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**Study on Heterogeneity of Passive Film
and Its Local Breakdown
by Scanning Electrochemical Microscopy**

(走査電気化学顕微鏡による不働態皮膜の不均一性と局部破壊に関する研究)

2001

Koji Fushimi

Preface

Since the discovery of 'fire', human beings have obtained a number of materials. Every civilization has been created, developed, and destroyed by the newest obtainable materials in respective eras as well as their applications and technologies. This tendency has been repeated until the present and will still be continued in the future. However, materials production does not proceed spontaneously. It requires huge amounts of energy as symbolized by purification processes in steel foundries. In contrast, it is natural thermodynamically that materials return to natural states in which little or no energy is expended. Corrosion of metallic materials is a typical spontaneous reaction (oxidation or sulfurization) that returns energy stored in materials during purification to the surrounding environment. Most engineering metals and alloys corrode in air, water, and electrolytic solutions. However, corrosion rates are strongly dependent on the materials themselves and their surface conditions as well as the surrounding environment. Materials frequently passivate even in wet environments due to formation of protective oxide films - so-called passive films. Passive films, the stability of which is much greater than the substrate itself, forms a high barrier against ion transport and sustains substrate corrosion resistivity. The study of passive films is one of the most important keys to investigate corrosion behavior and thereby decrease corrosion loss.

A number of theoretical and experimental approaches have attempted to elucidate passivity or passive films themselves. They are mainly classified as papers which deal with: i) fundamental models and ideas on passive films; ii) steady-state passive films' structure, stoichiometry, and properties; and iii) local breakdown of passive film. Among them, local breakdown of passive film is related directly to initiation of localized corrosion, which is the most dangerous corrosion behavior because it renders lifetime estimation difficult. Local breakdown of passive film might be related to weakened film sites with defective film structure or film thickness. However, it is hard to find sites where breakdown might start. This is the main reason why initiation of localized corrosion is still unclear though propagation is relatively well understood. For examination of precursive processes to localized corrosion onset, techniques for specifying precursor site locations and subsequent evolution are vitally necessary. This problem is significantly important for engineering and industry all over the world.

On the other hand, scanning electrochemical microscopy (SECM) is useful and powerful for *in-situ* evaluation of electrochemical reactivities at electrode surface local sites. This technique is one kind of scanning probe microscopy (SPM), but it can reveal localized reactivities in solution with a probe electrode. It is also useful to visualize distribution of

electroactive species and to fabricate the microstructure electrochemically.

In this thesis, SECM is applied in the field of corrosion. Here, active dissolution, passive, and trans-passive regions as well as oxygen evolution on electrodes are dealt. In addition to them, hydrogen evolution is also investigated using SECM. Furthermore, a state of the art technology, so-called 'liquid-phase ion gun (LPIG)', which can generate chloride ions locally to induce breakdown of passive film, is developed. This thesis consists of the following chapters.

Chapters 1-3 are devoted to fundamental concepts related basically throughout the thesis. Chapter 1 provides reported knowledge concerning passivity, passive film and its breakdown, and localized corrosion. Chapters 2 and 3 deal with methodologies of microelectrodes and SECM, respectively.

Instrumentation for the developed SECM apparatus and public experimental procedures are covered in Chapter 4. Although apparatus details have changed to fit individual investigation, basic SECM configurations and specifications are described. Preparation of microelectrodes is also illustrated in this chapter.

Chapters 5-10 are for practical aspects. In Chapters 5 and 6, experimental results and discussions for evaluation of heterogeneities of passive film formed on iron and titanium are reported, respectively. In Chapter 7, discussion is made for investigation of oxygen evolution on titanium. Micro-electrochemistry using SECM apparatus is employed to investigate active dissolution, passivation, and trans-passive dissolution of iron in Chapter 8. In Chapter 9, SECM is also used to measure hydrogen generation from magnetite during galvanic coupling with carbon steel. Current efficiency of hydrogen generation for the cathodic reaction during galvanic corrosion of carbon steel is estimated. In these chapters, the products from the specimen electrode surface can be detected with probe electrodes of SECM detected amperometrically. Chapter 10 introduces the LPIG technique which realizes local generation of chloride ions. Development and applications of LPIG to local breakdown of passive film formed on iron are reported.

Chapter 11 is the summary of this thesis. Initiation of localized breakdown of passive film investigated by SECM is concluded in the last chapter.

It may be risky for the author to assert that breakdown of passive film or the mechanism of localized corrosion is fully clarified by the SECM and/or LPIG technique. However, this thesis is the first to study corrosion phenomena using SECM to fully address the potential window of water, i.e., hydrogen evolution, active dissolution, passive and trans-passive region, and oxygen evolution.

Many people have assisted me. I would like to especially thank Prof. Masahiro Seo for his special guidance and suggestions in organizing numerous details and encouraging me to overcome my poor English. Prof. Toshio Narita, Prof. Hideaki Takahashi, Prof. Toshiaki Ohtsuka, Prof. Kazuhisa Azumi, Dr. Achim Walter Hassel and Dr. Fredrik Falkenberg also helped and their suggestions were invaluable. Furthermore, Tsuyoshi Okawa and Tomoko Yamamuro joined the study to get fruitful results. Finally I am grateful to my wife, Kumi, for her continuous love and support throughout my study.

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Sapporo, Japan

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1 Breakdown of passive film and localized corrosion

1.1 Corrosion loss

Since the discovery of 'fire', human beings have obtained a number of materials. Every civilization has been created, developed, and destroyed by the newest obtainable materials in respective era as well as their applications and technologies. This tendency has been repeated until the present and will still be continued in the future. Highly sophisticated technologies are based on developments and applications of many engineering materials. However, the materials production does not advance spontaneously. It needs a huge amount of energy as symbolized in the purification process in steel foundries. In contrast, it is natural thermodynamically that materials return to the state in which lesser or no energy is drained out. Most engineering metals and alloys return to states of oxides or sulfides due to release of energy to the environment which was obtained during their purification. This reaction is known as 'corrosion'.

At all times, some amount of engineering materials corrodes and tends to lose its function in industrial products. Only in Japan, it was reported that about 4.0 trillion yen, which is 0.77% of GNP, was lost through corrosion in 1997 (JSCE 2000). This value is one and half of that, 2.5 trillion yen, in 1975 while GNP in 1997 is 3.5 times that of 1975 (JSCE 1977). Although the industrial structure might be changed from a 'hard' type symbolized by manufacture to a 'soft' type represented by information technology (IT), it is notable that corrosion loss is still high. Large amounts of materials and energy are lost by corrosion. Stocks of energy and materials on earth are limited. It goes without saying that the study of corrosion is important to conserve these resources.

1.2 Passivity and passive film (Sato 1978, 1981, Schultze 2000)

1.2.1 *Definition of passive film*

Material corrosion rates depend on surface conditions and the surrounding environment as well as the material itself. Although noble metals such as platinum and gold are not corroded*, less noble metals like iron placed in acidic solutions corrode with evolution of

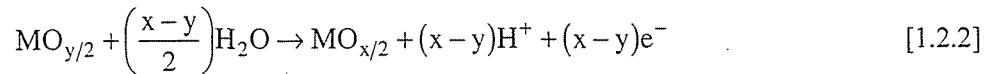
* It is well known that gold and platinum corrode in aqua regia (concentrated HCl and HNO₃ solution, mixed with the ratio of 3:1 by volume).

hydrogen. In concentrated HNO_3 , however, metallic iron suddenly becomes protective against corrosion some time after violent dissolution and gas evolution (Keir 1790). A sudden decrease of metal dissolution is also observed when metals are anodically polarized in acid and neutral solutions (Bonhoeffer 1941). The state of actively corroding metals under conditions where the bare substrate of metals would significantly react can be thus stable in the presence of a strong oxidant and/or by anodic polarization of the electrode. These alternative passivities are in fact electrochemically equivalent to one another. Thermodynamic arguments for oxide film formation were favored by Pourbaix. Figures 1.2.1 and 1.2.2 show the respective potential-pH diagrams of iron and titanium in a water system at 298 K (Pourbaix 1974). In many systems, the oxidation state of oxides increases with increased potential. The diagrams show stability of the metal and special oxides, depending on potential and pH. Passive behavior is due to inhibition of active dissolution by more or less spontaneous formation of a dense 'passive film' with limited ionic conductivity. The passive film, the stability of which is much greater than the substrate itself, has a high barrier against ion transport and sustains corrosion resistivity of the substrate.

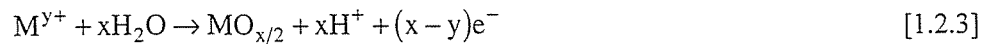
Passive films are formed from materials themselves and components of the environment including oxygen and water in contact with air or anodically with water as the following.



The anodic current density may be supplied from an outer circuit or is compensated by cathodic currents like hydrogen evolution in acidic media or oxygen reduction in neutral or alkaline media at open circuit conditions. Reaction 1.2.1 may proceed in steps via a lower oxide $\text{MO}_{y/2}$ which will be oxidized to the higher oxide $\text{MO}_{x/2}$ in the second step.



In addition to Equation 1.2.1, ions may be deposited from the electrolyte.



Problems of various hydration steps are omitted in Equation 1.2.1-3 for reasons of simplicity. Anodic potentials enhance passivation according to Equation 1.2.1-3, but trans-passivity and anodic breakdown cause the opposite effect. Cathodic polarization reduces or destabilizes passive films.

In general, the term 'passive film' is used mainly for films formed in aqueous solution, but in electric and other fields the definition includes all protective films against corrosion, even if they are deposited by any other technique rather than anodic polarization, e.g., PVD, or

oxidization by oxygen and steam. Passive films of the latter type are of the barrier type, i.e., they show low ionic and electronic conductivities at low and medium field strengths. Moreover, reactivity is negligible. In contrast to that, polished films have a large conductivity. Film formed on active metals for lead-acid batteries shows a large reactivity. These films will not be treated here. This thesis treats only anodic oxide films only forming on iron and titanium.

1.2.2 Previous investigations of passive film

Since discovery of 'passivity', a number of theoretical and experimental approaches have attempted to reveal passivity or passive films themselves. Topics found in the previous investigations about corrosion and passivity of iron through the 1960s are listed in Table 1.2.1.

Table 1.2.1 Topics found in previous investigations concerning the corrosion and passivity of iron through the 1960s

Topics	Reference
Discovery of iron passivity in concentrated nitric acid	Keir 1790
Existence of oxide films even in cases of invisible films	Schönbein 1836
Electronic conductivity of passive films on iron	Faraday 1836
Electron location model for passivity	Hittorf 1898
Acid resistivity theory	Tamman 1910
Flade potential for active/passive transient	Flade 1911
Iron-chromium alloy corrosion	Monnartz 1911
Active/passive oscillation	Hedge 1926
Stuffing of passive film	Evans 1927
Ellipsometric measurement	Freunlich 1927
Potential-pH diagram	Pourbaix 1938
Field assisted ion migration model	Mott 1940
Electrochemical approach using a potentiostat	Bonhoeffer 1941
Polarization curve	Bartlett 1945
Reciprocal logarithmic law	Cabrera 1949
Passivation current is the film dissolution current	Vetter 1954
Dependence of Flade potential upon pH, $\text{Fe}_3\text{O}_4/\gamma\text{-Fe}_2\text{O}_3$ transition	Göhr 1958
Active dissolution mechanism	Heusler 1958
Adsorption model of passivity	Uhlig 1958
Active dissolution mechanism	Bockris 1961
$\text{Fe}_3\text{O}_4/\gamma\text{-Fe}_2\text{O}_3$ model	Nagayama 1962
Place exchange mechanism	Sato 1963
Nonstoichiometric composition and n-type semiconductive property	Oshe 1970
.	.
.	.

Topics of investigations about passivity and passive film are classified into the following three.

- i) fundamental models and ideas on passive films
- ii) steady-state passive films' structure, stoichiometry and properties
- iii) breakdown of passive film

Although they have a mutually close connection, breakdown of passive film is a final problem based on the first two. It is directly related to localized corrosion, but its mechanism has not been clarified as described later. Breakdown of passive film still commands great interest from many corrosion researchers.

1.2.3 *Thickness and composition of passive film*

The anodic oxide film on iron or titanium in acid solution is classified with the barrier type of passive film which is an oxide polymer layer sustaining an electric field of 10^8 - 10^{10} V m⁻¹. The passive film formed on iron in acid solution, possessing the thickness of 1.6 nm V⁻¹ and consisting of an inner Fe₃O₄ and an outer γ -Fe₂O₃ barrier layer (Noda 1973, Vetter 1973, Sato 1975, Nishimura 1977). On the other hand, the passive film on iron in a neutral solution has two layers, one is a barrier layer for the inner and the other is a deposit layer for the outer one (Sato 1976). In pH 8.4 borate solution, the thickness of the barrier layer is a linear function of potential of about 1.7 nm V⁻¹, whereas the outer deposit layer thickness is nearly independent of potential (about 2.6 nm) except for potentials close to the passivation potential. The barrier layer is an iron(III) oxide in the passive potential region and contains iron(II) ions to some percentage in the trans-passive potential region as well as at low passivating potentials close to the active potential region, while the deposit layer is a hydrated iron(III) oxide or oxyhydroxide. Anions originating from electrolyte solution affect the barrier layer composition (Sato 1975, Seo 1977). The anion effect arises for two reasons. One is the initially formed, primary passive film which differs in different anion solutions and the other is the ion-selectivity of the deposit layer which is anion-selective in a boron-containing deposit layer (Nishimura 1977).

On the other hand, titanium behaves as a typical valve metal and the thicker barrier film forms on titanium to sustain larger potential difference compared with that of iron. Film thickness is a function of potential (Dyer 1978, Ohtsuka 1985). It increases linearly with potential in a potential region from -0.55 V to +7.5 V (RHE) under the condition of potentiostatic oxidation for 3.6 ks. The rate of thickness increase with potential is 2.4-2.8 nm V⁻¹ depending on solution. Breakdown of the anodic oxide film occurs at potentials higher than 7.5 V (RHE), beyond which a thick film formed. Optical interferometry (McAleer 1982) revealed that both oxygen evolution and rapid film thickening take place when the film is broken down. Investigation of the anodic oxide film of titanium stripped from the metal substrate using TEM (Yahalom 1970) detected that the anatase type of diffraction pattern for the anodic oxide film subjected to breakdown and crystallization. From the Raman spectroscopic measurements (Ohtsuka 1986), anodic oxide film is composed of the anatase type of TiO₂ and the film nature

changes from amorphous to crystalline oxide as the potential exceeds a certain value.

1.2.4 Properties of passive film

Properties of passive films in the steady state have been investigated by many researchers. Film thickness, thermodynamic properties, and electronic data of passive films differ in a wide range. Typical data are collected in Table 1.2.2.

Table 1.2.2 Typical data for passive films on iron and titanium (Schultze 2000)*

Metal	Oxide	$\rho / \text{g cm}^{-3}$	ϵ	$\Delta\epsilon_g / \text{V}$	E_{FB} / V	E_{OX} / V	N_D / cm^{-3}	ΔX	t_+	$(dd_i/dE) / \text{nm V}^{-1}$	d_0 / nm
Fe	$\text{Fe}_2\text{O}_3/\text{Fe}_3\text{O}_4$	5.2	-	1.9	0.4	-0.08	10^{20}	1.9	-	1.6	1.3**
Ti	TiO_2	3.4-4.2	7-114	3.2-3.8	0-0.3	-0.86	10^{20}	1.6	0.4	1.3-3.3	1.3-5.4

In Table 1.2.2, E_{OX} refers to the potential for a given oxide formed by Equation 1.2.1. It decreases with decreasing metal electronegativity, i.e., with increasing bond ionicity.

Electronic properties, particularly electronic conductivity, have been disputed in past years. Based on the present state of knowledge, it is highly probable that for most metals the passivating film is a poor electronic conductor ranging from semiconductor to insulator. Redox reactions, however, can occur by electronic tunneling if the passivating film is sufficiently thin. Oxygen evolution current on passivated zirconium was found to be in agreement with the electron tunneling current (Hartman 1964, Morozumi 1975). Redox reaction of $\text{Fe}(\text{CN})_6^{4-}/\text{Fe}(\text{CN})_6^{3-}$ were also observed to occur on passivated metal surfaces, although the exchange current density is significantly lower than that on platinum (Schultze 1976). In passivating semiconductive films, both the semiconduction and the tunnel mechanism are operative. An electronic band model was suggested for the passivating film on iron in neutral solution (Stimming 1976).

The passive film on iron shows n-type semiconductive properties in neutral sulfate solution estimated from photoelectric potential measurements (Oshe 1970). There is a strong relation between E_{OX} and electronegativity or band gap energy $\Delta\epsilon_g$ (Schultze 2000). The review of thermodynamic data gives an insight into the range of stability of passive films. On the other hand, fundamental kinetic phenomena, e.g., growth, the formation of duplex films with different oxidation states, or passivated metals stability in acid, cannot be explained by thermodynamics, but by kinetic arguments only. In Figures 1.2.1 and 1.2.2, electronic properties, such as the flat-

* ρ : density, ϵ : dielectric permittivity, $\Delta\epsilon_g$: band gap energy, E_{FB} : flatband potential, E_{OX} : equilibrium potential of oxide electrode, N_D : donor density, ΔX : difference of electronegativity, t_+ : transference number of cations, (dd_i/dE) : formation factor, and d_0 : initial oxide thickness

band potential, E_{FB} , and the positions of conduction and valence bands, E_{CB} and E_{VB} , are also included. They are convenient for considering electron transfer reaction processes at and in passive film.

1.2.5 Processes at metal/oxide film/solution system

For application, passive films should be stable which can be realized under special conditions needed for the use, but a typical feature is their variability under various conditions. Figure 1.2.3 shows a schematic diagram of possible reactions at the metal/oxide film/solution system. The most trivial processes are given as followings.

- a) growth or transfer of oxygen ions from the electrolyte into the oxide (i_{oxide})
- b) corrosion or transfer of metal ions from the oxide into the electrolyte (i_{dis})
- c) reduction of oxide according to the reverse reactions, Equations 1.2.1 to 1.2.3
- d) chemical dissolution when the charge transfer of metal ions is balanced with that of oxygen ions ($i = i_{oxide} + i_{dis} = 0$)
- e) structural modification as a result of changing conditions
- f) electron transfer reactions (i_{etr}), e.g. hydrogen or oxygen evolution
- g) capacitive charging (i_{charge})

A total current density, i_{total} , can be measured which consists of the partial anodic or cathodic current densities of all these processes:

$$i_{total} = i_{oxide} + i_{dis} + i_{etr} + i_{charge} \quad [1.2.4]$$

Any discussion of the processes presumes evaluation of partial current densities. If reactions are concentrated at special surface sites, the true local current densities will exceed the apparent current densities by an order of magnitude.

1.2.6 Growth of oxide film

Oxide films with low electronic conductivity grow by ion migration and diffusion. The transport is explained by the place exchange mechanism (Sato 1963) or field-assisted ion conduction (Cabrera 1949) which is common for ion transport in solids. The model yields an ohmic behavior for low field strengths ($\Delta V < 10^7 \text{ V m}^{-1}$) and an exponentially dependent current density, i , for high field strengths ($\Delta V > 10^9 \text{ V m}^{-1}$).

$$i = i_0 \exp(\beta \Delta V) \quad [1.2.5]$$

This also means that the field strength decreases due to growth.

** Pinkowski 1986

$$\Delta V = \frac{E - E_{\text{ox}}}{d_t} \quad [1.2.6]$$

Assuming a current efficiency of unity, the thickness of oxide film, d_t , is given from the charge, q , as the following

$$d_t = \frac{qM}{z\xi F\rho}, \quad [1.2.7]$$

where M is the molecular weight, ξ is the roughness factor, ρ is the density of the oxide, z is the number of electrons and F is the Faraday constant. Therefore, the oxide film growth rate is obtained from combination of Equations 1.2.5 and 1.2.7 as

$$\frac{dd_t}{dt} = \frac{Mi_0}{z\xi F\rho} \exp(\beta\Delta V) \quad [1.2.8]$$

This differential equation cannot be solved in a closed form but an approximation is given by the reciprocal logarithmic law (Cabrera 1949). Endless growth is predicted by Equation 1.2.8 when dissolution is ignored. If the formation rate according to Equation 1.2.8 is precisely compensated by dissolution, however, a steady state is obtained in actuality. Film thickness increases with increasing polarization potential and is calculated from the oxide formation factor, k , as the following.

$$d_t = k(E - E_{\text{ox}}) \quad [1.2.9]$$

However, k depends slightly upon experimental conditions including sweep rate and polarization time.

1.2.7 Electron transfer reactions

Outer sphere and inner sphere electron transfer reactions (ETR) at passive films are of great importance for overall corrosion processes due to their involvement in reduction processes since cathodic ETR can be coupled with anodic ion transfer reaction (ITR) of metal dissolution (Schmickler 1986, Schultze 1986). The rate of outer sphere ETR depends on position of the bands within the oxide, local potential, and probability of electron transfer by tunneling processes or direct electron transfer between the band and an electron level in the electrolyte (Schultze 1986). The exchange current density of a redox couple can be approximated by a linear relation with the of conduction band-energy level of the oxide relative to the Fermi level of the redox system (Schultze 1986). This relation has been proved for various outer sphere ETR as shown in Figure 1.2.4.

The probability, W , of direct elastic electron tunneling through a film is given as follows (Schultze 1978).

$$W = \exp\left(\frac{-2d_b\sqrt{2m_e\Delta\varepsilon}}{\hbar}\right) \quad [1.2.10]$$

where m_e is an effective mass of electron, d_b is barrier thickness, and $\Delta\varepsilon$ is barrier height for the electron-tunneling from an energy level of ε to energy level of conduction band edge, ε_{CB} . Precisely, ε_{CB} depends on film thickness, d_t , and then Equation 1.2.10 reforms as follows (Schmickler 1986).

$$W = \exp\left(\frac{-2\sqrt{2m_e}}{\hbar} \int_0^{d_t} \sqrt{\varepsilon_{CB}(x) - \varepsilon} dx\right) \quad [1.2.11]$$

The band-bending due to increasing donor density increases the probability, W . Furthermore, the donor in the film contributes formation of electron level for resonance electron tunneling. In the case of two steps-resonance electron tunneling via an energy level, ε_r , the probability is shown by (Schmickler 1986)

$$W = \left(\frac{W_1 W_2}{W_1 + W_2}\right) \delta(\varepsilon - \varepsilon_r) \quad , \quad [1.2.12]$$

where W_i is a probability at i th electron tunneling and $\delta(\varepsilon - \varepsilon_r)$ is a function for resonance electron tunneling at ε_r . In general, the probability of resonance process is higher than that of direct process. Moreover, thickness of electron tunneling, d_t , is influenced by band-bending in the film. Thickness of the space-charge layer, d_{sc} , in the film is given by the following equation (Memming 1983)

$$d_{sc} = \sqrt{\frac{2\varepsilon\varepsilon_0 kT}{N_D e^2}} \sqrt{\frac{e\Delta\varepsilon}{kT} - 1} \quad , \quad [1.2.13]$$

where N_D is a donor density. Equation 1.2.13 indicates that d_t also decreases with increasing donor density. Generally, the thin anodic oxide film on metal has high donor density (Heusler 1975).

For n-type semiconductive oxide films, e.g., iron and titanium oxides, ETR can take place via the conduction band at low potentials. Furthermore, the valence band usually is very low in the energetic scale, so ETR are impossible. On the other hand, p-type semiconductive oxide films, e.g., nickel, copper and noble metal oxides, represent exceptions to this rule.

For inner sphere ETR, such as the anodic oxygen evolution or cathodic hydrogen evolution, quantitative description is even more difficult since adsorption states of OH^- is unknown. For example, anodic oxygen evolution is possible by participation of the valence band, and a qualitative correlation between the overpotential and the position of the valence band can be established.

For oxidation or reduction of an oxide, some of the following are necessary conditions:

- a) The reaction should be possible due to thermodynamics ($E > E_{OX}$ for anodic processes).
- b) Redox reactions should not limit the potential ($E < E_{etr}$ for anodic processes).
- c) Electron transfer via the conduction or valence band should be possible if the process involves ETR.

Redox reactions of the oxide film depend on band position. The n-type oxides of iron and titanium should be oxidized and reduced via the conduction band. Reduction of Fe_2O_3 requires an ETR by tunneling of electrons from the conduction band resulting in dissolution of iron as Fe^{2+} . On the other hand, valve metals could be reduced by electrons from the conduction band at more negative potentials, but then hydrogen evolution takes place first.

1.3 Localized corrosion (Craig 1990, Frankel 1998)

Localized corrosion can be described as corrosion occurring at one part of a metal surface at a much higher rate than that over the remaining surface. It can take many forms (Scully 1975). It is of considerable importance, since many corrosion problems arise due to the following circumstance: although a suitable alloy may have been chosen for a particular environment in which it does not corrode generally, it may be particularly susceptible to localized corrosion. The lifetime of materials is considered as the time period when functions of materials degrade to critical levels due to corrosion. If materials corrode uniformly, the lifetime can be estimated easily from measurement of average corrosion rate in the environment of use. On the other hand, it is very difficult to estimate the lifetime in cases where materials corrode locally. Then, localized corrosion is the most dangerous type of corrosion. To avoid accidents due to localized corrosion, huge costs for maintenance or renewal are necessary.

Crevice corrosion arises commonly from differential aeration, where some form of restricted oxygen access is responsible. Since environmental changes can give rise to reactions that are different from those occurring anywhere else on the metal surface, the general phenomenon is referred to as occluded cell corrosion and will include crevice corrosion as well. Very small differences in potential can cause considerable concentration of anions within a crevice.

Pitting corrosion, which is also one of typical forms localized corrosion, is associated with breakdown of a protective film and it occurs frequently on a completely flat surface. It

occurs where the passive film suffers only local attack and is otherwise stable in the solution to which the metal is exposed. Pitting corrosion is initiated in the presence of aggressive anions, such as Cl^- ions. It is one of the most common yet insidious forms of corrosion attack but highly unpredictable and difficult to model. The role of passive films in pitting corrosion is classified into three parts.

- i) pit initiation
- ii) pit propagation
- iii) repassivation

The key parameter most often used to describe resistance of a metal to pitting is the breakdown potential, E_{BD} , or pitting potential, E_{pit} . Figure 1.3.1 illustrates the schematic polarization curve for explanation of E_{BD} and E_{pit} . At potentials lower than E_p , the metal surface is passive, whereas pitting occurs at potentials higher than E_p . The higher the breakdown potential, the more resistant metal is subjected to pitting.

1.3.1 Pit initiation

Initiation of pitting, i.e., the breakdown of the passive film, is the least understood aspect of pitting corrosion. Such breakdown is a rare occurrence that happens very rapidly on an extremely small scale, making difficult observation extraordinarily difficult. Depending on alloy composition, environment, potential, and exposure history, the passive films can have different thickness, structures, compositions, and protectiveness. Passage of a finite passive current density is evidence of continual reaction of the metal which results in film thickening, dissolution into the environment, or some combination of the above two. The view of the passive film as being a dynamic, rather than static, structure is critical to the proposed mechanism of passive film breakdown and pit initiation.

A number of models have been proposed to explain passive film breakdown in Cl^- containing solutions. Theories for passive film breakdown and pit initiation have been categorized into three main mechanisms that focus on passive film penetration, film breaking or adsorption as shown in Figure. 1.3.2 (Strehblow 1976).

Penetration mechanism requires transport of aggressive anions through the passive film to the metal/film interface as a rate-determining step (McBee 1974). According to the point-defect model (Lin 1981), incorporation of Cl^- into oxygen vacancy sites at the film/solution interface may provide increased concentration of cation vacancy, which moves to the metal/film interface to form voids and finally induce film breakdown.

