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Instability of nonequilibrium fluctuation in electrochemical nucleation.

II. Determination of the critical condition

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In the foregoing paper, part I, the mechanism of the fluctuations which are necessarily induced by the breakdown of the electrostatic equilibrium was examined. Consequently, it was found that nonspecific adsorption of ions onto electrode surface is essential to the progress of nucleation. It was also deduced that the critical condition for the unstable growth corresponds to the flat potential distribution in the diffuse layer within the electric double layer. Therefore, using the facts that at the stable region of the fluctuations, the electrode is kept in the electrostatic equilibrium and apparently behaves as an ideal polarized electrode, a method to determine the critical potential by the extrapolation from the stable region was theoretically developed. As a result, the critical potential equations corresponding to the flat distribution of the potential in the diffuse layer were obtained for various experimental conditions. By applying these equations to actual systems, the adsorbed states of ions at the interface can be examined. Therefore, the critical potential for silver nucleation onto platinum electrode in $\text{AgNO}_3 + \text{NaNO}_3$ solution were measured. Consequently, no intense specific adsorption of ions was observed, and it was concluded that a pair of Ag^+ ion and NO_3^- ion are simultaneously adsorbed by the electrostatic interaction. © 1995 American Institute of Physics.

I. INTRODUCTION

From the preceding paper, part I,¹ it has been shown that in the potential region where nonequilibrium fluctuations are kept stable, subsequent nucleation is depressed to minimum state. Hence, the substrate metal can be apparently be treated as an ideal polarized electrode, which is rigorously defined as the electrode at which no charge transfer across the metal-solution interface can occur, regardless of the potential externally imposed to the electrode.

At any fixed potentials, the electrode system attains a true state of equilibrium. However, this equilibrium is not of the familiar Nernstian type, but a state of electrostatic equilibrium in the electric double layer. Strictly speaking, no real electrode system can meet this stringent requirement; such equilibrium is easily broken by the thermal motion of solution particles. Physical quantities in a system not at Nernstian equilibrium fluctuate on the one side of electrostatic equilibrium in the direction to proceed reactions.

Therefore, if the system is stable for any fluctuations, it can approach ideal polarizability very closely though the range of imposed electrode potential is sufficiently restricted. However, in the case where the system is unstable, the fluctuations grow up with time, and the electrode reactions are accelerated with increasing faradaic current.

As shown in the preceding paper, such transition from stable state to unstable state occurs at a certain potential, i.e., the critical potential. To determine the critical potential in experiments, it will be shown in this paper that the extrapolation from the stable state can be used. Thus we can apply the usual theory of ideal polarized electrode to the determination of the critical potential.

In general, for ideal polarized electrodes, the plots of the electrode potential vs. either chemical potential of the component in question or its activity are referred to as the Esin

and Markov plots; the slope of the plot is called the Esin and Markov coefficient.²

The aim of this paper is to establish the expression of the critical potential with respect to the composition of the solution, i.e., the Esin and Markov relations corresponding to the critical condition of the instability. Then, the theoretical equations obtained are applied to determine the critical conditions of the cathodic deposition of silver onto platinum electrode in $\text{AgNO}_3 + \text{NaNO}_3$ solution. Namely, the electric charge coefficient for the silver nucleation will be examined from the theoretical and experimental points of view.

II. THEORY

In the present case, for simplicity, we will treat the solution containing only one supporting electrolyte in addition to the active metallic ion taking part in the nucleation.

Then, using a reference electrode (indicator electrode) reversible to one of three kinds of ions, metallic ion, and cation and anion of the supporting electrolyte, we will examine the potential difference between the working and indicator electrodes.

Furthermore, the expressions derived will be rewritten, corresponding to the case when the potential of the working electrode is measured with respect to a conventional reference electrode.

A. Critical potential coefficient with respect to indicator electrode

1. The case of minority metallic ion

At first, according to the literature,² we define the indicator electrode as an electrode reversible to one of the ions in the electrolyte solution. In addition, such particular ion is called the indicator ion. As mentioned above, we will treat a solution containing only three kinds of ions, i.e., active metallic ion which is classified as the minority ion, and anion

2and cation of the supporting electrolyte which form the majority ions. Here, the metallic ion, anion and cation will be denoted by the symbols m , $-$ and $+$, respectively. Therefore, if we measure the potential of the working electrode with respect to the indicator electrode reversible to either of the majority ions, the potential obtained should be expressed as $E^{*\pm}$; the symbol $*$ implies the quantity at the electrostatic equilibrium, and the symbol \pm denotes the quantity measured by the indicator electrode reversible to the cation $+$ or anion $-$. Hence, changing the chemical potential μ_{m-}^* of the salt $m-$ of the metallic ion m and anion $-$, we can measure the $E^{*\pm}$ which allows the derivation of the following Esin and Markov coefficient:³

$$\left(\frac{\partial E^{*\pm}}{\partial \mu_{m-}^*} \right)_{Q_M^*, \mu'} = - \frac{1}{\nu_{m-}^m} \left(\frac{\partial \Gamma_{mh'}^*}{\partial Q_M^*} \right)_\mu, \quad (1)$$

where subscript Q_M^* means that the surface excess of electric charge density on the metal phase is kept constant. Subscript μ' indicates that all chemical potentials are kept constant, other than the one with respect to which the differentiation is performed. Then, subscript μ denotes that constant composition of the solution is maintained. ν_{m-}^m is the number of moles of the metallic ion m per formula weight of the salt $m-$. $\Gamma_{mh'}^*$ represents the relative surface excess of the metallic ion m with respect to reference substance h' which is usually taken as the solvent, i.e.,

$$\Gamma_{mh'}^* = \Gamma_m^* - \nu_{m-}^m - \frac{x_{m-}}{x_{h'}} \Gamma_{h'}^*, \quad (2)$$

where Γ_m^* means the absolute surface excess of the metallic ion m ,⁴ and $\Gamma_{h'}^*$ is the absolute surface excess of the reference substance. x_{m-} and $x_{h'}$ are the mole fractions of the salt $m-$ and the reference substance h' in the homogeneous solution, respectively. Therefore, differentiating Eq. (2), we obtain

$$d\Gamma_{mh'}^* = d\Gamma_m^*. \quad (3)$$

Then, substituting Eq. (3) into Eq. (1), we have

$$\left(\frac{\partial E^{*\pm}}{\partial \mu_{m-}^*} \right)_{Q_M^*, \mu'} = - \frac{1}{\nu_{m-}^m} \left(\frac{\partial \Gamma_m^*}{\partial Q_M^*} \right)_\mu. \quad (4)$$

Here, Γ_m^* means the absolute surface excess, having an expression with the surface excess charge densities Q_{1m}^* and Q_{2m}^* of the metallic ion m in the Helmholtz layer and diffuse layer of the electric double layer, respectively, that is,

$$\Gamma_m^* = \frac{1}{z_m F} (Q_{1m}^* + Q_{2m}^*), \quad (5)$$

where z_m is ionic charge of the metallic ion and F is Faraday constant.

