Transient Analysis of Active Dissolution of Iron by Using Channel Flow Double Electrode[†]

Masayuki Itagaki^{††} and Tooru Tsuru

Department of Metallurgical Engineering, Faculty of Engineering, Tokyo Institute of Technology,
Tokyo 152, Japan

The active dissolution mechanism of iron in sulfuric acid solution has been investigated by the transient analysis with a channel flow double electrode (CFDE) system. The transient current after potential step is separated into partial electrochemical steps, which are Fe(II) dissolution and surface accumulation, using fast Fourier transformation (FFT) analysis with the dynamic collection efficiency, $N(\omega)$. The Fe(II) dissolution follows the formation of the adsorbed intermediate in the active dissolution potential region. The experimental results suggest the existence of two adsorbed species during the active dissolution of iron. The formation efficiency of adsorbed intermediate on the iron surface, $\Phi_f(\omega)$, and the dissolution efficiency of ferrous ions, $\Phi_{\text{diss}}(\omega)$, are calculated from the transient currents. The amplitude of $\Phi_{\text{diss}}(\omega)$ decreases and that of $\Phi_f(\omega)$ increases with the frequency. The numerical simulations for the active dissolution of iron have been performed on the basis of the reaction model involving two kinds of adsorbed species, and the elemental reaction rates have been estimated.

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I. Introduction

The active dissolution mechanism⁽¹⁾⁽²⁾ on metal in aqueous solution has been discussed by assuming the intermediate adsorbed on the metal surface. Therefore the more detailed investigation is necessary to obtain the informations concerning the adsorbed intermediate. With respect to the adsorbed intermediate, a few studies have been attempted using non-steady state measurements. The fractional coverage of the adsorbed intermediate has been calculated from the experimental results by the electrochemical impedance spectroscopy⁽³⁾. The charge for the adsorption has been measured directly from the transient currents on the collector electrode by imposing the current step to the iron working electrode with the CFDE system⁽⁴⁾.

In this paper, the transient currents are separated into dissolution and adsorption components in both time and frequency domains. With the examination of partial currents, the active dissolution mechanism of iron and its kinetics are discussed.

II. Principle

The collection efficiency at steady state, N_s , is calculated theoretically⁽⁵⁾ and verified experimentally⁽⁶⁾. A dissolution current, i_{diss} , is obtained with dividing a collector

electrode current, i_c , by N_s ,

$$i_{\text{diss}} = (n_w / n_c) i_c / N_s \quad (1)$$

where $n_w = 2$ (valency of the dissolution reaction of Fe(II) on the working electrode) and $n_c = 1$ (number of electron for the oxidation of Fe(II) to Fe(III) on the collector electrode). At non-steady state, collector electrode current contains the delay time when the emitted ions from the working electrode move over the gap between the working and collector electrodes. Therefore a transient current for dissolution must be calculated with the dynamic collection efficiency, $N(\omega)$, which is related to the frequency of emission. How to obtain a $N(\omega)$ will be mentioned later in this paper. The calculations for separation of the dissolution component from the total transient current in both time and frequency domains are shown as in the following. A dissolution efficiency, $\Phi_{\text{diss}}(\omega)$, which corresponds to the ratio of partial current of Fe(II) dissolution to the total current in the frequency domain, is given by,

$$\begin{aligned} \Phi_{\text{diss}}(\omega) &= (n_w / n_c) I_c(\omega) / \{ I_w(\omega) N(\omega) \} \\ I_c(\omega) &= \text{FFT} \{ i_c(t) \} \\ I_w(\omega) &= \text{FFT} \{ i_w(t) \} \end{aligned} \quad (2)$$

where $i_w(t)$ and $i_c(t)$ are transient currents on the working and collector electrodes, respectively, and $\text{FFT}\{X\}$ means the fast Fourier transformation of X . The formation efficiency of adsorbed species, $\Phi_f(\omega)$, on the working electrode is obtained by,

$$\Phi_f(\omega) = 1 - \Phi_{\text{diss}}(\omega). \quad (3)$$

On the other hand, partial transient currents of Fe(II) dis-

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^{††} Present address: Department of Industrial Chemistry, Faculty of Science and Engineering, Science University of Tokyo, Chiba 278, Japan.

solution, $i_{\text{diss}}(t)$, and adsorbed species formation, $i_f(t)$, in the time domain are given by,

$$i_{\text{diss}}(t) = (n_w/n_c) \text{IFFT}\{I_c(\omega)/N(\omega)\} \quad (4)$$

$$i_f(t) = i_w(t) - i_{\text{diss}}(t), \quad (5)$$

where $\text{IFFT}\{X\}$ means the inverse fast Fourier transformation of X .