Adsorption mechanism accepts a local adsorption of aggressive anions at special passive film

locations which should lead to higher dissolution of the passive film and, consequently, to its thinning or complete removal. Formation of chloride-nuclei at the film surface and its growth inward the film were proposed by Okada (Okada 1984). If a small amount of Cl^- adsorbs around a cation in the film to form a high-energy complex which will easily dissolve into the solution (Hoar 1967), the film is locally thinned and finally broken down. Moreover, adsorption or incorporation of Cl^- may introduce electron acceptor levels in the band gap of the film matrix, by which the potential distribution across the metal/film/solution interfaces is changed or a redox reaction via passive film is promoted (Sato 1981).

Film-breaking mechanism gives direct access of the electrolyte to the bare metal surface. In the chemico-mechanical theory (Hoar 1967.2), adsorption of Cl^- onto the film/solution interface may lead to a peptization due to mutual repulsion between adsorbed charged species, inducing cracks in the film due to sufficiently high repulsive forces. Furthermore, if the film pressure exceeds some critical value due to the decrease in surface tension by adsorption of Cl^- , the film may be broken down (Sato 1971).

As with most such situations, different mechanisms or combinations of these mechanisms may be valid for different metal/environment systems. In any case, passive film properties should be deteriorated due to contact with aggressive anions such as Cl^- ions since formation of iron-chloride complex ions such as FeCl_2^+ are thermodynamically stable (Seo 1975).

1.3.2 Pit propagation

The transition from pit nucleation to propagation is gradual, though not well understood. Still, a stochastic approach revealed that a large ensemble of pitting potential, E_{pit} , follows a normal distribution and probability for pitting (Shibata 1977). Several theories described pit growth after nucleation. Dissolution of metal ions in the pit and concomitant hydrolysis are a function of potential and pH (Galvele 1976, 1978). A threshold below which passivation is dominant and above which repassivation does not occur defines the potential at which the production rate of hydrogen ions due to hydrolysis is equal to the consumption rate of hydrogen evolution. Another model considers the rate-limiting step for pit development to be mass-transfer-controlled (Roy 1972). The rate at which ions diffuse out of or into the pit entirely determines the growth rate. Furthermore, there is considerable support for pit growth by salt film formation. Once saturation of a metallic salt proceeds within the pit, precipitation of a salt film occurs on the pit bottom (Beck 1974). The salt film is formed by metal cations and aggressive ions, most often chloride. Thus, further pit growth is controlled by transport across

this film.

1.3.3 Repassivation

For many metals in a variety of solutions, there exists a critical potential below which repassivation may occur and pitting ceases. This potential is referred as the repassivation potential, E_{RP} . If corrosion potential falls between pitting potentials E_{pit} , and E_{RP} , growing pits will continue to propagate. However, a metastability condition exists as pits initiate and attempt to reach stable propagation.

1.4 Purpose of the thesis

A number of researchers have investigated pitting corrosion processes. However, initiation has not been understood well, whereas propagation of localized corrosion has been clarified. Although initiation occurs at an extremely rapid rate with very small size, visualization of the site where local breakdown of passive film will take place has not been established. This is the reason why the initiation process of pitting is not understood.

Local passive film breakdown should take place at sites covered with thinner film or more defective film under the uniform environment and exposure history. Although this corrosion occurs electrochemically, merely conventional electrochemical measurements such as polarization with three electrodes cannot disclose the position of the weakest site initiating the breakdown. Therefore, for finding the weakest site of the passive film and pursuing the event from initiation of the local breakdown of passive film to pit propagation or repassivation, a state of the art technique has been needed urgently.

In recent years, considerable progress in accumulating knowledge of passivity has been seen. New optical, electron-optical, and electrochemical surface analytical techniques have allowed us to disclose molecular nature of passive films even several monolayers thick (Frankenthal 1978, Sato 1981, Froment 1983, Schultze 2000). However, initiation of local breakdown of passive film remains shrouded in darkness due to lack of investigating techniques. For accumulating fundamental knowledge about initiation of pitting corrosion and for decreasing corrosion loss, it is extremely important to investigate initiation of the local breakdown of passive film.

As described later, on the other hand, scanning electrochemical microscopy (SECM) is useful and powerful for *in-situ* evaluation of electrochemical reactivities at electrode surface local sites. This technique is one kind of scanning probe microscopy (SPM), but it can reveal

localized reactivities of solid surface in solution with a probe electrode. It is also useful to visualize distribution of electroactive species and to fabricate the microstructure electrochemically.

In this thesis, SECM is applied to the field of localized corrosion. Here, during active dissolution, passive, and trans-passive regions as well as oxygen evolution, distributions of surface reactions are investigated using SECM. In addition to them, hydrogen evolution is also observed by SECM. Furthermore, a new technology, the so-called 'liquid-phase ion gun (LPIG)', which can generate chloride ions locally to induce passive film breakdown, is developed to pursue local breakdown of passive film. Resistivity against passive film breakdown on iron is investigated with LPIG. This thesis consists of the following 11 chapters.

Chapters 1-3 are devoted to fundamental concepts related basically throughout the thesis. Chapter 1 provides reported knowledge concerning passivity, passive film and its breakdown, and localized corrosion. Chapters 2 and 3 deal with methodologies of microelectrodes and SECM, respectively.

Instrumentation for the developed SECM apparatus and common experimental procedures are covered in Chapter 4. Although apparatus details have changed to fit each investigation, basic SECM configurations and specifications are reported. Preparation of microelectrodes is also illustrated in this chapter.

Chapters 5-10 are for practical aspects. In Chapters 5 and 6, experimental results and discussions for evaluation of heterogeneities of passive film formed iron and titanium are reported, respectively. In Chapter 7, discussion is made for investigation of oxygen evolution on titanium. Micro-electrochemistry using the SECM apparatus is employed to investigate active dissolution, passivation, and trans-passive dissolution of iron in Chapter 8. In Chapter 9, SECM is also used to measure hydrogen generation from magnetite during galvanic coupling with carbon steel. Current efficiency of hydrogen generation for the cathodic reaction during galvanic corrosion of carbon steel is estimated. In these chapters, the products from the specimen electrode surface can be detected with probe electrodes of SECM amperometrically. Chapter 10 introduces the LPIG technique, which realizes local generation of chloride ions. Development and applications of LPIG to local breakdown of passive film formed on iron are reported.

Chapter 11 is the summary of this thesis.

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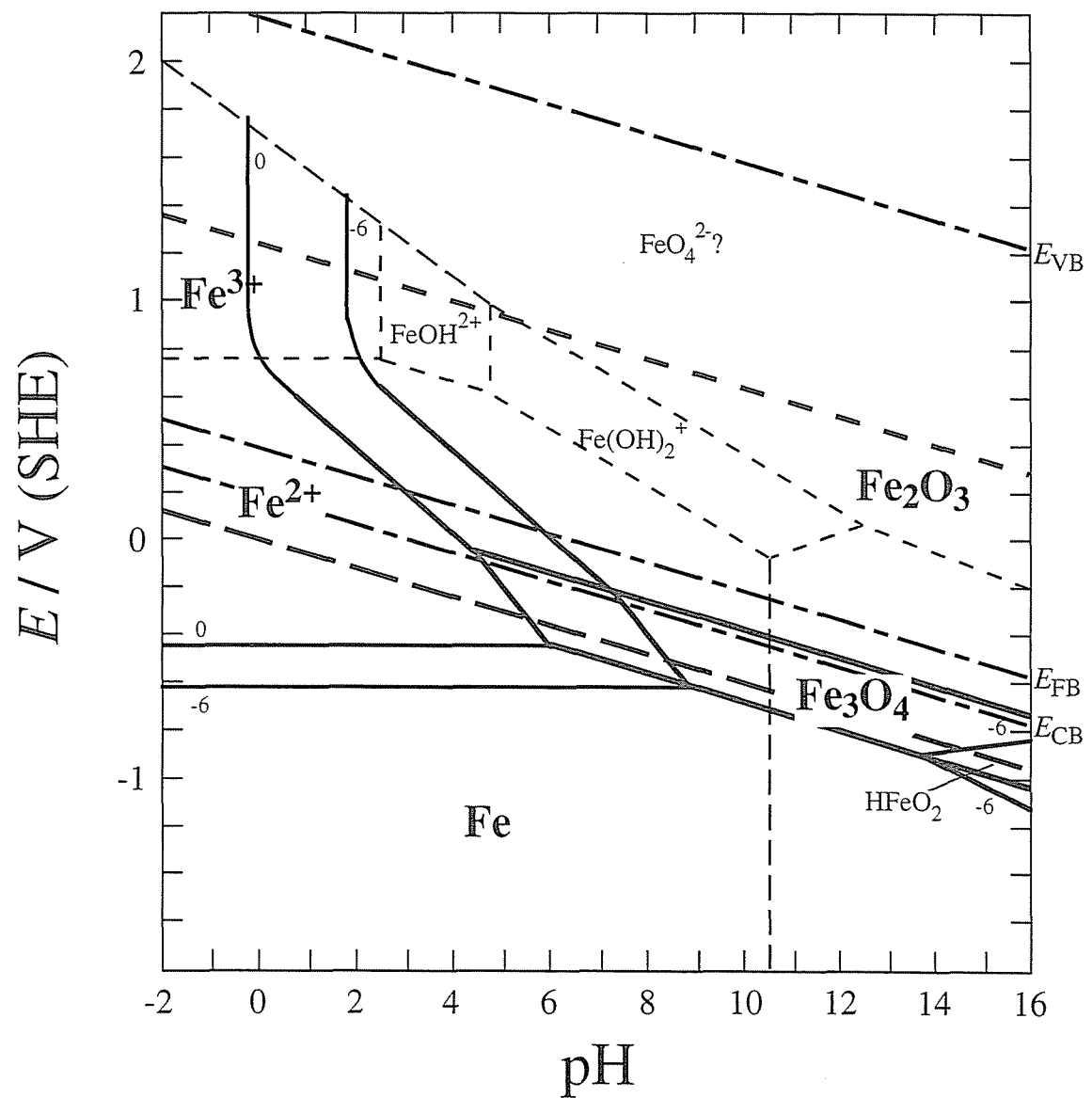


Fig. 1.2.1 Potential-pH diagram for the iron-water system at 298 K.

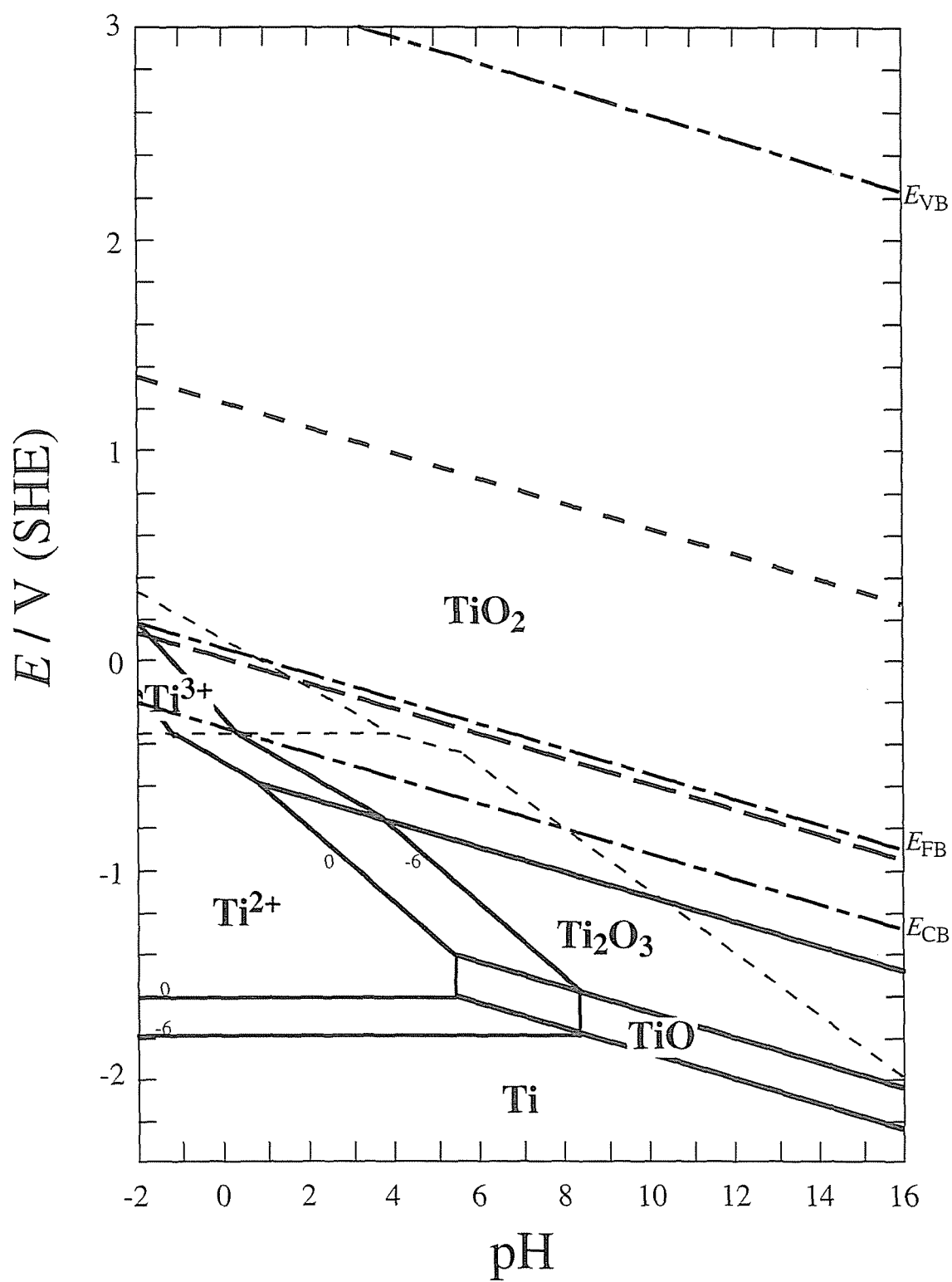


Fig. 1.2.2 Potential-pH diagram for the titanium-water system at 298 K.

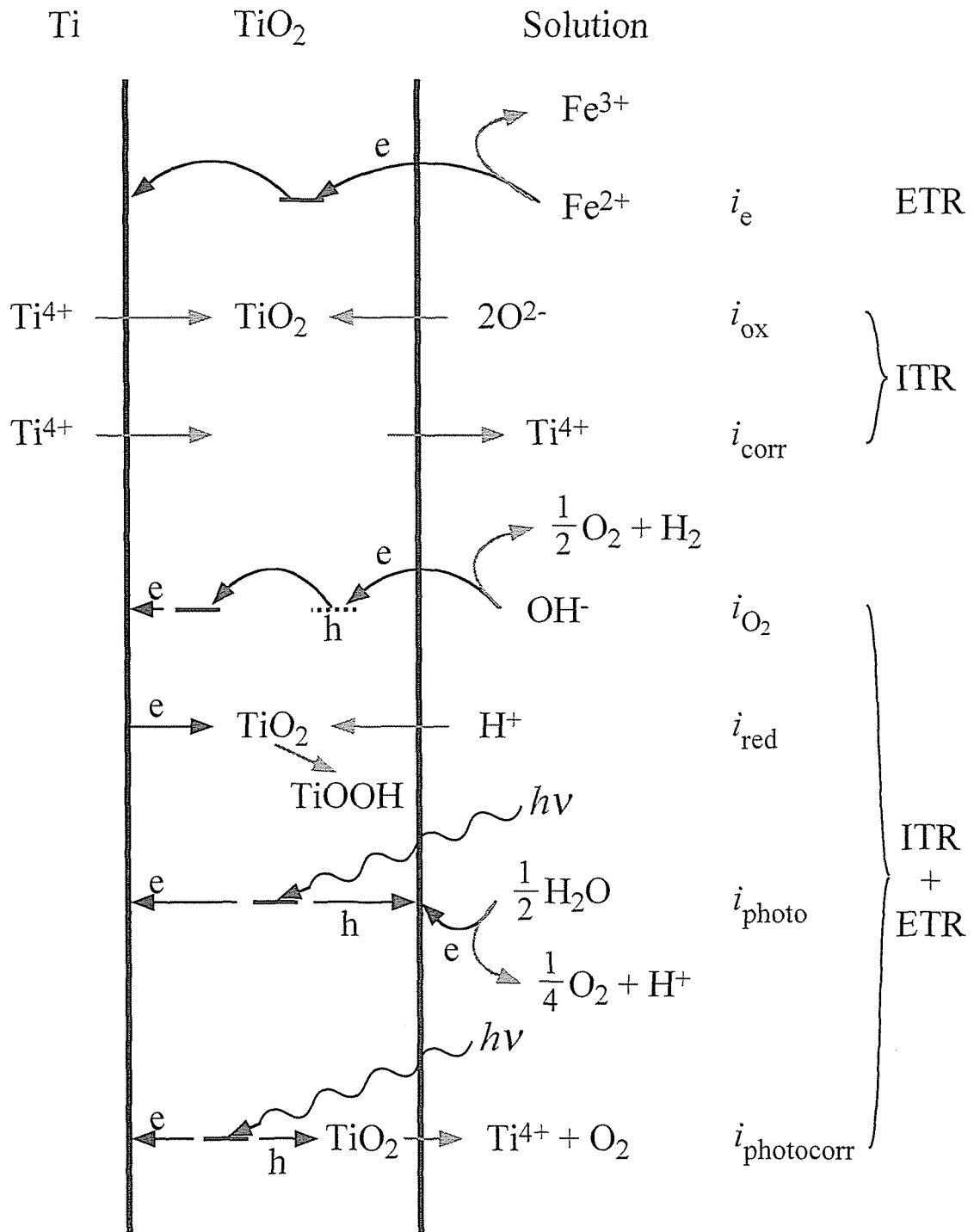


Fig. 1.2.3 Reaction processes at the Ti/TiO₂ film/solution system.

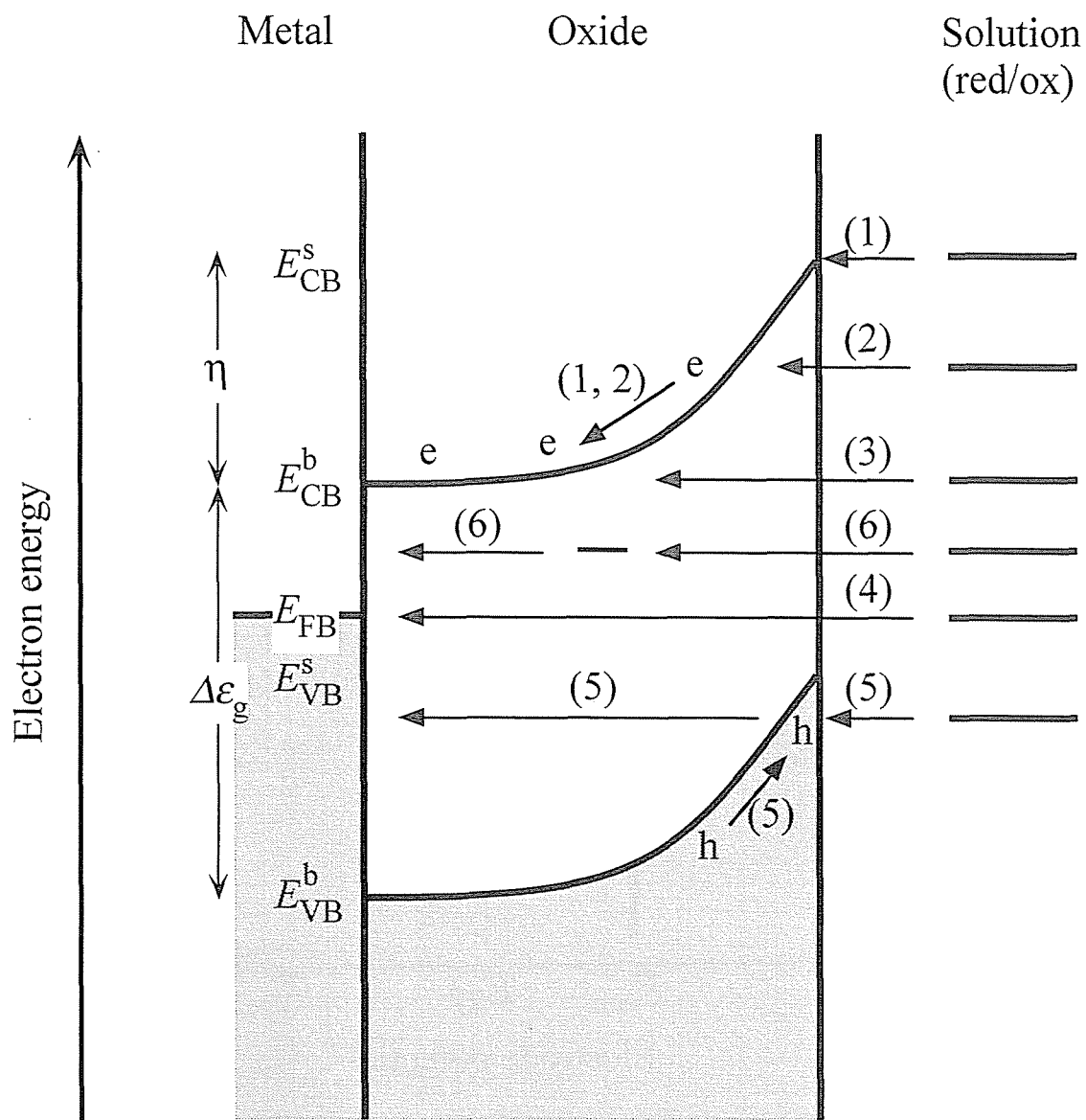


Fig. 1.2.4 Mechanism of electron transfer from redox system in solution to metal through oxide.

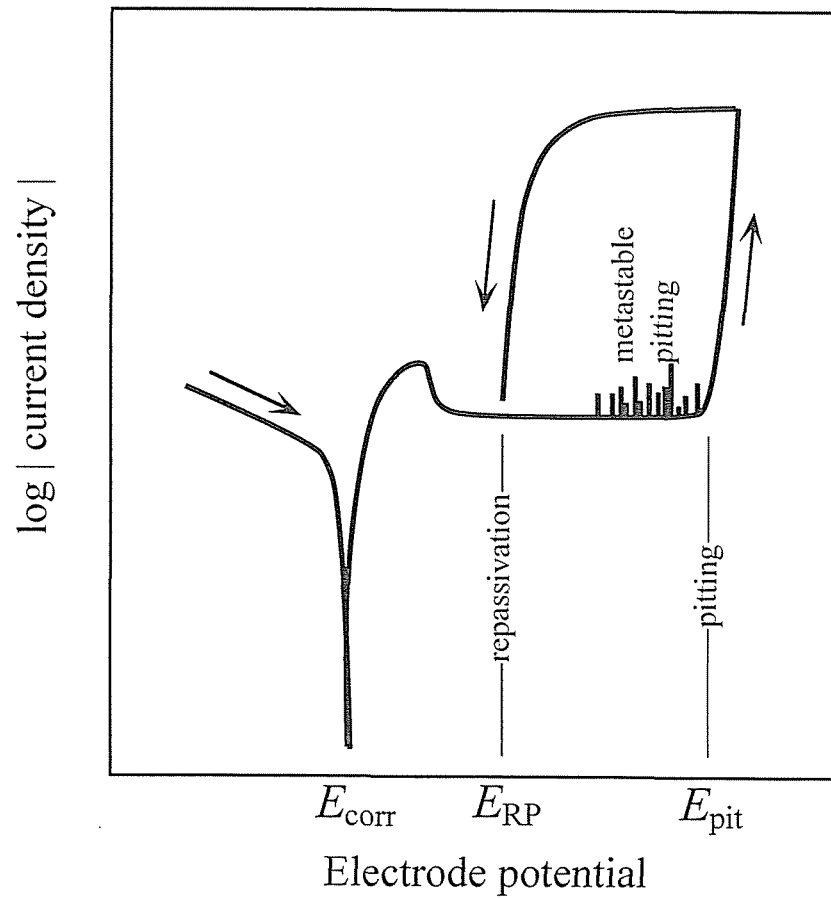


Fig. 1.3.1 Schematic diagram of potentiodynamic polarization curve of a spontaneously passive metal that is susceptible to pitting corrosion.

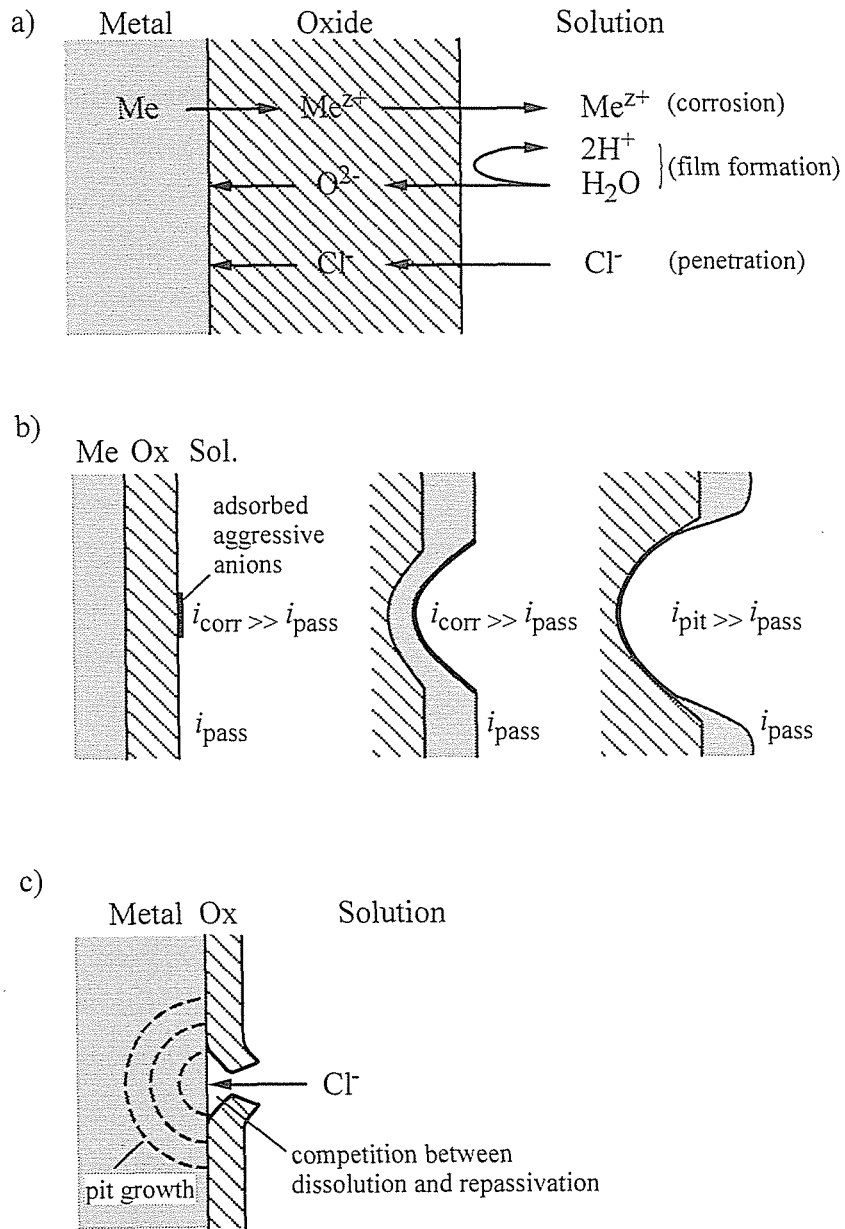


Fig. 1.3.2 Model of a passive metal surface for the processes leading to pit nucleation by a) penetration, b) adsorption, and c) film breaking mechanisms. (Strehblow 1976)

2 Microelectrodes

Microelectrodes, defined as electrodes of micrometer or smaller dimensions, have received considerable attention since the late 1970's in investigations by electroanalytical chemists. Although these small electrodes are inconvenient to generate large amounts of material, it is clear that their small size should make them useful to probe chemical composition of electroactive species in small spaces. Indeed, use of microelectrodes in amperometric measurement has been motivated by the need of very small electrode for *in vivo* biological studies (Davies 1942). The following features and benefits of microelectrodes (Aoki 1998) make these tools useful to improve quality of traditional electrochemical measurements.