By differentiating Eq. (A8) in Appendix A, the total differentiation of the chemical potential of the salt $m-$ is given as

$$d\mu_{m-}^* = \nu_{m-}^m RT d \ln a_m^*, \quad (6)$$

where a_m^* is the single-ion activity of the metallic ion m when the system is at an electrostatic equilibrium. Substituting Eqs. (5) and (6) into Eq. (4), it follows that

$$\left(\frac{\partial E^{*\pm}}{\partial \ln a_m^*} \right)_{Q_M^*, \mu'} = - \frac{RT}{z_m F} \left\{ \left(\frac{\partial Q_{1m}^*}{\partial Q_M^*} \right)_\mu + \left(\frac{\partial Q_{2m}^*}{\partial Q_M^*} \right)_\mu \right\}. \quad (7)$$

Now, we will introduce the critical condition to Eq. (7): In general, the following partial differentiation of Q_{2m}^* with respect to Q_M^* is derived,

$$\left(\frac{\partial Q_{2m}^*}{\partial Q_M^*} \right)_\mu = \left(\frac{\partial Q_{2m}^*}{\partial Q_2^*} \right)_\mu \left(\frac{\partial Q_2^*}{\partial Q_M^*} \right)_\mu. \quad (8)$$

Then, the expression, Eq. (B15) in Appendix B deduced from the critical condition is applied to Eq. (8). Therefore,

$$\left(\frac{\partial Q_{2m}^*}{\partial Q_M^*} \right)_\mu = 0 \quad (9)$$

holds for the critical condition.

Finally, substituting Eq. (9) into Eq. (7), we obtain the expression corresponding to the critical condition, i.e.,

$$\left(\frac{\partial E^{*\pm}}{\partial \ln a_m^*} \right)_{Q_M^*, \mu'} = - \frac{RT}{z_m F} \left(\frac{\partial Q_{1m}^*}{\partial Q_M^*} \right)_\mu, \quad (10)$$

where $E^{*\pm}$ in this equation is equal to the critical potential with respect to the indicator electrode reversible to either of the ions of the supporting electrolyte.

2. The case of majority ions of supporting electrolyte

In this case, we can arbitrarily choose either ion of the supporting electrolyte; the resultant equations are independent of such choice. Thus we will use the indicator electrode reversible to the cation $+$ of supporting electrolyte $+-$. Then, by means of the electrode, we measure the potential response dE^{*+} of the working electrode vs the change $d\mu_{+-}^*$ of the chemical potential with keeping Q_M^* and μ_{m-}^* constant.

Hence, the following Esin and Markov coefficient is obtained,² i.e.,

$$\left(\frac{\partial E^{*+}}{\partial \mu_{+-}^*} \right)_{Q_M^*, \mu'} = - \frac{1}{\nu_{+-}^-} \left(\frac{\partial \Gamma_{-h'}^*}{\partial Q_M^*} \right)_\mu, \quad (11)$$

where $\Gamma_{-h'}^*$ is the relative surface excess of the anion $-$ with respect to the reference substance h' , and ν_{+-}^- implies the number of moles of the anion per formula weight of the supporting electrolyte. Then,

$$d\Gamma_{-h'}^* = d\Gamma_{-}^* - \frac{z_m}{|z_-|} d\Gamma_m^*, \quad (12)$$

where z_- is ionic charge of the anion, including sign. Γ_{-}^* is the absolute surface excess of the same anion, related to the excess charge densities, Q_{1-}^* and Q_{2-}^* of the anion in the Helmholtz layer and the diffuse layer, i.e.,

$$\Gamma_{-}^* = \frac{1}{z_- F} (Q_{1-}^* + Q_{2-}^*). \quad (13)$$

Substituting Eqs. (5) and (13) into Eq. (12), and differentiating the resultant equation, it follows that

$$d\Gamma_{-h}^* = -\frac{1}{|z_-|F} (dQ_{1-}^* + dQ_{1m}^* + dQ_{2-}^* + dQ_{2m}^*). \quad (14)$$

On the other hand, differentiating Eq. (A4) in Appendix A, we have the expression concerning the chemical potential μ_{+-}^* , i.e.,

$$d\mu_{+-}^* = (\nu_{+-}^- + \nu_{+-}^+) RT d \ln a_{\pm}^*, \quad (15)$$

where ν_{+-}^+ indicates the number of moles of the cation + per formula weight of the supporting electrolyte, and a_{\pm}^* is the mean ionic activity of the supporting electrolyte at an electrostatic equilibrium.

Substitution of Eq. (14) into Eq. (11) provides the expression, as follows:

$$\left(\frac{\partial E^{*+}}{\partial \mu_{+-}^*} \right)_{Q_M^*, \mu'} = \frac{1}{\nu_{+-}^- |z_-| F} \left\{ \left(\frac{\partial Q_{1-}^*}{\partial Q_M^*} \right)_{\mu} + \left(\frac{\partial Q_{1m}^*}{\partial Q_M^*} \right)_{\mu} + \left(\frac{\partial Q_{2-}^*}{\partial Q_M^*} \right)_{\mu} + \left(\frac{\partial Q_{2m}^*}{\partial Q_M^*} \right)_{\mu} \right\}. \quad (16)$$

Hence, we will apply the critical condition to Eq. (16) as follows: In general, as well as Eq. (8), the partial differentiation of Q_{2-}^* with respect to Q_M^*

$$\left(\frac{\partial Q_{2-}^*}{\partial Q_M^*} \right)_{\mu} = \left(\frac{\partial Q_{2-}^*}{\partial Q_2^*} \right)_{\mu} \left(\frac{\partial Q_2^*}{\partial Q_M^*} \right)_{\mu} \quad (17)$$

holds. Then, the condition of electroneutrality at the interface is written in the form,

$$Q_M^* + Q_1^* + Q_2^* = 0. \quad (18)$$

Differentiating Eq. (18) with respect to Q_M^* , we obtain

$$\left(\frac{\partial Q_2^*}{\partial Q_M^*} \right)_{\mu} = - \left\{ 1 + \left(\frac{\partial Q_1^*}{\partial Q_M^*} \right)_{\mu} \right\}. \quad (19)$$

Hence, substituting Eq. (B20) in Appendix B and Eq. (19) into Eq. (17), we have

$$\left(\frac{\partial Q_{2-}^*}{\partial Q_M^*} \right)_{\mu} = - \frac{|z_-|}{z_+ + |z_-|} \left\{ 1 + \left(\frac{\partial Q_1^*}{\partial Q_M^*} \right)_{\mu} \right\}. \quad (20)$$

Considering the relation,

$$Q_1^* = Q_{1+}^* + Q_{1-}^* + Q_{1m}^*, \quad (21)$$

substitution of Eq. (B15) in Appendix B and Eq. (20) into Eq. (16) yields

$$\left(\frac{\partial E^{*+}}{\partial \mu_{+-}^*} \right)_{Q_M^*, \mu'} = \frac{1}{\nu_{+-}^- |z_-| F} \left[\frac{z_+}{z_+ + |z_-|} \left\{ \left(\frac{\partial Q_{1-}^*}{\partial Q_M^*} \right)_{\mu} \right\} \right]$$

$$+ \left(\frac{\partial Q_{1m}^*}{\partial Q_M^*} \right)_{\mu} \left\{ - \frac{|z_-|}{z_+ + |z_-|} \times \left\{ \left(\frac{\partial Q_{1+}^*}{\partial Q_M^*} \right)_{\mu} + 1 \right\} \right\}. \quad (22)$$

