

Chapter 2

Electrochemical Measurement of Wet Corrosion

Abstract The corrosion process consists of a combination of electrochemical oxidation and reduction reactions. Electrochemistry is founded of equilibrium and kinetic. The equilibrium phase diagram or potential-pH diagram can be drawn as a function of the solution pH and the potential from electrochemical thermodynamics, and one may predict from the diagram whether the metal in a specified environment is corroded or not. The corrosion current or rate is estimated from the electrochemical measurement of potential (E)-current (i) relationship. The corrosion current or the rate of corrosion loss can be estimated from the methods of the Tafel relation ($\log|i|$ vs. E relation) and the linear polarization (i vs. E relation). Electrochemical AC impedance or electrochemical impedance spectroscopy (EIS) was widely used for corrosion study. The electrode interface in the corrosion system is modeled from the impedance with an equivalent circuit constructed by electric elements of resistance, capacitance, inductance, and Warburg impedance. The corrosion mechanism may be discussed on the basis of the circuit.

Keywords Electrochemistry • Potential-pH diagram • Tafel • Linear polarization
Electrochemical impedance spectroscopy

2.1 Electrochemistry Related to the Corrosion Process

Because the corrosion of metals in aqueous solution comprises electrochemical reactions of oxidation of metal and reduction of environmental substances, the electrochemical treatment in experimental and theoretical aspects is applied to analysis of the corrosion process. The electrochemistry is founded on electrochemical equilibrium and kinetics. In the former, an equilibrium potential correspondent to a redox reaction is guided by application of chemical equilibrium. The equilibrium potential is defined by a potential at which the net reaction rate of the redox is “zero” and can be calculated from chemical potentials of the constituent compounds of the redox, and finally is described by the Nernst equation. In the latter, a reaction rate of a redox reaction is discussed on the relationship between

rate and potential difference from the equilibrium potential. The reaction rate, r , in electrochemistry can be converted to the reaction current, I , by using the Faraday's law.

$$(I/A) = z(r/\text{mol s}^{-1})(F/\text{C mol}^{-1}) \quad (2.1)$$

where z is the number of electrons involved in the redox and F the Faraday constant.

$$F/\text{C mol}^{-1} = 96495 \quad (2.2)$$

The current is usually normalized by a reaction area of the electrode, S , on which the redox reaction takes place.

$$(i/A \text{ cm}^{-2}) = (I/A)(S^{-1}/\text{cm}^{-2}) \quad (2.3)$$

where i is called current density (CD). The relationship between CD and potential difference from the equilibrium potential is arranged by the Butler–Volmer equation, where the potential difference accompanied by the increase of absolute of CD is called overpotential, polarization, or polarization potential.

The corrosion process is explained by similar procedures to those of the usual electrochemistry. Because the corrosion process involves more than one redox reaction, the potential at which the net CD is “zero” is different from the equilibrium potential of the redox reaction and the equilibrium of the redox is not established. The process that involves multiple redox reactions is called a mixed potential system. Instead of equilibrium potential, natural potential or open-circuit potential at which the net CD is “zero” in the mixed potential system is a starting condition, and the potential is called corrosion potential in the corrosion process. In the aspect of corrosion kinetics, a relationship between the CD and the overpotential that is difference from the corrosion potential is discussed.

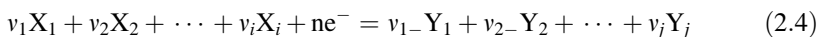
2.2 Redox Potential of Metals and Potential-pH Diagram

Metals suffer from anodic reactions of dissolution, oxide formation, and deposition of salt containing the metallic ion. For the corresponding redox reactions, the electrochemical equilibrium potentials are theoretically calculated from the electrochemical equilibrium theory. Pourbaix presented a diagram in which one can predict corrosive and anti-corrosive regions of individual metals [1]. He selected as basic nature of aqueous solution oxidative–reductive property and acidic–basic property. He plotted the equilibrium potentials of the various redox reactions related to the metal as a function of the pH value which is an index representing the acidic–basic property on X -axis and the potential, E , which is an index representing the oxidative–reductive property on Y -axis. From the plot, he predicted three regions in

which metallic state, metal covered by oxide, oxyhydroxide, or hydroxide, and metallic ions were individually stable. At the present, the plot has been known as the potential-pH diagram or the Pourbaix diagram and has been widely used for prediction of the corrosiveness of a specific metal in aqueous solution.

2.2.1 Electrochemical Potential and Equilibrium Potential

Initially, equilibrium of an electrochemical reaction and equilibrium potential are introduced. Under constant temperature and constant pressure, the equilibrium potential of the following electrochemical redox reaction



is determined by “zero” point of the summation of electrochemical potential of the individual species of the redox reaction written in the reduction direction.¹

$$\sum_j v_j \tilde{\mu}_j - \sum_i v_i \tilde{\mu}_i = 0 \quad (2.5)$$

where $\tilde{\mu}_i$ and $\tilde{\mu}_j$ are the electrochemical potentials of chemical species in the reactants X_i and in the products Y_j , respectively, and v_i and v_j are the respective stoichiometric numbers. When one follows the usual definition that the electrochemical potential complies chemical potential (μ_i) and electric potential ($z_i F \phi$),

$$\tilde{\mu}_i = \mu_i + z_i F \phi \quad (2.6)$$

where ϕ is a static electric potential of the phase in which the species, i , is present and z_i is a valence of the species i , including (+) or (−). From Eqs. 2.5 and 2.6, one can deviate the equilibrium potential, E .

$$nFE = -\Delta G = -\Delta G^0 - RT \left(\sum_j v_j \ln a_j - \sum_i v_i \ln a_i \right) \quad (2.7)$$

where n is a number of electrons included in reaction (2.4) and $a_{i(\text{or } j)}$ an activity of species i (or j), and ΔG is a change of Gibbs Free Energy defined by Eq. 2.8.

$$\Delta G = \sum_j v_j \mu_j - \sum_i v_i \mu_i \quad (2.8)$$

where ΔG^0 is a change of Gibbs Free Energy in Eq. 2.4 when the individual chemical species are present under the standard state. The value of ΔG^0 is calculated from the Gibbs Free Energy of standard formation referred from various

¹In the book, the electrochemical reaction under equilibrium is written in the reduction direction according to the rule of International Union for Pure and Applied Chemistry, IUPAC.

thermodynamic data books. Equation 2.7 is called the Nernst equation. In Eq. 2.7, the potential of the standard hydrogen electrode (SHE) is defined as $E = 0\text{ V}$ according to the IUPAC recommendation. In the definition, the following hydrogen electrode reaction on Pt electrode is assumed between the hydrogen gas at pressure of 10^5 Pa and hydrogen ion or proton at activity of 1.