Not only Faradaic processes but also non-Faradaic processes (mainly the charge of the electric double layer) are contained in $i_w(t)$, and non-Faradaic component is involved in $\Phi_f(\omega)$ and $i_f(t)$ in this analysis.

III. Experimental

1. Dynamic collection efficiency

Details of the CFDE have been described elsewhere⁽⁴⁾. Gold was used for the working and collector electrodes. The dimensions of the working and collector electrodes are 4 mm wide and 1 mm long along the flow direction, and the gap between these electrodes is 0.05 mm. The counter electrode was Pt and the reference electrode was a saturated Ag/AgCl/KCl electrode (SSE). The electrode potential, therefore, is represented with reference to SSE. The surfaces of electrodes were emery-polished down to #2000, and ultrasonically cleaned in methanol and doubly-distilled water successively before using in the measurements. The electrolyte solution was 0.5 kmol/m³ Na₂SO₄ containing 0.03 kmol/m³ K₃Fe(CN)₆, which is adjusted to pH 11 by the addition of NaOH. The electrolyte solution was prepared with doubly-distilled water and deaerated at least for two days by bubbling with high-purity N₂ gas. Average electrolyte flow rate in the channel (simply called as flow rate) was fixed at 73 cm/s and 225 cm/s.

The measurement of a dynamic collection efficiency, $N(\omega)$, was performed using a frequency response analyzer (FRA, NF Circuit Block 5020). Sinusoidal alternative current, $I_w(\omega)$, whose d.c.component was -20 mA and a.c.component was 5 mA (rms), was imposed to the working electrode. The reaction on the working electrode takes place without any surface accumulation;

The detection current, $I_c(\omega)$, was measured at the collector electrode (1.2 V), on which the emitted Fe(CN)_6^{4-} was oxidized again;

From these currents, $N(\omega)$ was determined at a certain frequency, ω ;

$$N(\omega) = (n_w/n_c) I_c(\omega) / I_w(\omega) \quad (8)$$

where $n_w = -1$ and $n_c = 1$.

2. Polarization curve and current responses by potential pulse

The experimental arrangement except electrodes was

same as one in the measurement of $N(\omega)$. The materials of the working and collector electrodes were pure iron (99.99%, Johnson Matthey) and gold, respectively. The following two kinds of electrolyte solutions were used;

(a) 1 kmol/m³ H₂SO₄ (pH 0.58)

(b) 0.1 kmol/m³ H₂SO₄ + 0.9 kmol/m³ Na₂SO₄ (pH 1.2)

The electrolyte solutions were deaerated with high-purity N₂ gas before and during measurement. The electrolyte flow rate was fixed at 225 cm/s.

In the measurement of polarization curve, the working electrode potential was scanned at 2 mV/s from -1.2 V. The Fe(II) dissolved from the working electrode was detected at the collector electrode (1.4 V) on which Fe(II) is oxidized to Fe(III).

In the measurement of transient current, a potential pulse (10 mV, 0.2 s) was superposed to the polarization potential of the working electrode. The transient currents on both working and collector electrode were measured by a dual-potentiostat and recorded into 2 channel transient convertor. The sampling time and number are 0.2 ms and 2048 points, respectively.