Here, using Eq. (A2) in Appendix A for electroneutrality, the following equations are obtained, i.e.,

$$\frac{1}{\nu_{+-}^- |z_-| F} \frac{z_+}{z_+ + |z_-|} = \frac{1}{(\nu_{+-}^+ + \nu_{+-}^-) |z_-| F}, \quad (23)$$

$$\frac{1}{\nu_{+-}^- |z_-| F} \frac{|z_-|}{z_+ + |z_-|} = \frac{1}{(\nu_{+-}^+ + \nu_{+-}^-) z_+ F}. \quad (24)$$

Substituting Eqs. (23) and (24) into Eq. (22), and then Eq. (15) into the resultant equation, we can eventually obtain the expression corresponding to the critical condition, as follows:

$$\left(\frac{\partial E^{*+}}{\partial \ln a_{\pm}^*} \right)_{Q_M^*, \mu'} = \frac{RT}{|z_-| F} \left\{ \left(\frac{\partial Q_{1-}^*}{\partial Q_M^*} \right)_{\mu} + \left(\frac{\partial Q_{1m}^*}{\partial Q_M^*} \right)_{\mu} - \frac{RT}{z_+ F} \left\{ \left(\frac{\partial Q_{1+}^*}{\partial Q_M^*} \right)_{\mu} + 1 \right\} \right\}, \quad (25)$$

where E^{*+} in this equation is equal to the critical potential with respect to the indicator electrode reversible to the cation + of the supporting electrolyte.

B. Critical potential coefficient with respect to conventional reference electrode

The electrode potential E^{*i} ($i = +$ or $-$) discussed in the preceding sections is measured from the potential E_{eq}^{*i} reversible to the cation + or anion $-$ by using the indicator electrode.

At the critical potential, E^{*i} is exhibited as

$$E^{*i} = E_W^* - E_{eq}^{*i}, \quad (26)$$

where E_W^* is the critical potential of the working electrode. This means that because E_{eq}^{*i} takes different values depending on the reversible ion (indicator ion), E^{*i} shows different behavior from E_W^* , which is inconvenient for comparing the observed values with the theoretical predictions. Therefore, instead of E^{*i} , we newly adopt the value E_{cr}^* defined by E_W^* which is measured from the constant reference electrode potential E_{ref}^* , as follows:

$$E_{\text{cr}}^* \equiv E_{\text{w}}^* - E_{\text{ref}}^*. \quad (27)$$

Substituting Eq. (26) into Eq. (27), we have

$$E_{\text{cr}}^* = E^{*i} + \Delta E^{*i}, \quad (28)$$

where

$$\Delta E^{*i} \equiv E_{\text{eq}}^{*i} - E_{\text{ref}}^*. \quad (29)$$

Hence, taking the cation + as the species of ion i , and making partial differentiation of Eq. (28) with respect to $\ln a_{\pm}^*$, the following expression is obtained:

$$\left(\frac{\partial E_{\text{cr}}^*}{\partial \ln a_{\pm}^*} \right)_{Q_M^*, \mu'} = \left(\frac{\partial E^{*+}}{\partial \ln a_{\pm}^*} \right)_{Q_M^*, \mu'} + \left(\frac{\partial \Delta E^{*+}}{\partial \ln a_{\pm}^*} \right)_{Q_M^*, \mu'}. \quad (30)$$

After substituting Eq. (25) and Eq. (C11) in Appendix C into Eq. (30), the dependence of the critical potential E_{cr}^* on the mean ionic activity of the supporting electrolyte as the salt of majority ions is derived

$$\left(\frac{\partial E_{\text{cr}}^*}{\partial \ln a_{\pm}^*} \right)_{Q_M^*, \mu'} = \frac{RT}{|z_-|F} \left\{ \left(\frac{\partial Q_{1-}^*}{\partial Q_M^*} \right)_{\mu} + \left(\frac{\partial Q_{1m}^*}{\partial Q_M^*} \right)_{\mu} \right\} - \frac{RT}{z_+ F} \left(\frac{\partial Q_{1+}^*}{\partial Q_M^*} \right)_{\mu}, \quad (31)$$

where the subscript μ' in this case means that the μ_{m-}^* is kept constant.

On the other hand, the partial differentiation of Eq. (28) for $i = \pm$ with respect to $\ln a_m^*$ leads to the expression of the dependence of E_{cr}^* on the single-ion activity of the metallic ion, i.e.,

$$\left(\frac{\partial E_{\text{cr}}^*}{\partial \ln a_m^*} \right)_{Q_M^*, \mu'} = \left(\frac{\partial E^{*\pm}}{\partial \ln a_m^*} \right)_{Q_M^*, \mu'} + \left(\frac{\partial \Delta E^{*\pm}}{\partial \ln a_m^*} \right)_{Q_M^*, \mu'}. \quad (32)$$

Thus, substituting Eq. (10) and Eq. (C12) in Appendix C into Eq. (32),

$$\left(\frac{\partial E_{\text{cr}}^*}{\partial \ln a_m^*} \right)_{Q_M^*, \mu'} = - \frac{RT}{z_m F} \left(\frac{\partial Q_{1m}^*}{\partial Q_M^*} \right)_{\mu} \quad (33)$$

is obtained; this coefficient has the same value as Eq. (10).

The critical coefficients derived above, correspond to the case when the metallic ion m is the minority ion, and the cation + and anion - of the supporting electrolyte form the majority ions.

On the contrary, we can also obtain the critical potential coefficient for the case when the cation + of the supporting electrolyte is taken as the minority ion, and the metallic ion m and the anion - form the majority ions. Such equations are easily obtained if the subscripts m and + are converted to + and m in Eqs. (31) and (33), respectively. That is, when the surface excess charge density Q_M^* on the metal phase and

the chemical potential μ_{+-}^* of the supporting electrolyte, i.e., the salt of the minority ions are kept constant, we can measure the critical potential as a function of mean ionic activity a_m^* of the salt of the majority ions, i.e., the metallic ion and the anion. In addition, the differential coefficient of the critical potential with respect to $\ln a_m^*$ is given by

$$\left(\frac{\partial E_{\text{cr}}^*}{\partial \ln a_m^*} \right)_{Q_M^*, \mu'} = \frac{RT}{|z_-|F} \left\{ \left(\frac{\partial Q_{1-}^*}{\partial Q_M^*} \right)_{\mu} + \left(\frac{\partial Q_{1+}^*}{\partial Q_M^*} \right)_{\mu} \right\} - \frac{RT}{z_m F} \left(\frac{\partial Q_{1m}^*}{\partial Q_M^*} \right)_{\mu}. \quad (34)$$

Moreover, for constant Q_M^* and μ_{m-}^* , the critical potential coefficient with respect to single ion activity a_{+}^* of the cation, the minority ion, is written by using Eq. (33), as follows:

$$\left(\frac{\partial E_{\text{cr}}^*}{\partial \ln a_{+}^*} \right)_{Q_M^*, \mu'} = - \frac{RT}{z_+ F} \left(\frac{\partial Q_{1+}^*}{\partial Q_M^*} \right)_{\mu}. \quad (35)$$