On the activity of ionic species, because the activities of individual ions formed from a salt compound cannot be determined, an average activity is substituted for the activities of individual ions of the salt electrolyte solution.²

2.2.2 Equilibrium Potential of Metal/Metal Ion Reaction

On a metal contact to an aqueous solution containing the metal ions, the following electrochemical reaction takes place.



The equilibrium potential can be written in the Nernst equation as the following way.

$$E = -\frac{1}{nF}\Delta G^0 - \frac{RT}{nF}\ln\left(\frac{a_{\text{M}}}{a_{\text{M}^{n+}}}\right) \quad (2.11)$$

When one defines the standard potential, E^0 , of M^{n+}/M reaction as the following equation.

$$E^0 = -(\Delta G^0/nF) \quad (2.12)$$

Equation 2.11 is simplified.

$$E = E^0 - \frac{RT}{nF}\ln\left(\frac{a_{\text{M}}}{a_{\text{M}^{n+}}}\right) \quad (2.13)$$

One can also refer the standard potential from various thermodynamic data books. In Eq. 2.13, since the activity of the pure solid metal is assumed at $a_{\text{M}} = 1$, the equilibrium potential is described as a function of the activity of the metallic

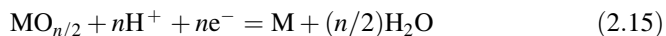
²For example, in an aqueous solution in which NaCl is dissolved, both Na^+ and Cl^- are present. Because the solution containing only Na^+ or Cl^- cannot be prepared due to the neutral condition in one phase, the standard state of the individual ions cannot be defined and thus the activity which is a ratio relative to the standard state cannot be defined.

ion. In the potential-pH diagram, Pourbaix chose $10^{-6} \text{ mol dm}^{-3} \text{ (M)}$ for concentration of the metallic ion. When one chooses for the standard condition the metal ion at a concentration of 1 M in the ideal solution, the activity is able to be replaced with the concentration in M in diluted solution. When introducing $T = 298 \text{ K}$ and $a_{M^+} = 10^{-6}$ into Eq. 2.13 and expressing the potential E in V versus SHE,

$$E = E^0 - (0.355/n) \quad (2.14)$$

2.2.3 Equilibrium Potential of Metal/Metal Oxide Reaction

The reaction of a system of metal (M)/metal oxide ($\text{MO}_{n/2}$)/aqueous solution (H_2O) can be described as the following way.



The corresponding Nernst equation is

$$E = -\frac{1}{nF} \Delta G^0 - \frac{RT}{nF} \ln \left(\frac{a_{\text{M}} a_{\text{H}_2\text{O}}^{n/2}}{a_{\text{MO}_{n/2}} a_{\text{H}^+}^n} \right) \quad (2.16)$$

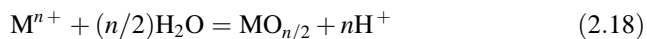
The activities of the pure solid metal and oxide, and water being a solvent can be $a_i = 1$ and when the temperature is assumed to be $T = 298 \text{ K}$, the equilibrium potential can be written as

$$E = E^0 - 0.0591 \text{ pH} \quad (2.17)$$

and becomes only a function of the solution pH value. In case of a multi-layered structure of the oxide film, the reaction of the outermost oxide layer determines the potential of metal covered by the oxide film.

2.2.4 Equilibrium of Metal Ion/Metal Oxide Reaction

When the concentration of metal ion is increased, a precipitation reaction occurs to form a metal oxide. Exactly, the precipitation reaction produces a hydrated oxide or a hydroxide, and however, we here replace it by the metal oxide for the simplification.



The precipitation equilibrium equation is

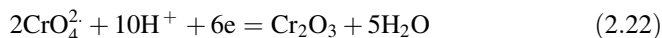
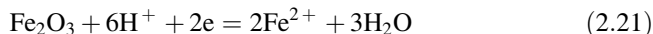
$$K_s = \frac{a_{\text{MO}_{n/2}} a_{\text{H}^+}^n}{a_{\text{M}^{n+}} a_{\text{H}_2\text{O}}^{n/2}} \quad (2.19)$$

From the activities of the metal, oxide, and water at $a_i = 1$ and from $T = 298 \text{ K}$ and $a_{\text{M}^{n+}} = 10^{-6}$, a specified pH value at which the precipitation starts to occur is estimated.

$$\text{pH} = \text{p}K_s + 6 \quad (2.20)$$

where $\text{p}K_s = -\log K_s$. The precipitation reaction (2.18) includes no electrons, and therefore, the specified pH value is not dependent of the potential.

There is another type of the precipitation reaction in which the precipitation is accompanied by a change of ionic valence. For example, in the cases of Fe/H₂O system and Cr/H₂O system, such type of reaction is possible.



In these reactions, the specific point at which the precipitation starts to occur is function of the both pH value and potential. For Eq. (2.21),

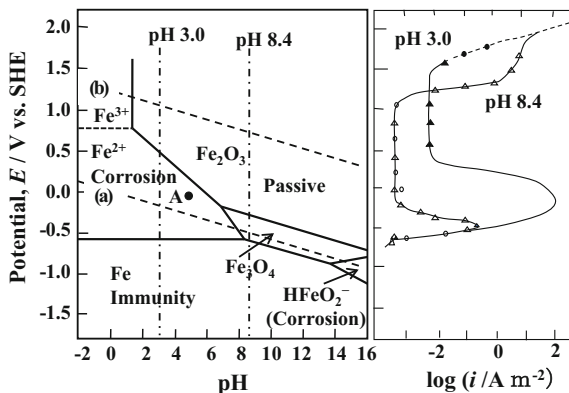
$$E = E^0 - \frac{(2.303)3RT}{F} \text{pH} - \frac{RT}{F} \ln a_{\text{Fe}^{2+}} \quad (2.23)$$

Under the condition of a constant activity of $a_{\text{Fe}^{2+}}$, the equilibrium potential changes with pH at a ratio of $0.177 \text{ V (pH)}^{-1}$ at $T = 298 \text{ K}$, and under the condition of a constant pH, it changes with Fe^{2+} concentration at a ratio of $0.059 \text{ V (decade of the concentration of Fe}^{2+})^{-1}$.