- (a) convenience in obtaining a steady-state current or semi steady-state current
- (b) less contribution for charging current
- (c) high sensitivity and rapid response of measurement
- (d) ability to measure chemical or electrochemical reaction rates under the steady-state
- (e) usability in solvents with low polarity or in solvents containing less electrolyte
- (f) capability to measure electrochemical reactions of an electrolyte itself
- (g) facility to monitor local events of electroactive species
- (h) induction of electrochemical interaction by combination of microelectrodes

Depending on experimental conditions, these features include improved temporal resolution of chemical and electrochemical reactions, much greater fluxes under diffusion-controlled conditions, and the possibility of allowing investigation of electrochemical processes in environments of high resistance. These advantages have made use of microelectrodes widespread to the extent up to today, use of micro-voltammetric electrodes is indeed ubiquitous among electrodes. Properties of microelectrodes cause them to be useful for high-speed applications and in resistive solvents. Steadily, microelectrodes have become more important tools for electrochemists.

Microelectrodes have been constructed in a number of different geometries, including inlaid disks, cylinders, and hemispheres, as well as inlaid bands and arrays. For any geometry, microelectrode fabrication is nontrivial, involving micromanipulation techniques and/or some lithographic methods used in fabrication of integrated circuits. Wightman described some of these methods and provided references to the literature (Wightman 1989). Furthermore, Baer described improved methods for construction of microdisk electrodes (Baer 1988). By far the most common geometry has been the inlaid disk; most electrochemists will confine their

attention to such electrodes. Preparation of a microdisk electrode, which is employed in this thesis, will be described in 4.1.

Use of microelectrodes mounted on micropositioners allows local concentration of electroactive species to be mapped in two dimensions. In this type of experiment, referred as scanning electrochemical microscopy (SECM), the microelectrode as a probe is scanned repeatedly across a sample surface while it is kept at a constant height above the sample (Engstrom 1986, Bard 1989, 1991). Current flowing through the microelectrode at each location is plotted against its x - y coordinate. In this way, a three-dimensional image that shows a distribution of local concentrations of electroactive species is obtained. This technique has been used to examine chemical or electrochemical distribution at the surface of biological samples or minerals, and it can be used even to map local electrochemical events at electrode surfaces.

This chapter first considers the diffusion problem in the context of potential-step experiments and then describes several advantages of microelectrodes in electrochemical experiments. The most beneficial use of a microelectrode as a probe for SECM will be discussed in the next chapter.

2.1 Diffusion operator

A reaction occurring at the surface of the electrode produces a concentration gradient in solution in the vicinity of the electrode which in turn gives rise to a diffusional flux of molecules. The diffusionally induced rate of change of concentration in solution is described by Fick's second law,

$$\frac{\partial c}{\partial t} = D \nabla^2 c, \quad [2.1.1]$$

where c and D are concentration and diffusion coefficients of diffusing species, respectively, t is time, and ∇^2 is the so-called Laplacian diffusion operator. The diffusion operator takes on different forms for each diffusion geometry such that Fick's second law has a unique solution for each electrode geometry. Finite element diagrams are used to explain nonlinear diffusion processes that take place at any electrode.

Consider the series of volume elements shown in Figure 2.1.1, which explains the terminology that will be used. Changes in concentration, c_j , must be estimated in any given volume element, j , with respect to diffusion time. The concentration change in any given volume element, j , will be due to a flux across interfaces between neighboring volume elements, $j-1$ and $j+1$, and can be expressed by

$$\frac{\Delta c}{\Delta t} = \frac{1}{V_j} \left[DA_{j+1} \frac{(c_{j+1} - c_j)}{\Delta x} - DA_j \frac{(c_j - c_{j-1})}{\Delta x} \right], \quad [2.1.2]$$

which takes the difference in the flux in mol s⁻¹ across each interface, and is divided by the volume of the element, V_j , to give desired units of concentration per time, mol dm⁻³ s⁻¹. For the case of planar diffusion $A_j = A_{j+1} = A$ and $V_j = A\Delta x$. Therefore, Equation 2.1.2 becomes

$$\frac{\Delta c}{\Delta t} = \frac{D}{\Delta x^2} (c_{j+1} - 2c_j + c_{j-1}), \quad [2.1.3]$$

which is the finite element form of Fick's second law for planar diffusion:

$$\frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial x^2}. \quad [2.1.4]$$

To derive Fick's second law for cylindrical and spherical geometries, one follows the same procedure using appropriate entries in Figure 2.1.1 for A_j , A_{j+1} , and V_j . In both cases, one must consider radial distance from the electrode center, r , in spite of x . For example, for cylindrical geometry,

$$\frac{\Delta c}{\Delta t} = \frac{2D}{\Delta r^2 (2j-1)} \left[j(c_{j+1} - c_j) - (j-1)(c_j - c_{j-1}) \right], \quad [2.1.5]$$

which can be rearranged to give

$$\frac{\Delta c}{\Delta t} = D \left[\frac{c_{j+1} - 2c_j + c_{j-1}}{\Delta r^2} - \frac{1}{\Delta r \left(j - \frac{1}{2} \right)} \frac{c_{j+1} - c_{j-1}}{2\Delta r} \right], \quad [2.1.6]$$

which is the finite element form of Fick's second law for cylindrical geometry,

$$\frac{\partial c}{\partial t} = D \left(\frac{\partial^2 c}{\partial r^2} + \frac{1}{r} \frac{\partial c}{\partial r} \right). \quad [2.1.7]$$

Fick's second law for spherical geometry, generated in identical fashion, is as follows.

$$\frac{\partial c}{\partial t} = D \left(\frac{\partial^2 c}{\partial r^2} + \frac{2}{r} \frac{\partial c}{\partial r} \right) \quad [2.1.8]$$

The appropriate form of Fick's second law is solved, subject to boundary conditions that describe a given experiment, to provide concentration profile information. The current-time or current-potential relationship is then obtained by evaluating flux at the electrode surface. The solution of the second-order differential equation, Equation 2.1.4, under the following boundary conditions, will give the diffusion-limited current, I_{limit} , and the concentration profile $c(x,t)$ for a macro-planar electrode (Bard 1980).

$$c(x, 0) = c^* \quad [2.1.9]$$

$$c(\infty, t) = c^* \quad [2.1.10]$$

$$c(0, t) = 0 \quad [2.1.11]$$

After Laplace transformation of Equation 2.1.4, application of conditions Equation 2.1.9 and Equation 2.1.10 yields

$$\bar{c}(x, s) = \frac{c^*}{s} + A(s) \exp\left(-\sqrt{\frac{s}{D}}x\right). \quad [2.1.12]$$

By applying the surface condition of Equation 2.1.11, the function $A(s)$ can be evaluated, and then $\bar{c}(x, s)$ can be inverted to obtain the concentration profile for diffusing species.

Transforming Equation 2.1.11 gives

$$\bar{c}(0, s) = 0, \quad [2.1.13]$$

which implies that

$$\bar{c}(x, s) = \frac{c^*}{s} \left[1 - \exp\left(-\sqrt{\frac{s}{D}}x\right) \right]. \quad [2.1.14]$$

The flux at the electrode surface is proportional to the current; specifically,

$$-J(0, t) = \frac{I(t)}{nFA} = D \left[\frac{\partial c(x, t)}{\partial x} \right]_{x=0}, \quad [2.1.15]$$

which is transformed to

$$\frac{\bar{I}(s)}{nFA} = D \left[\frac{\partial \bar{c}(x, s)}{\partial x} \right]_{x=0}. \quad [2.1.16]$$

The derivative in Equation 2.1.16 can be evaluated from Equation 2.1.14. Substitution yields

$$\bar{I}(s) = nFAc^* \sqrt{\frac{D}{s}} \quad [2.1.17]$$

and inversion produces the current-time response

$$I(t) = I_{\text{limit}}(t) = nFAc^* \sqrt{\frac{D}{\pi t}}, \quad [2.1.18]$$

which is known as the Cottrell equation (Cottrell 1902). Furthermore, inversion of Equation 2.1.12 yields

$$c(x, t) = c^* \operatorname{erf}\left(\frac{x}{2\sqrt{Dt}}\right). \quad [2.1.19]$$

In addition, under the steady-state conditions of Equation 2.1.4, the derivative of concentration

with time must be zero. Thus the differential in Equation 2.1.4 can be approximated in a linear fashion by

$$\frac{I_{\text{limit}}}{nFA} = \frac{D\{c^* - c(x)\}}{\delta}, \quad [2.1.20]$$

where δ is a thickness of diffusion layer.

2.2 Diffusion to micro-hemispherical and micro-disk electrodes

Diffusion of molecules to microelectrodes is identical to diffusion to macroelectrodes. However, planar, cylindrical, and spherical forms of Fick's second law, and combinations of those forms, are sufficient to describe diffusion to most microelectrode geometries. For the purpose of considering diffusion at microelectrodes, there are two categories of electrodes: i) diffusion occurs in a linear fashion and ii) diffusion occurs in a nonlinear fashion. The category i) consists of cylindrical and spherical electrodes. Since lines of flux (i.e., the pathway followed by material diffusing to the electrode) are straight, current density is the same at all points on the electrode. Thus, the diffusion problem is one-dimensional (i.e., distance from the electrode surface) and involves solution of the appropriate form of Fick's second law, Equation 2.1.7 or 2.1.8, either by Laplace transform methods as described in 2.1, or by digital simulation.

The potential-step experiment (i.e., chronoamperometry) at a micro-hemispherical electrode (e.g., a hanging mercury drop) illustrates consequences of diffusion geometry on the electrochemical response. In this case, Fick's second law expressed by Equation 2.1.8 is also adapted for diffusion of molecules. For an electrode with radius a , the following boundary conditions are given:

$$\text{at } a < r, \quad c(r, 0) = c^*, \quad [2.2.1]$$

$$c(\infty, t) = c^*, \quad [2.2.2]$$

$$c(a, t) = 0. \quad [2.2.3]$$

The substitution, $v(r, t) = rc(r, t)$, converts Equation 2.1.8 into an equation having similar form to the planar problem (Bard 1980).

$$\frac{\partial v}{\partial t} = D \frac{\partial^2 v}{\partial r^2} \quad [2.2.4]$$

Solution of Equation 2.2.4 with boundary conditions, Equations 2.1.1-3, gives the expression

for the concentration profile:

$$c(r, t) = c^* \left(1 - \frac{a}{r} \right) \operatorname{erfc} \left(\frac{r - a}{2\sqrt{Dt}} \right). \quad [2.2.5]$$

For long experimental time, then

$$c(r, \infty) = c^* \left(1 - \frac{a}{r} \right). \quad [2.2.6]$$

On the other hand, diffusion-limited current is given by the following expression:

$$I_{\text{limit}}(t) = nFADc^* \left(\frac{1}{\sqrt{\pi Dt}} + \frac{1}{a} \right), \quad [2.2.7]$$

where the first term is identical to the Cottrell equation, Equation 2.1.18, for macro-planar electrodes and the second is a time-independent term and sometimes referred as the “spherical correction”. Thus, one consequence of spherical geometry is that at long experimental time, the current approaches a nonzero steady-state value of

$$I_{\text{limit}} = \frac{nFADc^*}{a} = 2\pi nFDc^* a. \quad [2.2.8]$$

Fabrication of microelectrodes with the geometry of a disk embedded in an infinite insulating plane is easier to accomplish than forming spherical or hemispherical microelectrodes. The micro-disk electrode belongs to the category ii) at which nonlinear diffusion takes place. Lines of flux to a disk electrode do not coincide with simple geometries for which Fick’s second laws are derived as Equations 2.1.4, 7, and 8. Therefore, the diffusion problem must be expressed in two dimensions. Note that a line passing through the disk center and normal to the disk plane is a cylindrical axis of symmetry, so it is sensible to choose radial distance from this axis as one coordinate for the problem. Diffusion along this radial coordinate, r , is described by Equation 2.1.7. Also, diffusion along the coordinate, x , normal to the plane of the electrode, is described by Equation 2.1.4. Thus, the form of Fick’s second law which must be solved for a disk is

$$\frac{\partial c}{\partial t} = D \left(\frac{\partial^2 c}{\partial x^2} + \frac{1}{r} \frac{\partial c}{\partial r} + \frac{\partial^2 c}{\partial r^2} \right). \quad [2.2.9]$$

Several mathematical approaches to solving Equation 2.2.9 have been reported (Aoki 1981, Michael 1989, Mirkin 1992). Boundary conditions imposed by the electrode geometry are

$$\text{at } x = \infty \text{ or } 0 \leq x, \quad r = \infty, \quad c(x, r, t) = c^*, \quad [2.2.10]$$

$$\text{at } x = 0 \text{ and } 0 \leq r \leq a, \quad c(x, r, t) = 0, \quad [2.2.11]$$

$$\text{and at } x = 0 \text{ and } a < r, \quad \frac{\partial c}{\partial x} = 0. \quad [2.2.12]$$

The problem is closely analogous to the spherical diffusion case, but the equations are complex and a closed-form solution is impossible. Solutions in the form of integral equations are possible, but not very enlightening (Oldham 1991).

Saito (Saito 1968) was first to give clear insight into the steady-state nature of current at disk electrodes using a cylindrical coordinate system, resulting in diffusion-limited current.

$$I_{\text{limit}} = 4nFDc^*a \quad [2.2.13]$$

The diffusion-layer profile under steady-state conditions is given in Figure 2.2.1 and seen to be of a form similar to that for a spherical electrode. In fact, Equations 2.2.13 and 2.2.8 are identical when disk radius is equal to $\pi/2$ times that of a hemisphere as noted by Oldham (Oldham 1981). In addition, diffusion layer thickness of a disk can be shown, through combination of Equations 2.2.13 and 2.1.20, to be

$$\delta = \frac{\pi a}{4}. \quad [2.2.14]$$

On the other hand, Shoup (Shoup 1982) found the potential-step limiting current for a disk electrode inlaid in an infinitely large and coplanar insulator,

$$\frac{I_{\text{limit}}}{4nFDc^*a} = 0.7854 + \frac{0.8862}{\tau} + 0.2146 \exp\left(-\frac{0.7823}{\tau}\right), \quad [2.2.15]$$

where $\tau = \frac{2\sqrt{Dt}}{a}$. As time approaches infinity, Equation 2.2.15 coincides with Equation 2.2.13.

Furthermore Shoup (Shoup 1984) reported influence of insulation geometry on the limiting current at a disk electrode inlaid in a finite insulating plane with a radius of r^* ,

$$f(\tau^2, \rho_i) = \frac{I}{4nFDc^*a} = \frac{\pi}{2a} \int_0^a \left(\frac{\partial c}{\partial x} \right)_{x=0} r dr, \quad [2.2.16]$$

where an insulating coordinate, $\rho_i = a/r^*$, varies from 1 to 0 with increasing r^* as shown in Figure 2.2.1. $f(\tau^2, \rho_i)$ for long experimental time is changed from 1.0 to 1.4 decreasing with ρ_i . For an infinite insulating plane, then, Equation 2.2.16 coincides with Equation 2.2.13.

2.3 Applications of microelectrodes

Very small currents at microelectrodes have several experimental implications. small currents require more sophisticated current-measuring equipment. However, the reason for using a three-electrode cell controlled by a potentiostat largely disappears when microelectrodes are used. Reference electrodes can easily handle currents up to a few nanoamperes without

significant polarization so that most steady-state microelectrode experiments can be done using a two-electrode configuration.

Solution iR drop is a less serious problem than in experiments with conventional electrodes. Since the current is much smaller, larger solution resistivities can be tolerated; thus supporting electrolyte concentrations can be reduced or nonpolar solvents can be used. When current flows between a very small electrode and a large remote electrode, resistance is determined by size of the small electrode and can be shown to be (Newman 1970)

$$R = \frac{\rho_s}{4a}, \quad [2.3.1]$$

where ρ_s is solution resistivity. For a microelectrode in steady-state conditions, diffusion-limited current, I_{limit} , is proportional to the microelectrode radius, so that ohmic potential drop reaches a minimum independent of electrode size.

$$I_{\text{limit}} R = nFDc^* \rho_s \quad [2.3.2]$$

Furthermore, Oldham has shown (Oldham 1987) that $I_{\text{limit}} R$ drop is also independent of electrode geometry. For a one-electron process with $c^* = 1 \text{ mol m}^{-3}$, $D = 10^{-9} \text{ m}^2 \text{ s}^{-1}$, $\rho_s = 1 \text{ } \Omega \text{ m}$, the ohmic drop is about 0.1 mV.

Another important consequence of decreased area is a much smaller contribution of capacitive charging current. In a potential-step experiment, the capacitive charging current is a transient response,

$$I_c = \frac{\Delta\phi}{R} \exp\left(-\frac{t}{RC_d}\right), \quad [2.3.3]$$

where $\Delta\phi$ is the potential step, C_d is the double layer capacitance, and R is solution resistance. Since C_d is proportional to electrode surface area, the time constant for capacitive current decay, RC_d , decreases with electrode size so that the charging current transient is quite short-lived for smaller electrodes. The accessible time scale is therefore much shorter for microelectrodes.

Attainment of a steady-state current, together with removal of interference from ohmic potential drop and capacitive charging current, make potential-step measurement a more accurate and easily applied analytical technique when microelectrodes are used. Note that the steady-state flux of the diffusive species to microelectrodes of the order Dc^*/a , can be rather large for microelectrodes and increases as electrode diameter decreases. Indeed, this flux is frequently larger than the convective flux for a rotating disk electrode or an electrode in a stirred solution. This means that measurements at a microelectrode are relatively immune to stirring or other convective effects.

Consider the case where a one-electrode reaction takes place so rapidly at the

stationary microdisk electrode that the Nernst equation holds at the electrode surface. When the electrode potential, E , is swept linearly, the sigmoid shape of the voltammogram can be derived (Aoki 1984). Current on the forward scan is given as

$$I = \frac{4nFDc^*a}{1 + \exp\left\{-\frac{nF}{RT}(E^{0'} - E)\right\}}, \quad [2.3.4]$$

where $E^{0'}$ is a formal potential of the electrode. In addition, it was shown that the current on the rising part of the voltammetric wave follows the expression:

$$E = E_{1/2} + \frac{RT}{nF} \ln\left(\frac{I_{\text{limit}} - I}{I}\right) \quad [2.3.5]$$

Use of microelectrodes mounted on micropositioners allows local concentration of electroactive substances to be mapped in two dimensions. This type of experiment, referred as scanning electrochemical microscopy (SECM), has been described recently (Engstrom 1989, Bard 1989, 1991) as a new method for imaging surfaces in solution. Note that the specimen and probe form part of an electrochemical cell together with reference and counter electrodes. The microelectrode is repetitively scanned as a probe electrode across a specimen electrode surface while it is kept at a constant height above the sample. Current at each location is plotted against its x - y coordinate. In this way, a three-dimensional image showing local concentrations is produced. This technique has been used to examine chemical heterogeneity at the surface of biological samples or minerals; it can even be used to map local electrochemical events at surfaces of larger electrodes. The next chapter is concerned with instrumentation, principles, theories, and applications of SECM.

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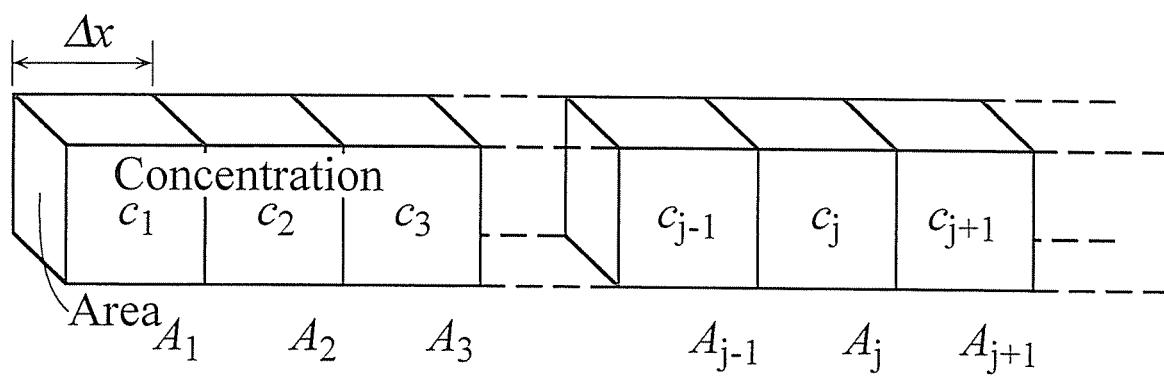


Fig. 2.1.1 Volume elements of the solution adjacent to an electrode.

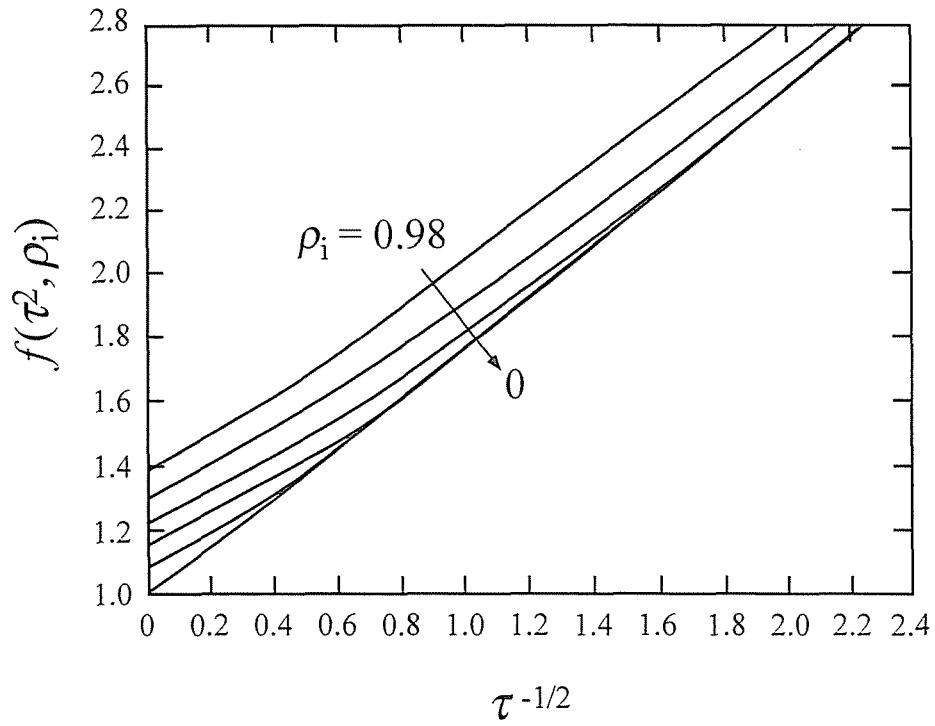


Fig. 2.2.1 Dimensionless current versus $\tau^{-1/2}$ at $\rho_i = 0.98$, 0.91, 0.80, 0.67, 0.50, and 0 (i.e. the disk in an infinite insulating plane). (Shoup 1984)

3 Scanning electrochemical microscopy (SECM)

Scanning electrochemical microscopy (SECM) has been developed (Engstrom 1989, Bard 1989, 1991) as an imaging tool for electrode surfaces in solution. Note that both probe and specimen form parts of an electrochemical cell together with reference and counter electrodes. The probe electrode detects Faradaic current at each local surface where an electrochemical or chemical reaction takes place. When the probe electrode is repeatedly scanned across the surface of a specimen electrode in x - y directions while kept at a constant height above the specimen, probe current at each location gives a three-dimensional image that shows distribution of electrochemical active species originating from the specimen surface. Furthermore, the probe electrode can be used to induce local electrochemical or chemical reactions due to generation of aggressive species toward the specimen surface. This chapter describes SECM: its instrumentation, principles, theories, and applications.

3.1 Basic apparatus of SECM

The SECM instrument consists basically of a combination of electrochemical and probe manipulation systems for acquiring high resolution data. A block diagram of general apparatus used for SECM experiments is shown in Figure 3.1.1. Apparatus consists of three major components.

- a) an electrochemical cell, in which four electrodes (specimen, probe, counter, and reference electrodes) are immersed into an electrolyte solution, slaved with a bipotentiostat with one or two potential programmers
- b) a series of movements and their controller which drives the probe electrode in x , y , and z directions
- c) a computer with a display system and interfaces for the above two components

Probe and specimen electrodes are controlled electrochemically as working electrodes by a bipotentiostat or two potentiostats. In cases using two potentiostats, each working electrode needs a counter electrode and a reference electrode, and a differential amplifier may be needed to prevent oscillation between two inside-electrical circuits. The bipotentiostat, otherwise, has a differential amplifier inside and can control independently potentials of two working electrodes versus a referential electrode during flowing currents between two working electrodes and a

counter electrode. In any cases, probe and specimen electrodes must be separated to hold potentials at E_p and E_s independently; currents, I_p and I_s , flowing through the probe and specimen electrodes, are monitored. Electrolyte solution filled into the electrochemical cell, in general, contains a mediator suitable to monitor desired response from the specimen surface. The probe electrode is also chosen for each experiment. The typical probe electrode is a microdisk electrode composed of noble metal, such as Pt, with a diameter of less than 10 μm . In 4.1, probe electrode manufacturing details will be explained. The probe electrode is generally mounted on the x - y - z positioning stages driven by their controller. Furthermore, either the probe or specimen electrode is often tilted in the θ_x and θ_y directions in order to maintain an electrode gap. These SECM instruments are controlled by a computer with interfaces which are used to acquire electrochemical signals (E_p , E_s , I_p , and I_s) and to control x - y - z - θ_x - θ_y probe electrode movements.

3.2 Principles of SECM

To understand SECM operation and response, behavior of a microelectrode is the most important because it is employed as a scanning probe in the SECM electrochemical cell. Consider a simple electrode reaction which is induced to occur at the microdisk electrode,



The species A is present in the solution in which specimen and probe electrodes are immersed and the probe electrode potential is held at a value that induces diffusion-limited conversion of species A to species B. If the probe electrode is located in the bulk solution sufficiently far from the specimen surface, current flowing through the probe electrode rapidly establishes a steady-state value expressed by Equation 2.2.13 (see Fig. 3.2.1a). In SECM, the probe electrode, which is a disk-shaped microelectrode, is close to the specimen surface within a few dimension of probe electrode diameter. As the probe electrode approaches the specimen surface, the concentration profile of species A around the probe tip is spatially perturbed by the specimen surface and observed current is altered from the unperturbed value. This probe current perturbation by the distance between probe and specimen electrodes constitutes SECM response.

Technique for using SECM can be used to investigate both conductive and insulating specimen surfaces. In the case of an insulating surface, when the probe electrode approaches the surface, reactant diffusion to the probe electrode is partially blocked by the surface and decreased current is detected at the probe electrode compared with the unperturbed value. This

effect is termed 'negative feedback' and is shown schematically in Figure 3.2.1b. On the other hand, when the probe electrode is close to a conducting surface, at which any species of B reaching to the surface are electrochemically transformed to species of A, a flux of A from the specimen surface to the probe electrode occurs in addition to some flux of A from the bulk solution to the probe electrode. Consequently, more of species A are produced than for the corresponding situation in bulk solution and probe current increases. This is termed 'positive feedback' and is also shown schematically in Figure 3.2.1c. Thus, probe current magnitude is governed by the electrochemical nature of the specimen surface and by distance between both electrodes. By scanning the probe electrode over the specimen surface at a constant gap and simultaneously recording probe current, a topographical image of the specimen surface can be obtained. The actual situation can be somewhat more complicated than the limited cases described above when the reaction rate on the specimen is governed by the rate of heterogeneous electron transfer kinetics rather than the rate of mass transfer.

In addition to amperometric feedback mode described above, other SECM modes of operation are possible. For example, in the substrate generation/tip collection (SG/TC) mode, current flowed through the probe electrode is used to monitor flux of electroactive species from the specimen surface. If the specimen is an electrode, this flux is generated by current flow at the specimen electrode, so the ratio of the probe and specimen currents, I_p/I_s , represents the probe collection efficiency. Alternatively, the specimen electrode can collect flux from the probe electrode.

