wave numbers, the fluctuations are kept stable, and the growth of the nuclei is depressed. In this case, the fluctuations are newly activated by the thermal motion, and then decrease with time. This phenomenon successively takes place in every moment and every place on the electrode surface. As a result, the electrode system approaches a steady state.

From these discussions, we can find a critical state between the unstable and stable states.

1. The first instability condition

The instability of the asymmetrical fluctuations induces the acceleration of nucleation and resultant increase of current. As will be mentioned in the next paper,³⁸ since fluctuations of this type has comparatively large autocorrelation distance about 100 μm , flat and large two-dimensional nuclei are expected to grow with the instability. In Eq. (71), the denominator of the first term on the right side is positive due to the large value of σ^* in the presence of large amount of supporting electrolyte. Therefore, the condition that the amplification factor takes positive value is fulfilled in the case when the first term of the numerator becomes positive. Equation (71) is simplified and integrated with regard to time, so that Eq. (73) is derived. Simultaneously, the first term of Eq. (71) corresponding to the first term of the numerator in Eq. (71) can be simply expressed, neglecting the other part $\Omega z_m F D_m k / RT$, as

$$F(\langle \Phi_2 \rangle) \equiv \pm \left(\frac{\partial \langle \Phi_1 \rangle}{\partial \langle \Phi_2 \rangle} \right)_{\mu} \int_0^t c_{cl} L_{\phi} dt, \quad (86)$$

where the unstable condition is equivalent to positive $F(\langle \Phi_2 \rangle)$ value, and + and - signs are ascribed to the cases of nonspecific and specific adsorption, respectively.

With Eq. (A16) in Appendix A, Eq. (86) is rewritten in the following form:

$$F(\langle\Phi_2\rangle) \equiv \mp \left\{ \left(\frac{\partial\langle\Phi_1\rangle}{\partial\langle\Phi_2\rangle} \right)_\mu \bigg/ \lambda \right\} \int_0^t c_{cr} \langle\Phi_2\rangle dt, \quad (87)$$

where the signs \pm are changed to \mp .

Here, since c_{cr} is positive as shown in Eq. (36) and $\langle\Phi_1\rangle$ remains negative for cathodic reaction, $F(\langle\Phi_2\rangle)$ should be examined for two different cases, nonspecific or weak specific adsorption and intense specific adsorption: In the case of nonspecific or weak specific adsorption, as mentioned in the foregoing section,

$$\left(\frac{\partial\langle\Phi_1\rangle}{\partial\langle\Phi_2\rangle} \right)_\mu > 0 \quad (88)$$

with $\langle\Phi_1\rangle < 0$ holds, so that

$$\langle\Phi_2\rangle < 0 \quad (89)$$

is derived. Important point for this case is to select the sign of minus in Eq. (87). Thus $F(\langle\Phi_2\rangle)$ becomes positive, then the instability takes place.

For intense specific adsorption, however, as also explained in the previous section,

$$\left(\frac{\partial\langle\Phi_1\rangle}{\partial\langle\Phi_2\rangle} \right)_\mu < 0 \quad (90)$$

with $\langle\Phi_1\rangle < 0$ holds. Therefore,

$$\langle\Phi_2\rangle > 0 \quad (91)$$

is dedicated. In consideration of intense specific adsorption, the sign of plus should be adopted in Eq. (87); $F(\langle\Phi_2\rangle)$ becomes negative, then the system remains stable and the asymmetrical fluctuations decrease with time.

In conclusion, the present discussion reveals the most important theoretical prediction that the cathodic deposition occurs if and only if there does not exist so intense specific adsorption to keep $(\partial\langle\Phi_1\rangle/\partial\langle\Phi_2\rangle)_\mu$ negative.

Using Eq. (B17) in Appendix B, the first instability conditions for the asymmetrical fluctuations are

$$\langle\Phi_2\rangle < 0 \quad \text{for} \quad \left(\frac{\partial Q_1^*}{\partial Q_2^*} \right)_\mu > -1. \quad (92)$$

From Eq. (92), it is concluded that even in the presence of specific adsorption, as long as the coefficient $(\partial Q_1^*/\partial Q_2^*)_\mu$ takes larger value than -1 , such instability will take place.