2.2.5 Potential-pH Diagram of Iron

As an example of the potential-pH diagram drawn from the above calculation, we introduce the diagram of iron in Fig. 2.1. For dissolved ionic species, there are Fe^{2+} and Fe^{3+} and further oxoacid ion species in alkaline pH solution. The multiple types of ionic species introduce slightly complicated diagram. It is, however, not difficult to draw the equilibrium lines corresponding the reactions of Fe/H₂O system. In Fig. 2.1, equilibrium lines of H₂O/H₂ and O₂/H₂O are added by dotted lines (a) and (b), respectively.

Fig. 2.1 Comparison between pH-potential diagram of iron and potential-current relation of iron in deaerated aqueous solution at 3.0 and 8.4



In the potential-pH diagram for iron as shown in Fig. 2.1a, Pourbaix proposed that the corrosion of iron was classified into the following three regions.

- (1) Immunity region: The potential is very low, and the bare metallic iron is stable. The corrosion hardly occurs.
- (2) Corrosion region: Ferrous (Fe^{2+}) and ferric (Fe^{3+}) ions are stable, and the corrosion of iron continuously occurs.
- (3) Passivity region: Iron oxides are stable, and the corrosion is inhibited by a barrier action of the oxide film.

As previously mentioned, Pourbaix assumed that the concentration of iron ions was 10^{-6} M. It is thought that if the concentration of dissolved ionic species is lower than 10^{-6} M, iron is held under the anti-corrosive state, and if the concentration is higher, corrosion is possibly progressed.

2.2.6 Prediction of Corrosiveness from the Potential-pH Diagram

By using the potential-pH diagram in Fig. 2.1, one can qualitatively predict corrosiveness of iron in an aqueous solution. For the prediction, the following measurement may be required.

- (1) pH of the solution
- (2) Corrosion potential E_{corr} of iron in the solution.
- (3) Redox potential E_{redox} of the solution: a potential of a polarizable electrode such as platinum and carbon immersed in the solution. The electrode can be purchased in a name of redox electrode.

From the solution pH and E_{corr} , one can judge which of the three regions iron electrode is located in. If E_{corr} is more negative than E_{redox} , i.e., if the redox compounds of the environment are polarized in the negative direction of potential, the anodic corrosion as a counter reaction is predicted to progress to a great degree.

When the corrosion potential of iron specimen is located in the corrosion region on the potential-pH diagram and the iron is predicted to suffer from the corrosion at a high corrosion rate, corrosion protection may be required. For example, at point A in Fig. 2.1 at which the environment is weakly acidic solution exposed to atmosphere, the iron specimen is located in the corrosion region. For the protection of the iron, three possibilities can be proposed. In the first, the potential of the iron is moved to the negative direction and made to be located in the immunity region. The method is correspondent to the cathodic protection, described in Sect. 1.5.1. For the cathodic protection, sacrificial anodes such as zinc, aluminum, magnesium, etc., are electrically contact to the iron specimen, or a negative current is supplied from an outer electric device to the iron specimen. In the second, the potential is inversely moved to the positive direction and is made to be located in the passivity region. The protection is correspondent to the anodic protection (see in Sect. 1.5.1). For the anodic protection, oxidative inhibitors and/or passivators are added in the aqueous environment. In the third, the aqueous environment is changed to an alkaline pH solution, and the iron is made to be located in the passivity region. The change in environment does not seem to be suitable actually. For the iron at point A in aqueous environment which includes only oxygen without other oxidants, only the oxygen reduction reaction is expected as the cathodic reaction. In such environment, if oxygen is removed, for example, by bubbling nitrogen gas and addition of hydrazine (N_2H_4), the corrosion may be much inhibited.

2.2.7 *Comparison of Current-Potential Relation with Potential-pH Diagram*

The potential-pH diagram was thermodynamically estimated from equilibrium potentials of redox reactions participating in corrosion reactions. The actual corrosion is based on the mixed potential system, and thus, the corrosion potential does not directly correspond to the equilibrium redox potentials. The corrosion potential exists between the equilibrium potential of the redox including the metal and its metal ion (M^{n+}/M) and that of the redox of environmental substances (see in Fig. 1.1). At the corrosion potential, the anodic positive current of the former redox reaction is coupled with the cathodic negative current of the latter redox.

In Fig. 2.1b, anodic CD in logarithmic scale of iron electrode is plotted against potential in pH 8.4 neutral borate and pH 3.0 acidic phosphate solution as comparison with potential-pH diagram [2, 3]. Although, in neutral solution, there is no corrosion region in the potential-pH diagram, an active dissolution region correspondent to the corrosion region appears in the CD-potential relation graph. In the

acidic solution, the active and passive potential regions are clearly seen in the CD-potential graph, corresponding to the corrosion and passivity region in the potential-pH diagram, respectively. The transient potential (passivation potential) from the active to the passive state is roughly in coincident with the formation potential of Fe_2O_3 .

2.3 Estimation of Corrosion Rate from Electrochemical Measurement

The combination of the electrochemical kinetics with electrochemical corrosion model enables us to estimate the corrosion CD and the corrosion mechanism. The corrosion rate is easily calculated from the corrosion CD according to the Faraday's law in Eq. 2.1.

