

Determination of the pH of Iso-Selectivity of the Interfacial Diffusion Layer of Fe

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Passive metal forms an interfacial diffuse layer on the surface of passive film by its reaction with H^+ or OH^- ions in solution depending on solution pH. There is a critical pH, called pH point of iso-selectivity (pH_{pis}) at which the nature of the diffuse layer is changed from the anion-permeable at $pH < pH_{pis}$ to the cation-permeable at $pH > pH_{pis}$. The pH_{pis} for a passivated Fe was determined by examining the effects of pH on the thickness of passive film and on the dissolution reaction occurring on the passive film under a galvanostatic reduction in borate-phosphate buffer solutions at various pH of 7~11. The steady-state thickness of passive film formed on Fe showed the maximum at pH 8.5~9, and further the nature of film dissolution reaction was changed from a reaction producing Fe^{3+} ion at $pH \leq 8.5$ to that producing FeO_2^- at $pH \geq 9$, suggesting that the pH_{pis} of Fe is about pH 8.5~9. In addition, the passive film formed at pH 8.5~9, pH_{pis} , was found to be the most protective with the lowest defect density as confirmed by the Mott-Schottky analysis. Pitting potential was decreased with increasing Cl^- concentration at $pH \leq 8.5$ due probably to the formation of anion permeable diffuse layer, but it was almost constant at $pH \geq 9$ irrespective of Cl^- concentration due primarily to the formation of cation permeable diffuse layer on the film, confirming again that pH_{pis} of Fe is 8.5~9.

Keywords : pH of iso-selectivity, Fe, passive film, galvanostatic reduction, Mott-Schottky analysis.

1. Introduction

Passivated metal actively interacts with H^+ and OH^- ions in aqueous solution, and so the outermost surface of passive film is covered with a layer of hydroxyl groups.¹⁾ Solution pH determines the surface charge of the passive film¹⁾ and hence dissolution reaction of the passive film.^{2),3)} As the dissolution reaction proceed, a film/solution interfacial diffuse layer is accumulated with the hydrated metal cation or anion depending on solution pH.^{4),5)} The diffuse layer concentrated with fixed hydrated metal cations or anions acts as a cation or anion rectifier, respectively, which is called anion-selective (or permeable) diffuse layer or cation-selective (or permeable) diffuse layer.^{4),5)} There is a critical pH, called pH point of iso-selectivity (pH_{pis}) at which the nature of the diffuse layer is changed from the anion-permeable at $pH < pH_{pis}$ to the cation-permeable at $pH > pH_{pis}$. In this regard, the ion-selectivity through the diffuse layer can be controlled by varying the solution pH with respect to the pH_{pis} .

It is well known that the pitting corrosion is caused

by the chemical attack of chloride ions (Cl^-) that have been adsorbed on the passive film.⁶⁾ Prior to the adsorption of Cl^- , they should be transported through the diffuse layer to the film. Is it possible to increase the resistance to pitting corrosion of Fe by forming a cation-selective diffuse layer on the passive film by controlling the solution pH higher than pH_{pis} ? We anticipate that the adsorption of Cl^- ions to the passive film on Fe will be significantly inhibited if a cation-selective diffuse layer is formed on the passive film, and vice versa. The research objective of the work is to determine pH_{pis} for Fe in a borate-phosphate buffer solution, and to examine the effects of Cl^- concentration on the resistance to pitting corrosion when the solution pH is lower or higher than the pH_{pis} .

2. Experiments

A three-electrode cell of 1 L multi-neck flask was used for electrochemical tests. Pure Fe (99.99 %) used as a working electrode was mounted in an epoxy resin with an exposed area of 0.13 cm^2 and polished to $6 \mu\text{m}$ with diamond suspension. A platinum counter electrode and a saturated calomel reference electrode (SCE) were used in

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the cell. All the electrode potentials were referred to the SCE scale. The electrochemical tests were conducted in deaerated borate-phosphate buffer solution (pH 6~11) prepared by mixing 0.2 M boric acid and 0.05 M citric acid with 0.1 M tertiary sodium phosphate solution.⁷⁾ Solution temperature was controlled at 25°C. The working electrode was cathodically cleaned at -1.0 V_{SCE} for 3 min before every electrochemical experiment.