From above discussions, the critical conditions are expressed as

$$\left(\frac{\partial\langle\Phi_1\rangle}{\partial\langle\Phi_2\rangle} \right)_\mu \langle\Phi_2\rangle = 0. \quad (93)$$

Therefore, we have two types of transitions from stable state to unstable state or vice versa; one is soft mode transition, where adsorption state of ionic species is constant, being $(\partial\langle\Phi_1\rangle/\partial\langle\Phi_2\rangle)_\mu > 0$ and only the diffuse layer overpotential $\langle\Phi_2\rangle$ reversibly changes from plus to minus or vice versa, i.e., such transition gradually occurs via the critical condition,

$$\langle\Phi_2\rangle = 0. \quad (94)$$

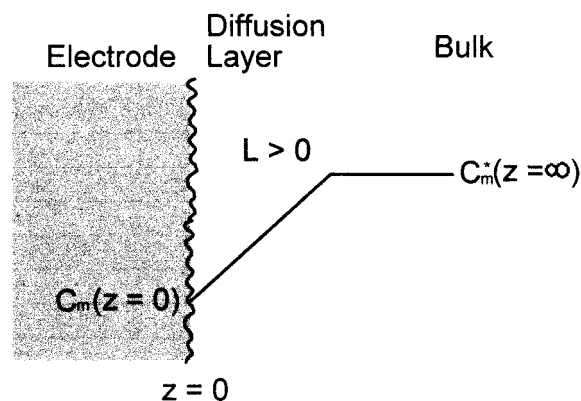


FIG. 4. Concentration distribution of depositing metal ion in the diffusion layer. For the concentration gradient, $L > 0$ always holds.

However, another type, hard mode transition is also possible. For example, at a certain potential, a transition from $(\partial Q_1^*/\partial Q_2^*)_\mu < -1$ to $(\partial Q_1^*/\partial Q_2^*)_\mu > -1$ owing to the change of the adsorption state occurs, so that unstable deposition suddenly starts. Namely, such transition is characterized by sudden phenomena because usually, the adsorption state may irreversibly alter. For cathodic reaction, $\langle\Phi_1\rangle$ always takes negative or zero value. Change of the sign of $(\partial\langle\Phi_1\rangle/\partial\langle\Phi_2\rangle)_\mu$ is thus forced to alter the sign of $\langle\Phi_2\rangle$. Therefore, at the critical state, $\langle\Phi_2\rangle$ must once converge to zero. That is, the critical condition is, using Eq. (B17) in Appendix B, given by

$$\langle\Phi_2\rangle = 0 \quad \text{accompanied with} \quad \left(\frac{\partial Q_1^*}{\partial Q_2^*} \right)_\mu = -1. \quad (95)$$

2. The second instability condition

When the asymmetrical fluctuations turn into an unstable state, the nucleation current progressively increases. The consequent result is the formation of diffusion layer. If the symmetrical fluctuations become secondarily unstable due to the thermal motion of solution particles, a lot of minute three-dimensional nuclei may start to grow domestically.

From Eq. (84), we can derive the unstable condition, i.e.,

$$\int_0^t L dt > 0. \quad (96)$$

For the nucleation after applying a constant potential step, as shown in Fig. 4, the sign of L remains positive, so that the above condition is always fulfilled. Therefore, the fluctuations grow unstably as long as the reaction proceeds.

This feature is different from the asymmetric case, i.e., this kind of instability is possible even on the anodic side of the critical potential so far as the electrode potential is on the cathodic side of the equilibrium potential. However, actually, since the reaction does not proceed if the first instability condition is not fulfilled, so that both conditions apparently agree with each other.

III. DISCUSSION

A. Mechanism of the first instability

The electrochemical potential fluctuation $\delta\mu_m^a$ of the metal ions in the double layer is expressed as a linear combination of the electrical potential variation and the concentration variation.

In consideration of nonspecific or at least weak specific adsorption, from Eq. (44), the potential variation ϕ_2^a at the projection ($z = \zeta^a > 0$) from the flat surface ($z = 0$) in the diffuse layer can be represented, neglecting ohmic drop, as follows:

$$\phi_2^a \approx +L_\phi \zeta^a, \quad (97)$$

where the sign of plus corresponds to the absence of the inversion of the sign of the probe electrode potential due to weak or nonspecific adsorption. Here, in the presence of large amount of supporting electrolyte, the total overpotential fluctuation ϕ_0^a of the double layer can be approximated by the overpotential fluctuation ϕ_1^a of the Helmholtz layer. Thus recalling Eqs. (40) and (97), we obtain the expression of ϕ_0^a at the projected portion, i.e.,

$$\begin{aligned} \phi_0^a &\approx \phi_1^a = \left(\frac{\partial \langle \Phi_1 \rangle}{\partial \langle \Phi_2 \rangle} \right)_\mu \phi_2^a \\ &\approx \left(\frac{\partial \langle \Phi_1 \rangle}{\partial \langle \Phi_2 \rangle} \right)_\mu L_\phi \zeta^a. \end{aligned} \quad (98)$$