In the corrosion electrochemistry, an anodic reaction (oxidation corrosion reaction) involved in the corrosion is coupled with a cathodic reaction of the environmental substances. At the corrosion potential (E_{corr}) under the natural immersion condition, both reactions hold a CD same as each other in magnitude and the CD corresponds to the corrosion CD (i_{corr}) of the metals. The changes of the both reaction CDs with potential follow the Butler–Volmer equation (Eq. 2.27) in which the anodic positive CD exponentially increases with more positive potentials and the cathodic negative CD is also increased in magnitude with more negative potentials.

$$i = i_{\text{corr}} \left(10^{(E-E_{\text{corr}})/\beta_A} - 10^{-(E-E_{\text{corr}})/\beta_C} \right) \quad (2.27)$$

where β_A and β_C are slopes of E versus $\log|i|$ for $i \gg 0$ and $-E$ versus $\log|i|$ for $i \ll 0$, respectively, and should be positive values in a unit of V. β_A and β_C are called anodic and cathodic Tafel slope. The CD, i can be measured by electrochemistry as a function of the potential applied and, however, the corrosion CD, i_{corr} is not directly measured. In the following sections, indirect estimation of i_{corr} is introduced.

2.4 Tafel Plot

In Eq. 2.27, when one changes potential in the more positive direction, i.e., one polarizes the metal electrode in the more anodic direction, the condition of $10^{(E-E_{\text{corr}})/\beta_A} \gg 10^{-(E-E_{\text{corr}})/\beta_C}$ can be established and the following equation is approximated.

$$(E - E_{\text{corr}})/\beta_A > 1 \quad i = i_{\text{corr}} \left(10^{(E - E_{\text{corr}})/\beta_A} \right) \quad (2.28)$$

Similarly, when one polarized it in the more negative direction, the following approximated equation is derived.

$$(E - E_{\text{corr}})/\beta_C < -1 \quad i = i_{\text{corr}} \left(-10^{-(E - E_{\text{corr}})/\beta_C} \right) \quad (2.29)$$

In Eq. 2.28, one converts it to a logarithmic CD.

$$\log|i| = \log i_{\text{corr}} + (E - E_{\text{corr}})/\beta_A \quad (2.30)$$

$$\frac{dE}{d \log|i|} = \beta_A \quad (2.31)$$

In Eq. 2.29, one also converts it to a logarithmic CD.

$$\log|i| = \log i_{\text{corr}} - (E - E_{\text{corr}})/\beta_C \quad (2.32)$$

$$-\frac{dE}{d \log|i|} = \beta_C \quad (2.33)$$

where β_A and β_C are anodic and cathodic Tafel slope, as described or are called anodic and cathodic Tafel coefficient. In the earlier than 1950, electrochemical measurement was done by current control (i.e., by galvanostatic condition), and CD was usually plotted as a control parameter on the X-axis and the potential as a responsible parameter on the Y-axis. The slope on the graph was described as the Tafel slope. Since 1960, the potentiostat has been generally used, and the control parameter is changed to potential. Since we usually plot the potential on the X-axis and CD on the Y-axis at present, the readers should take notice that the Tafel slope is a reciprocal of the slope on the graph of CD in logarithmic scale (Y-axis) versus potential (X-axis).

2.4.1 Estimation of Corrosion CD from Extrapolation of Tafel Lines

A typical illustration of $\log|i|$ versus E relation is shown in Fig. 2.2 in which we assumed the following parameters.

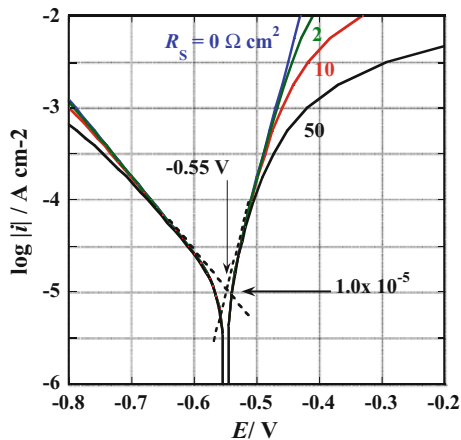
Anodic Tafel coefficient; $\beta_A = 0.04 \text{ V decade}^{-1}$

Cathodic Tafel coefficient; $\beta_C = 0.12 \text{ V decade}^{-1}$

Corrosion potential; $E_{\text{corr}} = 0.55 \text{ V}$

Corrosion current; $i_{\text{corr}} = 10^{-5} \text{ A cm}^{-2}$

Fig. 2.2 Relation between potential and current in logarithmic scale (the Tafel plot). In the plot, the following parameters are assumed; $\beta_A = 0.04$ V, $\beta_C = 0.12$ V, $E_{\text{corr}} = 0.55$ V and $i_{\text{corr}} = 1.0 \times 10^{-5}$ A cm $^{-2}$. For the calculation, the solution resistance is assumed to be $R_S = 0, 2, 10$ and $50 \Omega \text{ cm}^2$



In Fig. 2.2, deviations of the linear Tafel lines were plotted due to presence of solution resistance, R_S . From the intersection of the both extrapolated lines, one can estimate the corrosion potential, E_{corr} , and corrosion CD, i_{corr} . If $R_S = 0 \Omega \text{ cm}^2$, the intersection from the two extrapolated lines indicates that $E_{\text{corr}} = 0.55$ V and $i_{\text{corr}} = 10^{-5}$ A cm $^{-2}$. If $R_S = 50 \Omega \text{ cm}^2$, one needs to take a notice to draw the Tafel lines, as shown in the following section.

2.4.2 Limitation of Tafel-Line Extrapolation

There is attention paid for the Tafel-line extrapolation method. The first is length of the linear on the plot of $\log|i|$ versus E . For the extrapolation, one-decade length of the linear part may be required. In Fig. 2.2, the influence of the solution resistance on the deviation of the linear part is shown. When the solution resistance is $50 \Omega \text{ cm}^2$, it is impossible to hold one-decade length of the linear part. If the R_S value is relatively large, one should compensate the potential drop by R_S .

$$E = E_{\text{out}} - iR_S \quad (2.34)$$

where E_{out} and E are an output potential from the potentiostat and a potential imposed on the electrode/solution interface, respectively. The potential drop in the electrolyte solution, iR_S , is called solution resistance polarization or ohmic polarization. The actual R_S value can be estimated by an extrapolation to the high frequency limit on the electrochemical impedance spectrum (EIS). Because most potentiostats commercially available equip an automation device by which the solution resistance polarization (iR_S) can be compensated, one can use the device for relatively large R_S .