Polarization behavior of Fe was measured by potentiodynamic test at a scan rate of 1 mV·s⁻¹. To obtain a dependence of steady-state thickness of passive film (L_{ss}) on solution pH, passive film was potentiostatically grown on Fe at 0.6 V_{SCE} for 9 h, and then reduced galvanostatically at a cathodic current density of 10 μA·cm⁻². An influence of pH on the electronic properties of the passive film was examined by the Mott-Schottky analysis. For the analysis, the specimen was passivated at 0.6 V_{SCE} for 9 h, and the capacitance for the passive films was measured by sweeping potential in negative direction by 1 mV·s⁻¹ with excitation voltage of 10 mV (peak-to-peak) and frequency of 1000 Hz.⁸⁾ Finally, a dependence of the E_{pit} on solution pH and Cl⁻ concentration was investigated by potentiodynamic test at a scan rate of 1 mV·s⁻¹ in the borate-phosphate buffer solution at various pH (pH 7~10) and with various Cl⁻ concentration (0~0.5 M).

3. Results and discussion

3.1 Effects of pH on the polarization behavior

Fig. 1 showed polarization responses of Fe in deaerated borate-phosphate buffer solution at pH 6, 7, 8.5 and 10. The corrosion potential (E_{corr}) was about -0.8 V_{SCE} and passive state of Fe appeared in the solution at pH ≥ 7. In

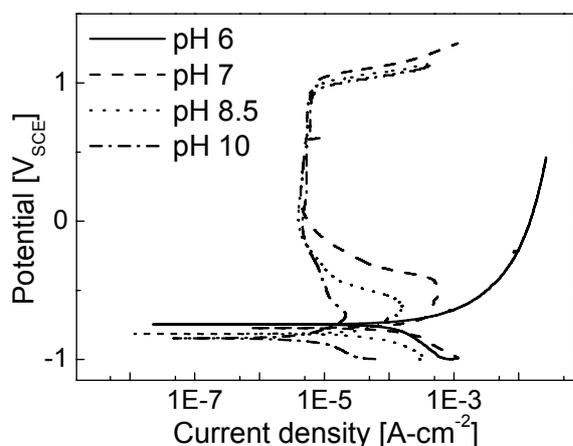


Fig. 1. Polarization responses of Fe in deaerated borate-phosphate buffer solution (pH 6, 7, 8.5 and 10) at 25°C with a scan rate of 1 mV·s⁻¹.

the solution at pH 7~10, the passive region of Fe extended from 0.1 V_{SCE} to 0.9 V_{SCE}. With an increase in pH, the overpotential for H₂ evolution increased, whereas the critical anodic current density at around -0.5 V_{SCE} decreased.¹⁰⁾ The primary passivation potential (E_{pp}) decreased with a slope (dE_{pp}/dpH) of -0.06 V·pH⁻¹,⁹⁾ as expected. Based on the data in Fig. 1, passive film on Fe was formed at film formation potential (E_{ff}) of 0.6 V_{SCE} in buffer solution at pH 7~11 for the subsequent electrochemical tests.

3.2 Effects of pH on thickness of the passive film

Among the numerous models on passivity of the metal, Point Defect Model (PDM) provides an analytical description of the growth and breakdown of passive films on metal surface on the atomic scale.^{3),10),11),12)} PDM suggests the dissolution reaction of the passive film at steady-state on metal M , which is $MO_{x/2} + xH^+ \rightarrow M^{\delta+} + (x/2)H_2O + (\delta-x)e^-$, where $MO_{x/2}$ = stoichiometric passive film. PDM provided several diagnostic criteria to identify the passive film under steady-state conditions.³⁾ As one of the criteria, a variance of steady-state thickness of the passive film (L_{ss}) as a function of pH is described as Eq. 1,

$$\left(\frac{\partial L_{ss}}{\partial pH} \right)_V = \left[\frac{1.1515n}{\gamma} - \beta \right] / \bar{\varepsilon} \quad (1)$$

where γ is a constant of F/RT (F ; Faraday constant), $\bar{\varepsilon}$ is a mean electric field strength across the passive film, n is kinetic order of the passive film dissolution reaction with respect to H^+ and β is a constant. The Eq. 1 is valid for both n-type and p-type semiconducting passive films. The positive or negative sign of n demonstrates the dissolution reaction of the passive film at steady-state depending on the solution pH.^{3),13)} Accordingly, it is possible to determine the critical pH where the film dissolution reaction is changed from the dependence of L_{ss} on pH.