On the other hand, according to Eq. (35), contribution of the concentration variation to the electrochemical potential is equal to $\{RT/c_{\text{cr}}\}c_m^a$. Therefore, the complete expression of the electrochemical potential fluctuation is

$$\delta\mu_m^a \approx z_m F \left(\frac{\partial \langle \Phi_1 \rangle}{\partial \langle \Phi_2 \rangle} \right)_\mu L_\phi \zeta^a + \frac{RT}{c_{\text{cr}}} c_m^a. \quad (99)$$

Here, as shown in Eqs. (29) and (30), the reaction equilibrium is supposed among active ions, adatoms and free electrons. However, the fluctuation of the electrochemical potential of free electrons is negligible, as discussed before, owing to their large mobilities. In addition, the fluctuation of the chemical potential of adatoms is also considered negligibly small because of the equilibrium between adatoms and lattice atoms, of which activities may be kept constant.

Therefore, approximately,

$$\delta\mu_m^a \approx 0 \quad (100)$$

is derived.

From Eqs. (99) and (100), it follows that

$$c_m^a \approx -\frac{z_m F}{RT} c_{\text{cr}} \left(\frac{\partial \langle \Phi_1 \rangle}{\partial \langle \Phi_2 \rangle} \right)_\mu L_\phi \zeta^a. \quad (101)$$

At the projection of nucleus $z = \zeta^a (> 0)$, the concentration fluctuation must take negative value owing to the depletion of the metal ions

$$c_m^a < 0 \quad \text{for } z = \zeta^a (> 0). \quad (102)$$

Using Eqs. (101) and (102), the unstable conditions in Eq. (92) can be deduced as follows:

$$\left(\frac{\partial \langle \Phi_1 \rangle}{\partial \langle \Phi_2 \rangle} \right)_\mu L_\phi > 0. \quad (103)$$

B. Mechanism of the second instability

As the reaction proceeds, outside the double layer, the diffusion layer develops gradually. At the same time, fluctuations of another type, symmetrical fluctuations take place due to the thermal motion, and corresponding nuclei start to grow.

In this case, nucleation also changes the electrochemical potential of the metal ions in the diffusion layer. However, on the contrary to the first instability, the potential term is negligible since it comes from ohmic drop which takes small value in the presence of large amount of the supporting electrolyte.

Therefore, the main part of the change is expressed only by the concentration term, i.e.,

$$\delta\mu_m^s \approx \frac{RT}{\langle C_m(x, y, 0, t) \rangle} c_m^s(x, y, \zeta^s, t)^s, \quad (104)$$

where at the top of projection $z = \zeta^s (> 0)$ resulting from the symmetrical fluctuations, c_m^s has the relation, according to Eq. (51),

$$c_m^s(x, y, \zeta^s, t)^s = c_m^s(x, y, 0, t)^s + L_\zeta \zeta^s, \quad (105)$$

where, as mentioned before, $\delta\mu_m^s \approx 0$ also holds. Substitution of Eq. (105) into this condition thus yields, at the surface,

$$c_m^s \approx -L_\zeta \zeta^s. \quad (106)$$

As discussed above, at the deposited portion $z = \zeta^s (> 0)$, the concentration fluctuation must take negative value

$$c_m^s < 0 \quad \text{for } z = \zeta^s (> 0). \quad (107)$$

Substituting Eq. (106) into Eq. (107), the unstable condition, $L > 0$, represented in Eq. (96) is derived. In the case of deposition, the concentration gradient is always kept positive. Thus the projection develops with time. In this case, we also find a kind of positive feed back cycle which makes the fluctuations unstable.

IV. CONCLUSIONS

Unstable growth of asymmetrical nonequilibrium fluctuations which arise from the breakdown of electrostatic equilibrium in the electric double layer leads to layer by layer two-dimensional nucleus formation, of which condition is written as

$$\langle \Phi_2 \rangle < 0 \quad \text{for } \left(\frac{\partial Q_1^*}{\partial Q_2^*} \right)_\mu > -1.$$

This kind of instability takes place from the cathodic polarization in the absence of the intense specific adsorption of ions: When there is no drastic change in the adsorption state, the critical state is described as follows:

$$\langle \Phi_2 \rangle = 0,$$

whereas in the case of the changing adsorption state,

$$\langle \Phi_2 \rangle = 0 \quad \text{accompanied with} \quad \left(\frac{\partial Q_1^*}{\partial Q_2^*} \right)_\mu = -1.$$

On the other hand, the symmetrical nonequilibrium fluctuations in the diffusion layer formed by the asymmetrical fluctuation yield minute three-dimensional nuclei on the electrode surface. The instability of the fluctuations occurs when the concentration gradient in the diffusion layer fulfills the following condition:

$$L > 0.$$

For cathodic deposition, L always takes positive value, so that these fluctuations always become unstable. Hence, mass flux variation coming from the symmetrical fluctuations increases with time; three-dimensional minute nuclei always grow with time.