IV. Experimental Results

1. Dynamic collection efficiency

The Nyquist plots of experimental results of $N(\omega)$ are shown in Fig. 1. At low frequency region, $N(\omega)$ is closed to the calculated value of $N_s(0.39)$ in both electrolyte flows. The amplitude, $|N(\omega)|$, decreases and the phase shift increases with the frequency. The phase shift decreases with increasing the electrolyte flow rate. This is due to the decrease of delay time of detection against the

Fig. 1 Nyquist plots of a dynamic collection efficiency $N(\omega)$ measured in 30 mol/m³ K₃Fe(CN)₆ solution. Electrolyte flow rate is (a) 73 cm/s, (b) 225 cm/s.

periodic time of alternative emission. The experimental limits of $N(\omega)$ are approximate 15 and 50 Hz at electrolyte flow rates 73 cm/s and 225 cm/s, respectively. These frequencies correspond to the limits of frequency analysis, and they are one order larger than one with RRDE⁽⁷⁾. In this paper, $N(\omega)$ at 225 cm/s was used for a high frequency analysis.

2. Polarization curves

Figure 2 shows the polarization curves on iron and the Fe(II) detection in the solutions (a) and (b). The open and solid symbols denote the working electrode current, i_w , and the Fe(II) dissolution current, i_{diss} , respectively. The i_{diss} is calculated from the i_c with eq. (1). In the polarization curve (i_w), the hydrogen evolution (cathodic) region and the active dissolution region are observed. The i_{diss} increases exponentially with the potential from

Fig. 2 Polarization curves and their dissolution currents of iron in sulfate solutions. Triangles and circles indicate the currents in the solutions (a) and (b), respectively. Open symbols show the working electrode currents and solid symbols show the dissolution currents of ferrous ion. The solution (a) is 1 kmol/m³ H₂SO₄, and (b) is a mixture of 0.1 kmol/m³ H₂SO₄ and 0.9 kmol/m³ Na₂SO₄.

Fig. 3 Change in current for (a) dissolution of ferrous ion and (b) formation of the adsorbed intermediate on iron electrode during the potential step from -0.48 V to -0.47 V in the solution (a).

the hydrogen evolution region to the active dissolution region, and the i_{diss} coincides with the i_w in the active dissolution region. It means that the i_{diss} represents the partial anodic current, on contrary to that the i_w is the sum of the anodic and cathodic currents. These results are in agreement with the previous investigation⁽⁴⁾ and the mixed potential theory of corrosion. In this paper, a reaction mechanism in the active dissolution potential region $\{-0.53$ V $\sim$ -0.44 V in the solution (a) and -0.48 V $\sim$ -0.40 V in the solution (b) $\}$ and kinetics of elemental reactions are discussed.

3. Transient currents after potential step

Figure 3 shows the transient currents, $\Delta i_{\text{diss}}(t)$ and $\Delta i_f(t)$, after the working electrode potential changes from -0.48 V to -0.47 V. These transient currents are calculated from $i_w(t)$ and $i_c(t)$ with Eqs. (4) and (5), and depicted within 30 ms after potential step. $\Delta i_{\text{diss}}(t)$ increases gradually after potential step. On the other hand, the current for charging the electric double layer is involved in $\Delta i_f(t)$ within about 0.2 ms, and its amount of charge is estimated less than $0.2 \mu\text{C}/\text{cm}^2$. It is reported that an ohmic coupling between the working and collector electrode influences the collector electrode current at non-steady state measurement with RRDE⁽⁸⁾. However, this contribution can be neglected in the CFDE measurement, because the electrolyte resistance of the CFDE system is only a few ohms, which is several tens times smaller than that of RRDE.

4. Dissolution efficiency of Fe(II) and formation efficiency of adsorbed species in the frequency domain

A dissolution efficiency of Fe(II), $\Phi_{\text{diss}}(\omega)$, and a formation efficiency of adsorbed species, $\Phi_f(\omega)$, are calculated from the transient currents with eqs. (2) and (3), respectively. Figure 4 shows the $\Phi_{\text{diss}}(\omega)$ and $\Phi_f(\omega)$ when the potential pulse from -0.43 V to -0.42 V is imposed to

Fig. 4 (a) The dissolution efficiency of ferrous ions $\Phi_{\text{diss}}(\omega)$ and (b) the formation efficiency of the adsorbed intermediate $\Phi_f(\omega)$, calculated with FFT, in the solution of (a) when potential pulse from -0.43 V to -0.42 V is imposed to the working electrode.