To examine the effects of solution pH on L_{ss} of Fe, galvanostatic reduction was performed on the passive films formed on Fe at 0.6 V_{SCE} for 9 h in deaerated borate-phosphate buffer solution at pH 7~11. The galvanostatic reduction curves for the passive film are presented in Fig. 2. The γ -Fe₂O₃ passive film⁸⁾ was reduced to Fe²⁺ at the arrest potential in the solution at each pH.¹³⁾ L_{ss} was calculated from the consumed charge during the galvanostatic reduction for γ -Fe₂O₃ in accordance with the following reduction equation, $Fe_2O_3 + 6H^+ + 2e^- \rightarrow 2Fe^{2+} + 3H_2O$ with a 100 % current efficiency.^{8),14)}

Fig. 3 showed the variance of L_{ss} as a function of pH. Clearly, the thickest passive film 5 nm thick was formed in the solution at pH 9. The slope (dL_{ss}/dpH)_V was

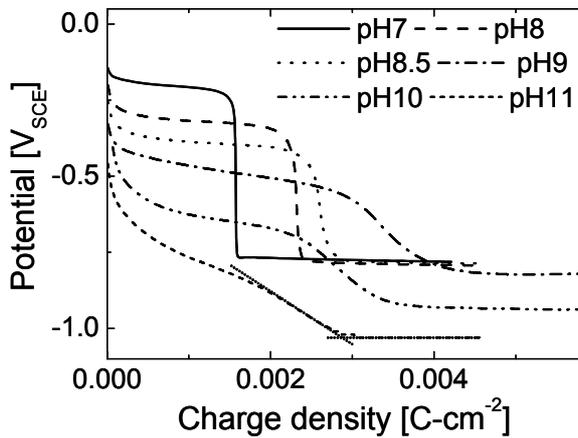


Fig. 2. Galvanostatic reduction for the passive film on Fe formed at 0.6 V_{SCE} for 9 h in deaerated borate-phosphate buffer solution (pH 7, 8, 8.5, 9, 10 and 11) at 25 °C. The passive film was reduced galvanostatically to cathodic current density of -10 μA-cm⁻².

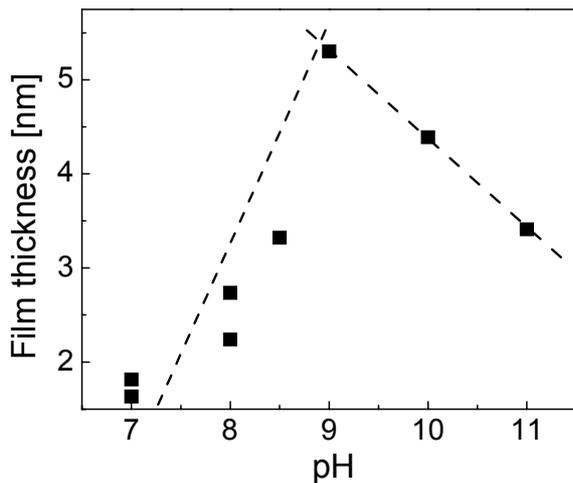


Fig. 3. L_{SS} of passive film on Fe as a function of pH, calculated from the consumed charge during the galvanostatic reduction shown in Fig. 2. The passive films were formed on Fe at 0.6 V_{SCE} for 9 h in deaerated borate-phosphate buffer solution (pH 7, 8, 8.5, 9, 10 and 11) at 25 °C.