As SECM techniques may be used with a wide range of electroactive species, it is possible to choose materials that may interact with the surface. The technique can therefore also be used to investigate chemical properties of the specimen surface. For example, species A may be capable of reacting at the specimen surface, depleting concentration of A near the probe electrode. A drop in measured current can then be interrogated to ascertain the nature of reaction taking place on the specimen surface.

3.3 Theories of SECM

Availability of well-developed quantitative theory covering various regimes of measurements and electrochemical mechanisms is a significant advantage of SECM. The different operating modes of SECM, such as feedback and generation/collection (G/C) modes, and steady-state and transient measurements, each require significantly different theoretical

descriptions. Quantitative treatments are available for both diffusion-controlled processes and finite kinetics as well as for more complicated mechanisms involving adsorption and homogeneous reactions in the electrodes-gap (Bard 1994). Most of reported theoretical results concern an SECM with a disk-shaped probe electrode. Other probe geometries are omitted from discussion here.

3.3.1 SECM in the feedback mode

Considerable complexity of SECM theory is due to cylindrical diffusion to the probe microelectrode and a thin layer-type diffusion space. The geometry shown in Figure 3.3.1 suggests a time-dependent diffusion problem for a simple quasi-reversible mediator in cylindrical coordinates as follows (Mirkin 1992):

at $0 < t$, $0 \leq r$, and $0 < z < d$,

$$\frac{\partial c_O}{\partial t} = D \left(\frac{\partial^2 c_O}{\partial x^2} + \frac{1}{r} \frac{\partial c_O}{\partial r} + \frac{\partial^2 c_O}{\partial z^2} \right) \text{ and } \frac{\partial c_R}{\partial t} = D \left(\frac{\partial^2 c_R}{\partial x^2} + \frac{1}{r} \frac{\partial c_R}{\partial r} + \frac{\partial^2 c_R}{\partial z^2} \right); \quad [3.3.1]$$

$$\text{at } t = 0, 0 \leq r, \text{ and } 0 < z < d, c_O(t, r, z) = c_O^* \text{ and } c_R(t, r, z) = 0; \quad [3.3.2]$$

$$\text{at } 0 < t, 0 \leq r, \text{ and } z = 0, j_p(t, r) = D_O \left(\frac{\partial c_O}{\partial z} \right)_{z=0} = -D_R \left(\frac{\partial c_R}{\partial z} \right)_{z=0}; \quad [3.3.3]$$

$$\text{at } 0 < t, 0 \leq r, \text{ and } z = d, j_s(t, r) = -D_O \left(\frac{\partial c_O}{\partial z} \right)_{z=d} = D_R \left(\frac{\partial c_R}{\partial z} \right)_{z=d} \quad [3.3.4]$$

$$I_p(t) = 2\pi nF \int_0^a j_p(t, r) r dr \text{ and } I_s(t) = 2\pi nF \int_0^r j_s(t, r) r dr, \quad [3.3.5]$$

where r and z are respective spatial variables for radius direction and normal to electrode-surface, t is time, a and r_s are respective radii of the probe and specimen electrodes, d is distance between probe and specimen electrodes, $c(t, r, z)$ is concentration of electroactive species, c^* is its bulk value, D is the diffusion coefficient, j is the diffusion flux, and I is the total Faradaic current. The subscript, O , relates to the oxidized form and R to reduced form; subscripts p and s refer to probe and specimen electrodes, respectively. Faradaic current is expressed as:

$$I = nFj(t, r, 0) = nF \{ k_f c_O(t, r, 0) - k_b c_R(t, r, 0) \}; \quad [3.3.6]$$

$$\text{at } a < r, j_p(t, r, 0) = 0; \quad [3.3.7]$$

$$\text{and at } r_s < r, j_s(t, r, 0) = 0. \quad [3.3.8]$$

If the specimen is an insulator,

$$j_s \equiv 0. \quad [3.3.9]$$

Rate constants for oxidation, k_b , and reduction, k_f , at probe and specimen electrodes are given by Butler-Volmer equations (Bard 1980)

$$k_f = k^0 \exp\left\{-\frac{\alpha n F}{RT}(E - E^{0'})\right\} \quad [3.3.10]$$

$$k_b = k^0 \exp\left\{\frac{(1-\alpha)nF}{RT}(E - E^{0'})\right\}, \quad [3.3.11]$$

where k^0 is the standard rate constant, E is the electrode potential, $E^{0'}$ is the formal potential, and α is the transfer coefficient.

Above formulation implies that the overall process is confined to the thin layer of solution between the probe electrode with its insulating sheath and the specimen electrode. This is an approximation because the insulating sheath surrounding the probe electrode is not infinitely thick and the condition

$$\text{At } r^* < r, \quad c_O(t, r, z) = c_O^* \text{ and } c_R(t, r, z) = 0 \quad [3.3.12]$$

can be used to account for the finite value of the sheath radius, r^* . However, calculations (Mirkin 1992, Bard 1992) showed that differences caused by the infinite sheath approximation are negligible in the case of a conductive specimen and can be easily taken into account for an insulating one. Furthermore, actual glass sheath geometry is conical rather than cylindrical and is always imperfect. Therefore, r^* is the least reliable parameter in SECM theory and one should avoid using it in calculations.

Although the above problem can be solved for the most general case of unequal diffusion coefficients, this would require a quite cumbersome numerical or analytical treatment (Martin 1997). Most computational results reported for a non-steady-state process were obtained for $D_O = D_R$ because this leads to $c_O + c_R = c^*$ and reduces system Equation 3.2.1 to a single equation. It is convenient to use dimensionless variables:

$$\mathbf{R} = \frac{r}{a} \quad [3.3.13]$$

$$\mathbf{Z} = \frac{z}{a} \quad [3.3.14]$$

$$\mathbf{C} = 1 - \frac{c}{c_O^*} \quad [3.3.15]$$

$$\mathbf{T} = \frac{tD}{a^2} \quad [3.3.16]$$

$$\mathbf{J} = \frac{ja}{Dc_O^*} \quad [3.3.17]$$

Thus, the problem solution can be obtained in terms of dimensionless currents $I_p(T)$ and $I_s(T)$

$$I_p(T) = -\frac{\pi}{2} \int_0^1 J_p(T, R) R dR \quad [3.3.18]$$

$$I_s(T) = -\frac{\pi}{2} \int_0^{\frac{r}{a}} J_s(T, R) R dR \quad [3.3.19]$$

and $I_p(T)$ and $I_s(T)$ are equal to physical currents normalized by the diffusion-limiting current of the probe electrode given by Equation 2.2.13.

$$I = \frac{I}{I_{p,limit}} \quad [3.3.20]$$

Numerical calculation with the alternating-direction implicit (ADI) finite difference method is applied to solve the relation between the high spatial resolution required at both probe and specimen electrodes and the relatively large matrix for the solution gap between probe and specimen electrodes. A large number of volume elements and hundreds of iterations are necessary to calculate the potentiostatic transient to a steady-state value (Bard 1991.2, 1992, Unwin 1991). Analysis of simulation results (Bard 1991.2) revealed several time regions typical for SECM transients. In the short time region (less than 1 ms), an SECM transient follows closely the microdisk transient, then starts to deviate and finally levels at a constant value of I_p . For a conductive substrate, $I_p > I_{p,limit}$. The smaller the distance between probe and specimen electrodes, the earlier the deviations between SECM and microdisk transients. The deviation time is related to diffusion of species across the gap separating the probe and specimen electrodes. This time can be determined experimentally and can be used to evaluate the diffusion coefficient.

Similarly, transients computed for different rates of an irreversible heterogeneous reaction showed a microdisk-type behavior at short time (Bard 1992). Current magnitude at longer time and its eventual steady-state value are determined by the value of the dimensionless heterogeneous rate constant.

$$K_{b,s} = \frac{k_{b,s} a}{D} \quad [3.3.21]$$

A conductive specimen behaves as $K_{b,s} \rightarrow \infty$ while an insulating specimen behaves as $K_{b,s} \rightarrow 0$.

3.3.2 SECM in the generation/collection mode

In the feedback mode of SECM operation, the overall redox process is essentially confined to the thin layer between the probe and specimen electrodes. The generation/collection

mode (G/C) situation, especially when the specimen electrode is a generator and the probe electrode is a collector (SG/TC mode), is quite different since the probe electrode tip travels within a thick diffusion layer generated from the surface of the specimen electrode. Rigorous theoretical description is problematic because:

- i) the moving probe electrode stirs the diffusion layer of specimen electrode - disturbances are especially significant when the probe electrode is an amperometric sensor and has its own diffusion layer.
- ii) when the specimen electrode is huge, no steady-state can be achieved.
- iii) when the probe electrode is close to the specimen electrode, it blocks diffusion to its surface, and this screening effect is hard to take into account because of imperfect geometry of the insulating sheath of probe electrode.

The potentiometric probe electrode is a passive sensor. It does not change the concentration profile of electroactive species generated or consumed chemically or electrochemically at the surface of specimen electrode. A consistent theoretical treatment can be proposed only for a steady-state condition when a small specimen generates stable species. Concentration of such species can be measured by an ion-selective micro sensor (Horrocks 1993) as a function of probe position. The potentiometric SECM experiment yields the probe electrode potential, E_p , as a function of distance between probe and specimen electrodes. To establish a concentration distribution by SECM, one needs to use a calibration curve, which is a relation between E_p and c . A typical form of such a dependence will be obeyed in

$$E_p = E' + A \log c, \quad [3.3.22]$$

where E' is a constant and A is the experimentally determined slope equal to 0.059 V for an ideal one-electron Nernstian reaction at room temperature.

There are two significantly different G/C SECM modes of operation. The substrate generation/tip collection (SG/TC) mode as shown schematically in Figure 3.3.2a was historically the first type of SECM measurement performed (Engstrom 1986, 1987, 1988). The aim of these experiments was to probe the diffusion layer generated by the large specimen electrode using a much smaller probe electrode as an amperometric sensor. However, the following shortcomings limit SG/TC mode applicability in addition to theoretical problems listed in the beginning of this section:

- i) the process at a large specimen electrode is always non-steady state.
- ii) a large specimen current may cause significant IR -drop.
- iii) collection efficiency, the ratio of I_p/I_s , is low.

The tip generation/substrate collection (TG/SC) mode as shown in Figure 3.3.2b, on

the other hand, was found to be better (Lee 1991, Zhou 1992). The TG/SC experiment, unlike the feedback mode of SECM, includes simultaneous measurements of both current transients of probe and specimen electrodes. For uncomplicated processes at short time, current flowing through the specimen electrode is initially close to zero and grows as probe electrode current decreases as shown in Figure 3.3.3, until differences between them vanishes. At a steady state, these quantities are almost identical if $L (= d/a)$ is not very large (Lee 1991, Zhou 1992). Under these conditions, the generated species for the probe electrode predominantly diffuses to the large specimen electrode, rather than escaping from the electrode gap. For a process with a coupled chemical reaction, there are large differences between I_s and I_p , and both quantities provide important kinetic information. The TG/SC theory for a process with a second order chemical reaction was considered elsewhere (Zhou 1992). The TG/SC mode of SECM operation is certainly advisable for kinetic measurements, while SG/TC mode can be used for monitoring corrosion, enzymatic reactions, and other heterogeneous processes at the specimen surface.

3.4 Application modes

The SECM can be used in a variety of ways:

- i) as an electrochemical tool to study electrode processes and coupled homogeneous reactions
- ii) as an imaging device, i.e., microscope
- iii) for fabrication at high resolution

Details of each use are as follows.

3.4.1 *Electrochemical tool*

In applying SECM to study on electrode reactions, the x - y scanning feature is usually not used. Measurements with SECM in this mode combine many features of microelectrodes and thin layer electrochemistry (Hubbard 1970) with a number of advantages. The flux to a microelectrode spaced a distance d from a conductive specimen is of the order of Dc/d , independent of probe radius a when $d < a$. This means that very high fluxes, and thus high currents, can be obtained. Applications based on this feature to the determination of heterogeneous electron-transfer reaction rates are discussed herein.

The SECM can also serve, in the G/C mode, in the same manner as a rotating ring disk electrode (RRDE) (Albery 1971) or channel flow double electrode (CFDE) (Matsuda 1968, Aoki 1977, 1978). The SECM approach has advantages that different specimens can be

examined easily, i.e., without difficulties in fabricating RRDEs, and that higher fluxes between electrodes are available without need to rotate the electrodes or otherwise cause convection in solution. Moreover, in the TG/SC mode, collection efficiency, I_s/I_p , in absence of perturbing homogeneous chemical reactions is near unity as compared with significantly lower values in practical RRDEs and CFDEs. Finally, although transient SECM measurements are possible, most applications have involved steady-state currents which are easier to measure and are not perturbed by factors like double-layer charging and Faradic processes of adsorbed species.

It is useful to consider the tiny electrode area and gap volume probed in SECM. Consider a probe of radius $a = d/2$ spaced at a distance, d , from a conductive specimen. The SECM allows one to make quantitative electrochemical measurements in very small domains, $\pi d^3/4$, with small amounts of material, $4c/\pi d^3$. Measurements are made possible by positive feedback, which acts as a probe signal amplifier because of repeated cycling of electroactive molecules between probe and specimen electrodes. This factor also suggests that SECM may be useful in accelerated stability testing and analysis in very small volumes (Unwin 1992).

3.4.2 Imaging tool

The SECM can be employed to image surfaces of different types of specimens, both insulators and conductors, immersed in solutions. In this application, the mediator and electrolyte must be chosen to be compatible with the surface type and surface processes to be probed. For example, if a particular surface species or specimen-substrate, S_R , is to be oxidized, redox potential of mediator pair, O/R, must be more positive than that of the pair, S_O/S_R , so that the following reaction occurs spontaneously and rapidly.



Generally, mediator pairs are chosen to be those that show rapid, usually one-electron, heterogeneous reactions at the probe electrode. A wide range of suitable redox couples, which are often also used in other applications, are available for both aqueous and non-aqueous media and span a wide range of potential. Some typical couples are given in Table 3.4.1 (Bard 1994).

A particular advantage of SECM in imaging applications, compared with other types of scanning probe microscopy (SPM), is that the response observed is based on fairly rigorous theory, and hence measured current can be employed to estimate distance between probe and specimen electrodes. Resolution attainable with SECM depends upon probe radius, a . The highest resolution reported to date is of the order of 30-50 nm. It is unlikely that SECM could ever attain atomic or molecular resolution found with scanning tunneling microscopy (STM) and atomic force microscopy (AFM) due to difficulty in fabricating suitably insulated angstrom-

size SECM probes. Also, tunneling current will be preferable to SECM response when smaller

Table 3.4.1 Selected redox mediators in aqueous solution of pH 7

Mediator or redox reaction	$E_{\text{redox}} / \text{V (SHE)}$
4,4'-Dimethyl-1,1'-trimethylene-2,2'-bipyridyl	-0.69
$\text{Co(sepalchrate)}^{3+} + e^- \rightleftharpoons \text{Co(sepalchrate)}^{2+}$	-0.54
$(\text{Methyl viologen})^{2+} + e^- \rightleftharpoons (\text{Methyl viologen})^+$	-0.45
$\text{Anthraquinone-2-sulfonate} + 2e^- \rightleftharpoons \text{Hydroquinone}$	-0.22
$\text{Co(en)}_3^{3+} + e^- \rightleftharpoons \text{Co(en)}_3^{2+}$	-0.22
Methylene blue	0.01
$\text{Ru(NH}_3)_6^{3+} + e^- \rightleftharpoons \text{Ru(NH}_3)_6^{2+}$	0.05
$\text{FeEDTA}^- + e^- \rightleftharpoons \text{FeEDTA}^{2-}$	0.12
$1,2\text{-Naphthoquinone} + 2e^- \rightleftharpoons \text{Hydroquinone}$	0.14
$\text{Ru(en)}_3^{3+} + e^- \rightleftharpoons \text{Ru(en)}_3^{2+}$	0.18
$\text{TMPD}^+ + e^- \rightleftharpoons \text{TMPD}$	0.27
$1,4\text{-Benzoquinone} + 2e^- \rightleftharpoons \text{Hydroquinone}$	0.28
$\text{Co(bpy)}_3^{3+} + e^- \rightleftharpoons \text{Co(bpy)}_3^{2+}$	0.32
$\text{Fe(CN)}_6^{3-} + e^- \rightleftharpoons \text{Fe(CN)}_6^{4-}$	0.361*, 0.36
$\text{CoEDTA}^- + e^- \rightleftharpoons \text{CoEDTA}^{2-}$	0.38
$\text{Co(phen)}_3^{3+} + e^- \rightleftharpoons \text{Co(phen)}_3^{2+}$	0.327*, 0.38
$\text{Ferrocene}^+ + e^- \rightleftharpoons \text{Ferrocene}$	0.44
$\text{W(CN)}_8^{3-} + e^- \rightleftharpoons \text{W(CN)}_8^{4-}$	0.49
$\text{Co(C}_2\text{O}_4)_3^{3-} + e^- \rightleftharpoons \text{Co(C}_2\text{O}_4)_3^{4-}$	0.57
1,1-Dicarboxylic acid ferrocene	0.64
$\text{Mo(CN)}_8^{3-} + e^- \rightleftharpoons \text{Mo(CN)}_8^{4-}$	0.77
$\text{Os(bpy)}_3^{3+} + e^- \rightleftharpoons \text{Os(bpy)}_3^{2+}$	0.84
$\text{Ru(CN)}_6^{3-} + e^- \rightleftharpoons \text{Ru(CN)}_6^{4-}$	0.86
$\text{Ru(bpy)}_2(\text{NH}_3)_2^{3+} + e^- \rightleftharpoons \text{Ru(bpy)}_2(\text{NH}_3)_2^{2+}$	0.88
$\text{IrCl}_6^{2-} + e^- \rightleftharpoons \text{IrCl}_6^{3-}$	1.00
$\text{Fe(bpy)}_3^{3+} + e^- \rightleftharpoons \text{Fe(bpy)}_3^{2+}$	1.07
$\text{Fe(phen)}_3^{3+} + e^- \rightleftharpoons \text{Fe(phen)}_3^{2+}$	1.13*, 1.07
$\text{Br}_2 + e^- \rightleftharpoons 2\text{Br}^-$	1.087
$\text{Ru(phen)}_3^{3+} + e^- \rightleftharpoons \text{Ru(phen)}_3^{2+}$	1.22
$\text{Ru(bpy)}_3^{3+} + e^- \rightleftharpoons \text{Ru(bpy)}_3^{2+}$	1.27

TMPD: N,N,N',N'-Tetramethyl-p-Phenylenediamine, * Bard 1985

probes are brought sufficiently close to a conductive specimen.

3.4.3 Fabrication tool

The SECM can be employed to carry out high-resolution fabrication on surfaces using variants of conventional electrochemical approaches, i.e., electrodeposition, electroplating, and etching. For example (Hüsser 1989), the probe electrode can be lowered into a polymer film containing a metal ion such as Ag^+ and metal structures can be formed by electrodeposition of

metal while the probe electrode is moved in a desired travel. Specimen, e.g., metals (Craston 1988) or semiconductors (Mandler 1990), can be etched by generation of an oxidant such as $\text{Os}(\text{bpy})_3^{3+}$ or Br_2 while the probe electrode is moved near the specimen surface. Such SECM etching can also be performed by making the specimen electrode the anode and moving the cathodic probe electrode near it. As with imaging, in general, resolution attainable in fabrication is of the order of the probe electrode diameter. For choosing a suitable mediator, electrolyte, and solution pH, however, resolution is achieved at values less than one third of the probe electrode diameter by the focusing effect for diffusive species from the probe electrode by a scavenger species contained in the solution (Borgwarth 1999).

3.4.4 *Modified SECMs*

Resolution attainable with SECM is largely governed by the probe electrode size and distance separating probe and specimen electrodes. With a probe electrode of very small diameter, scanning the probe electrode in close proximity to the specimen surface and measuring probe current becomes difficult because stray vibrations or irregularities in the specimen surface can cause a crash of the probe electrode. For high resolution, the SECM must be operated in constant current mode, as is often used with the STM or AFM, where distance is adjusted by a closed feedback loop to movement in the z direction to maintain I_p constant. This is straightforward (Wipf 1992) when the specimen is either all conductive or all insulating because feedback can be set to counter a change in current by either moving the probe electrode closer to a conductive surface or further away from an insulating surface. However, for specimens containing both types of regions, a method of recognizing the surface nature is more complicated. One approach (Wipf 1993) is to modulate motion of the probe electrode normal to the specimen surface and record dI_p/dz . Over a conductor, a probe electrode movement away from the specimen surface causes a decrease in probe current, whereas an increase occurs over an insulator. Probe currents over a conductor and an insulator are out of phase by 180 degree. Thus, one can identify the conductive or insulating nature of the specimen surface by detecting the in-phase or out-phase component of the modulated current.

As described above, SECM is one kind of SPMs. Thus, SECM apparatus can be mounted on other apparatus of SPM with the modified probe electrode. Even SECM with submicron resolution has been realized by using AFM (Zhu 1997, Williams 1998). In this case, the probe electrode tip is employed as one counter electrode and collects local current density for dissolution of certain MnS inclusions in stainless steel.

Combination of SECM with photoelectrochemical microscopy (PEM) has been used

to locate pitting precursor sites on a polycrystalline titanium by Smyrl and colleagues (Casillas 1995, Sukanto 1995, James 1996). The tip of an optical fiber coated with noble metal is used as a modified probe electrode and gives SECM and/or PEM images for the same specimen surface without changing the probe. Moreover, it is possible to image *in-situ* both roughness and electrochemical activity of the surface in liquid by using shear-force feedback method (James 1998, Mesias 1999). Distance between probe and specimen electrodes is normally regulated by monitoring damping of the oscillations of a resonating probe by a tuning fork as it encounters viscous damping near the specimen surface. By this method, the probe electrode can be kept at a constant height above the specimen surface without contact.

Localized electrochemical impedance spectroscopy (LEIS) for mapping AC impedance distribution, as a function of frequency, has proven to be a valuable test method for characterization and quantification of organic coating degradation (Lillard 1995, Zou 1997), galvanic corrosion (Lillard 1992), and pitting corrosion (Annergren 1997) in aqueous media. In LEIS, as in traditional AC impedance methods, a sinusoidal voltage perturbation between the working electrode and reference electrodes is maintained by driving an AC current between the working electrode and a distant counter electrode with a potentiostat. Local AC impedances are then derived from the ratio of applied AC voltage and local AC solution current density. The local AC current density is obtained from potential difference measurements near the electrode surface using a probe consisting of two microelectrodes. Local AC solution current density is derived by measuring AC potential difference between microelectrodes, and using their known separation distance and solution conductivity.

Scanning vibrating electrode technique (SVET), in which the probe electrode is mounted on a bimorph piezoelectric reed which vibrates the probe normal to the specimen surface at a characteristic frequency. This SVET has been used to investigate initiation of stress corrosion cracking (Isaacs 1988.1), surface heterogeneity (Isaacs 1987), precipitation in aged duplex stainless steels (Jiang 1992), and galvanic corrosion (Isaacs 1998.2).

The scanning droplet cell (SDC) has been used for investigating aluminum and gold surfaces and for cathodic modification of an aluminum surface (Hassel 1997, 1999, 2000.1). It allows application for all common electroanalytical techniques arbitrarily for small areas on the electrode surface. In combination with SECM, it has been used for understanding progression of heterogeneities of a titanium surface reaction (Hassel 2000.2).

3.5 SECM for corrosion research

The SECM has already been used in the field of corrosion. Investigation of the oxidized surface on chromium (Lee 1990) by using methyl viologen(II) ions and $\text{Fe}(\text{CN})_6^{4-}$, and on titanium by using $\text{Ru}(\text{NH}_3)_6^{3+}$ (Wei 1995) illustrated their insulating properties. Precursor processes of pitting corrosion taking place on titanium by Br^- were investigated well by Smyrl and colleagues (Casillas 1993, 1994, 1995, James 1989, Sukanto 1995). Spatially-localized electrochemical reactivities of oxide films on titanium or tantalum were actively investigated using $\text{Fe}(\text{CN})_6^{4-}$, $\text{Ru}(\text{NH}_3)_6^{3+}$, Br^- , and I^- as mediators (Basame 1995, 1998, 1999.1, 1999.2). On the other hand, recently, dissolution of MnS inclusions in stainless steel during initiation of pitting corrosion was investigated in an aqueous solution containing I^- (Paik 2000). Although these studies stressed SECM utility, the redox system added as a mediator in solution may alter electrochemical reactivities of oxide film if the redox system adsorbs strongly on the oxide film or reacts with the film.

In contrast, Wipf et al employed a solution containing trichloroacetic acid and locally generated chloride ions at a probe electrode of SECM to investigate local breakdown of passive films on stainless steel (Wipf 1994) and iron (Still 1997). Local generation of aggressive anions is effective to study precursor processes of pitting corrosion because location of precursor sites can be specified. However, influence of thickness or defective structure of passive films on resistivity against film breakdown has not been well evaluated.