Fig. 5 Potential dependence of the formation efficiency of the adsorbed intermediate at $f=1$ Hz. Open and solid symbols denote the formation efficiencies in the solutions (a) and (b), respectively.

the working electrode. The amplitude of $\Phi_{\text{diss}}(\omega)$ is about unity at low frequency and decreases at high frequency. The phase shift of $\Phi_{\text{diss}}(\omega)$ is approximately zero at low frequency and increases with the frequency. This result shows a similar tendency to the result by Benzekri *et al.*⁽⁷⁾ On the other hand, the amplitude of $\Phi_f(\omega)$ increases with the frequency, and its slope in log-log plots is about unity. The phase shift of $\Phi_f(\omega)$ keeps positive value and decreases with the frequency. These results indicate that the dissolution of Fe(II) dominates at low frequency region and that the formation of adsorbed species gets predominant as the frequency increases. The amplitude of $\Phi_{\text{diss}}(\omega)$ does not depend remarkably on the potential between -0.47 V and -0.40 V in the solution (a). On the other hand, amplitude of $\Phi_f(\omega)$ depends on the potential. To investigate the potential dependence of $\Phi_f(\omega)$, the amplitude at frequency $f=1$, $|\Phi_f(2\pi)|$, is chosen and plotted against the potential in Fig. 5. Both results in the solutions (a) and (b) show a minimum value, and $|\Phi_f(2\pi)|$ increases with the pH value.

V. Discussion

1. Analysis in the time domain

The active dissolution mechanism of iron can be roughly classified into two groups, namely catalytic mechanism⁽¹⁾ and consecutive (non-catalytic) mechanism⁽²⁾. It is reported that the active dissolution mechanism depends on the thermal pretreatment⁽⁹⁾ and electrode potential⁽⁷⁾. In this paper, only consecutive dissolution path is considered for simplification.

It is also reported that the formation of divalent adsorbed species, $\text{Fe(II)}_{\text{ad}}$, follows the formation of Fe(I)_{ad} at high potential⁽³⁾. Therefore the following reaction is assumed:

Fig. 6 Relationship between the change of the dissolution current of ferrous ions and the stored charge of the adsorbed intermediate during potential step (a) $-0.48 \sim -0.47$ V, (b) $-0.47 \sim -0.46$ V, (c) $-0.46 \sim -0.45$ V, (d) $-0.45 \sim -0.44$ V in the solution (a).

The reaction rate constant K_i is assumed to obey the Tafel law; $K_i = k_i \exp(b_i E)$, where k_i is the reaction rate constant at $E=0$ V in an arbitrary potential scale and b_i is the Tafel constant. In this analysis, the fractional coverage of Fe(I)_{ad} and $\text{Fe(II)}_{\text{ad}}$ are represented by θ_1 and θ_2 , respectively, and maximum charge densities of Fe(I)_{ad} and $\text{Fe(II)}_{\text{ad}}$ are represented by γ_1 and γ_2 , respectively. In Fig. 3, the integration of $\Delta i_f(t)$ corresponds to the charge for the formation of adsorbed species, ΔQ , on the working electrode. Moreover, $\Delta i_{\text{diss}}(t)$ corresponds to the amount of Fe(II) dissolution. Figure 6 shows the plots of ΔQ and $\Delta i_{\text{diss}}(t)$ after the potential step (10 mV) is superposed to the polarization potential of the working electrode. The initial values for 2 ms after potential step are not plotted in Fig. 6 to avoid the influence of electric double layer. Figure 6 shows that ΔQ is proportional to $\Delta i_{\text{diss}}(t)$ and that its slope, a , increases with the potential. This slope, a , means the dissolution coefficient, which corresponds to the ratio of amount of Fe(II) dissolution to the fractional coverage of adsorbed species. Furthermore, the potential dependences of a in the solutions (a) and (b) are shown in Fig. 7. The dissolution coefficients, a , in both solutions (a) and (b) coincide with the thick straight line at low potential, and deviate from this line at high potential.