APPENDIX A

The electrical potential distribution $\Phi(x, y, z, t)$ in the diffuse layer is determined by the electrostatic component and the nonequilibrium fluctuation, as follows:

$$\Phi(x, y, z, t) = \Phi^*(z, t) + \phi(x, y, z, t)_{\text{non}}. \quad (\text{A1})$$

Using the current conservation law Eq. (21), we can conclude that the nonequilibrium fluctuation does not yield any electric charge. Therefore, $\Phi(x, y, z, t)$ as well as $\Phi^*(z, t)$ should fulfill the following Poisson equation, i.e.,

$$\nabla^2 \Phi(x, y, z, t) + \frac{1}{\epsilon} \rho(x, y, z, t) = 0, \quad (\text{A2})$$

where $\Phi(x, y, z, t)$ is measured from the critical state, and $\rho(x, y, z, t)$ is the electric charge per unit area of electrode, and ϵ is the dielectric constant.

Hence, if it can be assumed that the total concentration $C_i(x, y, z, t)$ of the ion i as well as the electrostatic component $C_i^*(z, t)$ takes Boltzmann distribution in the diffuse layer with the concentration in the critical state $C_i(z = \infty^+)_{\text{cr}}$, it is expressed as

$$C_i(x, y, z, t) = C_i(z = \infty^+)_{\text{cr}} \exp \left\{ -\frac{z_i F}{RT} \Phi(x, y, z, t) \right\}, \quad (\text{A3})$$

where $z = \infty^+$ means the outside of the electric double layer, which is equal to $z = 0$ in the scale of the fluctuation.

According to Eq. (A3), we can define the fluctuation equation of the metal ionic concentration following the Boltzmann distribution, i.e.,

$$c_m(x, y, z, t)^a = -\langle c_m(x, y, 0, t)_{\text{cr}}^a \rangle \exp \left\{ \frac{z_m F}{RT} \Phi(x, y, z, t) \right\}, \quad (\text{A4})$$

where $\langle c_m(x, y, 0, t)_{\text{cr}}^a \rangle$ is the area average of the critical asymmetrical concentration fluctuation at the electrode surface, which is for simplicity defined positive. In the present case, the fluctuation $c_m(x, y, z, t)^a$ is defined as the depletion from the equilibrium state, i.e., the metal ion is electrically treated like having negative charge, so that the charge num-

ber $z_m (> 0)$ must be replaced by $-z_m (< 0)$. In the presence of large amount of supporting electrolyte, the variation of the diffuse-layer potential is small enough to assume

$$|\Phi(x, y, z, t)| \ll \frac{RT}{z_m F}. \quad (\text{A5})$$

From Eqs. (A4) and (A5), the following equation is thus obtained:

$$c_m(x, y, z, t)^a = -\langle c_m(x, y, 0, t)_{\text{cr}}^a \rangle \left\{ 1 + \frac{z_m F}{RT} \Phi(x, y, z, t) \right\}. \quad (\text{A6})$$

Hence, the concentration fluctuation from the critical state is newly defined as

$$c_m(x, y, z, t)^{+a} = c_m(x, y, z, t)^a + \langle c_m(x, y, 0, t)_{\text{cr}}^a \rangle. \quad (\text{A7})$$

Here, $\langle c_m(x, y, 0, t)_{\text{cr}}^a \rangle$ is a constant, so that any of the calculations of the fluctuations such as the root mean square and the gradient give the same values as for $c_m(x, y, z, t)^{+a}$ and $c_m(x, y, z, t)^a$. This is because such calculations are performed for space-variable parts. Therefore, as shown in Eq. (37), the term $c_m(x, y, z, t)^a + \langle c_m(x, y, 0, t)_{\text{cr}}^a \rangle$ can be effectively replaced to $c_m(x, y, z, t)^a$. Thus we redefine $c_m(x, y, z, t)^a$ as $c_m(x, y, z, t)^{+a}$. Using the discussion for Eq. (A7), Eq. (A6) is thus rewritten as

$$c_m(x, y, z, t)^a = -\frac{z_m F}{RT} c_{\text{cr}} \Phi(x, y, z, t), \quad (\text{A8})$$

where for simplicity

$$c_{\text{cr}} \equiv \langle c_m(x, y, 0, t)_{\text{cr}}^a \rangle \quad (> 0). \quad (\text{A9})$$