The other origin of the deviation from linear Tafel line is a contribution of diffusion of reactive species in the solution. Due to the slow diffusion rate,

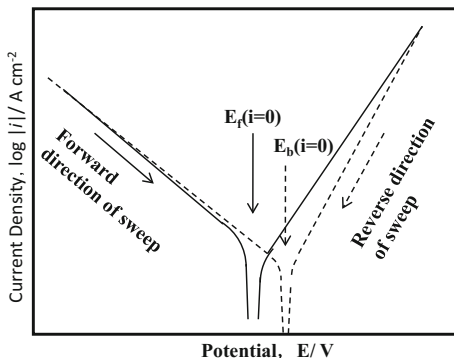
difference in concentration of the species between the surface and the solution bulk is generated, and the potential, E , imposed at the interface is decreased.

$$E = E_{\text{out}} - E_D \quad (2.35)$$

where E_D is a potential drop between the electrode surface and the solution bulk due to the concentration difference originated by the diffusion. The potential drop due to the slow diffusion is called the concentration polarization. The removal of the contribution of the diffusion is able to be done by using a rotating electrode or a liquid flow cell. By using computer simulation, the compensation of the contribution of the diffusion may be possible [4].

The potential sweep method is generally applied to the measurement of the Tafel relation. It should be noticed that the Tafel lines and zero-current potential possibly changed with the sweep directions when the corrosion CD is relatively small. Such change occurs when the property of the metal surface is changed with the potential applied. In the electrode imposed by a negative potential, adsorbed and absorbed hydrogen atoms exist on the surface and surface layer, and the surface works as a reductive surface. In the surface imposed by a positive potential, inversely, surface is covered by oxide/hydroxide and oxidative adsorbed species, working as an oxidative surface. The change of surface property with potential induces difference of the zero-current potential between the sweep directions, which is schematically illustrated in Fig. 2.3. The difference of the zero-current potential is increased with the smaller corrosion CD and with the larger sweep rate. The exact corrosion potential may be located between the two zero-current potentials. In order to avoid the difference in the zero-current potential, the potential-logarithm of CD relation should be separately measured from the corrosion potential: For the anodic region, one potential sweep in the direction to positive is performed and for the cathodic region, the other potential sweep in the negative direction. The effect of the sweep rate on the potential-logarithm of CD curve may still remain. In order to avoid the effect of the sweep rate, one needs to impose a much smaller sweep rate. It is recommended that the Tafel relation is measured at so small sweep rate that the curve of potential logarithm of CD may not depend on the sweep rate.

Fig. 2.3 Schematic plot for change of $\log|i|$ versus E curve with the direction of potential sweep



2.5 Linear Polarization Resistance

Equation 2.17 can be converted to the following.

$$\left(10^{(E-E_{\text{corr}})/\beta_A}\right) = \exp[(2.303)(E-E_{\text{corr}})/\beta_A] \quad (2.36)$$

$$\left(10^{-(E-E_{\text{corr}})/\beta_C}\right) = \exp[-(2.303)(E-E_{\text{corr}})/\beta_C] \quad (2.37)$$

Under a condition of $2.303 (E-E_{\text{corr}})/\beta_A \ll 1$, Eq. 2.36 is approximated to Eq. 2.38.

$$\exp[(2.303)(E-E_{\text{corr}})/\beta_A] = 1 + (2.303)(E-E_{\text{corr}})/\beta_A \quad (2.38)$$

under a condition of $|(E-E_{\text{corr}})/\beta_C| \ll 1$, similarly Eq. 2.37 is approximated.

$$\exp[-(2.303)(E-E_{\text{corr}})/\beta_C] = 1 - (2.303)(E-E_{\text{corr}})/\beta_C \quad (2.39)$$

If substituting Eqs. 2.38 and 2.39 into Eq. 2.27,

$$i = i_{\text{corr}}(E - E_{\text{corr}})(2.303) \left(\frac{1}{\beta_A} + \frac{1}{\beta_C} \right) \quad (2.40)$$

According to Eq. 2.40, CD is proportional with potential under the condition of $E \cong E_{\text{corr}}$. The ohmic law is established approximately. A ratio of the potential to CD possesses a unit of $\Omega \text{ cm}^2$ and is called the polarization resistance [4, 5].

$$R_P = \left(\frac{dE}{di} \right)_{E \cong E_{\text{corr}}} = \frac{1}{2.303 i_{\text{corr}}} \frac{1}{\left(\frac{1}{\beta_A} \right) + \left(\frac{1}{\beta_C} \right)} \quad (2.41)$$

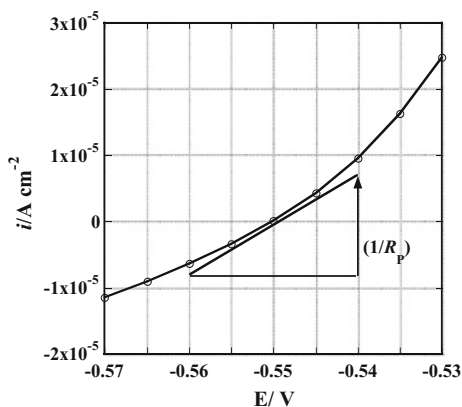
From Eq. 2.41, corrosion CD, i_{corr} , can be calculated [5, 6]. Because β_A and β_C are assumed to be constant for one corrosion system, the equation to estimate i_{corr} is simplified.

$$i_{\text{corr}} = (K/R_P) \quad (2.42)$$

where K is a term including β_A and β_C .

$$K = \frac{1}{2.303 \left[\left(1/\beta_A \right) + \left(1/\beta_C \right) \right]} = \frac{\beta_A \beta_C}{2.303(\beta_A + \beta_C)} \quad (2.43)$$

Fig. 2.4 Potential-CD relation near corrosion potential, $E_{\text{corr}} = 0.55 \text{ V}$ and reciprocal of polarization resistance R_p . The parameters assumed for calculation are same to those in Fig. 2.2



In Fig. 2.4, the potential-CD curve is drawn in neighborhood of the corrosion potential, E_{corr} , under the same condition as those in Fig. 2.3 with $R_s = 0 \Omega \text{ cm}^2$. In Fig. 2.4, one sees the linear relation between the potential applied and CD. The slope (di/dE) in Fig. 2.4 at the neighborhood of E_{corr} , becomes the reciprocal of the polarization resistance, R_p .