The Fe(II) dissolution current is proportional to the fractional coverage, θ_1 , with the reaction (10):

Fig. 7 Potential dependence of the dissolution coefficient a . Open and solid symbols denote the dissolution coefficients in the solutions (a) and (b), respectively.

$$i_{\text{diss}}(t) = 2FK_2\theta_1 \quad (12)$$

At a constant potential, eq. (12) is transformed into,

$$\Delta i_{\text{diss}}(t) = 2FK_2\Delta\theta_1. \quad (13)$$

The charge stored on the working electrode, ΔQ , is composed of the charges of Fe(I)_{ad} and $\text{Fe(II)}_{\text{ad}}$;

$$\Delta Q = \gamma_1\Delta\theta_1 + \gamma_2\Delta\theta_2. \quad (14)$$

The dissolution coefficient, a , is written by,

$$a = \Delta i_{\text{diss}}(t) / \Delta Q. \quad (15)$$

Equations (13) and (14) are substituted into eq. (15),

$$\begin{aligned} a &= 2FK_2\Delta\theta_1 / (\gamma_1\Delta\theta_1 + \gamma_2\Delta\theta_2) \\ &= (2FK_2/\gamma_1) / \{1 + (\gamma_2\Delta\theta_2/\gamma_1\Delta\theta_1)\} \end{aligned} \quad (16)$$

From eq. (16), the dissolution coefficient, a , is determined by the reaction rate constant, K_2 , and the ratio of adsorbed charges, $(\gamma_2\Delta\theta_2/\gamma_1\Delta\theta_1)$. The charge ratio of Fe(I)_{ad} and $\text{Fe(II)}_{\text{ad}}$ at steady state is calculated from reaction (11);

$$\gamma_2\theta_2/\gamma_1\theta_1 = K_3/K_{-3} = k_3/k_{-3} \exp(b_3 - b_{-3})E \quad (17)$$

As $(b_3 - b_{-3}) > 0$ in eq. (17), $\gamma_2\theta_2/\gamma_1\theta_1$ increases exponentially with the potential. And $\gamma_2\theta_2/\gamma_1\theta_1$ increases with increasing the pH value, because k_3 is proportional to a pH value. Assuming that $\gamma_2\Delta\theta_2/\gamma_1\Delta\theta_1$ is quite small at low potential ($1 \gg (\gamma_2\Delta\theta_2/\gamma_1\Delta\theta_1)$),

$$a = 2FK_2/\gamma_1 \quad (18)$$

$$= \{2Fk_2 \exp(b_2E)\} / \gamma_1. \quad (19)$$

Equation (19) is transformed into logarithm:

$$\log a = -\log(\gamma_1/2F) + \log k_2 + b_2E. \quad (20)$$

The equation of the straight line in Fig. 7 is

$$\log a = 8.1 + E/0.08. \quad (21)$$

Assuming that $\gamma_1 = 0.001 \text{ C/cm}^2$ and $F = 96500 \text{ C/mol}$,

k_2 and b_2 are determined with comparison of eq. (20) with eq. (21). Then K_2 is obtained as,

$$K_2 = 0.80 \exp(29E). \quad (22)$$

Because $\gamma_2\theta_2/\gamma_1\theta_1$, increases with potential in eq. (17), it is supposed that $(\gamma_2\Delta\theta_2/\gamma_1\Delta\theta_1)$ also increases with potential and contributes to the dissolution coefficient, a . Therefore, $(\gamma_2\Delta\theta_2/\gamma_1\Delta\theta_1)$ can not be neglected at high potential in eq. (16), and leads to the decrease of a at high potential. On the next section, the potential and pH dependences of $(\gamma_2\Delta\theta_2/\gamma_1\Delta\theta_1)$ and a will be discussed.

2. Simulation in the frequency domain

On the basis of reactions (9)–(11), the simulations of $\Phi_{\text{diss}}(\omega)$ and $\Phi_f(\omega)$ are performed and the elemental reaction rates are obtained.