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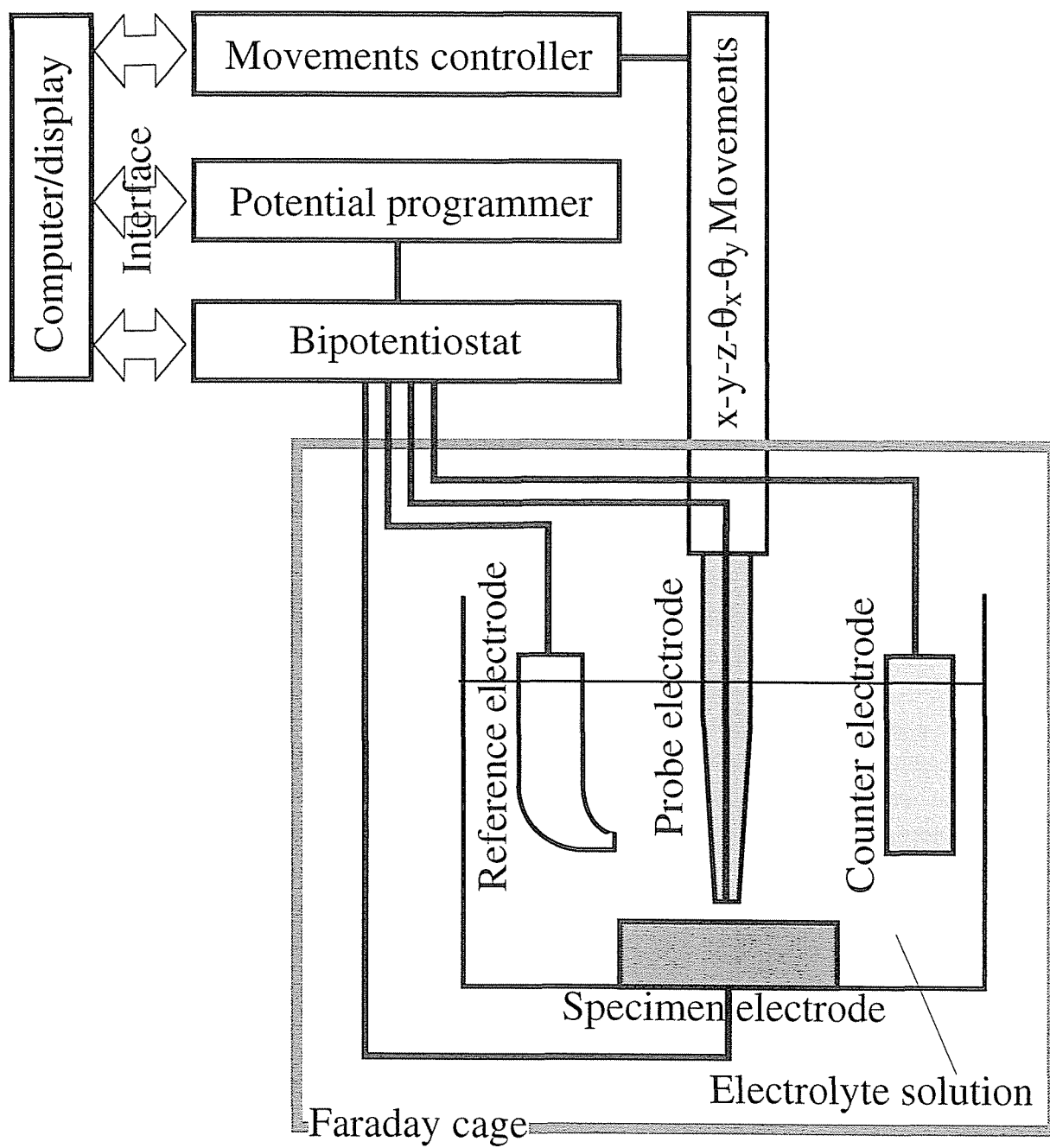


Fig. 3.1.1 Block diagram of SECM apparatus

a)
$$I_{\text{limit}} = 4nFD_A c_A^* a$$

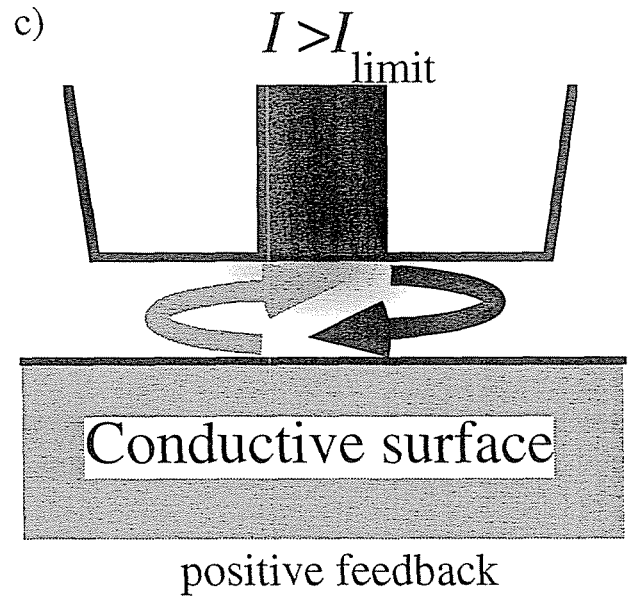
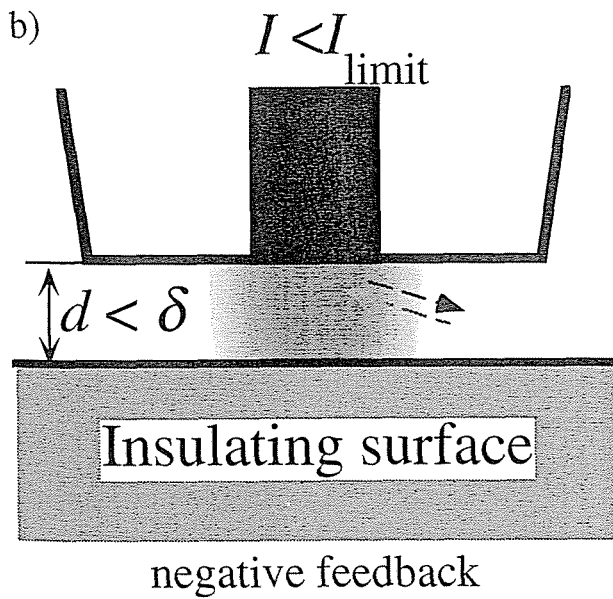
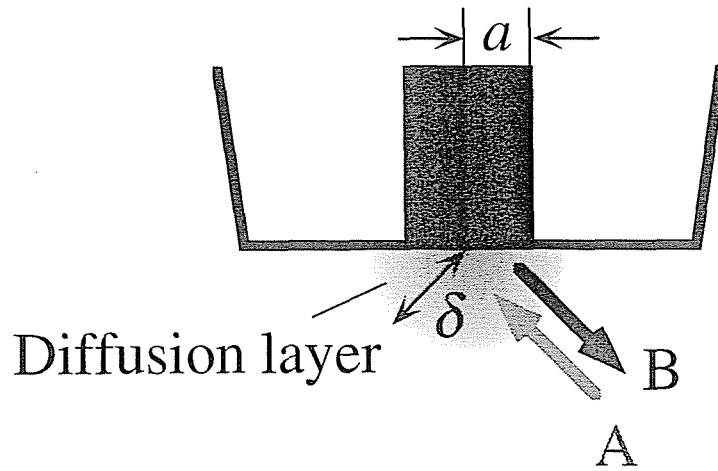


Fig. 3.2.1 Schematic diagram of the diffusion layer at the tip of probe electrode located a) at bulk solution or closed to the surface of b) insulating or c) conductive specimen electrode. d_{dl} is diffusion layer thickness.

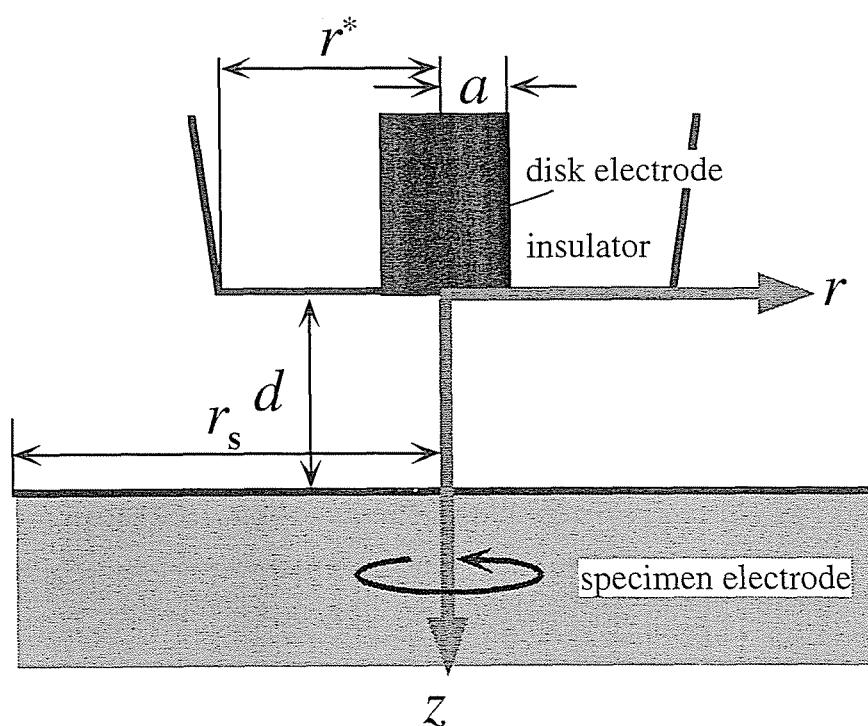
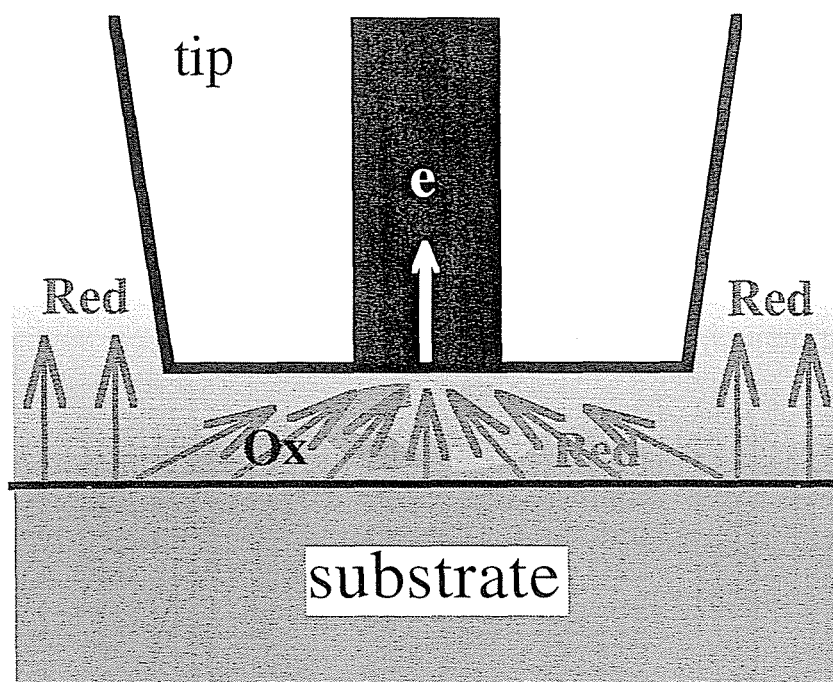


Fig. 3.3.1 Micro-disk electrode and planar specimen in an axis-symmetric system.

a) SG/TC mode



b) TG/SC mode

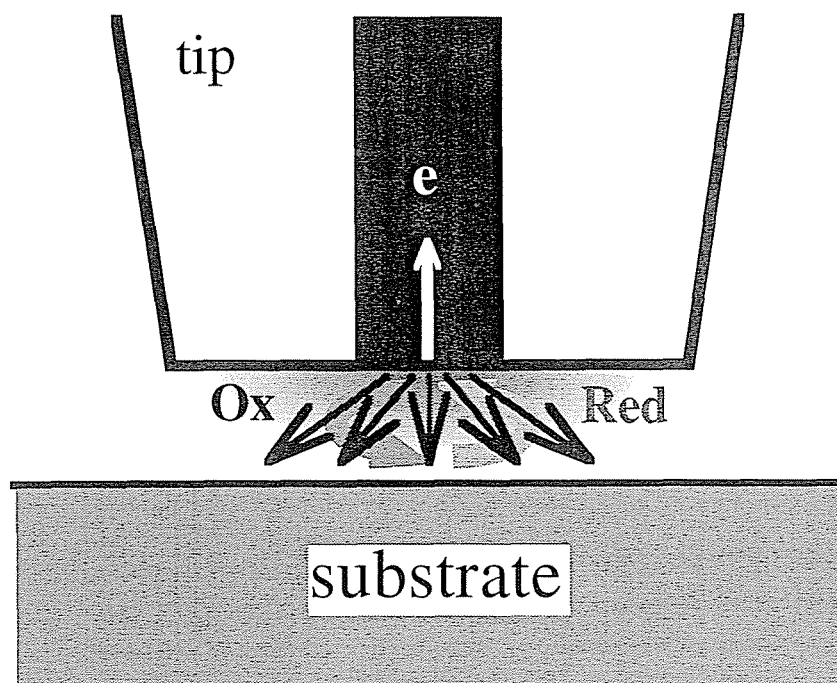


Fig. 3.3.2 Schematic diagram of the diffusion layer at the tip of probe electrode in a) SG/TC mode and b) TG/SC mode.

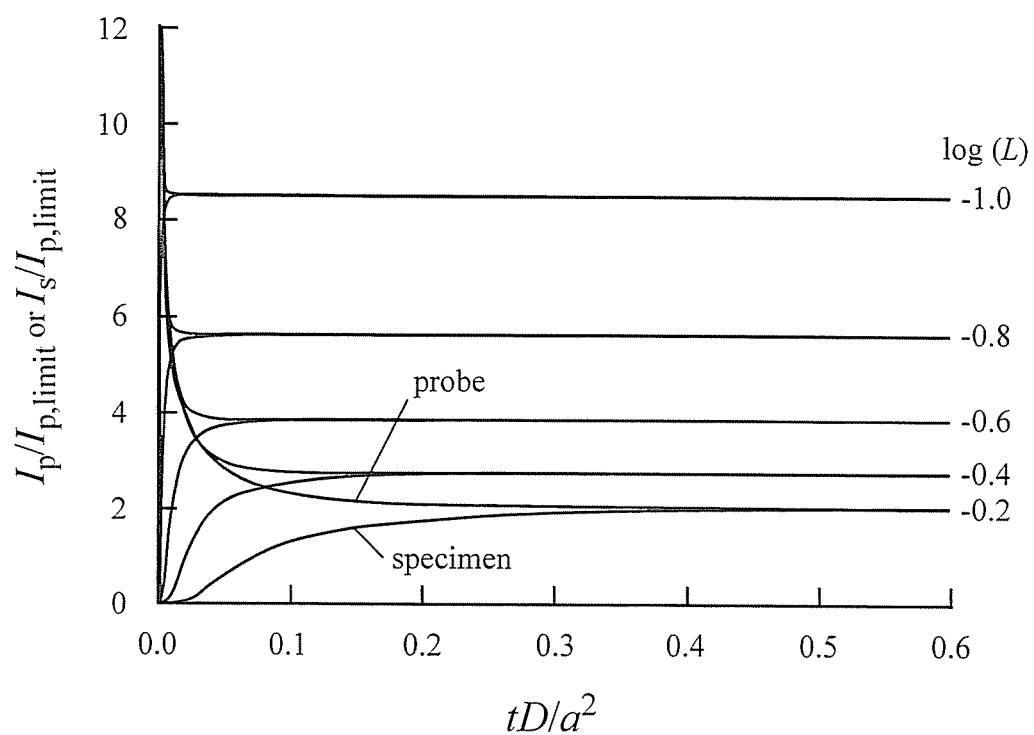


Fig. 3.3.3 Transients of probe and specimen currents under diffusion-controlled conditions in TG/SC mode. (Zhou 1992)

4 Experimental apparatus and procedures

4.1 Preparation of the probe microelectrode

The most popular type of probe electrode used for SECM experiments is a microdisk electrode which is surrounded by an insulator, such as glass, as shown in Figure 4.1.1. Construction of this kind of probe electrode is largely based on fabrication techniques for disk-shaped microelectrodes described in the literature (Fleischmann 1987, Wightman 1989). The procedure for fabricating the typical probe microelectrode used in this thesis is detailed here. Other methods for fabricating different types of probe microelectrodes suitable for SECM are detailed in reports of Wightman (Wightman 1989) and Bard (Bard 1994).

A fine wire of noble metal, such as Pt or Au, is welded or glued with silver paste (Fujikura Kasei Co., D-500) to a copper wire with a diameter less than 0.5 mm for an electrical contact and ease of handling. The wire is then placed in a glass capillary (length of 50-100 mm, inner and outer diameters of about 2.0 and 2.4 mm, respectively) and sealed with a helix-heating wire (Narishige Co., MF-77). The glass should melt around the fine wire for 1-2 mm at the assembly tip. For alternative preparation of microdisk electrodes, epoxy resin is employed to seal the fine wire to thermal sensitive metal, such as Ag, and a carbon rod into glass. In this case, the open end of the glass capillary is connected to a vacuum line to draw the highly viscous resin into the capillary. The sealed end of the glass capillary is then mechanically polished with a diamond whetstone (#5000) on a turntable (Narishige Co., EG-400) until the wire cross-section is exposed. At an open end of the glass, a copper wire is sealed with solder or epoxy resin. For cleaning the exposed surface of the microelectrode composed of Pt or carbon, the electrode is polarized cyclically in the potential range between hydrogen evolution and oxygen evolution in 1 mol dm⁻³ sulfuric acid until the same voltammogram is obtained.

4.2 Characterization of the microelectrode

Microelectrodes are first characterized by cyclic voltammetry. Figure 4.2.1 shows the typical cyclic voltammogram (CV) for 0.03 mol dm⁻³ K₄Fe(CN)₆ solution or 0.03 mol dm⁻³ K₃Fe(CN)₆ solution using a microelectrode composed of Pt wire with a diameter of 5 μm. Microelectrode radius, however, can be estimated from the diffusion-limiting plateau current,

$I_{p,limit}$, by using the relation for a disk-shaped microelectrode of Equation 2.2.13. As the diffusion coefficient (Adams 1969) of $Fe(CN)_6^{4-}$ is $6.3 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$ or that of $Fe(CN)_6^{3-}$ is $7.6 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$, calculated diameter of the electrode used in Figure 4.2.1 is about $5 \text{ }\mu\text{m}$ which is in good agreement with the measured diameter of the fine wire used.

4.3 Instrumentation of SECM

A basic SECM instrument was discussed in 3.1. Here, the SECM instrument developed and used for this thesis will be clarified. Figure 4.3.1 shows a block diagram of the apparatus mainly used for SECM experiments in this thesis. Apparatus consists of three major components:

- a) an electrochemical cell, in which four electrodes (specimen, probe, counter, and reference electrodes) are immersed and slaved with a bipotentiostat and a potential programmer.
- b) a series of movements and their controller which drives a probe electrode in x , y , and z directions and tilts it in θ_x and θ_y directions.
- c) computer with a display system and interfaces for above two components.

Detailed specifications of each apparatus are explained below.

4.3.1 Electrochemical cell

The electrochemical cell composed of PVC has four electrodes, i.e. probe, specimen, counter, and reference electrodes. Although preparation and characterization of the probe electrode was illustrated in 4.1 and 4.2, the probe electrode mainly used was a Pt microelectrode with a $10 \text{ }\mu\text{m}$ diameter. The specimen electrode was generally embedded into epoxy resin (Struers, Epofix) after wiring and held on the electrochemical cell by the holder composed of PTFE or PVC. Probe and specimen electrodes will be detailed along with the electrolyte solution filling the electrochemical cell later in each chapter. On the other hand, a wired Pt foil was employed as the counter electrode. Furthermore, a commercially served Ag/AgCl/saturated KCl electrode (TOA Electronics Ltd., HS-205C) was used as the reference electrode using a Lugin capillary into which an aged-saturated KNO_3 was embedded. All potentials were converted to a standard hydrogen electrode (SHE).

A bipotentiostat (Hokuto Denko Co., HAL-1512mM2) specially built for this SECM controls independently probe and specimen electrode potentials, E_p and E_s , versus the reference electrode during current flow between two working electrodes and the counter electrode. A

potential programmer (Hokuto Denko Co., HB-105A or Echo Electronics Co., ENP-70U) was used to change E_p linearly with time or stepwise. Furthermore, a potentiostat (Solartron, SI1287) was often employed to prepare the microelectrode, i.e. to check diameter, clean or oxidize the surface. Detailed specifications of electrochemical apparatus are included below.

a) Hokuto Denko Co., HAL-1512mM2

Potentials of the two working electrodes, i.e. probe and specimen electrodes, can be controlled independently by an electrometer and/or a potentiostat as the following: electrometer-electrometer; electrometer-potentiostat; potentiostat-electrometer; and potentiostat-potentiostat.

As an electrometer,

Input impedance: $> 10 \text{ G}\Omega$

Dark current: $< 1 \text{ pA}$

Sampling rate: $5 \mu\text{s}$

As a potentiostat,

Output voltage range: 15 V

Output current range: 100 mA

Setting voltage range: 10 V

Full scale current range: $100 \text{ p to } 100 \text{ mA}$

Adjustment resolution: $< 0.1\%$

Sampling rate: 0.5 ms

Interface: IEEE488 (GP-IB)

b) Solartron, SI1287

Output voltage range: 14.5 V

Output current range: 2 A

Full scale current range: $200 \text{ n to } 2 \text{ A}$

Input impedance: $> 10 \text{ G}\Omega$

Dark current: $< 1 \text{ nA}$

DC sweep: analog ramp rate: $0.1 \mu\text{ to } 100 \text{ V s}^{-1}$

Interface: IEEE488 (GP-IB)

c) Hokuto Denko Co., HB-105A

Channels: 1

Output voltage range: 10 V

DC sweep: analog ramp rate: $1 \mu\text{ to } 150 \text{ V s}^{-1}$

Adjustment resolution: $< 0.01\%$

Interface: IEEE488 (GP-IB)

d) Echo Electronics Co., ENP-70U

Channels: 4

Output voltage range: $0 \text{ to } +10\text{V or } -5 \text{ to } +5 \text{ V}$

Maximum resolution: $2.44 \text{ mV (12-bit for } 10 \text{ V)}$

Minimum step duration: $< 1 \text{ ms for the step from } 0 \text{ to } 10\text{V}$

Interface: IEEE488 (GP-IB)

4.3.2 Probe movement

Three types of x - y - z - θ_x - θ_y positioning stages driven by drivers and controllers were used to scan the probe electrode. Manual adjustment in x - y - z - θ_x - θ_y directions, moreover, was enabled for the specimen electrode. Respective specifications are shown in Table 4.3.1.

Table 4.3.1 Specifications of drivers and controllers *

Direction	Pro.	Stage	Driver (num.)	Driving type	Controller	Accuracy
PC-controlled (type I)						
x - y	CP	LD-947	AME-15 (2)	SME	M9103	$0.1 \mu\text{m step}^{-1}$
z	CP	LS-141	AME-25 (1)	SME	M9103	$0.1 \mu\text{m step}^{-1}$
θ_x - θ_y	CP	TD-101	AME-15 (2)	SME	M9103	$2 \times 10^{-9} \text{ deg. step}^{-1}$
PC-controlled (type II)						
x - y	SI	-	SP-2200 (1)	DC motor	SP-4200	$0.01 \mu\text{m step}^{-1}$
z	CP	LS-141	AME-25 (1)	SPE	M9103	$0.1 \mu\text{m step}^{-1}$
θ_x - θ_y	CP	TD-101	AME-15 (2)	SME	M9103	$2 \times 10^{-9} \text{ deg. step}^{-1}$
PC-controlled (type III)						
x	CP	-	ALS-902-H04 (1)	linear-motor	LMC-2	$0.04 \mu\text{m step}^{-1}$
y	CP	LS-941	AME-15 (1)	SME	M9103	$0.1 \mu\text{m step}^{-1}$
z	CP	LS-141	AME-25 (1)	SME	M9103	$0.1 \mu\text{m step}^{-1}$
	PI	LS-648	P-841.40 (1)	piezoelectric	E-610.S0	$0.04 \mu\text{m step}^{-1}$
θ_x - θ_y	CP	TD-101	AME-15 (2)	SME	M9103	$2 \times 10^{-9} \text{ deg. step}^{-1}$
Manual						
x - y	CP	LD-947-S1	-	-	-	-
Z	MS	CZ-351	-	-	-	-
	CP	LV-637-1	-	-	-	-
θ_x - θ_y	CP	TD-602	-	-	-	-

4.3.3 System controller

These SECM instruments are controlled by a personal computer and an IEEE488 (GP IB) board (Hewlett Packard, 82341D or National Instruments, PCMCIA-GPIB), which is used to acquire electrochemical signals (E_p , E_s , I_p , and I_s) via the bipotentiostat and to control x - y - z - θ_x - θ_y movements of the probe via the position-controllers. Programs for these purposes are written in two languages (Hewlett Packard, HP VEE version 4.0 and Microsoft, Visual Basic version 5.0). The SECM images are made by commercially available software (Wave Metrics Inc., Igor Pro version 3.12).

4.3.4 Miscellaneous

To monitor position of the probe electrode tip above the specimen surface, a CCD

* CP: Chuo Precision Indust., SI: Seiko Instruments, PI: Physik Instrumente, MS: Meiritsu Seiki Co., SME: stepping-motor encoding

camera (Olympus, H100-014-000-HM60), with 250 times magnification at a monitor, was used. An optical microscope was also employed to monitor distance between the probe electrode and the specimen surface.

The electrochemical cell and manipulation system of the probe electrode were located in a Faraday cage, the inside of which was controlled thermostatically at 298 ± 0.1 K by a PID thermostat. The Faraday cage was, moreover, located on an air-suspending anti-vibration table (Sigma Koki, HOA-107LA).

4.4 Chemicals and materials

Super-purified chemicals produced by Kanto Chemical Co. were employed for all experiments. Milli-Q water was served for all aqueous solutions. Chemicals and metals used in this thesis are listed in Table 4.4.1.

Details of materials used for electrodes are described below.

a) Iron

A polycrystalline iron of 99.9% purity in the form of a sheet (5 mm x 5 mm x 1 mm annealed at 873 K in vacuum) was employed as the specimen electrode in Chapters 5, 8, and 10. Average grain diameter is larger than 200 μm .

b) Titanium

Polycrystalline titanium of 99.5% purity (impurities: C=0.009, N=0.004, O=0.101, H=0.0013, and Fe=0.036%) in the form of a rod (10 mm diameter annealed at 1023 K in vacuum) was used as the specimen electrode in Chapters 6 and 7. Average grain diameter is about 100 μm .

c) Platinum

Purity of platinum (Nilaco Co.) used as electrodes for various purposes was above 99.98%. Platinum wire with 5, 10, 20, 50 or 100 μm diameter was employed for probe electrodes. Preparation of the probe electrode was previously described in 4.1. Furthermore, platinum wire and foil were used for the standard specimen electrode in 4.5. Platinum plate with a size of 5 mm x 5 mm x 0.5 mm was used as the model specimen system in Chapter 9. In general, the counter electrode was composed of platinum foil and wires.

Table 4.4.1 Used chemicals

chemicals	purity / %	object	misc.
agar	-	salt bridge	
boric acid/ H_3BO_3	99.5	electrolyte solution	
ethanol/ $\text{C}_2\text{H}_5\text{OH}$	99.5	degreasing, etch-pit method	
	in vol.		
2-ethoxyethanol/ $\text{C}_2\text{H}_5\text{OC}_2\text{H}_4\text{OH}$	98.0	electropolishing of Ti	
Formic acid/ HCOOH	98.0	etch-pit method	
hydrochloric acid/ HCl	35-37	LPIG formation	
hydrogen peroxide/ H_2O_2	34.5	etch-pit method	
iron(III) chloride/ FeCl_3	99.0	etch-pit method, detection of Fe^{3+}	hexahydrate
iron(II) sulfate/ FeSO_4	99-102	detection of Fe^{2+}	heptahydrate
methanol/ CH_3OH		electropolishing of Ti	
2-methoxyethanol/ $\text{CH}_3\text{OC}_2\text{H}_4\text{OH}$	99.0	electropolishing of Ti	
nitric acid/ HNO_3	60-61	nital solution, etch-pit method	
perchloric acid/ HClO_4	60-62	electropolishing of Ti	
potassium chloride/ KCl	99.5	salt bridge, detection of Cl^-	
potassium hexacyanoferrate(III)/ $\text{K}_3\text{Fe}(\text{CN})_6$	99.0	mediator	trihydrate
potassium hexacyanoferrate(II)/ $\text{K}_4\text{Fe}(\text{CN})_6$	99.5	mediator	
potassium nitrate/ KNO_3	99.0	salt bridge	
silver(I) chloride/ AgCl	99.5	LPIG formation	
sodium chloride/ NaCl	99.5	pitting formation	
sodium sulfate/ Na_2SO_4	99.0	electrolyte solution	anhydrous
sodium tetraborate/ $\text{Na}_2\text{B}_4\text{O}_7$	99-103	electrolyte solution	decahydrate
sulfuric acid/ H_2SO_4	96.0	electrolyte solution, pH control, probe electrode cleaning	

d) Silver

For LPIG microelectrode, silver wire with a diameter of 180 or 50 μm and 99.9% purity was employed. Furthermore, silver wire with 100 μm diameter and 99.99% purity was employed to measure Cl^- concentration in the narrow gap between the LPIG microelectrode and the specimen surface.

e) Carbon

Graphite reinforcement carbon (GRC) rod is commercially available as a mechanical pencil lead and has good electrochemical performance as reported elsewhere (Aoki 1989). A microelectrode for Fe^{3+} or Fe^{2+} detection was prepared from GRC rod (Mitsubishi Pencil Co., B 0.3mm) with a 0.3 mm diameter. According to a technical note (Kawakubo 1982), the lead was made by: dispersing 75-80 natural graphite into a 12-13% organic binder and 8% spindle oil mixture; squeezing the dispersed graphite into rod form; then dehydrating the rod at 373-573 K to prevent rod deformation; and finally sintering it at ca. 1273 K under an inert gas atmosphere.

Lead impurity was limited to 2.05 ppm Cd, 1.20 ppm Sb, 0.65 ppm Sb and 0.65 ppm.

4.5 Specification of instruments

A standard specimen electrode, which was composed of a platinum disk with a 500 μm diameter and a platinum ring with a 50 μm width and embedded into epoxy resin as shown in Figure 4.5.1 was prepared to evaluate specification of developed SECM. A platinum probe electrode with a 10 μm diameter was polarized at -0.1 V (SHE) while the specimen platinum disk was polarized at 0.9 V (SHE) in deaerated pH 8.4 borate solution containing 0.03 mol dm^{-3} $\text{K}_3\text{Fe}(\text{CN})_6$. As a mediator, $\text{Fe}(\text{CN})_6^{3-}/\text{Fe}(\text{CN})_6^{4-}$ is often used and its redox reaction proceeds with an outer-sphere type of electron transfer.