In general, the electric charge density has the relationship

$$\rho(x, y, z, t) = \sum_j z_j F C_j(x, y, z, t). \quad (\text{A10})$$

Here, the electroneutrality outside the double layer approximately gives

$$\sum_{j \neq m} z_j C_j^*(z = \infty) = 0, \quad (\text{A11})$$

where $C_j(z = \infty^+) = C_j^*(z = \infty)$ is again used.

Debye's length, λ is defined as

$$\lambda \equiv \left(\frac{\epsilon RT}{F^2 \sum_i z_i^2 C_i^*(z = \infty)} \right)^{1/2}. \quad (\text{A12})$$

By recalling Eqs. (A3), (A5), (A10), (A11), and (A12), Equation (A2) can be rewritten in the form

$$\nabla^2 \Phi(x, y, z, t) = \frac{1}{\lambda^2} \Phi(x, y, z, t). \quad (\text{A13})$$

After averaging Eq. (A13) in x and y directions, it follows that

$$\frac{\partial^2}{\partial z^2} \langle \Phi(x, y, z, t) \rangle = \frac{1}{\lambda^2} \langle \Phi(x, y, z, t) \rangle \quad (\text{A14})$$

The solution of Eq. (A14) is given as

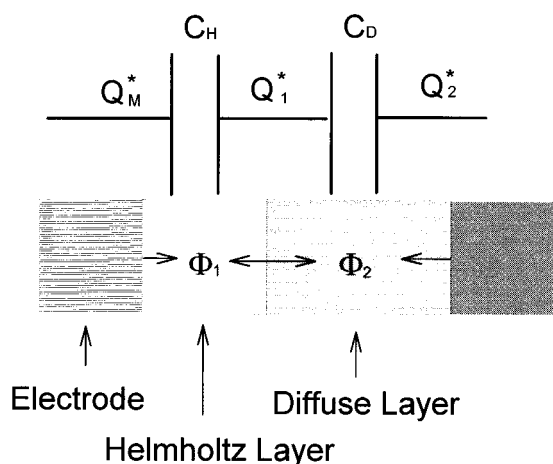


FIG. 5. Diagram of equivalent circuit near the electrode surface. C_H : differential capacity per unit area of the Helmholtz layer, C_D : differential capacity per unit area of the diffuse layer, Q_M^* : electric charge density on the electrode side, Q_1^* : electric charge density in the Helmholtz layer, Q_2^* : electric charge density in the diffuse layer,

$$\langle \Phi(x, y, z, t) \rangle = \langle \Phi(x, y, 0, t) \rangle \exp(-z/\lambda). \quad (\text{A15})$$

Therefore, the potential gradient at the flat outer Helmholtz plane, $z=0$ is

$$\left\{ \frac{\partial \langle \Phi(x, y, z, t) \rangle}{\partial z} \right\}_{z=0} = -\frac{\langle \Phi_2 \rangle}{\lambda}, \quad (\text{A16})$$

where $\langle \Phi_2 \rangle \equiv \langle \Phi(x, y, 0, t) \rangle$.

Furthermore, after averaging Eq. (A8) in x and y directions, the resultant equation based on the active ionic concentration fluctuation in the diffuse layer is differentiated with respect to z . Since the constant term c_{cr} can be removed as mentioned in Eq. (A7), we can also obtain the concentration fluctuation gradient of the metal ions at the flat outer Helmholtz plane, that is,

$$\left\{ \frac{\partial \langle c_m(x, y, z, t)^a \rangle}{\partial z} \right\}_{z=0} = -\frac{z_m F}{RT} c_{cr} \left\{ \frac{\partial \langle \Phi(x, y, z, t) \rangle}{\partial z} \right\}_{z=0}. \quad (\text{A17})$$

Substituting Eq. (A16) into Eq. (A17), the concentration gradient is

$$\left\{ \frac{\partial \langle c_m(x, y, z, t)^a \rangle}{\partial z} \right\}_{z=0} = \frac{z_m F}{\lambda RT} c_{cr} \langle \Phi_2 \rangle. \quad (\text{A18})$$

APPENDIX B

An ideal electric double layer is, as shown in Fig. 5, considered as an electric system of two condensers made of the Helmholtz layer and diffuse layer.