C. Measurement of electric charge coefficient

Using the formula

$$\left(\frac{\partial Q_1^*}{\partial Q_2^*} \right)_{\mu} = \left(\frac{\partial Q_1^*}{\partial Q_M^*} \right)_{\mu} / \left(\frac{\partial Q_2^*}{\partial Q_M^*} \right)_{\mu} \quad (36)$$

and substituting Eq. (18) into Eq. (36), we obtain the electric charge coefficient playing an important role for the instability of the nonequilibrium fluctuations in part I,¹ i.e.,

$$\left(\frac{\partial Q_1^*}{\partial Q_2^*} \right)_{\mu} = - \left(\frac{\partial Q_{1+}^*}{\partial Q_M^*} \right)_{\mu} / \left\{ 1 + \left(\frac{\partial Q_{1m}^*}{\partial Q_M^*} \right)_{\mu} \right\}. \quad (37)$$

Here, differentiating Eq. (21) with respect to Q_M^* , the quantity $(\partial Q_{1+}^* / \partial Q_M^*)_{\mu}$ is deduced as

$$\left(\frac{\partial Q_{1+}^*}{\partial Q_M^*} \right)_{\mu} = \left(\frac{\partial Q_{1+}^*}{\partial Q_M^*} \right)_{\mu} + \left(\frac{\partial Q_{1-}^*}{\partial Q_M^*} \right)_{\mu} + \left(\frac{\partial Q_{1m}^*}{\partial Q_M^*} \right)_{\mu}. \quad (38)$$

Therefore, to determine the value of the charge coefficient in Eq. (37) experimentally, it is necessary to provide each term on the right side of Eq. (38) with measurable quantities, i.e., the critical potential coefficients.

Derivation of the coefficients is classified into two cases depending on which ion, metallic ion or cation of the supporting electrolyte is chosen as the minority ion. The results are shown in Eqs. (31) and (33)–(35). From these equations, it is concluded that each charge coefficient can be derived from the arbitrary choice of three equations from the four equations. For example, using Eqs. (31), (33), and (35),

$$\left(\frac{\partial Q_{1+}^*}{\partial Q_M^*} \right)_{\mu} = - \frac{z_+ F}{2.303 RT} \left(\frac{\partial E_{\text{cr}}^*}{\partial \log_{10} a_{+}^*} \right)_{Q_M^*, \mu'}, \quad (39)$$

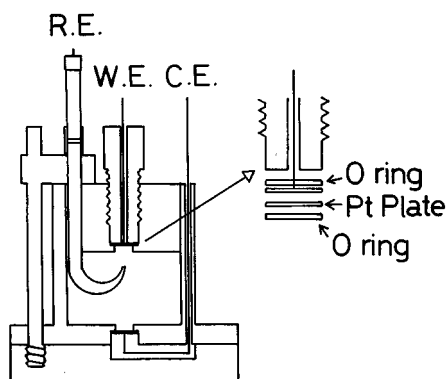


FIG. 1. Schematic configuration of electrolytic cell. W.E.: working electrode, C.E.: counter electrode, R.E.: reference electrode

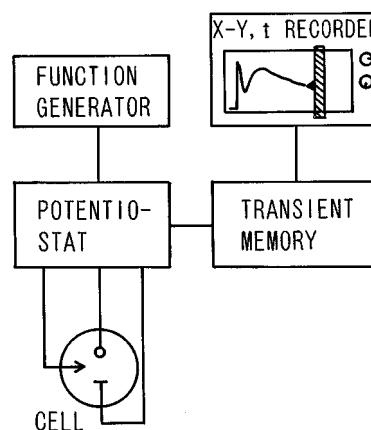


FIG. 2. Block diagram of cell system.

$$\left(\frac{\partial Q_{1-}^*}{\partial Q_M^*} \right)_\mu = \frac{|z_-|F}{2.303RT} \left\{ \left(\frac{\partial E_{cr}^*}{\partial \log_{10} a_{\pm}^*} \right)_{Q_M^*, \mu'} + \frac{z_m}{|z_-|} \left(\frac{\partial E_{cr}^*}{\partial \log_{10} a_m^*} \right)_{Q_M^*, \mu'} - \left(\frac{\partial E_{cr}^*}{\partial \log_{10} a_+^*} \right)_{Q_M^*, \mu'} \right\}, \quad (40)$$

$$\left(\frac{\partial Q_{1m}^*}{\partial Q_M^*} \right)_\mu = - \frac{z_m F}{2.303RT} \left(\frac{\partial E_{cr}^*}{\partial \log_{10} a_m^*} \right)_{Q_M^*, \mu'}. \quad (41)$$

The potential coefficient in Eq. (34) can be obtained both from the data directly measured by the experiments and from the calculation with the other charge coefficients decided above.

III. EXPERIMENT

A cell made of acrylic resin which was used in experiments is shown in Fig. 1. Working and counter electrodes were round platinum plates of 12 mm in diameter and 0.5 mm in thickness and attached to the upper and bottom parts of the cell from the behind of the panels by screw caps. As shown in the figure, cylindrical spaces were made in front of the both electrodes. The working electrode at the top was set toward the counter electrode at the bottom, being face to face each other. All these settings were made to prevent natural convection.

An Ag/AgCl electrode in a solution saturated with KCl was used as a reference electrode, which was settled adjacent to the working electrode through a Luggin capillary tip filled with agar-agar gel saturated by KNO_3 to regulate the potential of the working electrode. The distance between the working electrode and the capillary tip was kept constant for assuring constant resistance of the solution. The temperature was kept at $27 \pm 1^\circ \text{C}$.

Prior to experiments, working electrode was activated by cyclic potential sweeps in a vessel filled with 1 M NaNO_3 .

Immediately after attaining constant activity, the working electrode was transferred to the cell filled with solution containing AgNO_3 with NaNO_3 as a supporting electrolyte. The water was twice distilled, and before experiments, dissolved O_2 was removed by bubbling N_2 gas for more than 10 min.

Experiments were carried out as follows; first, the electrode potential was set at the rest potential, then the potential was swept in the cathodic direction to start the silver nucleation on the platinum electrode. Sweep rate was regulated by a potentiostat (Potentio-Galvanostat 2090, Toho Technical Research) via a function generator (FG-02, Toho Technical Research). Current transient was recorded by a XY recorder (F-42P, Riken Electronics). Figure 2 shows the block diagram of the electrode system.

As shown in Fig. 3, extrapolation of the current transient obtained from the potential sweep determines the critical potential. After verifying that the data obtained was independent of the sweep rate, the rate was determined as $2.0 \times 10^{-3} \text{ V s}^{-1}$.

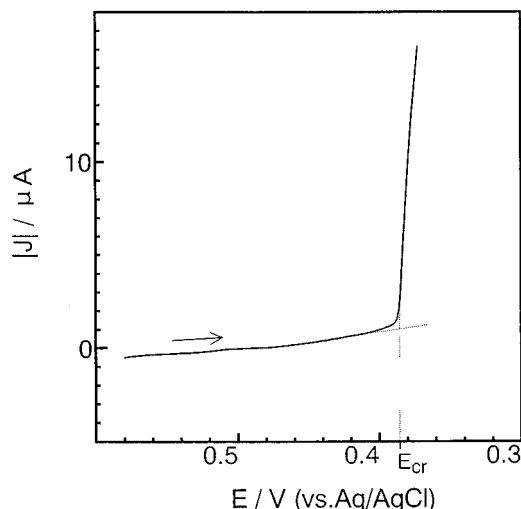


FIG. 3. Diagram for critical potential measurement: Sweep rate is $2.0 \times 10^{-3} \text{ V s}^{-1}$, $[\text{AgNO}_3] = 1 \text{ mol m}^{-3}$, $[\text{NaNO}_3] = 1000 \text{ mol m}^{-3}$, $T = 300 \text{ K}$.