2.5.1 Measurement of Linear Polarization Resistance

For the measurement of polarization resistance, R_p , firstly one measures the corrosion potential, E_{corr} , then a small potential or small CD is imposed, and the response CD or potential change is measured. The measurement can be finished in a much shorter time period compared with the Tafel extrapolation method.

For the polarization resistance, four methods are considered, which is shown in Fig. 2.5. By using square wave potential (Fig. 2.5a) and CD (Fig. 2.5b), R_p can be calculated as the following.

$$R_p = \Delta E / \Delta i \quad (2.44)$$

Imposition of sine wave of potential and response of sine wave of CD (Fig. 2.5c) are AC impedance method (see Sect. 2.6), and the impedance, Z , becomes complex number including the phase retardation, θ between E and i .

$$Z = (\Delta E / \Delta i) \exp j\theta \quad (2.45)$$

where j is an imaginary unit, $j^2 = -1$. The impedance is a function of frequency imposed and for the measurement of polarization resistance, enough low frequency is required to reach the phase retardation of the impedance at 0° , as discussed in Sects. 2.5.2 and 2.6.

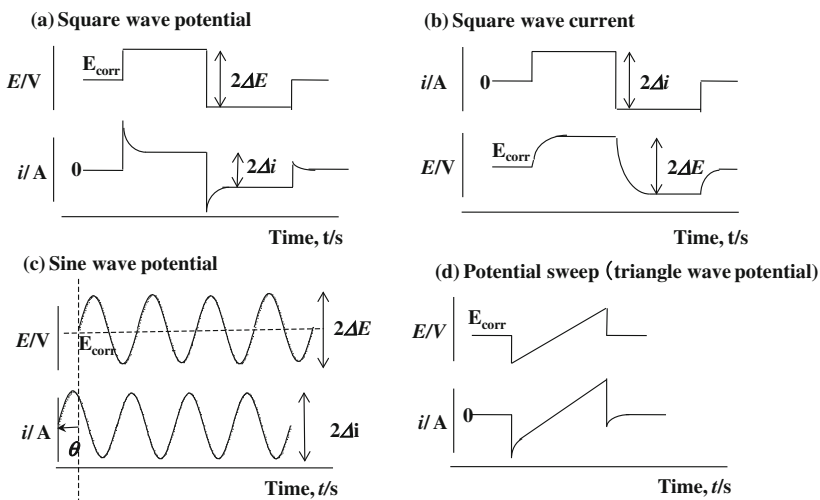


Fig. 2.5 Measurement techniques of polarization resistance

By using triangle wave of potential, R_P is estimated by the following.

$$R_P = \frac{dE/dt}{di/dt} \quad (2.46)$$

where dE/dt is a ratio of increase of the potential to time (i.e., sweep rate) and di/dt is a ratio of increase of CD to time in the linear part of the response function.

2.5.2 Requirement of Period (or Frequency) and Amplitude

To measure the polarization resistance in an allowable error, the amplitude and the period or frequency of the imposed signal must be suitably selected. We assume a simple equivalent circuit correspondent to the corrosive interface as shown in Fig. 2.6. The circuit consists of a parallel circuit connected in series with the solution resistance (R_S). The parallel circuit comprises a polarization resistance at the corrosion interface (R_P) and a double-layer capacitance (C_{DL}). In order to evaluate the polarization resistance, the measurement period three times longer than the time constant τ_P of the R_P - C_{DL} circuit is required.

$$\tau_P = R_P C_{DL} \quad (2.47)$$

For example, when we assume $R_P = 10^5 \Omega \text{ cm}^2$ which may be a maximum resistance for the corrosion without barrier oxides and $C_{DL} = 10^{-4} \text{ F cm}^{-2}$ which

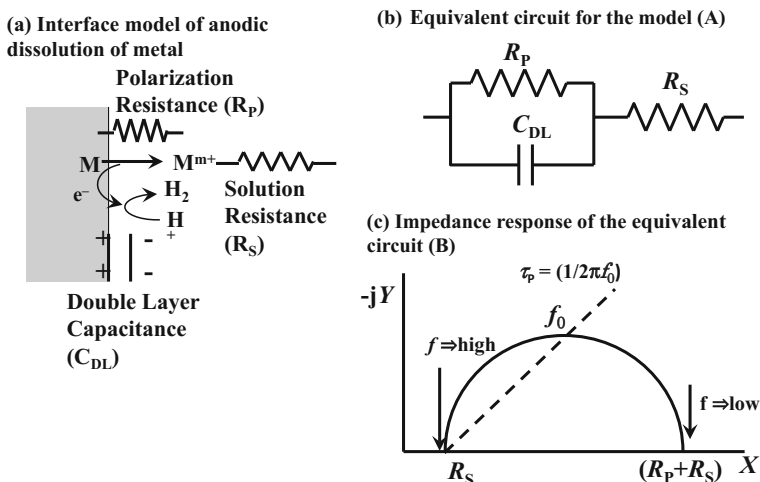


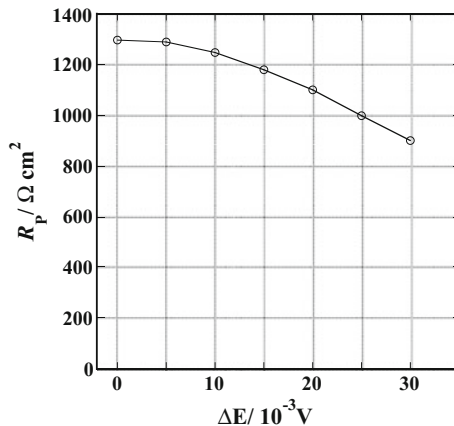
Fig. 2.6 **a** Schematic model of the interface accompanied by anodic dissolution of metal, **b** Equivalent circuit for the model (a), and **c** impedance response plotted on complex plane (Nyquist plot)

may be also maximum value for bare metal surface, $\tau_p = 10$ s. If one use the period of $T = 50$ s (frequency, 0.02 Hz) for the measurement, the polarization resistance method is applicable to almost all corrosion systems [6, 7].