Before discussion we adopt the following notations:

C_H : differential capacity per unit area of the Helmholtz layer, C_D : differential capacity per unit area of the diffuse layer, C_0 : total capacity of the double layer per unit area, $\langle \Phi_1 \rangle$: average overpotential of the Helmholtz layer, $\langle \Phi_2 \rangle$: av-

erage overpotential of the diffuse layer, $\langle \Phi_0 \rangle$: total average overpotential of the double layer, Q_M^* : electric charge density on the electrode side, Q_1^* : electric charge density in the Helmholtz layer, Q_2^* : electric charge density in the diffuse layer.

Here, C_H and C_D are defined as

$$\left(\frac{\partial \langle \Phi_1 \rangle}{\partial Q_M^*} \right)_\mu \equiv \frac{1}{C_H}, \quad (\text{B1})$$

$$-\left(\frac{\partial \langle \Phi_2 \rangle}{\partial Q_2^*} \right)_\mu \equiv \frac{1}{C_D}. \quad (\text{B2})$$

Then, C_0 is given as

$$\left(\frac{\partial \langle \Phi_0 \rangle}{\partial Q_M^*} \right)_\mu \equiv \frac{1}{C_0}. \quad (\text{B3})$$

In general, the electroneutrality exists among Q_M^* , Q_1^* , and Q_2^* , i.e.,

$$Q_M^* + Q_1^* + Q_2^* = 0. \quad (\text{B4})$$

Keeping the chemical potentials of all components constant, we differentiate Eq. (B4) with respect to Q_2^* ; then

$$\left(\frac{\partial Q_M^*}{\partial Q_2^*} \right)_\mu = -\left\{ \left(\frac{\partial Q_1^*}{\partial Q_2^*} \right)_\mu + 1 \right\}. \quad (\text{B5})$$

With Eq. (B5), the following equation can be derived:

$$\begin{aligned} \left(\frac{\partial \langle \Phi_2 \rangle}{\partial Q_M^*} \right)_\mu &= \left(\frac{\partial \langle \Phi_2 \rangle}{\partial Q_2^*} \right)_\mu \left(\frac{\partial Q_2^*}{\partial Q_M^*} \right)_\mu \\ &= -\left(\frac{\partial \langle \Phi_2 \rangle}{\partial Q_2^*} \right)_\mu \left\{ \left(\frac{\partial Q_1^*}{\partial Q_2^*} \right)_\mu + 1 \right\}. \end{aligned} \quad (\text{B6})$$

Here, the total average overpotential which is measured from the critical potential is expressed as

$$\langle \Phi_0 \rangle = \langle \Phi_1 \rangle + \langle \Phi_2 \rangle. \quad (\text{B7})$$

Both sides of Eq. (B7) are differentiated with regard to Q_M^* , then it follows that:

$$\left(\frac{\partial \langle \Phi_0 \rangle}{\partial Q_M^*} \right)_\mu = \left(\frac{\partial \langle \Phi_1 \rangle}{\partial Q_M^*} \right)_\mu + \left(\frac{\partial \langle \Phi_2 \rangle}{\partial Q_M^*} \right)_\mu. \quad (\text{B8})$$

Substituting Eq. (B6) into Eq. (B8), we obtain

$$\begin{aligned} \left(\frac{\partial \langle \Phi_0 \rangle}{\partial Q_M^*} \right)_\mu &= \left(\frac{\partial \langle \Phi_1 \rangle}{\partial Q_M^*} \right)_\mu - \left(\frac{\partial \langle \Phi_2 \rangle}{\partial Q_2^*} \right)_\mu \left\{ \left(\frac{\partial Q_1^*}{\partial Q_2^*} \right)_\mu + 1 \right\}. \end{aligned} \quad (\text{B9})$$

Substitution of Eqs. (B1), (B2), and (B3) into Eq. (B9) gives following relation:

$$\frac{1}{C_0} = \frac{1}{C_H} + \frac{1}{C_D \left\{ \left(\frac{\partial Q_1^*}{\partial Q_2^*} \right)_\mu + 1 \right\}}. \quad (\text{B10})$$

On the other hand, substituting Eq. (B2) into Eq. (B6), then

$$\left(\frac{\partial\langle\Phi_2\rangle}{\partial Q_M^*}\right)_\mu = \frac{1}{C_D \left\{ \left(\frac{\partial Q_1^*}{\partial Q_2^*}\right)_\mu + 1 \right\}} \quad (\text{B11})$$

is obtained.