The mass balance of two kinds of adsorbed species are,

$$\gamma_1(d\theta_1/dt) = F\{(1 - \theta_1 - \theta_2)K_1 + K_{-3}\theta_2 - (K_2 + K_3)\theta_1\} \quad (23)$$

$$\gamma_2(d\theta_2/dt) = 2F(K_3\theta_1 - K_{-3}\theta_2). \quad (24)$$

Since $d\theta_1/dt = d\theta_2/dt = 0$ at steady state, the fractional coverages at steady state are calculated from eqs. (23) and (24) as follows:

$$\Theta_1 = K_1K_{-3} / (K_1K_{-3} + K_2K_{-3} + K_1K_3) \quad (25)$$

$$\Theta_2 = K_1K_3 / (K_1K_{-3} + K_2K_{-3} + K_1K_3) \quad (26)$$

Assuming that a sinusoidal alternative potential is imposed to the working electrode; $E = E_0 + |\Delta E| \exp(j\omega t)$, eqs. (23) and (24) become,

$$\begin{aligned} j\omega\gamma_1 d\theta_1 &= F\{[b_1K_1(1 - \Theta_1 - \Theta_2) + b_{-3}K_{-3}\Theta_2 \\ &\quad - (b_2K_2 + b_3K_3)\Theta_1] dE \\ &\quad - (K_1 + K_2 + K_3) d\theta_1 + (K_{-3} - K_1) d\theta_2\} \end{aligned} \quad (27)$$

$$\begin{aligned} j\omega\gamma_2 d\theta_2 &= 2F\{[b_3K_3\Theta_1 - b_{-3}K_{-3}\Theta_2] dE \\ &\quad + K_3 d\theta_1 - K_{-3} d\theta_2\}. \end{aligned} \quad (28)$$

From eqs. (27) and (28), the differentiations of fractional coverages with respect to the potential, $(d\theta_1/dE)$, $(d\theta_2/dE)$ are calculated as follows:

$$d\theta_1/dE = (C_{13}C_{22} - C_{12}C_{23}) / (C_{11}C_{22} - C_{12}C_{21}) \quad (29)$$

$$d\theta_2/dE = (C_{11}C_{23} - C_{13}C_{21}) / (C_{11}C_{22} - C_{12}C_{21}), \quad (30)$$

where

$$C_{11} = j\omega\gamma_1 / F + K_1 + K_2 + K_3$$

$$C_{12} = K_1 - K_{-3}$$

$$C_{13} = b_1K_1 - (b_1K_1 + b_2K_2 + b_3K_3)\Theta_1 - (b_1K_1 + b_{-3}K_{-3})\Theta_2$$

$$C_{21} = -K_{-3}$$

$$C_{22} = j\omega\gamma_2 / 2F + K_{-3}$$

$$C_{23} = b_3K_3\Theta_1 - b_{-3}K_{-3}\Theta_2.$$

The charge balances for total current, I_w , and dissolution current, I_{diss} , are given by,

$$I_w = F\{K_1(1 - \theta_1 - \theta_2) - K_{-3}\theta_2 + (K_2 + K_3)\theta_1\} \quad (31)$$

$$I_{\text{diss}} = 2FK_2\theta_1. \quad (32)$$

The differentiations of I_w and I_{diss} with respect to potential are calculated as follows,

$$\begin{aligned} dI_w/dE = F \{ & b_1 K_1 (1 - \Theta_1 - \Theta_2) + (b_2 K_2 + b_3 K_3) \Theta_1 \\ & - b_{-3} K_{-3} \Theta_2 + (K_2 + K_3 - K_1) (d\Theta_1/dE) \\ & - (K_1 + K_{-3}) (d\Theta_2/dE) \} \end{aligned} \quad (33)$$

$$dI_{\text{diss}}/dE = 2F \{ b_2 K_2 \Theta_1 + K_2 (d\Theta_1/dE) \}. \quad (34)$$

The dissolution efficiency of Fe(II) is obtained from eqs. (33) and (34).

$$\Phi_{\text{diss}}(\omega) = (dI_{\text{diss}}/dE) / (dI_w/dE) \quad (35)$$

Furthermore, the formation efficiency of adsorbed species is also calculated as follows,

Fig. 8 The simulated results of (a) the dissolution efficiency of ferrous ions $\Phi_{\text{diss}}(\omega)$ and (b) the formation efficiency of the adsorbed intermediate $\Phi_f(\omega)$ in the solution (a) at -0.42 V $K_1 = 4.0 \exp(38E)$, $K_2 = 0.80 \exp(29E)$, $K_3 = 3.5 \exp(20E)$, $K_{-3} = 1.0 \times 10^{-9} \exp(-38E)$, $\gamma_1 = 0.001 \text{ Ccm}^{-2}$, $\gamma_2 = 0.002 \text{ Ccm}^{-2}$.