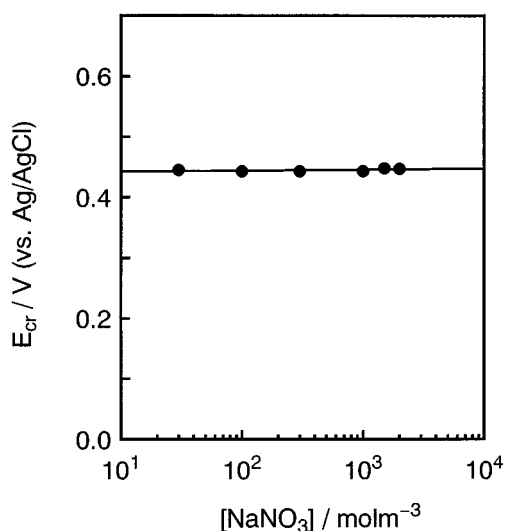


FIG. 4. Dependence of critical potential on NaNO_3 concentration in the case where Ag^+ ion is minority ion and NaNO_3 is majority salt: $[\text{AgNO}_3]=20 \text{ mol m}^{-3}$, $T=300 \text{ K}$.

IV. RESULTS AND DISCUSSION

Figure 4 shows the results of the critical potential measurement; in the case of majority salt of NaNO_3 and minority ion of Ag^+ , the concentration of NaNO_3 was varied at constant Ag^+ ionic concentration. The slope of the plot was equal to zero.

Subsequently,

$$\left(\frac{\partial E_{\text{cr}}^*}{\partial \ln a_{\pm}^*} \right)_{Q_M^*, \mu'} = 0.0 \quad \text{V} \quad (42)$$

is obtained.

Figure 5 exhibits the experimental results obtained with changing Ag^+ ionic concentration instead of NaNO_3 concentration under the same situation as Fig. 4. Namely,

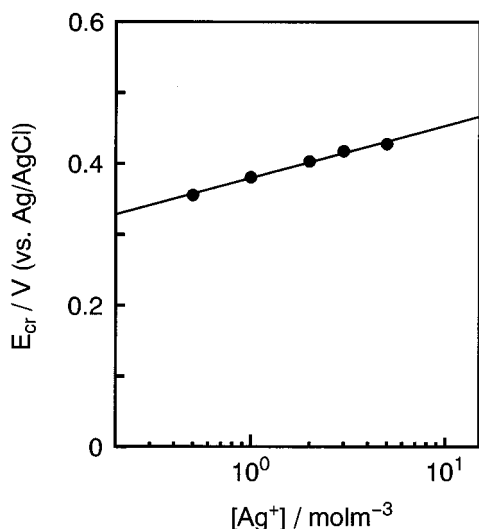


FIG. 5. Dependence of critical potential on Ag^+ ionic concentration in the case where Ag^+ ion is minority ion and NaNO_3 is majority salt: $[\text{NaNO}_3]=300 \text{ mol m}^{-3}$, $T=300 \text{ K}$.

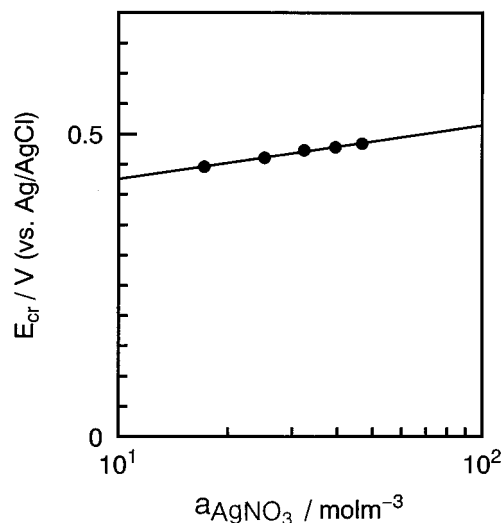


FIG. 6. Dependence of critical potential on AgNO_3 activity in the case when Na^+ ion is minority ion and AgNO_3 is majority salt: $[\text{NaNO}_3]=1 \text{ mol m}^{-3}$, $T=300 \text{ K}$.

$$\left(\frac{\partial E_{\text{cr}}^*}{\partial \ln a_m^*} \right)_{Q_M^*, \mu'} = 3.21 \times 10^{-2} \quad \text{V} \quad (43)$$

is derived.

On the contrary, in the case where AgNO_3 is a majority salt and Na^+ ion is minority ion, Fig. 6 indicates the critical potentials measured with changing mean activity of AgNO_3 calculated by the use of the data in the literature⁵ at constant Na^+ ionic concentration. As a result,

$$\left(\frac{\partial E_{\text{cr}}^*}{\partial \ln a_m^*} \right)_{Q_M^*, \mu'} = 3.83 \times 10^{-2} \quad \text{V} \quad (44)$$

was obtained.

In the same case as Fig. 6, in Fig. 7, the critical potential

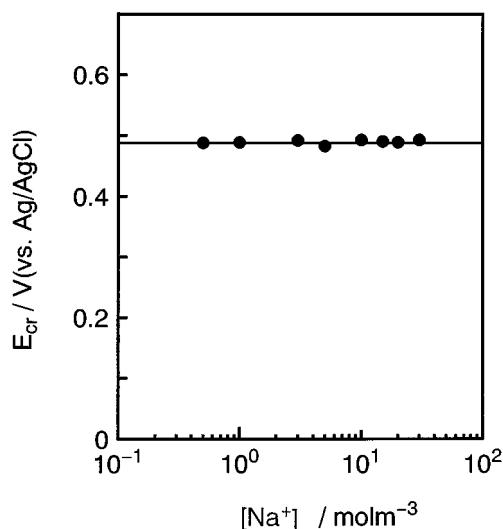


FIG. 7. Dependence of critical potential on Na^+ ionic concentration in the case where Na^+ ion is minority ion and AgNO_3 is majority salt: $[\text{AgNO}_3]=80 \text{ mol m}^{-3}$, $T=300 \text{ K}$.

was measured as the Na^+ ionic concentration was altered in the solution with constant AgNO_3 concentration. Then, the experimental result is

$$\left(\frac{\partial E_{\text{cr}}^*}{\partial \ln a_+^*} \right)_{Q_M^*, \mu'} = 0.0 \quad \text{V}. \quad (45)$$

If we obtain only three of the four data mentioned above, we can calculate the rest from the three data by using Eqs. (31) and (33)–(35).