Using Eqs. (B1), (B11), and the equation

$$\left(\frac{\partial\langle\Phi_1\rangle}{\partial\langle\Phi_2\rangle}\right)_\mu = \left(\frac{\partial\langle\Phi_1\rangle}{\partial Q_M^*}\right)_\mu \bigg/ \left(\frac{\partial\langle\Phi_2\rangle}{\partial Q_M^*}\right)_\mu, \quad (\text{B12})$$

the following equation is derived:

$$\left(\frac{\partial\langle\Phi_1\rangle}{\partial\langle\Phi_2\rangle}\right)_\mu = \frac{C_D}{C_H} \left\{ \left(\frac{\partial Q_1^*}{\partial Q_2^*}\right)_\mu + 1 \right\}. \quad (\text{B13})$$

Here, electric charge in the diffuse layer is given as

$$Q_2^* = \epsilon \left(\frac{\partial\langle\Phi(x,y,z,t)\rangle}{\partial z} \right)_{z=0}. \quad (\text{B14})$$

Then, substituting Eq. (A16) into Eq. (B14), we obtain

$$Q_2^* = - \frac{\epsilon\langle\Phi_2\rangle}{\lambda}. \quad (\text{B15})$$

Substitution of Eq. (B15) into Eq. (B2) yields the expression of the capacity of the diffuse layer, i.e.,

$$C_D = \frac{\epsilon}{\lambda}. \quad (\text{B16})$$

Finally, after substituting Eq. (B16) into Eq. (B13), we obtain the expression of the differential overpotential coefficient

$$\left(\frac{\partial\langle\Phi_1\rangle}{\partial\langle\Phi_2\rangle}\right)_\mu = \frac{\epsilon}{\lambda C_H} \left\{ \left(\frac{\partial Q_1^*}{\partial Q_2^*}\right)_\mu + 1 \right\}. \quad (\text{B17})$$

APPENDIX C: LIST OF SYMBOLS

$C_m(x,y,z,t)$	concentration of depositing metal ion, mol m^{-3}
$C_m^*(z,t)$	electrostatic equilibrium component of $C_m(x,y,z,t)$, mol m^{-3}
$c_m(x,y,z,t)$	fluctuation of $C_m(x,y,z,t)$, mol m^{-3}
$C_j(x,y,z,t)$	concentration of ion j , mol m^{-3}
$C_j^*(z=\infty)$	bulk concentration of ion j , mol m^{-3}
$C_j^*(z,t)$	electrostatic equilibrium component of $C_j(x,y,z,t)$, mol m^{-3}
$c_j(x,y,z,t)$	fluctuation of $C_j(x,y,z,t)$, mol m^{-3}
C_{ad}^*	electrostatic equilibrium component of surface concentration of adatoms, mol m^{-2}
$c_{\text{ad}}(x,y,t)$	fluctuation of adatom concentration, mol m^{-2}
c_{cr}	average critical concentration fluctuation of depositing metal ions, mol m^{-3}
$c_m(x,y,z,t)_D^a$	asymmetric concentration fluctuation arising from the diffusion of depositing metal ions, mol m^{-3}
$c_i(x,y,z,t)^{+a}$	asymmetric concentration fluctuation of ion i from the critical state, 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, F m^{-2}
C_D	differential capacity per unit area of the diffuse layer, F m^{-2}
C_0	total capacity of the double layer per unit area, F m^{-2}
D_m	diffusion coefficient of depositing metal ion, $\text{m}^2 \text{s}^{-1}$
D_j	diffusion coefficient of ion j , $\text{m}^2 \text{s}^{-1}$
D_{ad}	surface diffusion coefficient of adatoms, $\text{m}^2 \text{s}^{-1}$
$f(t)$	function defined by Eq. (71)
F	Faraday's constant, $96\,487 \text{ mol equiv.}^{-1}$
$F(\langle\Phi_2\rangle)$	function defined by Eq. (86)
$g(t)$	function defined by Eq. (80)
i	unit of imaginary number
$\mathbf{J}(x,y,z,t)$	current density vector, A m^{-2}
$\mathbf{J}^*(t)$	electrostatic equilibrium component of $\mathbf{J}(x,y,z,t)$, A m^{-2}
$\mathbf{j}(x,y,z,t)$	fluctuation of $\mathbf{J}(x,y,z,t)$, A m^{-2}
\mathbf{j}_{flux}	mass flux of metal ions from the solution phase to the interface, $\text{mol m}^{-2} \text{s}^{-1}$
\mathbf{j}_{surf}	mass flux of adatoms by the surface diffusion, $\text{mol m}^{-2} \text{s}^{-1}$
j_{inc}	mass flux of adatoms by the incorporation to crystal lattice, $\text{mol m}^{-2} \text{s}^{-1}$
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}
L_m	average concentration fluctuation gradient at the outer Helmholtz plane, mol m^{-4}
L_ϕ	average potential gradient at the outer Helmholtz plane, V m^{-1}
L	average concentration gradient in the diffusion layer, mol m^{-4}
\mathbf{n}	unit normal vector of the electrode surface
Q_M^*	electric charge density on the electrode side, C m^{-2}
Q_1^*	electric charge density in the Helmholtz layer, C m^{-2}
Q_2^*	electric charge density in the diffuse layer, C m^{-2}
$(\partial Q_1^* / \partial Q_2^*)_ \mu$	electric charge coefficient of the double layer
R	universal gas constant, $8.3143 \text{ J mol}^{-1} \text{ deg}^{-1}$
t	time, s
T	absolute temperature, K
x, y, z	variables in Cartesian-coordinate system, m
z_m	charge number of depositing metal ion including sign
z_j	charge number of ion j including sign
γ^*	isotropic surface free energy, J m^{-2}
ϵ	dielectric constant, F m^{-1}
$Z(x,y,t)$	surface height at the outer Helmholtz plane, m