2.16×10^{-7} for the solutions at $\text{pH} \leq 8.5$ and -0.945×10^{-7} cm-pH⁻¹ for those at $\text{pH} \geq 9$, respectively, as shown in Fig. 3. For either n- or p-type semiconductor passive film, L_{SS} varies linearly with pH as predicted by Eq. 1. The Eq. 1 contains 3 unknown constants, $\bar{\varepsilon}$, β and n , and it was reported that the $\bar{\varepsilon}$ in the passive film on Fe was $(1\text{--}6) \times 10^6$ V-cm⁻¹,^(11),8) and the constant β was less than -0.01.⁽¹¹⁾ Thus, the n , the kinetic order for the dissolution of γ -Fe₂O₃ with respect to H⁺ can be calculated by substituting $\bar{\varepsilon} = 2 \times 10^6$ V-cm⁻¹,⁽⁸⁾ and $\beta = -0.015$,⁽¹¹⁾ $n > 0$ for the

$\text{pH} \leq 8.5$ and $n < 0$ for $\text{pH} \geq 9$, respectively. The change in the sign (+ or -) of n was interpreted by Macdonald et al.,⁽³⁾ as that the positive sign of n demonstrated that the dissolution of the passive film on Fe at $\text{pH} \leq 8.5$ preceded by protonation of the surface, while the negative sign of n at $\text{pH} \geq 9$ was preceded by an ionization of surface hydroxyl groups of the passive film, respectively.⁽³⁾ Therefore, the film dissolution reaction at the steady-state can be predicted as $\text{Fe}_2\text{O}_3 + 6\text{H}^+ \rightarrow 2\text{Fe}^{3+} + 3\text{H}_2\text{O}$ at $\text{pH} \leq 8.5$ and $\text{Fe}_2\text{O}_3 + \text{H}_2\text{O} \rightarrow 2\text{FeO}_2^- + 2\text{H}^+$ at $\text{pH} \geq 9$,^(2),10) respectively.

Galvanostatic reduction test results showed that the dissolution reaction of the passive film at the steady-state was changed at pH 8.5–9. The product ions from the film dissolution reaction at steady-state were Fe³⁺ in hydrated form at $\text{pH} \leq 8.5$ and FeO₂⁻ at $\text{pH} \geq 9$, respectively. As the dissolution reaction proceed, in the solution at $\text{pH} \leq 8.5$, the cation (hydrated Fe³⁺) would accumulate at the film/solution interfacial diffuse layer and, likewise, anion (FeO₂⁻) would accumulate at the diffuse layer in the solution at $\text{pH} \geq 9$, and hence, the diffuse layers showed anion-selectivity at $\text{pH} \leq \text{pH} 8.5$ and cation-selectivity at $\text{pH} \geq \text{pH} 9$, respectively. Thus, the galvanostatic results demonstrated that the pH 8.5–9 is pH_{pis} of the interfacial diffuse layer formed on the passivated Fe in borate-phosphate buffer solution, and the other anion species in the solution such as Cl⁻ can be easily transported through the anion-selective interfacial diffuse layer at $\text{pH} \leq 8.5$, while the transport of Cl⁻ through cation-selective diffuse layer would be inhibited at $\text{pH} \geq 9$. For this reason, it is expected that passive film breakdown by Cl⁻ will take place actively in the solution at pH lower than 8.5–9, while it will be significantly reduced at pH higher than 8.5–9.

3.3 Effects of pH on electronic properties of the passive film

Effects of solution pH on the electronic properties of the passive film were investigated by the Mott-Schottky analysis. For the Mott-Schottky analysis, the specific interfacial capacitance, C , is obtained from $C = 1/\omega Z''$, where ω is the angular frequency and Z'' is the imaginary part of the specific impedance. Assuming that the double-layer capacitance is sufficiently high, it is neglected in a series combination with the space-charge capacitance, and hence, the measured capacitance, C , is equal to the space-charge capacitance, C_{SC} .⁽¹⁵⁾ Based on the Mott-Schottky theory, the C_{SC} of n-type semiconductor is given by Eq. 2.