In the present case, for example, the data obtained in Eq. (44) will be computed from the data of Eqs. (42), (43), and (45): First, substituting Eqs. (42), (43), and (45) into Eq. (40), it follows that

$$\left(\frac{\partial Q_{1-}^*}{\partial Q_M^*} \right)_{\mu} = 1.05. \quad (46)$$

Then, substitution of Eq. (43) into Eq. (41) leads to

$$\left(\frac{\partial Q_{1m}^*}{\partial Q_M^*} \right)_{\mu} = -1.05. \quad (47)$$

Furthermore, we substitute Eq. (45) into Eq. (39), so that

$$\left(\frac{\partial Q_{1+}^*}{\partial Q_M^*} \right)_{\mu} = 0.0 \quad (48)$$

is derived. Finally, substitution of Eqs. (46), (47), and (48) into Eq. (34) gives

$$\left(\frac{\partial E_{\text{cr}}^*}{\partial \ln a_m^*} \right)_{Q_M^*, \mu'} = 4.14 \times 10^{-2} \quad \text{V}. \quad (49)$$

Comparing this value with that of Eq. (44), it is obvious that both data are in good agreement with each other. From these results, it is concluded that the experimental data obtained indicate no discrepancy between each other, and show correct values.

Here, Eqs. (46)–(48) express the variations of electric charges of adsorbed species in the Helmholtz layer when the unit charge on the electrode side is altered. From this point of view, the summation of Eqs. (46) to (48) indicates the absence of specific adsorption, i.e., electroneutrality in the Helmholtz layer. As usually expected, Eq. (48) reveals that Na^+ ions does not change the adsorption state.^{6,7}

Consequently, Eqs. (46) and (47) indicated that the same amounts of charges, i.e., 1.05 units of Ag^+ ions and NO_3^- ions behave like a ion pair, adsorbing to or desorbing from the electrode.

Finally, we will obtain the charge coefficient which has much importance to the instability of asymmetrical fluctuation, i.e., substituting Eqs. (46)–(48) into Eq. (38), we can reckon, as mentioned before,

$$\left(\frac{\partial Q_1^*}{\partial Q_M^*} \right)_{\mu} = 0.0. \quad (50)$$

Substitution of Eq. (50) into Eq. (37) allows

$$\left(\frac{\partial Q_1^*}{\partial Q_2^*} \right)_{\mu} = 0.0. \quad (51)$$

From this result, according to the foregoing paper,¹ the instability in the present case belongs to the case where the charge coefficient $(\partial Q_1^* / \partial Q_2^*)_{\mu}$ is larger than -1 .

Thence, the instability takes place when $\langle \Phi_2 \rangle$ becomes minus;

$$\langle \Phi_2 \rangle < 0 \quad \text{and} \quad \left(\frac{\partial \langle \Phi_1 \rangle}{\partial \langle \Phi_2 \rangle} \right)_{\mu} > 0 \left(\left(\frac{\partial Q_1^*}{\partial Q_2^*} \right)_{\mu} > -1 \right). \quad (52)$$

V. CONCLUSIONS

The critical potential in a solution system containing active metallic ion and single supporting electrolyte was theoretically derived, which corresponds to the critical condition, $\langle \Phi_2 \rangle = 0$, for the asymmetrical nonequilibrium fluctuations.

The theoretical equations obtained were depicted in the form of the potential coefficient against the activity of ion or salt. In spite of three ionic components, four equations were obtained, so that the electric charge coefficients describing the adsorption states of three ions can be derived from the arbitrary choice of three equations from the four equations. Hence, we can ascertain the validity of the equations from both aspects of calculation and experiment, i.e., by determining the residual potential coefficient from the calculation and experiments.

Experimental demonstration was performed for silver nucleation onto platinum electrode in $\text{AgNO}_3 + \text{NaNO}_3$ solution. The adsorption behaviors of silver ion, sodium ion and nitrate ion were also examined by means of the electric charge coefficients. Consequently, they suggested the absence of specific adsorption of ions; it was found that electrostatic interaction induces the 1:1 adsorption of Ag^+ ion and NO_3^- ion. However, Na^+ ion was never adsorbed during cathodic polarization.

Finally, the electric charge coefficient which has much importance to the instability of the asymmetrical fluctuations was determined, i.e.,

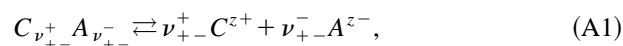
$$\left(\frac{\partial Q_1^*}{\partial Q_2^*} \right)_{\mu} = 0.0.$$

From the above result, it was concluded that the instability in the present case is caused by the absence of specific adsorption of ions, and that the unstable condition is given as

$$\langle \Phi_2 \rangle < 0 \quad \text{with} \quad \left(\frac{\partial \langle \Phi_1 \rangle}{\partial \langle \Phi_2 \rangle} \right)_{\mu} > 0.$$

APPENDIX A: CHEMICAL POTENTIALS OF THE SALTS OF MINORITY AND MAJORITY IONS

For a supporting electrolyte, i.e., a salt of majority ions, we may write a following formal dissociation equilibrium:



where C and C^{z+} mean the atom and cation coming from the supporting electrolyte, respectively. Similarly, A and A^{z-}

mean the atom and anion from the same salt, respectively. The ν 's indicate the number of moles of cation or anion per formula weight of the salt. Since the salt is electrically neutral, the following equation:

$$\nu_{+-}^+ z_+ = \nu_{+-}^- |z_-| \quad (\text{A2})$$

holds.

Corresponding to the above equilibrium, there is an equation relating the chemical potential μ_{+-} of the supporting electrolyte to the electrochemical potentials $\bar{\mu}_+$ and μ_- of its constituent ions, that is,

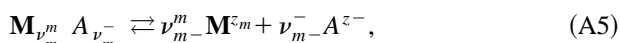
$$\mu_{+-} = \nu_{+-}^+ \bar{\mu}_+ + \nu_{+-}^- \bar{\mu}_-. \quad (\text{A3})$$

It is also convenient to employ the activity of the salt instead of the chemical potential. From Eq. (A3), we have

$$\mu_{+-} = \mu_{+-}^0 + (\nu_{+-}^+ + \nu_{+-}^-) RT \ln a_{\pm}, \quad (\text{A4})$$

where μ_{+-}^0 is the standard chemical potential of the salt and a_{\pm} is the mean ionic activity.

Then, for the metallic active ion, i.e., a minority cation, we may express the following formal equilibrium in relation to the majority anion of the supporting electrolyte,



where \mathbf{M} and \mathbf{M}^{z_m} are the metallic atom and ion, respectively. z_m means the ionic charge of the metallic ion, including sign. Since the salt in Eq. (A5) as well as Eq. (A1) is electrically neutral, the following equation is also derived

$$\nu_{m-}^m z_m = \nu_{m-}^- |z_-|. \quad (\text{A6})$$

From Eq. (A5), we obtain an equation relating the chemical potential of the salt to the electrochemical potentials of its constituent ions

$$\mu_{m-} = \nu_{m-}^m \bar{\mu}_m + \nu_{m-}^- \bar{\mu}_-. \quad (\text{A7})$$

In this case, the chemical potential μ_{m-} is determined by the activity of the metallic ion owing to its minority. Therefore,

$$\mu_{m-} = \mu_{m-}^0 + \nu_{m-}^m RT \ln a_m, \quad (\text{A8})$$

where μ_{m-}^0 is the standard chemical potential of the salt in the presence of constant large amount of supporting electrolyte, and a_m means the single-ion activity of the metallic ion.