$Z^*(x, y)$	electrostatic equilibrium component of $Z(x, y, t)$, m	μ	subscript denoting constant composition of the solution being maintained
$\zeta(x, y, t)$	fluctuation of $Z(x, y, t)$, m	non	subscript indicating the total nonequilibrium fluctuation
$\zeta^0(t)$	amplitude of $\zeta(x, y, t)$, m		
λ	Debye's length, m		
$\mu_{\text{ad}}(x, y, t)$	chemical potential of adatoms, J mol^{-1}		
$\delta\mu_{\text{ad}}$	fluctuation of $\mu_{\text{ad}}(x, y, t)$ J mol^{-1}		
$\bar{\mu}_m(x, y, z, t)$	electrochemical potential of depositing metal ions, J mol^{-1}		
$\delta\bar{\mu}_m(x, y, z, t)$	fluctuation of $\bar{\mu}_m(x, y, z, t)$, J mol^{-1}		
$\bar{\mu}_e(x, y, t)$	electrochemical potential of free electrons in the metal phase, J mol^{-1}		
$\rho(x, y, z, t)$	electric charge per unit area of electrode, C m^{-2}		
σ^*	electric conductivity, S m^{-1}		
$\Phi(x, y, z, t)$	electrostatic potential, V		
$\Phi^*(z, t)$	electrostatic equilibrium component of $\Phi(x, y, z, t)$, V		
$\phi(x, y, z, t)$	fluctuation of $\Phi(x, y, z, t)$, V		
Φ_1	potential difference of the Helmholtz layer, V		
Φ_2	potential difference of the diffuse layer, V		
$\phi_1(x, y, t)$	fluctuation of Φ_1 , V		
$\phi_2(x, y, z, t)$	fluctuation of Φ_2 , V		
$(\Phi_1)_{\text{rev}}$	potential value measured by the probe electrode, V		
$(\partial\Phi_1)/(\partial\Phi_2)_\mu$	differential overpotential coefficient		
$\phi^0(z, t)$	amplitude of $\phi(x, y, z, t)$, V		
$\phi_2^0(z, t)$	amplitude of $\phi_2(x, y, z, t)$, V		
$\psi(x, y, t)$	fluctuation of the chemical potential of adatoms by the change of surface form, J m^{-2}		
Ω	molar volume of depositing metal, $\text{m}^3 \text{mol}^{-1}$		
$\langle \rangle$	symbol for averaging in x and y directions		
∇	$\equiv (\partial/\partial x, \partial/\partial y, \partial/\partial z)$		
∇^2	$\equiv \partial^2/\partial x^2 + \partial^2/\partial y^2 + \partial^2/\partial z^2$		
∇_{\perp}	$\equiv (\partial/\partial x, \partial/\partial y)$		
∇_{\perp}^2	$\equiv \partial^2/\partial x^2 + \partial^2/\partial y^2$		
∇_{\perp}^4	$\equiv \partial^4/\partial x^4 + \partial^4/\partial y^4$		
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 states		

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