As discussed in 3.3.2, the TG/SC mode is available above the disk surface. On the other hand, in case of the platinum ring of the specimen in an open circuit, the feedback mode is available above the ring surface as discussed in 3.3.1.

Figure 4.5.2 shows probe current as a function of a distance, d , between the probe electrode and specimen surface when the probe electrode was moved more closely to the specimen surface of epoxy resin or platinum disk. At distance more than 60 μm which is several times as much as the probe electrode diameter, the probe current stabilizes, which coincides with the limiting current. At distances less than 40 μm , however, probe current decreases with decreasing d above the epoxy resin, indicating that negative feedback takes place. On the other hand, probe current increases with decreasing d above the platinum disk, implying that positive feedback takes place.

Figures 4.5.3a and b shows current images of the probe and specimen electrodes, respectively, when the 10 μm diameter probe electrode was scanned above the specimen electrode at a 5 μm distance. From the probe current image, it is easy to distinguish the components of epoxy resin, platinum disk and platinum ring. In the specimen current image, furthermore, the epoxy resin part cannot be distinguished from the platinum ring although it is distinguishable from the platinum disk. This results from that the epoxy resin and platinum ring are isolated. Figure 4.5.3c shows current profiles through probe and specimen electrodes, respectively, when the probe electrode was scanned along the dashed line drawn in Figures 4.5.3a and b. In these profiles, both currents change dramatically at the boundary between platinum disk and epoxy resin. In the case where the current changing at the boundary obeys an

error function characterized by the standard deviation, σ , lateral resolutions of current image can be defined by the value of 2σ which correspond to a distance between 14% and 86% of a difference in current as depicted in Figure 4.5.4b. Probe current differentiated with respect to a scanning distance, $\partial I_p/\partial x$, can be approximately expressed by a normal distribution around the boundary as shown in Figure 4.5.4c. Therefore, lateral resolutions of probe and specimen current images are respectively 16 μm and 21 μm from Figure 4.5.4b. These values are two times as much as the diameter of the probe electrode, 10 μm , as mentioned in 3.4.2.

4.6 Conclusions

Details of an SECM apparatus and probe electrodes used for this thesis were discussed. The probe current image and specimen current image for the standard specimen electrode, which consisted of Pt disk and ring embedded into epoxy resin, were measured with the TG/SC and feedback mode in deaerated pH 8.4 borate solution containing $\text{Fe}(\text{CN})_6^{3-}$ as a mediator. Probe current decreased by the approach of the probe electrode to the epoxy-resin surface, while it increased by the approach to the platinum surface. Distinctions between epoxy resin and each platinum part were more clear in the probe current image than in the specimen current image. Lateral resolution of the probe current image was about 20 μm which was two times as much as the probe electrode diameter of 10 μm .

References

- | | |
|--------------------|--|
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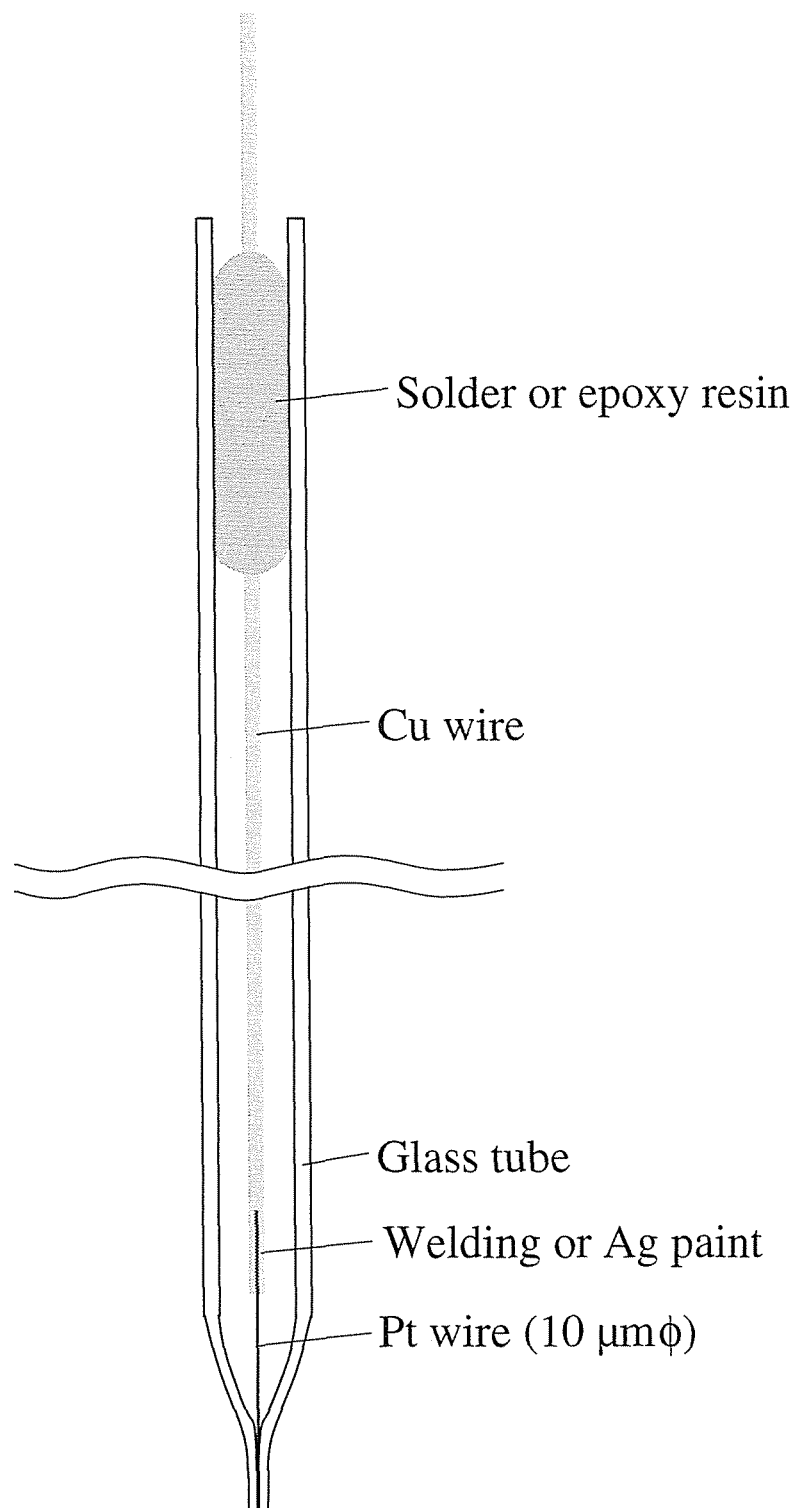


Fig. 4.1.1 Structure of probe electrode for SECM.

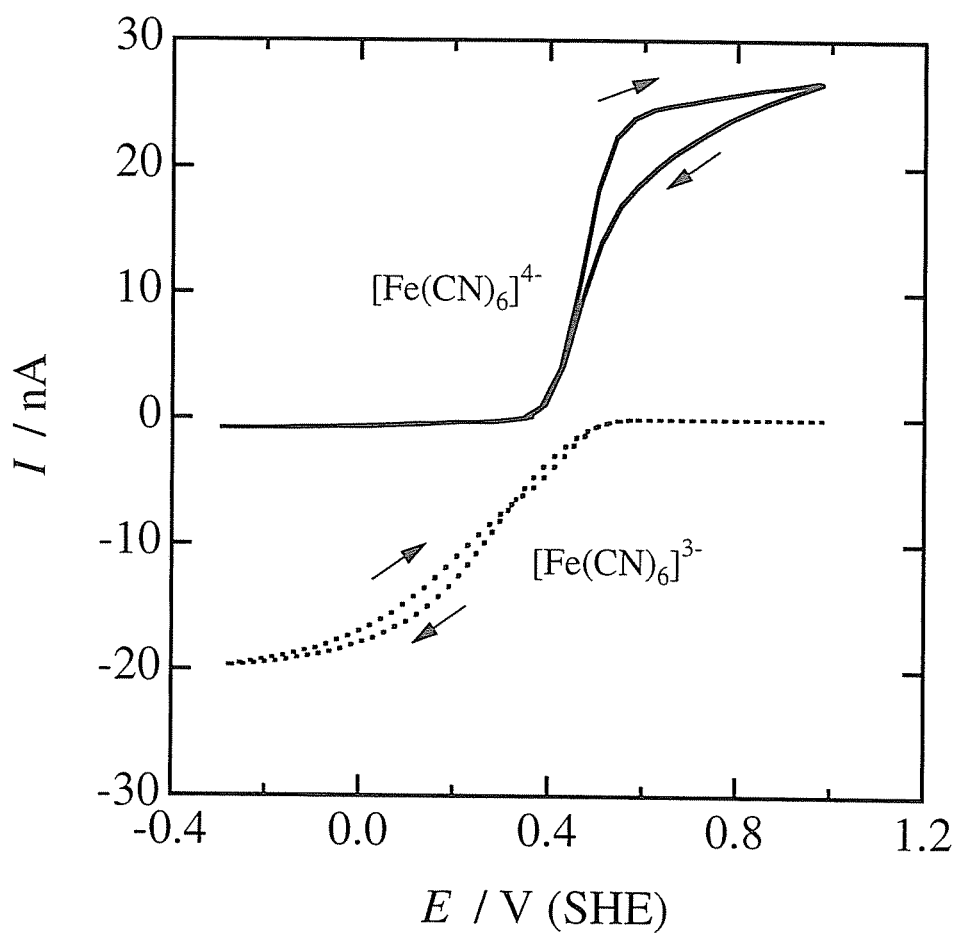


Fig. 4.2.1 Cyclic voltammogram of Pt micro-disk electrode with a diameter of $5\ \mu\text{m}$ in deaerated pH 8.4 borate solution containing $0.03\ \text{mol dm}^{-3}$ $\text{K}_4\text{Fe}(\text{CN})_6$ (—) and $\text{K}_3\text{Fe}(\text{CN})_6$ (.....). Potential sweep rate was $0.1\ \text{V s}^{-1}$.

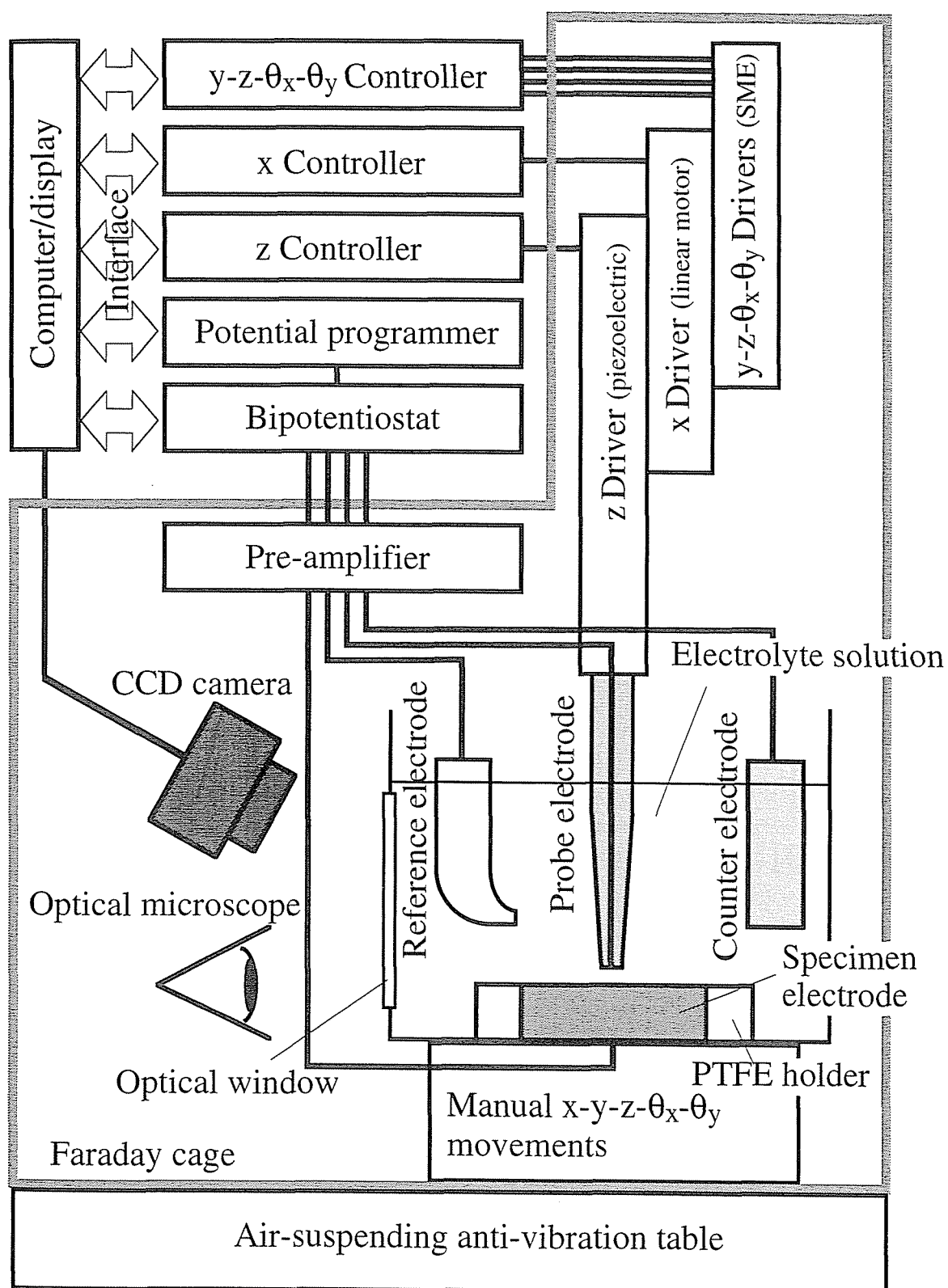


Fig. 4.3.1 Block diagram of SECM apparatus mainly used for experiments.

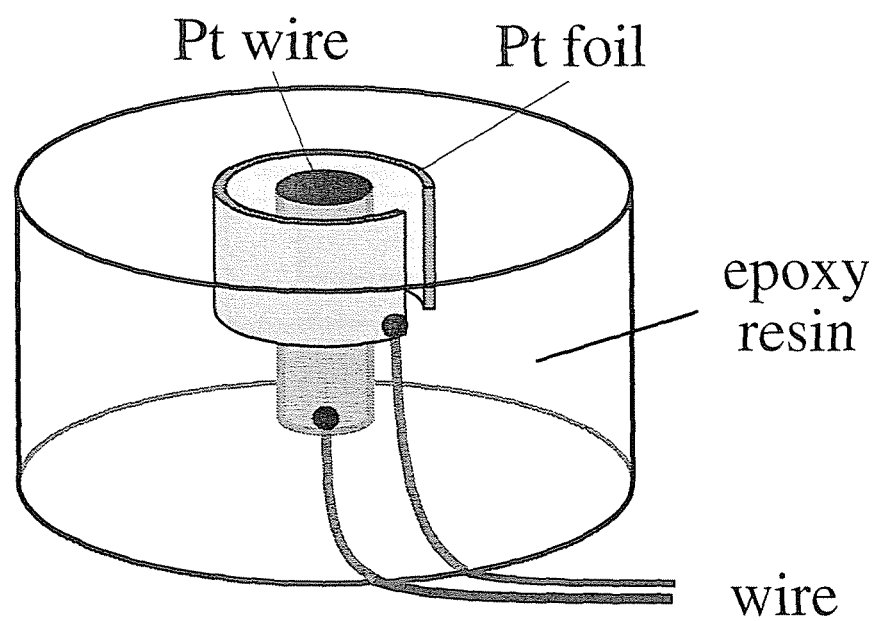


Fig. 4.5.1 Standard specimen electrode with Pt wire and foil embedded into epoxy resin.

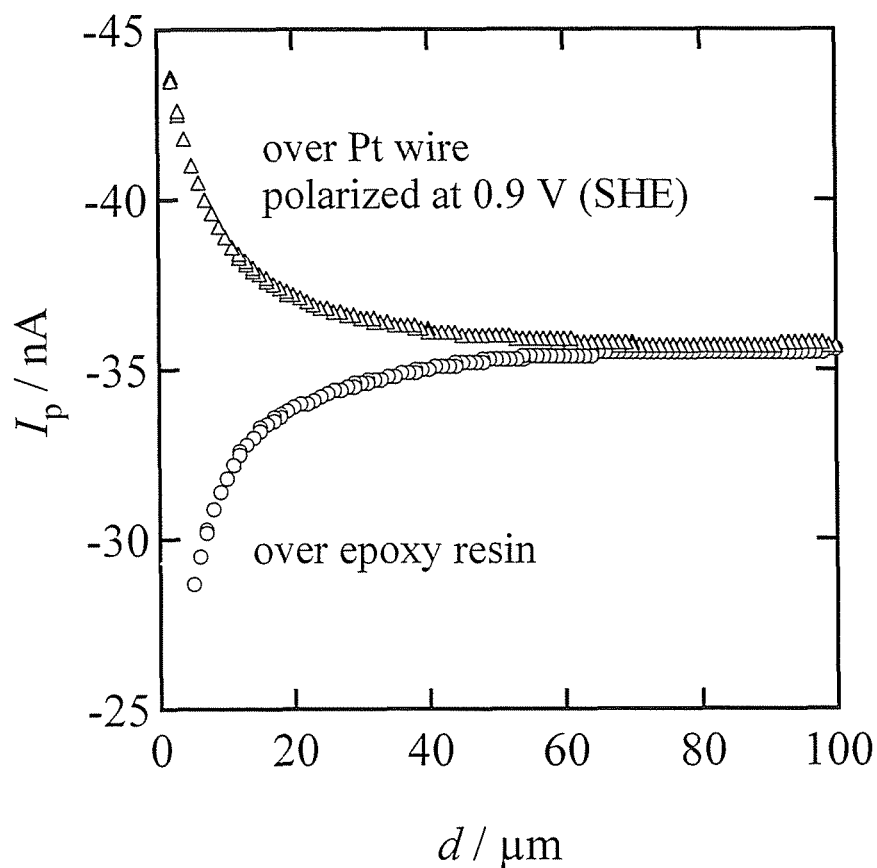


Fig. 4.5.2 Probe current, I_p , measured as a function of distance between probe electrode and standard specimen electrode, d , when the probe electrode with a diameter of 10 μm approached the epoxy resin ($\circ$) and Pt wire (Δ). The probe electrode and Pt disk in the standard specimen electrode were polarized at -0.1 V (SHE) and 0.9 V (SHE), respectively, in deaerated pH 8.4 borate solution containing $0.03 \text{ mol dm}^{-3} \text{ K}_3\text{Fe}(\text{CN})_6$.

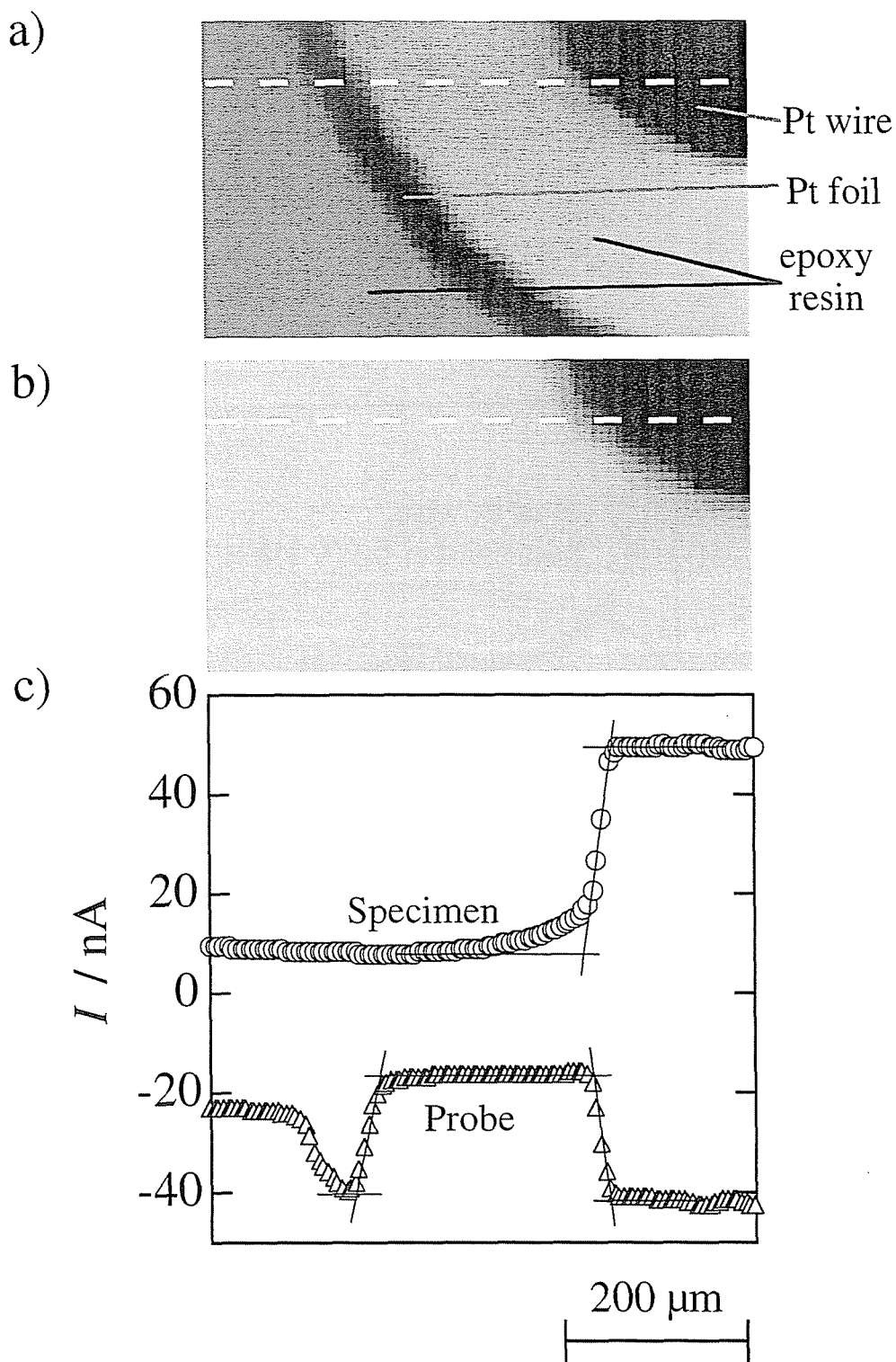


Fig. 4.5.3 a) Probe current image and b) specimen current image obtained when the probe electrode with a diameter of 10 μm was scanned over the standard specimen electrode surface. The probe electrode and Pt wire in the specimen electrode were, respectively, polarized at -0.1 V (SHE) and 0.9 V (SHE), whereas the Pt foil in the specimen electrode was in an open circuit, in deaerated pH 8.4 borate solution containing 0.03 mol dm^{-3} $\text{K}_3\text{Fe}(\text{CN})_6$.
c) Current profiles of probe and specimen electrodes obtained when the probe electrode was scanned along the dashed line drawn on the current images.

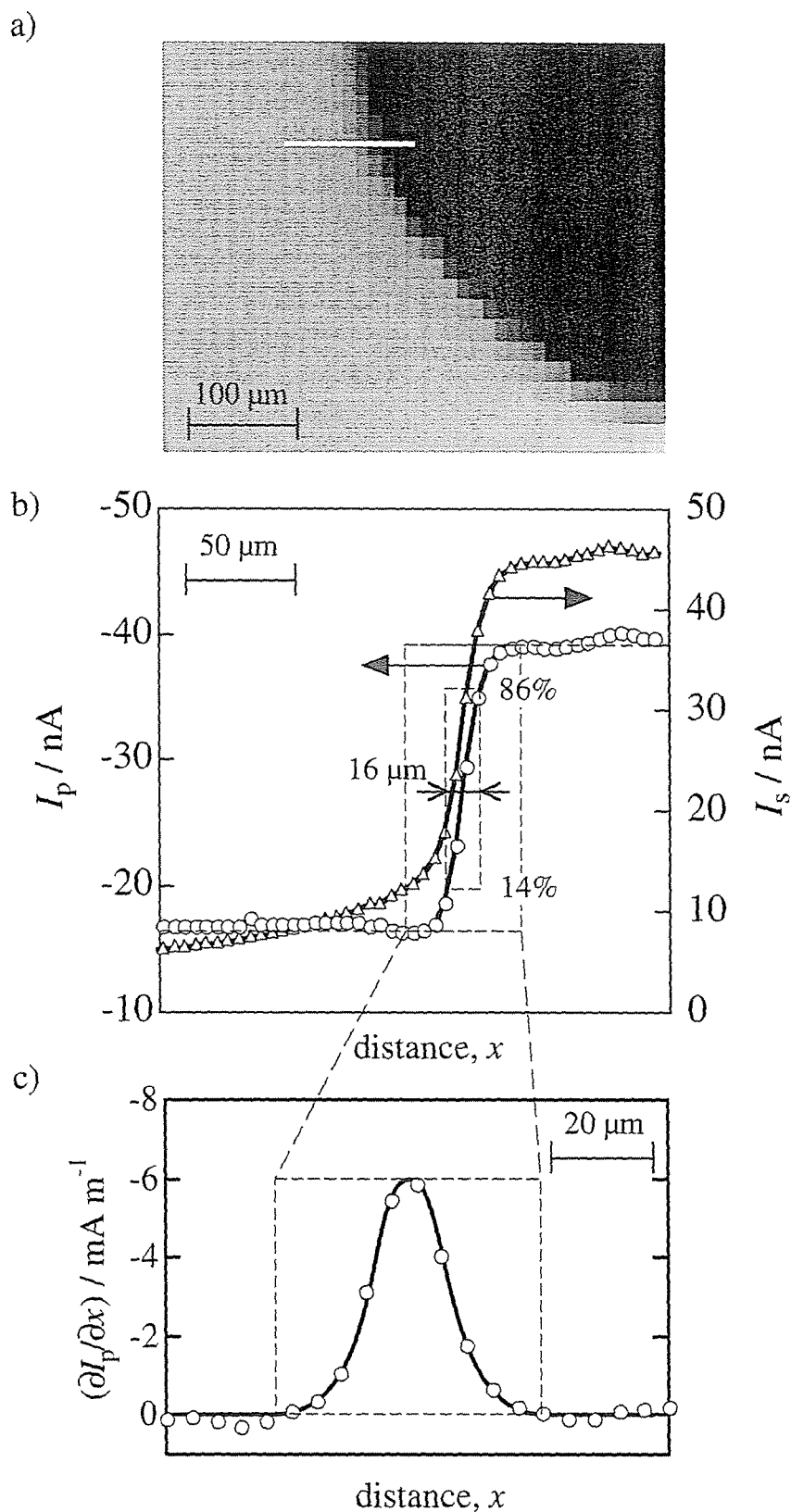


Fig. 4.5.4 a) Magnified probe current image of Fig. 4.5.4a.
b) Probe and specimen current profiles along the white line in Fig. 4.5.5b.
c) Profile of the derivative of I_p with x , $(\partial I_p / \partial x)$, at the boundary between epoxy resin and Pt disk.

5 Heterogeneity of passive film on a polycrystalline iron electrode

5.1 Introduction

Passive films formed on metals and alloys sustain corrosion resistivities of substrates. A local breakdown of passive film eventually leads to localized corrosion such as pitting. Evaluation of electrochemical reactivities at local sites of passive film is important for better understanding precursor process of localized corrosion. For an *in-situ* evaluation of local electrochemical reactivities, SECM is useful and powerful. Bard et al used SECM to examine the surface of oxide films formed on chromium (Lee 1990) or on titanium (Wei 1995) and showed their insulating properties. Smyrl et al investigated precursor processes of pitting corrosion taking place on titanium (Casillas 1993, 1994, 1995, James 1996, Sukamto 1995) by SECM. Although these studies using SECM provided the first step for investigating precursor processes of pitting, distribution of difference in thickness or defective structure of passive films, which would be directly related to local film breakdown, has not been evaluated well.