Fig. 9 Simulated results of the amplitude of the formation efficiency of the adsorbed intermediate at $f=1$ Hz. Open and solid symbols denote the formation efficiencies in the solutions (a) and (b), respectively. The rate constants and the maximum charge densities of the adsorbed species in solution (a) refer to Fig. 8. Those in the solution (b) are followed as $K_1 = 20 \exp(38E)$, $K_2 = 0.80 \exp(29E)$, $K_3 = 17.5 \exp(20E)$, $K_{-3} = 1.0 \times 10^{-9} \exp(-38E)$, $\gamma_1 = 0.001 \text{ Ccm}^{-2}$, $\gamma_2 = 0.002 \text{ Ccm}^{-2}$.

$$\Phi_f(\omega) = 1 - \Phi_{\text{diss}}(\omega). \quad (36)$$

Assuming the reaction constants and the other parameters, $\Phi_{\text{diss}}(\omega)$ and $\Phi_f(\omega)$ are simulated from eqs. (35) and (36) (Fig. 8). The amplitude of $\Phi_{\text{diss}}(\omega)$ is about unity in the range between 1 Hz and 100 Hz, and decreases slightly as the frequency increases. The phase shift of $\Phi_{\text{diss}}(\omega)$ is about zero at 1 Hz and increases with increasing with frequency. On the other hand, the amplitude of $\Phi_f(\omega)$ increases as the frequency increases, whose slope is approximate unity. The phase shift of $\Phi_f(\omega)$ keeps positive value in the range between 1 Hz and 100 Hz. These simulated results are in agreement with the experimental ones. Figure 9 depicts the potential dependence of simulated amplitude at 1 Hz, $|\Phi_f(2\pi)|$. In the simulated results in Fig. 9, the reaction rate constants, K_1 and K_3 , in the solution (b) are five times larger than those in the solution (a). $|\Phi_f(2\pi)|$ in both solutions show minimum values, and this is in agreement with the experimental result in Fig. 5.

The total current at steady state, i_w , is calculated from the following equation and depicted in Fig. 10:

$$i_w = F \{ K_1 + (-K_1 + K_2 + K_3) \Theta_1 - (K_1 + K_{-3}) \Theta_2 \} \quad (37)$$

The i_w increases exponentially with the potential and depends on the pH value. The simulated currents are always positive on the contrary to that experimental currents have cathodic region. This is caused by neglecting the cathodic reaction in this simulation. Then the simulated currents correspond to the anodic partial currents. The potential dependences of fractional coverages, which are simulated from eqs. (25) and (26), are depicted in Fig. 11. The fractional coverages, Θ_1 and Θ_2 , increase exponentially with the potential. Θ_2 is much smaller than Θ_1 at low potential, and Θ_2 increases rapidly at high potential and influences the dissolution coefficient, a .

Fig. 10 Simulated results of polarization curves. Circles and triangles indicate the current densities in the solutions (a) and (b), respectively. The rate constants and the maximum charge densities of the adsorbed species refer to Figs. 8 and 9.

Fig. 11 Simulated results of steady state coverages of the adsorbed intermediate. Circles and triangles indicate the coverages in the solutions (a) and (b), respectively. Open and solid symbols show the Θ_1 and Θ_2 , respectively. The rate constants and the maximum charge densities of the adsorbed species refer to Figs. 8 and 9.

Fig. 12 Simulated results of the dissolution coefficient a and $\gamma_2\Delta\theta_2/\gamma_1\Delta\theta_1$. Circles and triangles indicate dissolution coefficient and $\gamma_2\Delta\theta_2/\gamma_1\Delta\theta_1$, respectively. Open and solid symbols denote the simulated results in the solutions (a) and (b), respectively. The rate constants and the maximum charge densities of the adsorbed species refer to Figs. 8 and 9.