$$\frac{1}{C_{SC}^2} = \frac{2}{\varepsilon \varepsilon_0 e N_D} \left(E_{app} - E_{FB} - \frac{kT}{e} \right) \quad (2)$$

where ε is the dielectric constant of the oxide (12 for γ

$-\text{Fe}_2\text{O}_3^8)$, ϵ_0 is the vacuum permittivity (8.854×10^{-14} F-cm $^{-1}$), e is the charge of an electron, N_D is the donor density in the passive film, E_{app} is the applied potential, E_{FB} is the flat band potential and k is the Boltzmann constant. Thus, for n-type semiconductors, C_{SC}^{-2} versus E_{app} should be linear with positive slopes which are inversely proportional to the N_D .

Fig. 4 showed Mott-Schottky plots for the passive film formed on Fe at 0.6 V $_{SCE}$ for 9 h in deaerated borate-phosphate buffer solution (pH 7, 8.5 and 10). E_{FB} of the passive films appeared in the range of -0.18~-0.45 V $_{SCE}$ and decreased linearly with pH having a gradient of $dE_{FB}/dpH = -0.06$ V-pH $^{-1}$, as expected. The Mott-Schottky plots exhibited one linear region with a positive slope, confirming

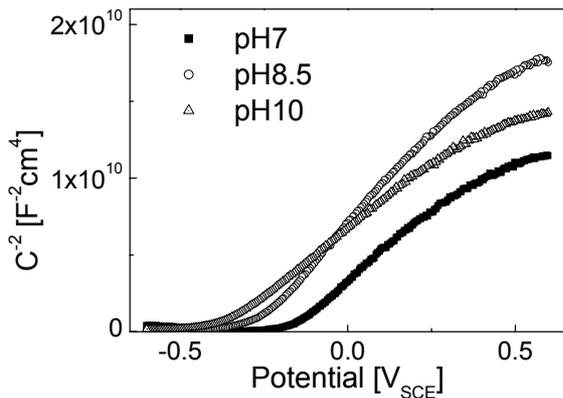


Fig. 4. Mott-Schottky plots for the passive film on Fe formed at 0.6 V $_{SCE}$ for 9 h in deaerated borate-phosphate buffer solution (pH 7, 8.5 and 10) at 25 °C. The Mott-Schottky plots were measured with excitation voltage of 10 mV and frequency of 1 kHz.

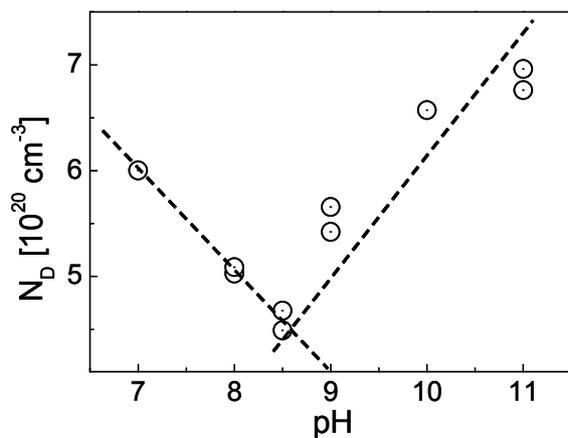


Fig. 5. Donor density (N_D) in the passive film on Fe as a function of pH calculated from the slopes of the Mott-Schottky plots in Fig. 4. The passive films were formed at 0.6 V $_{SCE}$ for 9 h in deaerated borate-phosphate buffer solution (pH 7, 8, 8.5, 9, 10 and 11) at 25 °C.

n-type semiconducting passive film for $\gamma\text{-Fe}_2\text{O}_3$. The dominant and detectable donor species in the n-type passive film is oxygen vacancy, VO^{2+} .^{3),12)}

N_D of the passive films calculated from the slope in the linear region of the Mott-Schottky plots, and it is presented as a function of solution pH in Fig. 5. The N_D is in the range of $(4\text{--}6) \times 10^{20}$ cm $^{-3}$, which is well consistent with those in the previous reports.⁸⁾ N_D decreased linearly with solution pH 7 to pH 8.5 followed by the lowest value of N_D at pH 8.5 and then increased again linearly with increase in pH. Consequently, the most protective passive film with the lowest N_D was formed in the buffer solution at pH 8.5~9 as shown in the Fig. 5. It is significant that the pH at which the thickest passive film is formed is well corresponded to that at which the most protective passive film with the lowest N_D is formed as confirmed by comparing Fig. 5 with Fig. 3.