In Chapters 5 and 6, SECM is applied to evaluate heterogeneity of passive films formed on iron and titanium electrodes, respectively. In this chapter, SECM is first applied to evaluate heterogeneity of passive films formed on a pure iron electrode in deaerated pH 8.4 borate solution.

5.2 Experimental

5.2.1 Specimen preparation

The iron specimen used in experiments was a polycrystalline iron plate with a purity above 99.9 %. Surface preparation of the iron specimen depending on the aim of research was performed with the following two procedures:

- i) the iron specimen was mechanically polished with α -alumina abrasives to a size of 0.05 μm , rinsed with doubly distilled water, and finally dried with nitrogen gas.
- ii) after mechanical polishing with the above procedure, the iron specimen was subjected to chemical etching in ethanol solution containing 10 vol.% nitric acid for 15 s to remove the mechanical polishing layer, i.e., the bibby layer, rinsed with doubly distilled water, and finally dried with nitrogen gas.

Two iron plates (5 mm x 10 mm x 0.2 mm) prepared with procedure i) were embedded into epoxy resin as shown in Figure 5.2.1. The cross section (5 mm x 0.2 mm) of each plate was mechanically polished again with α -alumina abrasives to give a two-banded iron electrode. This type of iron electrode was employed to examine difference in thickness of passive films formed on two iron bands at different potentials. On the other hand, the iron plate (7.5 mm x 10 mm x 1.5 mm) prepared with procedure ii) was mounted on a specimen holder with epoxy resin. A limited surface area (7.5 mm x 10 mm) of the plate was exposed to solutions. The latter type of iron electrode was employed to examine passive film heterogeneity depending on iron substrate grain-orientation.

Both types of iron electrodes were cathodically polarized in deaerated pH 6.5 borate solution under a constant current density of $5 \mu\text{A cm}^{-2}$ to remove an air-formed oxide film. After cathodic polarization, the iron electrodes were potentiostatically passivated at E_f for 3.6 ks in deaerated pH 8.4 borate solution to form passive films.

5.2.2 SECM measurement

The SECM apparatuses (types I and II in Table 4.3.1) were used for this experiment. A platinum microdisk electrode with a diameter of 10 μm was used as a probe electrode. Procedure for the probe electrode preparation was described in 4.1. As a mediator of the redox reaction on the passivated iron surface, $\text{K}_4\text{Fe}(\text{CN})_6$ was employed. After passivation, deaerated pH 8.4 borate solution containing 0.03 mol dm^{-3} $\text{K}_4\text{Fe}(\text{CN})_6$ was introduced into the SECM cell, and then potentials of probe and iron electrodes were respectively controlled at $E_p = 1.2 \text{ V}$ and $E_s = 0.1 \text{ V (SHE)}$ with the bipotentiostat. In this condition, $\text{Fe}(\text{CN})_6^{4-}$ oxidation proceeds on the probe electrode, whereas reduction of $\text{Fe}(\text{CN})_6^{3-}$ produced on the probe electrode proceeds on the iron electrode. It is known that the flat band potential, E_{FB} , of the passive film on iron is -0.16 V (SHE) in pH 8.4 borate solution (Azumi 1987). The passive film on iron in the solution may be cathodically reduced at potentials lower than E_{FB} . Therefore, $E_s = 0.1 \text{ V (SHE)}$ higher than E_{FB} was chosen to avoid any changes in thickness of the passive film during measurement of the probe current image.

The TG/SC mode was employed to obtain the probe current image. When distance between probe and specimen electrodes is shorter than thickness of the diffusion layer of $\text{Fe}(\text{CN})_6^{4-}$ diffusing to the probe electrode formed in bulk solution, oxidation of $\text{Fe}(\text{CN})_6^{4-}$ on the probe electrode is enhanced or retarded just above the iron surface local sites. In this experiment, distance between probe and specimen electrodes, d , is controlled so that the value of probe current is about 0.6 times as much as the limiting current measured when the probe electrode is

located more than 200 μm far from the specimen electrode.

5.2.3 Miscellaneous

Surface roughness of the iron specimen subjected to chemical etching was measured by a surface profilometer (Tokyo Seimitsu Co., Surfcom) equipped with a diamond tip (diameter of 0.01 μm) for surface tracing. After measurement of a probe current image, an optical micrograph of the same region was taken for comparison with the probe current image. Furthermore, orientation of each crystal grain on the substrate iron surface was examined by an etch-pit method (Hayakawa 1979, Kinoshita 1979). Three solutions (a), (b), and (c) as described in Table 5.2.1 were prepared for an etch-pit method.

Table 5.2.1 Solutions prepared for an etch-pit method.

	Chemicals	Mixing ratios in volume	Immersion order and period
(a)	HCl : H ₂ O ₂ : H ₂ O	1 : 10 : 100	i) 10 s
(b)	sat.-FeCl ₃ aq. sol. : HNO ₃ : H ₂ O	2 : 1 : 10	ii) 50 s, iv) 30 s
(c)	HCOOH : H ₂ O ₂ : C ₂ H ₅ OH	1 : 1 : 1 : 1	iii) 10 s

The iron specimen was immersed into these solutions in the following order: i) solution (a) for 10 s; ii) solution (b) for 50 s; iii) solution (c) for 10 s; and iv) solution (b) for 30 s. After each immersion, the iron specimen was rinsed with doubly distilled water. This etching treatment showed the pit shape depending on orientation of each grain. Each pit was composed mainly of low index planes ($\{100\}$ and $\{110\}$) of a polyhedron (Vetter 1970, Hayakawa 1979, Kinoshita 1979) as shown in Figure 5.2.2. Shape of each pit was confirmed with SECM observations as shown in Figure 5.2.3, from which the grain orientation was evaluated.

5.3 Results and Discussion

5.3.1 Probe current as a function of distance between probe and iron electrodes

Figure 5.3.1 shows probe current change when a probe electrode with a 20 μm diameter was advanced toward the epoxy resin and the two iron bands passivated at $E_f = 0.4$ V and 0.8 V (SHE) in deaerated pH 8.4 borate solution. The probe electrode and two iron bands were polarized at $E_p = 0.9$ V and $E_s = 0.2$ V (SHE), respectively, in deaerated pH 8.4 borate solution containing 0.03 mol dm⁻³ K₄Fe(CN)₆. Thereon, Fe(CN)₆⁴⁻ oxidation to Fe(CN)₆⁴⁺ proceeds on the probe electrode under a diffusion-limiting condition from Figure 4.2.1. Probe

current, I_p , decreases with decreasing distance between the probe and specimen surface, d , apparently indicating that the passive iron surface is insulating. However, the tendency of decreasing I_p is in the order of: the epoxy resin > the iron band passivated at $E_f = 0.8$ V (SHE) > the iron band passivated at $E_f = 0.4$ V (SHE). This means that the passivated iron surface is semiconductive and its conductivity is dependent on E_f as discussed later. On the other hand, $|I_s|$ increases with decreasing d , indicating that any cathodic reactions are promoted on the passivated iron surface by advancing the probe electrode to the surface.

Similarly, after the iron electrode was passivated at $E_f = 0.4, 0.6, 0.8$ or 1.0 V (SHE) for 3.6 ks in deaerated pH 8.4 borate solution, probe current, I_p , was measured as a function of d at $E_p = 1.2$ V and $E_s = 0.1$ V (SHE) in deaerated pH 8.4 borate solution containing 0.03 mol dm^{-3} $\text{K}_4\text{Fe}(\text{CN})_6$. In Figure 5.3.2, probe current normalized with a limiting probe current, $I_p/I_{p,\text{limit}}$, was plotted versus d . The value of $I_p/I_{p,\text{limit}}$ decreases with decreasing d , indicating that the passive iron surface is semiconductive. Moreover, at d less than $15 \text{ }\mu\text{m}$, the value of $I_p/I_{p,\text{limit}}$ decreases with increasing E_f .

It is known that the passive film on iron has a semiconductive property of n-type with a band gap energy, ΔE_g , of 1.6-2.0 eV (Schultze 1976, 2000, Wilhelm 1979) as described in 1.2.4. Ellipsometrical results as shown in Figure 5.3.3 (Sato 1971, Azumi 1985) indicate that thickness of passive films formed on iron in pH 8.4 borate solution increases linearly from 1 nm to 5 nm with increasing film formation potential, E_f . In the experiment, the potential of passive iron electrode is held at $E_s = 0.1$ V (SHE) which is lower than the edge potential of conduction band, E_{CB} , of iron oxide in pH 8.4 solution as shown in Fig. 1. 2. 1. Since the estimated potential of redox reaction ($\text{Fe}(\text{CN})_6^{3-/4-}$) is higher than flat band potential, E_{FB} , there are two possible processes of the electron transfer through the passive film for reduction of $\text{Fe}(\text{CN})_6^{3-}$ which diffuses from the platinum probe electrode as illustrated in Fig. 5.3.4. One is an elastic tunneling across the film for transfer reaction of electrons between the passivated metal substrate and redox system in solution when film is sufficiently thin (less than 3 nm) for tunneling. The probability, W , of direct electron tunneling is theoretically derived in Equation. 1.2.10 (Schultze 1978). In this case, the barrier thickness, d_b , in Equation. 1.2.9 can be regarded as the film thickness, d_f .

$$W = \exp\left(\frac{-2d_f\sqrt{2m_e\Delta E}}{\hbar}\right) \quad [5.3.1]$$

Alternative process of the electron transfer is an indirect elastic tunneling through the conduction band in the space charge layer of film. In this case, the thickness of the space charge layer, d_{SC} , influences the probability of indirect electron tunneling as shown in Equation 5.3.2.

$$W = \exp\left(\frac{-2d_{sc}\sqrt{2m_e\Delta\epsilon}}{\hbar}\right) \quad [5.3.2]$$

The thickness of the space charge layer, d_{sc} , is given by Equation 1.2.13 (Memming 1983).

$$d_{sc} = \sqrt{\frac{2\epsilon\epsilon_0 kT}{N_D e^2}} \sqrt{\frac{e\Delta\epsilon}{kT} - 1} \quad [1.2.13]$$

Equation 1.2.13 indicates that d_{sc} decreases with increasing donor density, N_D . Azumi reported (Azumi 1987) that N_D of the passive film on iron increases with decreasing film thickness, d_f . Therefore, the increase in d_f implies the decrease in probability of indirect tunneling of electrons. In both processes, therefore, the probability of electron transfer reaction irrespective of direct or indirect tunneling decreases with increasing d_f .

Probe current change as a function of d , i.e. decrease in I_p and increase in $|I_s|$ in Figure 5.3.1 and decrease in $I_p/I_{p,limit}$ at d less than 15 μm in Figure 5.3.2 with increasing E_f , i.e. film thickness, reflect redox reactivity of passive iron surface. It is known that the redox current of Fe(CN)_6^{4-} and Fe(CN)_6^{3-} on iron electrode passivated in pH 8.4 borate solution decreased with increasing film thickness (Schultze 1975). Results of Figures 5.3.1 and 5.3.2 are consistent with them. In principle, therefore, the probe current image measured by scanning probe electrode with a diameter of 10 μm in x and y directions at d less than 15 μm can evaluate difference in thickness of passive films on iron. In Figure 5.3.2, $I_p/I_{p,limit} = 0.6$ corresponds to $d = 5 \mu\text{m}$, which is employed later to obtain probe current images.

5.3.2 Evaluation of difference in thickness of passive films from probe current image

Figure 5.3.5b shows the probe current image of the specimen electrode with two iron bands embedded into epoxy resin as shown in Figure 5.3.5a when the probe electrode with a diameter of 20 μm was employed. The two iron bands were anodically polarized at $E_f = 0.8 \text{ V}$ and 0.4 V (SHE) for 3.6 ks to form passive films with different thickness (3.3 nm and 4.4 nm), respectively, prior to measurement of the probe current image. Figure 5.3.5b illustrates that probe current flowed above the epoxy resin surface is relatively low compared with that above the iron band surfaces because the epoxy resin surface is insulating. Moreover, higher probe current flows are noticeable above the iron surface covered with the thinner passive film, proving that difference in thickness of passive films on iron can be evaluated from the probe current image. Figure 5.3.5c shows the probe current profile along the dashed line drawn in Figure 5.3.5b. Lateral resolution of the probe current image was estimated to be 40 μm from the probe current profile at the boundary between epoxy resin and iron plate with passive film formed at 0.4 V, which was two times the diameter of the probe electrode. Furthermore, Figures

5.3.5d and 5.3.5e respectively show the specimen current image and profile simultaneously obtained with Figures 5.3.5b and 5.3.5c. Above the thinner passive film, the higher specimen current flows were comparable with those above the thicker film. However, lateral resolution of the specimen current image was estimated to be 80 μm , which was about two times the size of the probe current image.

In the case where the smaller probe electrode was employed, lateral resolution was significantly improved. Figures 5.3.6a and 5.3.6b respectively show the probe current image and profile of the specimen electrode with two iron bands embedded into epoxy resin. The two iron bands were anodically polarized at $E_f = 0.6$ V and 1.0 V (SHE) for 3.6 ks to form passive films with different thickness (3.8 nm and 4.9 nm), respectively, prior to measurement of the probe current image. Lateral resolution of the probe current image was estimated to be 23 μm from the probe current profile at the boundary between epoxy resin and iron plate with passive film formed at 1.0 V, which was slightly larger than two times the diameter of the probe electrode. Furthermore, the line profiles of probe current above the iron plate surface covered with thicker passive film (4.9 nm) are rather smooth, indicating that passive film formed at 1.0 V (SHE) is more uniform than that formed at 0.6 V (SHE).

5.3.4 *Heterogeneity of passive film associated with orientation of the substrate crystal grain*

Figure 5.3.7a shows a probe current image measured after the iron electrode surface with distinctive crystal grains was passivated at 1.0 V (SHE) for 3.6 ks. The probe current profile along the dashed line drawn in Figure 5.3.7a is also shown in Figure 5.3.7b. Moreover, Figure 5.3.8 shows an optical micrograph of the same surface region where the probe current image was measured. The index planes described on the optical micrograph represent orientation of each crystal grain evaluated from the etch pit shape. It is seen from comparison of Figures 5.3.7a and 5.3.8 that shapes of patch patterns on the probe current image coincide completely with shapes of crystal grains on the iron surface. Furthermore, the probe current flowed above the grain surface oriented to $\{100\}$ plane is less than that above the grain surface oriented to $\{110\}$ or $\{111\}$ plane. At first, surface roughness of the iron surface has to be taken into consideration to explain grain orientation dependence of the probe current. The measured surface roughness profile as shown in Figure 5.3.9 indicated that the $\{100\}$ grain surface is concave, while the $\{110\}$ or $\{111\}$ grain surface is convex, and that the height difference at the boundary between the $\{100\}$ and $\{110\}$ grains is about 0.4 μm . Assuming similar redox reactivities of $\{100\}$ and $\{110\}$ grains, change in probe current between $\{100\}$ and $\{110\}$ grains originating only from geometry can be easily estimated using the normalized probe current vs.

distance curve at $E_f = 1.0$ V (SHE) in Figure 5.3.2. The estimated change in probe current corresponding to height difference of $0.4\text{ }\mu\text{m}$ at the grain boundary is 0.6 nA . On the other hand, the real change in probe current at the grain boundary obtained from Figure 5.3.7b is 1.4 nA which is 2.3 times the estimated value. The change of 0.8 nA in probe current at the boundary between $\{110\}$ and $\{100\}$ crystal grains still remains even after correction of probe current is made for height difference at the grain boundary. This result supports the argument that difference in thickness of passive films formed on $\{110\}$ and $\{100\}$ crystal grains would reflect on the probe current image of Figure 5.3.6a or probe current profile of Figure 5.3.7b. It is expected that passive film formed on the $\{110\}$ grain is thinner than that on the $\{100\}$ grain since probe current above the $\{110\}$ grain is larger than that above the $\{100\}$ grain.

Kudelka et al (Kudelka 1997) measured thickness of passive films formed on a polycrystalline titanium electrode by anisotropy micro-ellipsometry (Michaelis 1993) and found that passive film formed on the (0001) grain with high packing density of the substrate surface is thinner than that on the (xxx0) grain with low packing density. In case of iron, packing density of the $\{110\}$ grain surface is higher than that of the $\{100\}$ grain surface. Similar relation between thickness of passive film and packing density of the substrate grain may hold for iron as well as titanium. The reason why the thinner passive film is formed on the substrate grain with higher packing density is not well understood, although it is probable that high packing density hinders penetration of electric field into the metal surface and suppresses passive film growth (Kudelka 1997). Further experiments are necessary to confirm the dependence of passive film thickness on orientation of substrate iron grains.

5.4 Conclusions

To evaluate difference in thickness of passive film formed on iron in deaerated pH 8.4 borate solution containing $\text{Fe}(\text{CN})_6^{4-}$ as a mediator, SECM was applied. The following conclusions were drawn:

- i) Difference in thickness of passive films formed on iron could be evaluated from the current flowing through the probe electrode, on which $\text{Fe}(\text{CN})_6^{4-}$ was oxidized to $\text{Fe}(\text{CN})_6^{3-}$, and the iron electrode, on which $\text{Fe}(\text{CN})_6^{3-}$ diffused from the probe electrode was reduced to $\text{Fe}(\text{CN})_6^{4-}$.
- ii) Lateral resolution of probe current image was two times the diameter of the employed probe electrode.

- iii) The probe current image of a polycrystalline iron passivated surface showed heterogeneity. Shapes of patch patterns on the probe current image coincided completely with shapes of crystal grains on the substrate iron surface.
- iv) Probe current passed above the grain surface which was oriented to a {100} plane was less than that above the grain surface oriented to either a {110} or a {111} plane.
- v) Grain orientation dependence of probe current was ascribed to difference in thickness of passive films formed on crystal grains.

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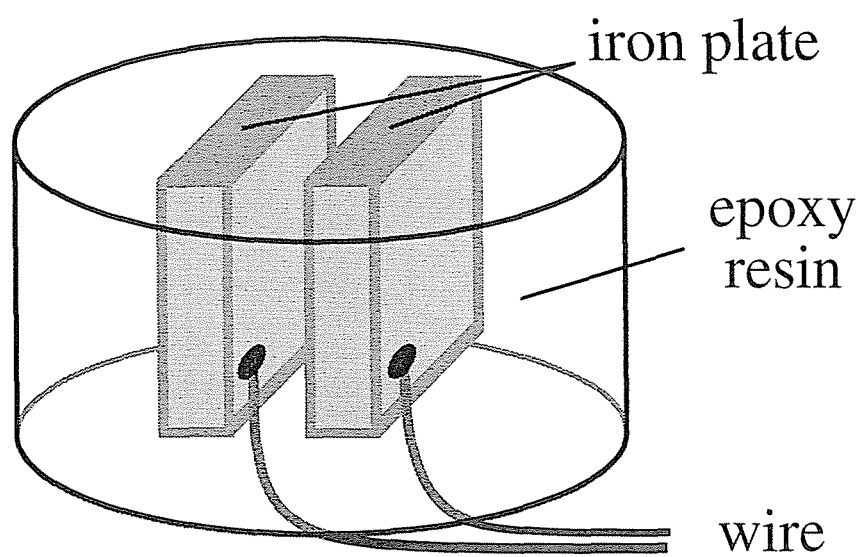


Fig. 5.2.1 Specimen electrode with two iron plates separately embedded into epoxy resin.
The distance between two iron plates was about 200 μm .

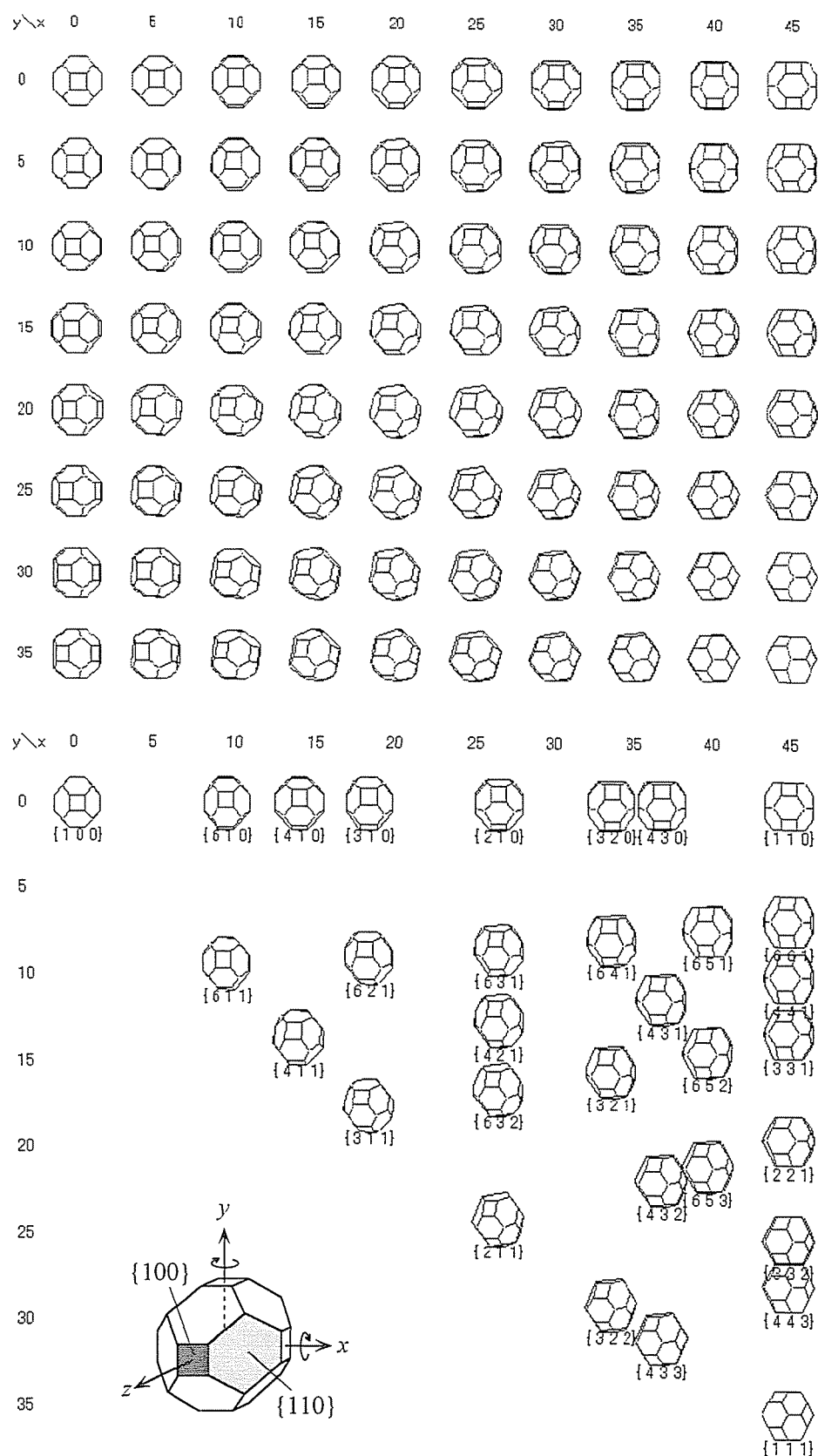


Fig. 5.2.2 Top views (from the z axis) of polyhedrons, which correspond to the shapes of etch pits on iron surface, rotated in the x and y axes.

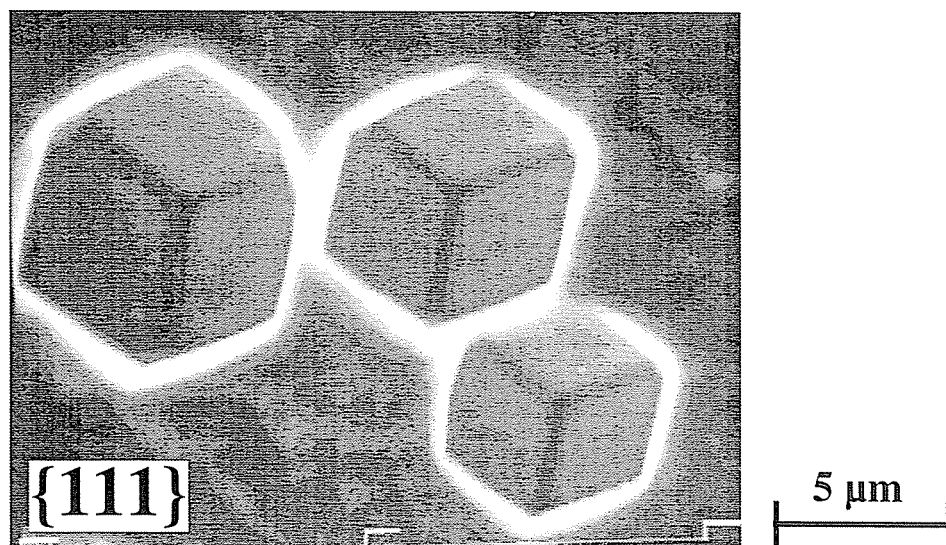
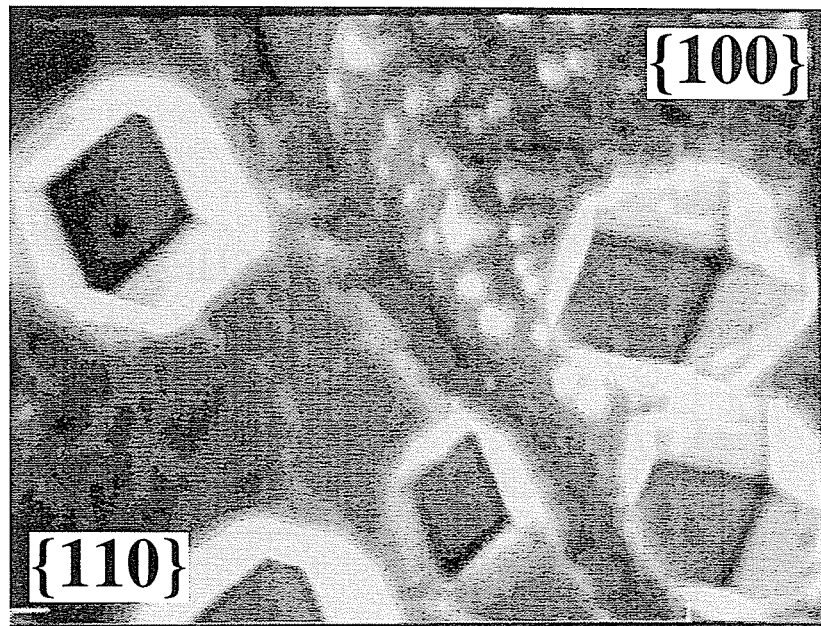


Fig. 5.2.3 SEM images of iron surface after the formation of etch pits.