APPENDIX B: ELECTRIC CHARGE COEFFICIENT FOR DIFFUSE LAYER

In the preceding paper, part I,¹ it was shown that the Faradaic current induced by the nonequilibrium fluctuations yields no electric change in the solution. Therefore, the concentration distribution in the diffuse layer of the electric double layer can be described by the Boltzmann distribution similar to that at the completely electrostatic equilibrium, i.e.,

$$\langle C_i(z) \rangle = \langle C_i(\infty^+) \rangle \exp\left(-\frac{z_i F}{RT} \langle \Phi \rangle\right), \quad (\text{B1})$$

where, for simplicity, we will exhibit the average in x and y directions parallel to the electrode surface by the symbol $\langle \rangle$, and then $\langle C_i(z) \rangle \equiv \langle C_i(x, y, z, t) \rangle$, $\langle C_i(\infty^+) \rangle \equiv \langle C_i(x, y, 0, t) \rangle$

and $\langle \Phi \rangle \equiv \langle \Phi(x, y, 0, t) \rangle$. Here, $z = \infty^+$ means the immediate location outside the double layer; in comparison with the scale of the fluctuations, the value of ∞^+ can be neglected and equated with zero in the fluctuation scale.

Since we are now discussing the potential near the critical potential,

$$\left| \frac{z_i F}{RT} \langle \Phi \rangle \right| \ll 1. \quad (\text{B2})$$

Under the condition of Eq. (B2), as shown in Appendix A of the preceding paper, the potential gradient in the diffuse layer is exhibited in the form,

$$\frac{\partial \langle \Phi \rangle}{\partial z} = -\frac{\langle \Phi \rangle}{\lambda}, \quad (\text{B3})$$

where λ denotes the Debye length,

$$\lambda \equiv \frac{1}{F} \sqrt{\frac{\epsilon RT}{\sum_j z_j^2 \langle C_j(\infty^+) \rangle}}. \quad (\text{B4})$$

Here, expanding Eq. (B1) under the condition of Eq. (B2), we obtain the expression of the surface excess of ion i at a plane parallel to the surface in the diffuse layer, i.e.,

$$\langle C_i(z) \rangle - \langle C_i(\infty^+) \rangle = -\frac{z_i F}{RT} \langle C_i(\infty^+) \rangle \langle \Phi \rangle. \quad (\text{B5})$$

With boundary conditions,

$$\langle \Phi \rangle = 0 \quad \text{for } z = \infty^+ \text{ (outside the double layer)}, \quad (\text{B6})$$

$$\langle \Phi \rangle = \langle \Phi_2 \rangle \quad \text{for } z = 0 \text{ (outer Helmholtz plane)}. \quad (\text{B7})$$

Integrating Eq. (B5) from $z=0$ to $z=\infty^+$, the absolute surface excess Γ_{2i}^* over the diffuse layer is deduced. Here, the symbol $*$ means electrostatic quantity.

With the aid of Eq. (B3),

$$\begin{aligned} \Gamma_{2i}^* &= -\frac{z_i F}{RT} \langle C_i(\infty^+) \rangle \int_0^{\infty^+} \langle \Phi \rangle dz \\ &= \frac{z_i F \lambda}{RT} \langle C_i(\infty^+) \rangle \int_{\langle \Phi_2 \rangle}^0 d\langle \Phi \rangle \\ &= -\frac{z_i F \lambda}{RT} \langle C_i(\infty^+) \rangle \langle \Phi_2 \rangle, \end{aligned} \quad (\text{B8})$$

where $\langle \Phi_2 \rangle$ implies the averaged potential difference between both sides of the diffuse layer. Hence, the total electric charge density Q_{2i}^* of ion i over the whole diffuse layer is given by

$$Q_{2i}^* = z_i F \Gamma_{2i}^*, \quad (\text{B9})$$

where z_i is ionic charge of ion i including sign. Substitution of Eq. (B8) into Eq. (B9) yields

$$Q_{2i}^* = -\frac{(z_i F)^2 \lambda}{RT} \langle C_i(\infty^+) \rangle \langle \Phi_2 \rangle. \quad (\text{B10})$$

On the other side, the total electric charge density in the diffuse layer is, using the usual electric double layer theory,⁸ given by

$$Q_2^* = \epsilon \left(\frac{\partial \langle \Phi \rangle}{\partial z} \right)_{z=0}. \quad (\text{B11})$$

Substituting Eq. (B3) into Eq. (B11), we have

$$Q_2^* = - \frac{\epsilon \langle \Phi_2 \rangle}{\lambda}. \quad (\text{B12})$$

Therefore, the electric charge coefficient of ion i in the diffuse layer is described by Eqs. (B4), (B10), and (B12), as follows:

$$\left(\frac{\partial Q_{2i}^*}{\partial Q_2^*} \right)_\mu = \frac{(z_i F)^2 \lambda^2}{\epsilon R T} \langle C_i(\infty^+) \rangle = \frac{z_i^2 \langle C_i(\infty^+) \rangle}{\sum_j z_j^2 \langle C_j(\infty^+) \rangle}. \quad (\text{B13})$$

Thus from Eq. (B13),

$$\sum_i \left(\frac{\partial Q_{2i}^*}{\partial Q_2^*} \right)_\mu = 1 \quad (\text{B14})$$

is obtained. Here, for the minority metallic ion of $i = m$, it approximately follows from Eq. (B13) that

$$\left(\frac{\partial Q_{2m}^*}{\partial Q_2^*} \right)_\mu = 0. \quad (\text{B15})$$

Therefore, for the majority ions of the supporting electrolyte, the electroneutrality also approximately holds, as follows:

$$\sum_i z_i \langle C_i(\infty^+) \rangle = 0 \quad \text{for } i \neq m. \quad (\text{B16})$$

In this case, since a single salt is present as the supporting electrolyte in the solution, recalling $\langle C_+(\infty^+) \rangle = C_+^*(z = \infty)$ and $\langle C_-(\infty^+) \rangle = C_-^*(z = \infty)$, we have the electroneutrality from Eq. (B16), i.e.,

$$z_+ C_+^*(z = \infty) = |z_-| C_-^*(z = \infty). \quad (\text{B17})$$

On the other hand, neglecting the presence of the minority ion, the following equation corresponding to the cation $+$ is obtained:

$$\left(\frac{\partial Q_{2+}^*}{\partial Q_2^*} \right)_\mu = \frac{z_+^2 C_+^*(z = \infty)}{z_+^2 C_+^*(z = \infty) + z_-^2 C_-^*(z = \infty)}. \quad (\text{B18})$$

Substituting Eq. (B17) into Eq. (B18), it follows that:

$$\left(\frac{\partial Q_{2+}^*}{\partial Q_2^*} \right)_\mu = \frac{z_+}{z_+ + |z_-|}. \quad (\text{B19})$$

For the anion $-$, by the similar procedure,

$$\left(\frac{\partial Q_{2-}^*}{\partial Q_2^*} \right)_\mu = \frac{|z_-|}{z_+ + |z_-|} \quad (\text{B20})$$

is obtained.

APPENDIX C: DEPENDENCE OF THE INDICATOR ELECTRODE POTENTIAL ON THE CHEMICAL POTENTIAL OF SUPPORTING ELECTROLYTE WHEN USING CONVENTIONAL REFERENCE ELECTRODE

In this case, the indicator electrode is reversible to the cation of the supporting electrolyte, so that we may write a formal equilibrium



where C and C^{z+} mean the atom and cation coming from the supporting electrolyte, respectively.