3.4 Effects of pH on the resistance to pitting corrosion

Previous experiments on the passive film formed on Fe in deaerated borate-phosphate buffer solution (pH 7~11) demonstrated that the most protective passive film with the highest thickness and the lowest defect density was formed in the solution at pH 8.5~9. Thus, effects of solution pH and concentration of Cl $^-$ ([Cl]) on the resistance to film breakdown were examined quantitatively by measuring the pitting potential (E_{pit}) as a function of solution pH and [Cl] by potentiodynamic tests in borate-phosphate buffer solution containing Cl $^-$ at various pH. The results are shown in Fig. 6 and Fig. 7.

It is evident from Fig. 6 that E_{pit} increased linearly with pH 7 to pH 8.5, however it converged to about -0.2 V $_{SCE}$ irrespective of Cl $^-$ concentration at pH ≥ 9 . Further, E_{pit} decreased linearly with [Cl] in the solution at pH ≤ 8.5 ,

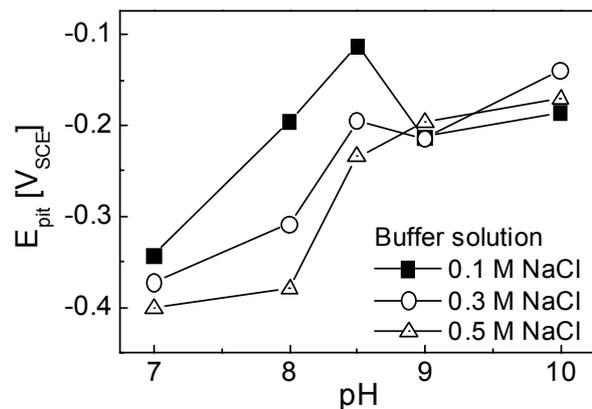


Fig. 6. Dependence of E_{pit} of Fe on pH in borate-phosphate buffer solution (pH 7, 8, 8.5, 9 and 10) with various Cl $^-$ concentration (0.1, 0.3 and 0.5 M NaCl).

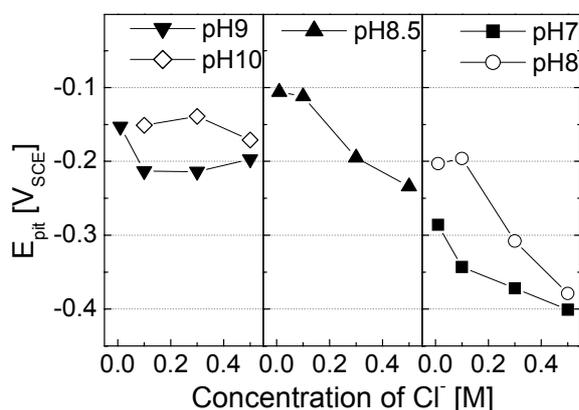


Fig. 7. Dependence of E_{pit} of Fe on concentration of Cl^- in borate-phosphate buffer solution (pH 7, 8, 8.5, 9 and 10) with various Cl^- concentration (0.01, 0.1, 0.3 and 0.5 M NaCl).