In the actual corrosion system, the metal is often covered with corrosion products, adsorption layer of inhibitors, and passive oxide film. The polarization resistance in the system occasionally becomes values larger than $10^6 \Omega \text{ cm}^2$. When the steel is covered by a hydrated iron oxide layer, the apparent double-layer capacitance becomes large values from 10^{-3} to $10^{-2} \text{ F cm}^{-2}$ because the $\text{Fe}^{3+}/\text{Fe}^{2+}$ redox couple in the hydrated oxide layer apparently accumulates a large charge. When the corrosion system includes the large polarization resistance or the large double-layer capacitance, the time constant is larger than 100 s and the imposing signal with a period longer than 500 s may be required. Because the imposition of the signal with the period as long as 500 s may be not realistic, one must pay attention to the measurement of a metal covered by surface layer such as corrosion products, adsorption layer, etc.

The basic equation of the polarization resistance (Eq. 2.40) was derived from a condition of linear approximation of the response signal. If the amplitude of the imposition signal is larger, the deviation from the linear approximation is larger. Figure 2.7 indicates the polarization resistance calculated from Eq. 2.44 as a function of amplitude of the imposed potential signal. When drawing the curve in Fig. 2.7, the same parameters as those in Figs. 2.2 and 2.4 were assumed. The polarization resistance presumed is calculated at $1.31 \times 10^4 \Omega \text{ cm}^{-2}$ from the parameters. The deviation from the theoretical resistance is 10% at 15 mV amplitude and 20% at 20 mV. If the amplitude is smaller on the contrary, the response

Fig. 2.7 Change of polarization resistance estimated by linear approximation with potential width applied. The parameters for calculation of the polarization resistance are same to those in Fig. 2.2



signal is also smaller and the precise measurement may be more difficult. We can thus propose that the amplitude at 15 mV may be suitable for the easy measurement of the polarization resistance, though the resistance includes 10% error.

2.5.3 “K” Value for Calculation of Corrosion Rate

For estimation of the corrosion CD from the polarization resistance, the proportional constant, K , is required (Eq. 2.42). Because the K value is theoretically a function of the Tafel coefficients, β_A and β_C (Eq. 2.41), it is possible to estimate the corrosion CD precisely with the Tafel coefficients that was previously measured.

When one considers the polarization resistance method as a monitoring technique of the corrosion rate, immediate evaluation of the corrosion CD is desirable without use of the Tafel coefficients. From the parameters used in Figs. 2.2 and 2.4,

$$(\beta_A = 0.04 \text{ V}, \beta_C = 0.12 \text{ V}) \quad K = 0.013 \text{ V} \quad (2.48)$$

When one uses the anodic Tafel coefficient, $\beta_A = 0.06 \text{ V}$, reported for anodic dissolution reaction of metal,

$$(\beta_A = 0.06 \text{ V}, \beta_C = 0.12 \text{ V}) \quad K = 0.017 \text{ V} \quad (2.49)$$

and when the cathodic reaction is kinetically controlled by diffusion process of oxygen,

$$(\beta_A = 0.04 \text{ V}, \beta_C = \text{infinite}) \quad K = 0.026 \text{ V} \quad (2.50)$$

The corrosion CD estimating from the polarization resistance is dependent on the K value, changing in double degree with the K values assumed. If one allows an error in logarithmic scale of $\pm \log(2) = \pm 0.3$ for corrosion CD, it is possible to continuously monitor of the corrosion CD with assumption of a suitable K value [7, 8].

2.6 AC Impedance

In electrochemistry, frequency response analyzer (FRS) becomes popular, and many studies have been presented by electrochemical impedance. The technique is at present known as electrochemical impedance spectroscopy (EIS). EIS has also been applied to corrosion electrochemistry by many authors.

2.6.1 Differential AC Impedance

As shown in Fig. 2.5c, we consider that AC potential signal is imposed, and the response CD is measured. The sine wave of potential is represented as a complex number with an amplitude ΔE and an angular frequency ω ($= 2\pi f$; f is frequency)

$$E = E_0 + \Delta E \exp j(\omega t) \quad (2.51)$$

$$dE/dt = j\omega \Delta E \exp j(\omega t) \quad (2.52)$$

According the Euler's formula

$$\exp j(\omega t) = \cos(\omega t) + j \sin(\omega t) \quad (2.53)$$

When the amplitude and phase retardation of the response CD are Δi and θ , respectively,

$$i = i_0 + \Delta i \exp j(\omega t + \theta) \quad (2.54)$$

$$di/dt = j\omega \Delta i \exp j(\omega t + \theta) \quad (2.55)$$

The impedance is defined by a ratio of AC potential to AC current, and the electrochemical impedance, Z , is written by a differentiated form.

$$Z = dE/di = (dE/dt)/(di/dt) = (\Delta E/\Delta i) \exp j(-\theta) = |Z| \exp j(-\theta) \quad (2.56)$$

where $|Z|$ is amplitude of the impedance in unit $\Omega \text{ cm}^2$. According to the Euler's equation,

$$Z = |Z|[\cos(-\theta) + j \sin(-\theta)] = X - jY \quad (2.57)$$

Since the impedance changes with frequency, it is described as a function of frequency. For the graphic expression, the complex plane plot of $-Y$ versus X as shown in Fig. 2.6c and the Bode plot of $\log|Z|$ versus $\log(f)$ and θ versus $\log(f)$ have been used.

2.6.2 Electric Elements Constructing Impedance

The AC response on the electrode interface is simulated by an equivalent electric circuit. The circuit is made of electric elements of resistor, condenser, and coil, and the other element specified for the interfacial diffusion process, i.e., Warburg impedance. In Fig. 2.8, the relationship between AC potential imposed and AC current responded in the former three elements is illustrated.

AC current through the resistor exhibits no phase retardation against the potential, and the amplitude of the AC current exhibits no change with frequency.

$$Z = R = \Delta E / \Delta I \quad (\theta = 0) \quad (2.58)$$

R is a ratio of potential to current, called resistance.

When the AC potential is imposed on a condenser (or capacitor), the charge Q is harmonically changed with the AC potential.