The differentiations of fractional coverages with respect to the potential, $d\theta_1/dE$ and $d\theta_2/dE$, are obtained from Fig. 11 and the charge ratio ($\gamma_2\Delta\theta_2/\gamma_1\Delta\theta_1$) is calculated:

$$\gamma_2\Delta\theta_2/\gamma_1\Delta\theta_1 = (\gamma_2/\gamma_1)\{(d\theta_2/dE)/(d\theta_1/dE)\} \quad (38)$$

The charge ratio ($\gamma_2\Delta\theta_2/\gamma_1\Delta\theta_1$) and dissolution coefficient, a , which is obtained from substitution of ($\gamma_2\Delta\theta_2/\gamma_1\Delta\theta_1$) into eq. (16), are shown in Fig. 12. In Fig. 12, a shows the maximum value in both solutions. The decreasing of a at high potential is originated by the in-

creasing of ($\gamma_2\Delta\theta_2/\gamma_1\Delta\theta_1$), and peak potential depends on the pH value.

VI. Conclusions

Active dissolution mechanism has been analyzed by the transient technique with CFDE and following conclusions are obtained.

The dynamic collection efficiency in the frequency domain of CFDE system, $N(\omega)$, which involves the delay time of detection due to the traveling time between the working and collector electrodes, has been measured. The $N(\omega)$ depends on the frequency of the working electrode current. The $N(\omega)$ shows the same value as steady state collection efficiency, N_s , in the very low frequency region, and its amplitude decreases as the frequency increases. The transient currents which flow on the iron working electrode have been separated into dissolution and accumulation components using the $N(\omega)$ in both time and frequency domains. The active dissolution mechanism of iron in sulfuric acid solution has been explained by the reaction model involving the two adsorbed species. The numerical simulations have been performed and the elemental reaction rates have been estimated.

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Nomenclature

a	dissolution coefficient
E	potential of the working electrode, V
F	Faraday constant, C/mol
i_w	current on the working electrode at steady state, A/cm ²
i_c	current on the collector electrode at steady state, A/cm ²
i_{diss}	dissolution current at steady state, A/cm ²
$i_w(t)$	transient current on the working electrode, A/cm ²
$i_c(t)$	transient current on the collector electrode, A/cm ²
$i_{diss}(t)$	dissolution current of Fe(II), A/cm ²
$i_f(t)$	formation current of adsorbed species, A/cm ²
I_w	working electrode current which is function of frequency and potential, A/cm ²
I_{diss}	dissolution current which is function of frequency and potential, A/cm ²
$I_w(\omega)$	current on the working electrode in the frequency domain, A/cm ²
$I_c(\omega)$	current on the collector electrode in the frequency domain, A/cm ²
N_s	collection efficiency at steady state
$N(\omega)$	collection efficiency in the frequency domain
n_w	valency of reaction on the working electrode

n_c	valency of reaction on the collector electrode	γ_1	maximum charge density of Fe(I)_{ad} , C/cm^2
K_i	reaction rate constant	γ_2	maximum charge density of $\text{Fe(II)}_{\text{ad}}$, C/cm^2
k_i	reaction rate constant at $E=0$ V for an arbitrary potential scale		
b_i	Tafel constant		
ΔQ	charge for the formation of adsorbed species, C/cm^2		
$\Phi_{\text{diss}}(\omega)$	dissolution efficiency of Fe(II) in the frequency domain		
$\Phi_f(\omega)$	formation efficiency of adsorbed species in the frequency domain		
θ_1	fractional coverage of Fe(I)_{ad} , cm^{-2}		
θ_2	fractional coverage of $\text{Fe(II)}_{\text{ad}}$, cm^{-2}		
Θ_1	fractional coverage of Fe(I)_{ad} at steady state, cm^{-2}		
Θ_2	fractional coverage of $\text{Fe(II)}_{\text{ad}}$ at steady state, cm^{-2}		

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