whereas it converged to a constant value of about -0.2 V_{SCE} irrespective of $[\text{Cl}^-]$ at $\text{pH} \geq 9$ as shown in Fig. 7. The results demonstrated that the adsorption of Cl^- to the passive film surface is changed depending on the solution pH whether it is higher or lower than the pH_{pis} . At pH lower than the pH_{pis} , Cl^- appears to be easily accessible to the passive film on Fe due to formation of anion-selective layer on the passive film. On the other hand, in the solution with pH greater than pH_{pis} , transport of Cl^- onto the passive film would be significantly inhibited due primarily to the formation of cation-selective diffuse layer on the film. Thus, E_{pit} should be decreased with $[\text{Cl}^-]$ in solution at pH lower than the pH_{pis} , whereas it would be converged to a constant value of E_{pit} in solution at pH greater than the pH_{pis} , as demonstrated in Fig. 6 and Fig. 7. The results clearly demonstrated that pH_{pis} of Fe is pH 8.5~9 in borate-phosphate buffer solution, and that Cl^- attack on the passive film on Fe is significantly reduced in solution at pH greater than the pH_{pis} due primarily to the formation of cation-selective diffuse layer formed on the film.

4. Conclusions

(1) Polarization test showed that a stable passive state on Fe was extended from 0.1 V to 0.9 V in the solution at pH 7 to 10. With an increase in solution pH, overpotential for H_2 evolution increased, the critical anodic current density decreased, and passivation potential (E_{pp}) decreased with a slope ($dE_{\text{pp}}/d\text{pH}$) of $-0.06 \text{ V}\cdot\text{pH}^{-1}$.

(2) The steady-state thickness of passive film formed on Fe showed the maximum at pH 8.5~9, and further the nature of film dissolution reaction was changed from a reaction producing Fe^{3+} ion at $\text{pH} \leq 8.5$ to that producing FeO_2^- at $\text{pH} \geq 9$, suggesting that the pH_{pis} of Fe is about pH 8.5~9. Thus, it is expected that the diffuse layers shows anion-selectivity at $\text{pH} \leq 8.5$ and cation-selectivity at $\text{pH} \geq 9$, respectively.

(3) The passive film formed on Fe at 0.6 V_{SCE} for 9 h exhibited n-type semiconductivity with a donor density of $4\text{--}6 \times 10^{20} \text{ cm}^{-3}$ depending on the solution pH. The most protective passive film with the lowest defect density was formed in the solution at pH 8.5~9 or at pH_{pis} .

(4) E_{pit} for Fe was decreased with increasing Cl^- concentration at $\text{pH} \leq 8.5$ due probably to the formation of anion-selective diffuse layer, but it was almost constant at $\text{pH} \geq 9$ irrespective of Cl^- concentration due primarily to the formation of cation-selective diffuse layer on the film, confirming again that pH_{pis} of Fe is 8.5~9.

References

1. E. McCafferty, *J. Electrochem. Soc.*, **146**, 2863 (1999).
2. M. Pourbaix, Atlas of Electrochemical Equilibria in Aqueous Solutions, First English ed., Pergamon Press, Oxford (1966).
3. D.D. Macdonald, S.R. Biaggio, and H. Song, *J. Electrochem. Soc.*, **139**, 170 (1992).
4. M. Sakashita and N. Sato, *Corros. Sci.*, **17** 473 (1977).
5. N. Sato, *Electrochim. Acta*, **41**, 1525 (1996).
6. A. John Sedriks, Corrosion of Stainless Steels, 2nd, Wiley-Interscience publication, Ch. 4
7. G.J. Shugar, T. Ballinger, Chemical Technicians' Ready Reference Handbook, 3rd Ed., p. 655, McGraw Hill, New York, (1990).
8. S.J. Ahn and H.S. Kwon, *J. Electroanal. Chem.*, **579**, 311 (2005).
9. N. Sato, *Corros. Sci.*, **37**, 1947 (1995).
10. D.D. Macdonald, *J. Electrochem. Soc.*, **139**, 3434 (1992).
11. D.D. Macdonald and M.U. Macdonald, *J. Electrochem. Soc.*, **137**, 2395 (1990).
12. S.J. Ahn and H.S. Kwon, *J. Electrochem. Soc.*, **152**, B482 (2005).
13. E. Sikora and D.D. Macdonald, *J. Electrochem. Soc.*, **147**, 4087 (2000).
14. K.N. Goswami and R.W. Staehle, *Electrochim. Acta*, **16**, 1895 (1971).
15. S.J. Ahn and H.S. Kwon, *Electrochim. Acta*, **49**, 3347 (2004).