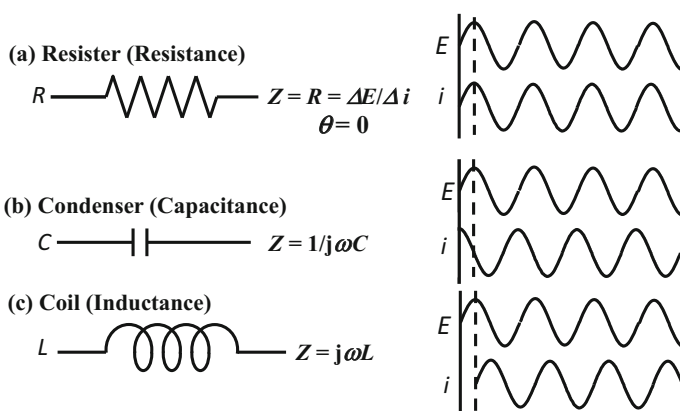


Fig. 2.8 Scheme of current response to AC potential applied to three elements of resister, condenser, and coil

$$Q = \Delta Q \exp j(\omega t) \quad (2.59)$$

$$\Delta Q = C \Delta E \quad (2.60)$$

where C is called capacitance, which represents capability of charge accumulation in the capacitor. The AC current with the change of Q is shown in the following.

$$i = dQ/dt = C \Delta E j \omega \exp j(\omega t) \quad (2.61)$$

$$di/dt = C \Delta E (j \omega)^2 \exp j(\omega t) \quad (2.62)$$

The impedance is described as the following.

$$Z = dE/di = (1/j\omega C) = (1/\omega C) \exp j(-\pi/2) \quad (2.63)$$

where the relation of $(1/j) = -j = \exp j(-\pi/2)$ is used according the Euler's equation. The impedance of the capacitor possesses a phase retardation at -90° (Fig. 2.8b), and the amplitude increases with decrease of frequency. Simply, the more AC current flows with the higher frequencies.

When the AC current is imposed on a coil (or inductor), the back electromotive force is induced across the coil and the potential induced is proportional to the rate of change of current with a proportional constant (inductance, L).

$$E = L(di/dt) \quad (2.64)$$

$$di/dt = (1/L) \Delta E \exp j(\omega t) \quad (2.65)$$

If using Eq. 2.52 for dE/dt , the impedance is written as the following,

$$\begin{aligned} Z &= (dE/dt)/(di/dt) = [j\omega \Delta E \exp j(\omega t)] / [(1/L) \Delta E \exp j(\omega t)] \\ &= j\omega L = \omega L \exp j(\pi/2) \end{aligned} \quad (2.66)$$

The impedance of the coil possesses a phase retardation at $+90^\circ$, and the amplitude of impedance decreases with decrease of frequencies.

The Warburg impedance originates in a concentration wave induced by an interfacial reaction and propagated in the interfacial layer of the solution. The wave is gradually attenuated with the increasing distance from the interface and the distance which the wave reaches decreases with increase of frequencies. The Warburg impedance is described by a complex quality with real and imaginary part of equal magnitude [9, 10].

$$Z = (W/\omega^{1/2})(1 - j) \quad (2.67)$$

W is the Warburg parameter described in the following.

$$W = \frac{RT}{n^2 F^2} \frac{1}{c_0 \sqrt{D}} \quad (2.68)$$

where c_0 is a concentration at the bulk solution of the species diffused, and D is a diffusion constant of the species in the solution [9, 10].

2.6.3 Equivalent Circuit and Frequency Response

The AC response of the electrode interface is analyzed from an equivalent circuit approximating the interfacial structure. The equivalent circuit is constructed from the resistance, conductance, inductance, and Warburg impedance element.

We consider the simple equivalent circuit as shown in Fig. 2.6b at which a charge transfer resistance, R_p , is connected in parallel with a double-layer capacitance, C_{DL} and the parallel circuit is in series connected with a solution resistance, R_s . The impedance of the circuit is written as

$$Z = R_s + \frac{1}{(1/R_p) + j\omega C_{DL}} \quad (2.69)$$

When ω is very high, the second term is approximated as 0 and thus,

$$\omega \rightarrow \infty, Z = R_s \quad (2.70))$$

When ω is extremely low, $j\omega C_{DL}$ is approximated as 0 and thus,

$$\omega \rightarrow 0, Z = R_s + R_p \quad (2.71)$$

From the high frequency and low frequency limits, the values of R_s and R_p are determined. In frequencies between the two limits, a semicircle is drawn with changing frequencies on the complex plane plot (Fig. 2.6). When we take a frequency f_0 at which the real part is equal to the imaginary part in the second term of Eq. 2.69, we can write the following equation.

$$(1/R_p) = (2\pi f_0) C_{DL} \quad (2.72)$$

$$R_p C_{DL} = 1/(2\pi f_0) = \tau_p \quad (2.73)$$

where τ_p is a time constant of the R_p - C_{DL} parallel circuit, and the locus at f_0 is placed on the top of the semicircle. Inversely, if we find a frequency f_0 from the top of the semicircle, we can determine a value of C_{DL} from Eq. 2.73.

Actual corrosion system may be more complicated due to solid corrosion products, adsorption layers, and oxide films covering the surface. The equivalent

circuit corresponding to the corrosion system may be complicated, and however, the circuit is constructed from a combination of the three electric elements and Warburg impedance. Further the constant phase element must be considered which represents an incomplete capacitance. The more detail on constructing the equivalent circuit may be seen in the references [9, 10].

2.7 Summary

The electrochemistry on corrosion was founded on equilibrium and kinetics.

- (1) Equilibrium: The equilibrium phase diagram or potential-pH diagram was drawn as a function of the solution pH and the potential. The solution pH that is an index of acid–base property of the solution was plotted on X-axis, and the potential that is an index of oxidation–reduction property of the solution was plotted on Y-axis. From the diagram, one can predict whether a metal in a specified environment is corroded or not.
- (2) Kinetics: The corrosion current or rate is estimated from the electrochemical measurement of potential-current relationship. From the relationship in a relatively large range of potential around the corrosion potential, the corrosion current can be determined by the Tafel extrapolation method. The relationship in a relatively small range is approximated as a linear function, and from the slope in the linear function, the polarization resistance can be calculated. Because reciprocal of the polarization resistance is proportional to the corrosion current, the corrosion current or rate is calculated with assuming the proportional constant.
- (3) As an application of the corrosion kinetics, electrochemical AC impedance was introduced for corrosion study. The electrode interface in the corrosion system can be modeled by an equivalent circuit constructed by the electric elements of resistance, capacitance, inductance, and Warburg impedance.

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