Therefore, the chemical potential μ_c^* (metal) of the pure substance comprising the indicator electrode may be expressed in terms of the electrochemical potential $\bar{\mu}_+^*$ (sol) of that ion in the solution and the electrochemical potential $\bar{\mu}_e^*$ (metal) of the electron in the metal phase of the indicator electrode, i.e.,

$$\mu_c^* (\text{metal}) = \bar{\mu}_+^* (\text{sol}) + z_+ \bar{\mu}_e^* (\text{metal}). \quad (\text{C2})$$

Here, the chemical potential μ_c^* (metal) is assumed constant, so that the differentiation of both sides of Eq. (C2) yields

$$d\bar{\mu}_e^* (\text{metal}) = - \frac{1}{z_+} d\bar{\mu}_+^* (\text{sol}). \quad (\text{C3})$$

Since the potential of the indicator electrode shows the equilibrium potential E_{eq}^{*+} corresponding to Eq. (C1), the relationship between such potential and the electrochemical potential of the electron is expressed as

$$dE_{\text{eq}}^{*+} = - \frac{1}{F} d\bar{\mu}_e^* (\text{metal}). \quad (\text{C4})$$

Owing to the constant potential E_{ref}^* of the conventional reference electrode,

$$d\Delta E^{*+} = dE_{\text{eq}}^{*+} \quad (\text{C5})$$

is obtained by using the expression,

$$\Delta E^{*+} \equiv E_{\text{eq}}^{*+} - E_{\text{ref}}^*. \quad (\text{C6})$$

Thus, substituting Eqs. (C3) and (C4) into Eq. (C5),

$$d\Delta E^{*+} = \frac{1}{z_+ F} d\bar{\mu}_+^* (\text{sol}) \quad (\text{C7})$$

is obtained.

Here, $d\bar{\mu}_+^* (\text{sol})$ indicates the change in the electrochemical potential of the majority cation in the solution. However, we know that the whole system is electrically neutral, and therefore, the mole numbers of all the charged components can not be independent.

Thus if we change the electrochemical potential of the cation, the electrochemical potential of the anion is also changed. So, we can consider that such change is equal to that of the averaged chemical potential; the change is shared between its constituent electrochemical potentials.

The averaged chemical potential is, thus, using Eq. (A3) in Appendix A, defined as

$$\mu_{CA}^* \equiv \frac{\mu_{+-}^*}{\nu_{+-}^+ + \nu_{+-}^-}. \quad (C8)$$

Substituting Eq. (A4) in Appendix A into Eq. (C8), and differentiating the resultant equation, we have

$$d\mu_{CA}^* = RT d \ln a_{\pm}^*. \quad (C9)$$

From the above discussion, taking

$$d\bar{\mu}_+^*(\text{sol}) = d\mu_{CA}^* \quad (C10)$$

and substituting Eqs. (C9) and (C10) into Eq. (C7), we finally obtain the expression for the indicator electrode reversible to the cation of the supporting electrolyte when using the conventional reference electrode, i.e.,

$$\left(\frac{\partial \Delta E^{*+}}{\partial \ln a_{\pm}^*} \right)_{Q_M^*, \mu'} = \frac{RT}{z_+ F}. \quad (C11)$$

Since the indicator electrode reversible to the cation or anion of the supporting electrolyte is inert to the change of activity of the metal ion, then

$$\left(\frac{\partial \Delta E^{*\pm}}{\partial \ln a_m^*} \right)_{Q_M^*, \mu'} = 0. \quad (C12)$$

APPENDIX D: LIST OF SYMBOLS

a	Activity; subscript indicates species
a_{\pm}	mean ionic activity of supporting electrolyte
A	atom arising from supporting electrolyte
$A^{\pm-}$	anion arising from supporting electrolyte
$C_i(z)$	concentration of ion i , $\equiv C_i(x, y, z, t)$, mol m^{-3}
C	atom arising from supporting electrolyte
C^{z+}	cation arising from supporting electrolyte
E^*	electrode potential measured with respect to superscripts
	\pm indicator electrode reversible to either ion of the supporting electrolyte
	$+$ indicator electrode reversible to the cation of the supporting electrolyte
	$-$ indicator electrode reversible to the anion of the supporting electrolyte
E_{eq}^{*i}	electrode potential reversible to the cation ($i=+$) or anion ($i=-$) by using the indicator electrode, V
E_{ref}^*	constant reference electrode potential, V
E_W^*	critical potential of the working electrode, V
E_{cr}^*	critical potential measured from constant reference electrode potential E_{ref}^* , V
F	Faraday's constant, 96 487 C equiv. ⁻¹
M	metal atom
M^{z_m}	metal ion
Q_M^*	total excess charge density on the metallic side of the double layer, C m^{-2}
Q_1^*	excess charge density in the Helmholtz layer, C m^{-2}
Q_{1+}^*	component of Q_1^* equivalent to surface excess of cation in the Helmholtz layer, C m^{-2}
Q_{1-}^*	component of Q_1^* equivalent to surface excess of anion in the Helmholtz layer, C m^{-2}
Q_{1m}^*	component of Q_1^* equivalent to surface excess of metallic ion in the Helmholtz layer, C m^{-2}

Q_2^*	excess charge density in the diffuse layer, C m^{-2}
Q_{2+}^*	component of Q_2^* equivalent to surface excess of cation in the diffuse layer, C m^{-2}
Q_{2-}^*	component of Q_2^* equivalent to surface excess of anion in the diffuse layer, C m^{-2}
Q_{2m}^*	component of Q_2^* equivalent to surface excess of metallic ion in the diffuse layer, C m^{-2}
R	universal gas constant, 8.3143 J mol ⁻¹ deg ⁻¹
T	absolute temperature, K
z	charge number of ion including sign; subscripts indicate species
Γ	surface excess, mol m^{-2}
	single subscript: nonrelativized surface excess of indicated component
	two subscripts: surface excess of component indicated by first subscript relative to component indicated by second subscript
Γ_{2i}^*	absolute surface excess of ion i over the diffuse layer, mol m^{-2}
ϵ	dielectric constant, F m ⁻¹
λ	Debye's length, m
μ	chemical potential, subscript indicates species, superscript 0 indicates standard chemical potential, J mol ⁻¹
$\bar{\mu}$	electrochemical potential, subscript indicates species, J mol ⁻¹
ν	stoichiometric coefficient, superscript: $+$, cation of supporting electrolyte; $-$, anion of supporting electrolyte; m , metallic ion; subscript designates cation and anion of salt in question
Φ	electrostatic potential, V
Φ_2	potential difference of the diffuse layer, V
$\langle \rangle$	symbol of the average in x and y directions
∞^+	symbol indicating immediate location outside the double layer which is equivalent to electrode surface, $z=0$ in the scale of fluctuation
∞	symbol indicating location outside the diffusion layer, i.e., bulk of the solution

Superscript

$*$	superscript denoting electrostatic equilibrium
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Subscript

Q_M^*	subscript denoting the surface excess of electric charge density on the metallic phase being kept constant
μ	subscript denoting that chemical potentials of all the components are kept constant
μ'	subscript denoting all chemical potentials being kept constant, other than the one with respect to which the differentiation is performed
$+$	subscript denoting cation of supporting electrolyte
$-$	subscript denoting anion of supporting electrolyte
m	subscript denoting metallic ion
CA	subscript denoting average value concerning supporting electrolyte
1	subscript indicating the Helmholtz layer
2	subscript indicating the diffuse layer

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