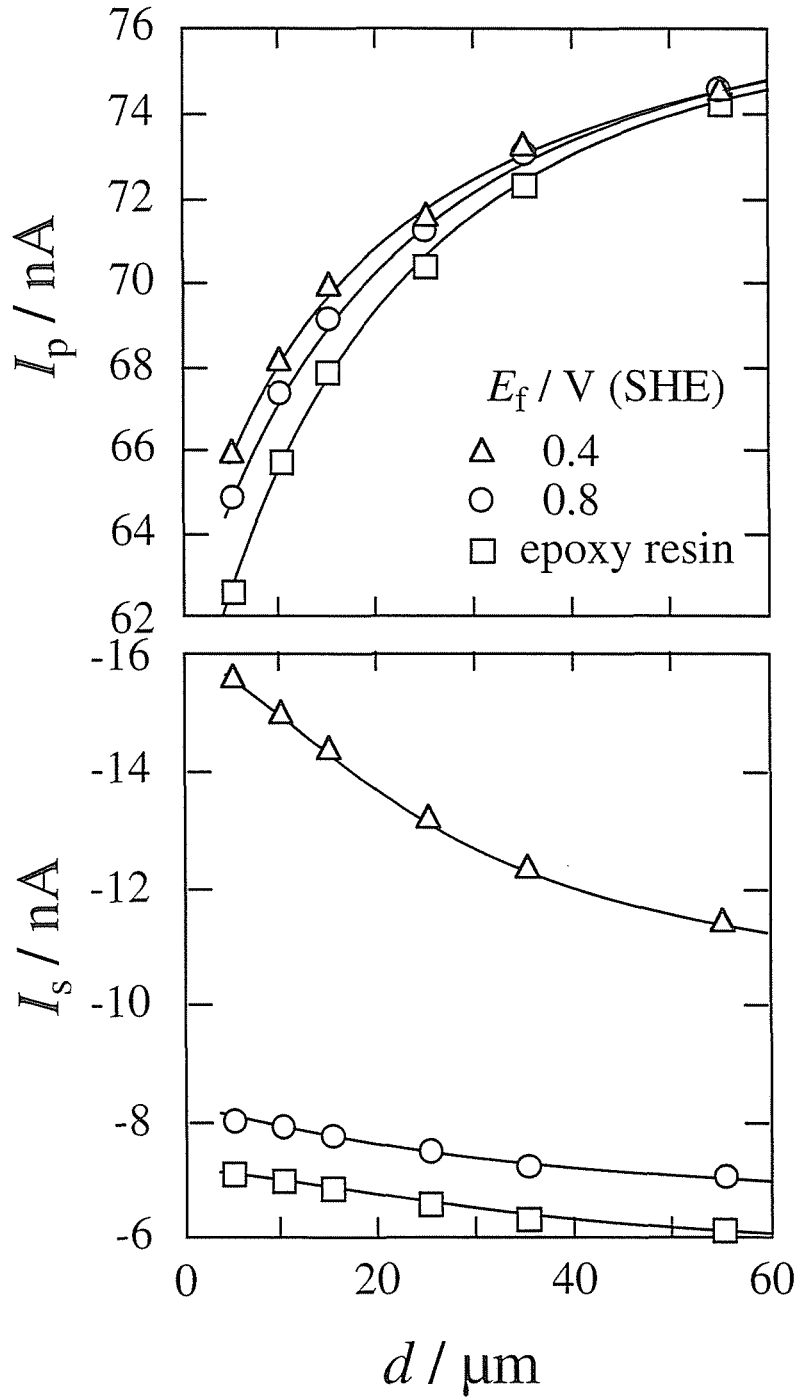


Fig. 5.3.1 Probe and specimen currents, I_p and I_s , measured as a function of distance between probe and specimen electrodes, d , when the probe electrode with a diameter of $20 \mu\text{m}$ approached the epoxy resin and to the iron bands passivated at $E_f = 0.4$ V and 0.8 V (SHE) in deaerated pH 8.4 borate solution. The probe electrode and iron bands were polarized at 0.9 V and 0.2 V (SHE), respectively, in deaerated pH 8.4 borate solution containing 0.03 mol dm^{-3} $\text{K}_4\text{Fe}(\text{CN})_6$.

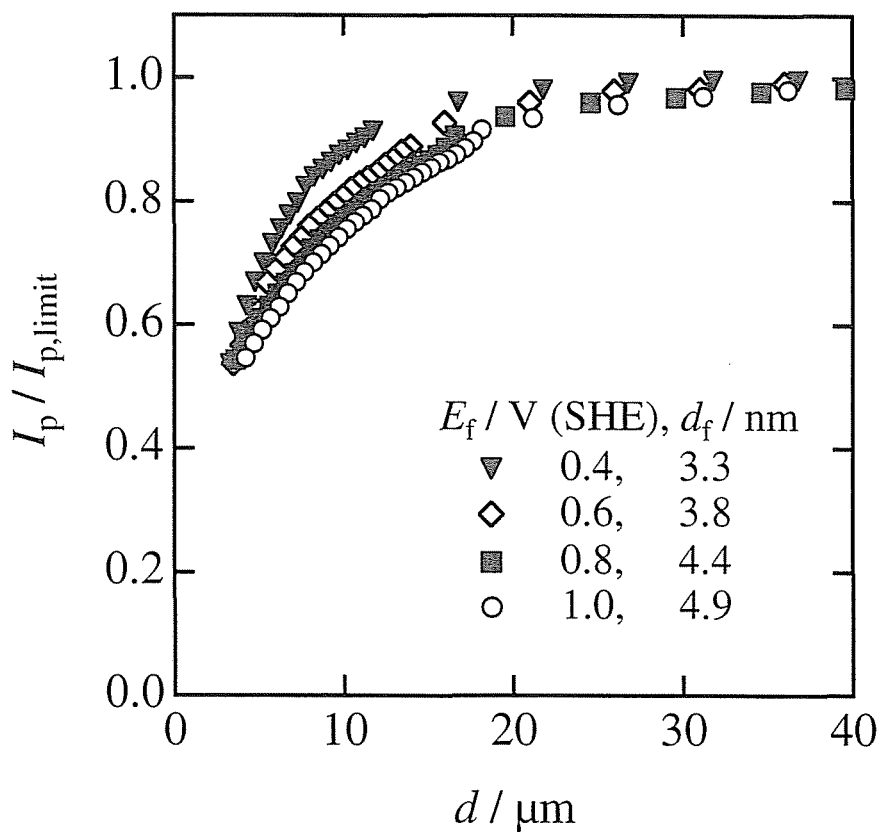


Fig. 5.3.2 Normalized probe current, $I_p / I_{p,limit}$, as a function of distance between probe and iron electrodes, d . The probe and iron electrodes were polarized at 1.2 V and 0.1 V (SHE), respectively, in deaerated pH 8.4 borate solution containing $0.03 \text{ mol dm}^{-3} \text{ K}_4\text{Fe(CN)}_6$ after the iron electrode was passivated at $E_f = 0.4, 0.6, 0.8$ or 1.0 V (SHE) for 3.6 ks in deaerated pH 8.4 borate solution. Thickness of passive film, d_f , was from Azumi 1985.

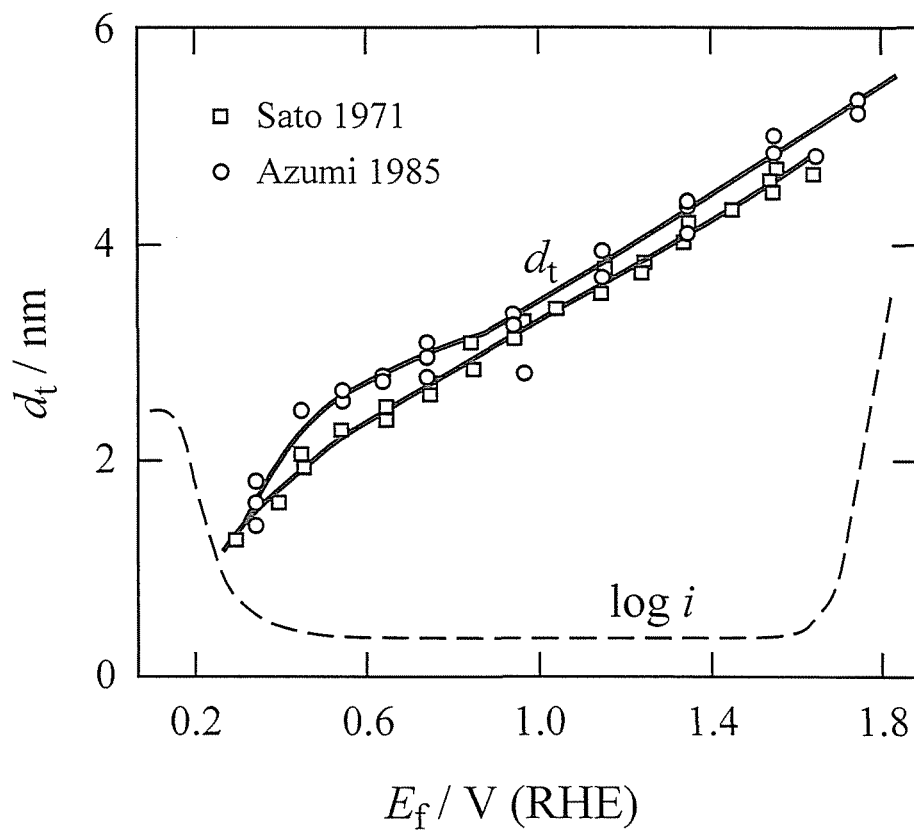


Fig. 5.3.3 Ellipsometrical film thickness of passive film, d_t , formed on iron (Sato 1971, Azumi 1985). The film was formed by anodic polarization at E_f for 3.6 ks in pH 8.4 borate solution

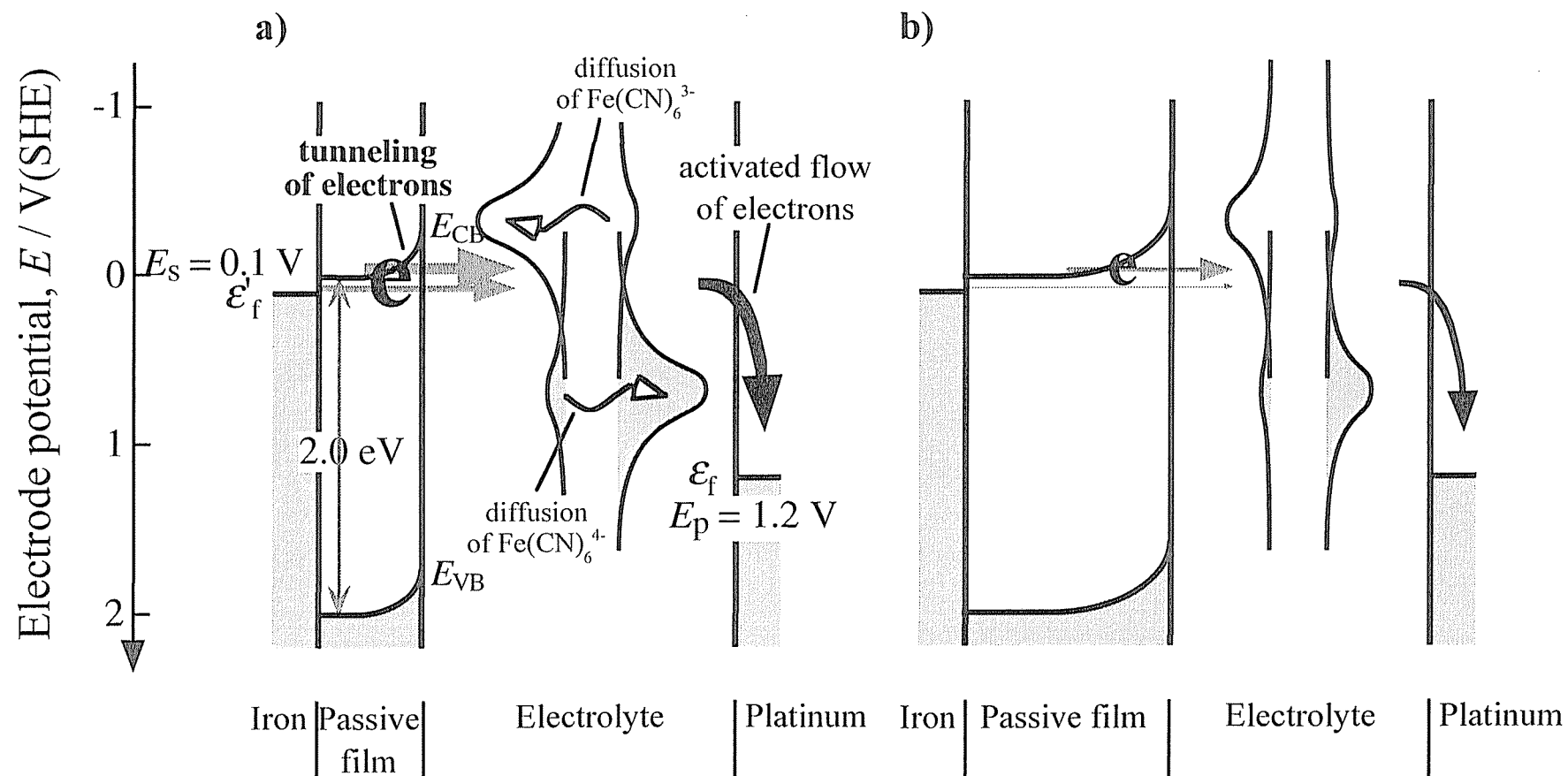


Fig. 5.3.4 Schematic illustration by an electronic band model for charge transfer between iron electrode with a) thin or b) thick passive film, $\text{Fe(CN)}_6^{3-}/\text{Fe(CN)}_6^{4-}$ redox system and platinum probe electrode.

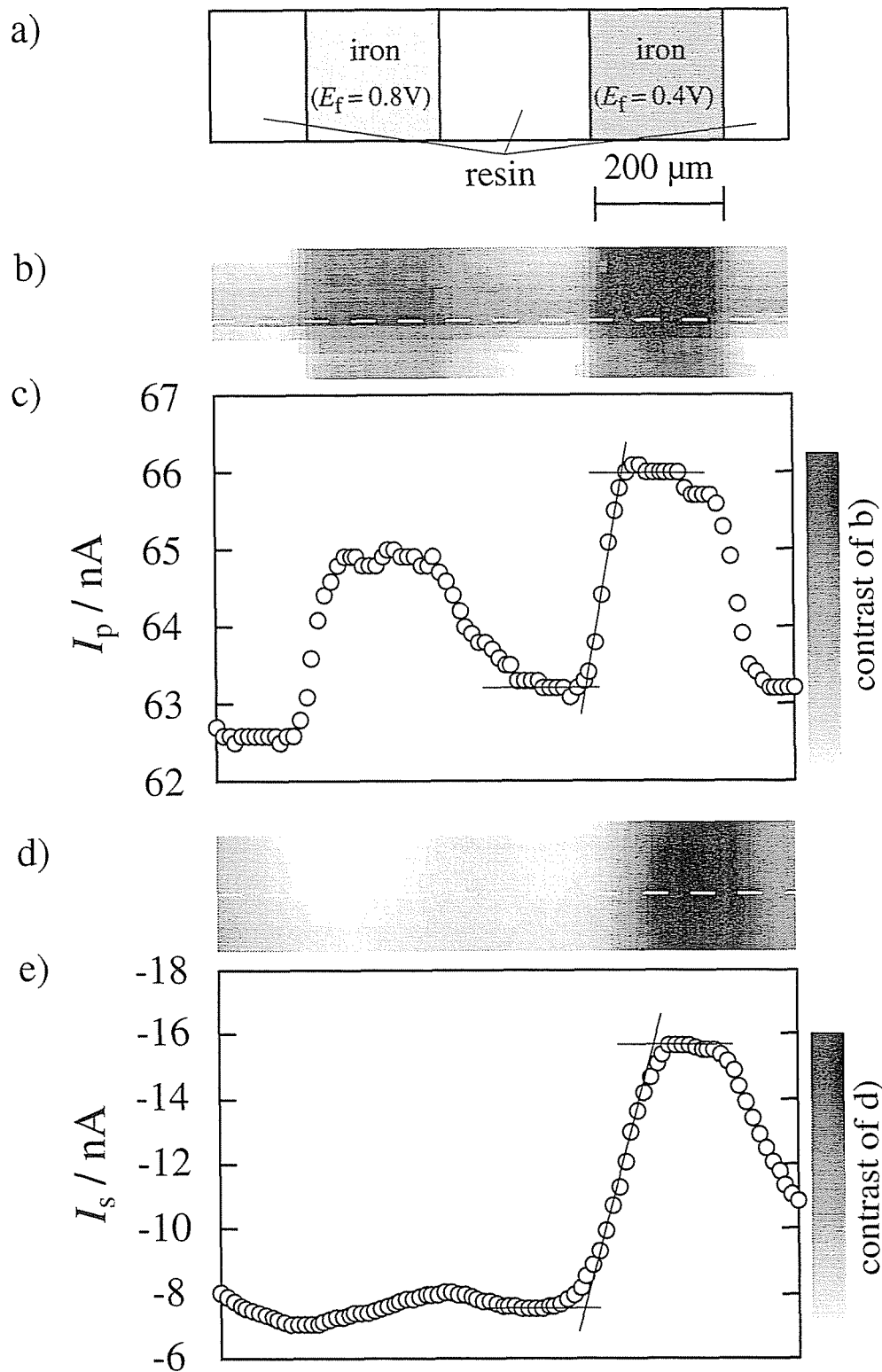


Fig. 5.3.5 a) Top view of specimen electrode. b) Probe current image and d) specimen current image obtained when the probe electrode with a diameter of $20\text{ }\mu\text{m}$ was scanned over the specimen electrode surface with two iron bands passivated at $E_f = 0.4$ and 0.8 V (SHE), respectively, in deaerated pH 8.4 borate solution. The probe electrode and iron bands were polarized at 0.9 V and 0.2 V (SHE), respectively, in deaerated pH 8.4 borate solution containing $0.03\text{ mol dm}^{-3}\text{ K}_4\text{Fe}(\text{CN})_6$. c) Probe current profile and e) specimen current profile obtained when the probe electrode was scanned along the dashed line drawn on the current images.

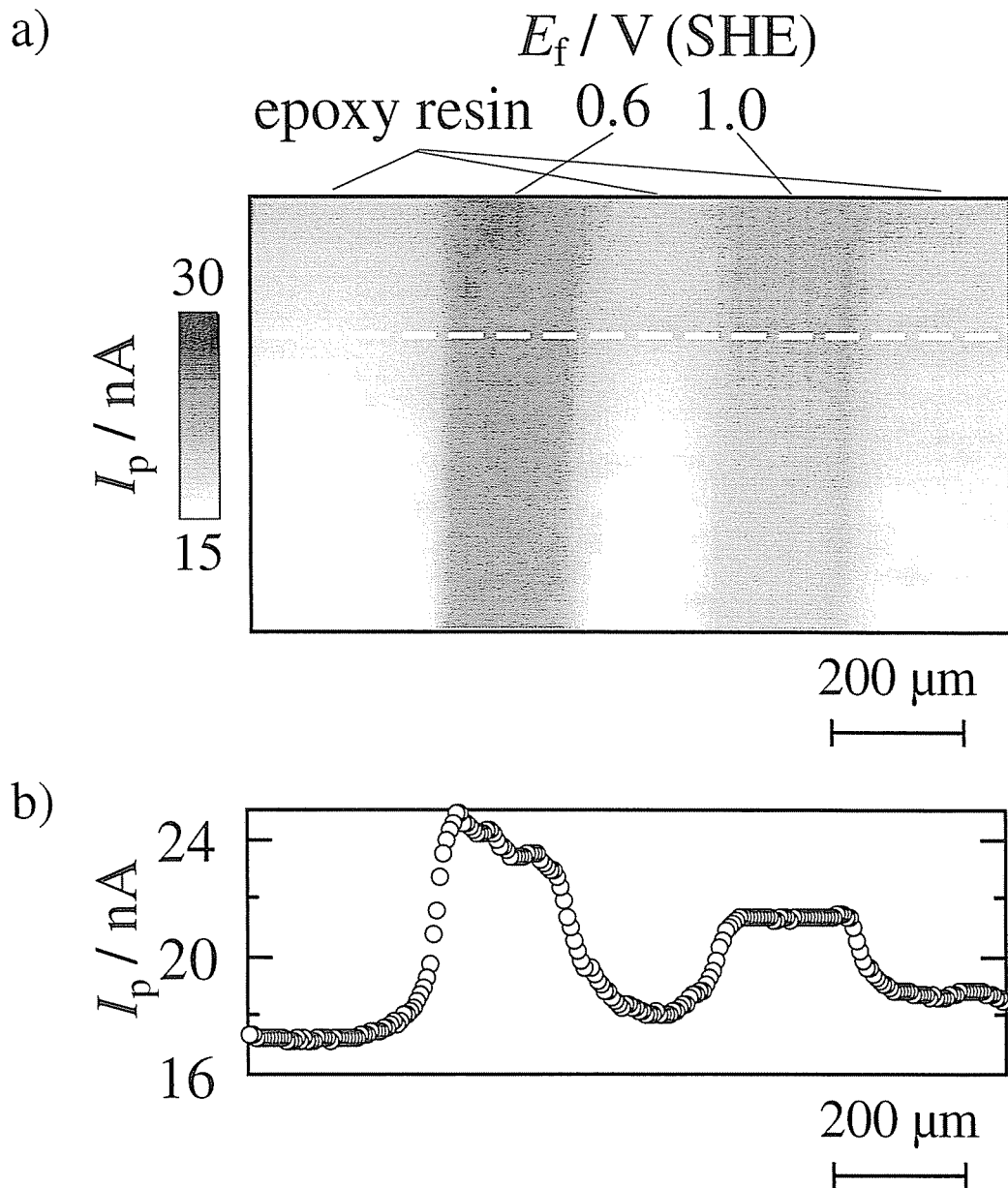


Fig. 5.3.6 a) Probe current image of the specimen electrode with two iron bands embedded into epoxy resin. The two iron bands were anodically polarized at $E_f = 0.6 \text{ V}$ and 1.0 V (SHE) for 3.6 ks to form passive films with different thickness of 3.8 and 4.9 nm (Sato 1974), respectively, prior to the measurement of the probe current image. For measurement of the probe current image, the probe and iron electrodes were polarized at 1.2 V and 0.1 V (SHE), respectively, in deaerated pH 8.4 borate solution containing $0.03 \text{ mol dm}^{-3} \text{ K}_4\text{Fe}(\text{CN})_6$.

b) Probe current profile along the dashed line drawn in Fig. 5.3.5b.

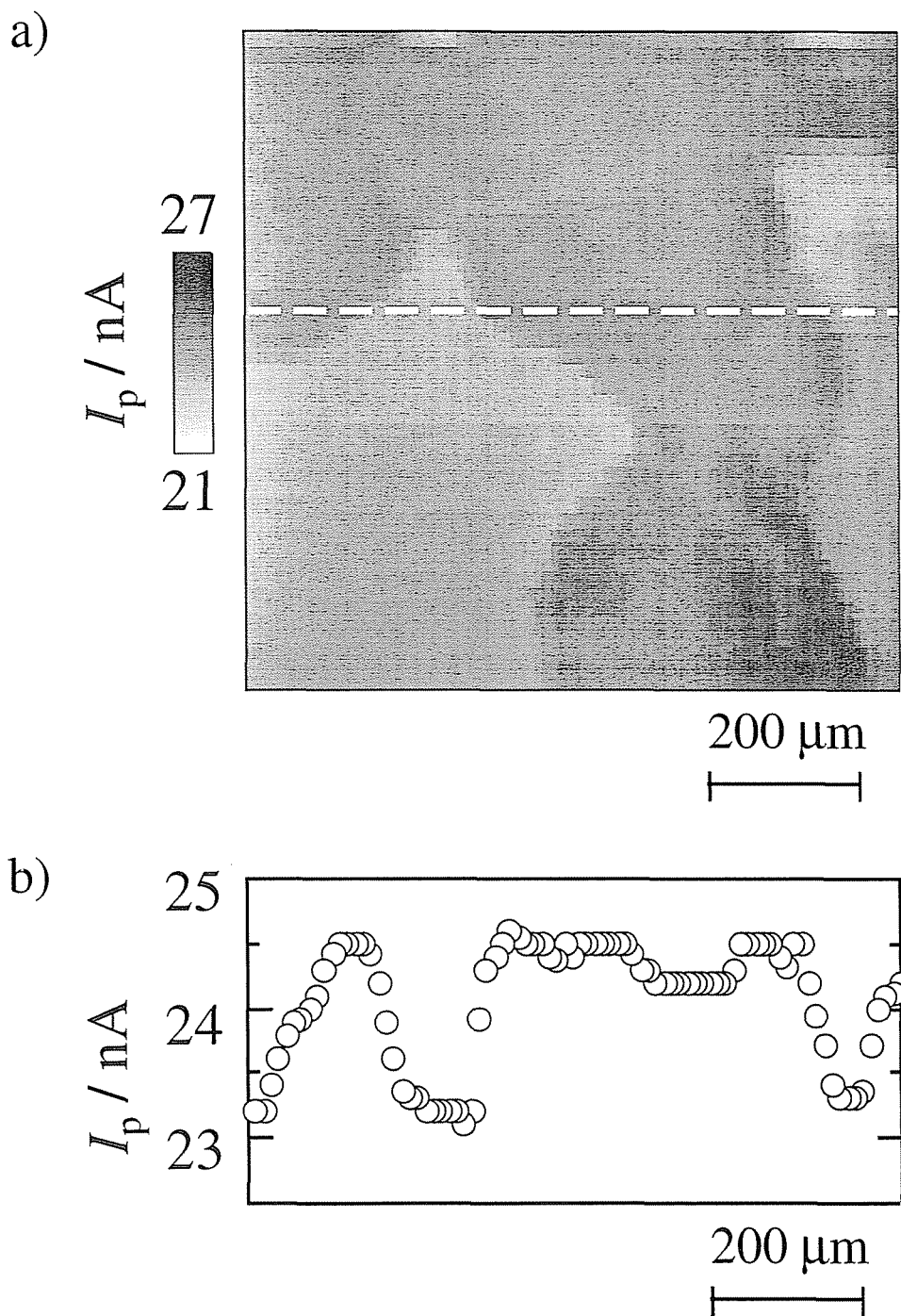
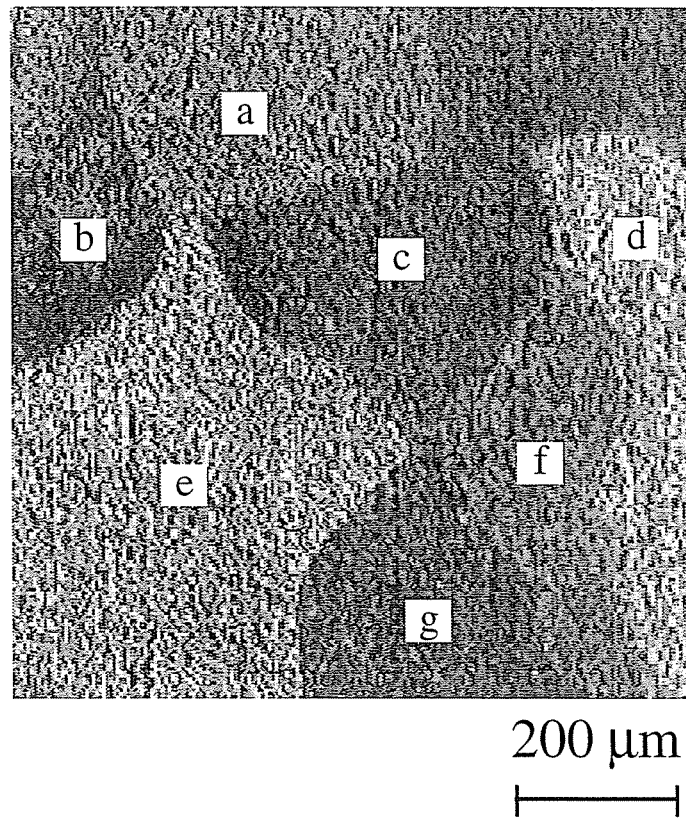


Fig. 5.3.7 a) Probe current image measured after the iron electrode surface with distinctive crystal grains was passivated at 1.0 V (SHE) for 3.6 ks. For measurement of the probe current image, probe and iron electrodes were polarized at 1.2 V and 0.1 V (SHE), respectively, in deaerated pH 8.4 borate solution containing $0.03 \text{ mol dm}^{-3} \text{ K}_4\text{Fe}(\text{CN})_6$. b) Probe current profile along the dashed line drawn in Fig. 5.3.6a.



Index plane		rotation angle	
		[100]	[010]
a	$(\bar{0}11)$	-10°	5°
b	(111)	0°	-5°
c	(101)	-5°	15°
d	(001)	10°	0°
e	$(0\bar{0}1)$	10°	0°
f	(101)	-10°	5°
g	(101)	0°	15°

Fig. 5.3.8 Optical micrograph of the same surface region where the probe current image was measured in Fig. 5.3.6a.
Index planes described on the optical micrograph represent orientation of each crystal grain evaluated from the etch pit shape. The real deviation from the index plane is described with rotation angles about [100] and [010] axes in the table.

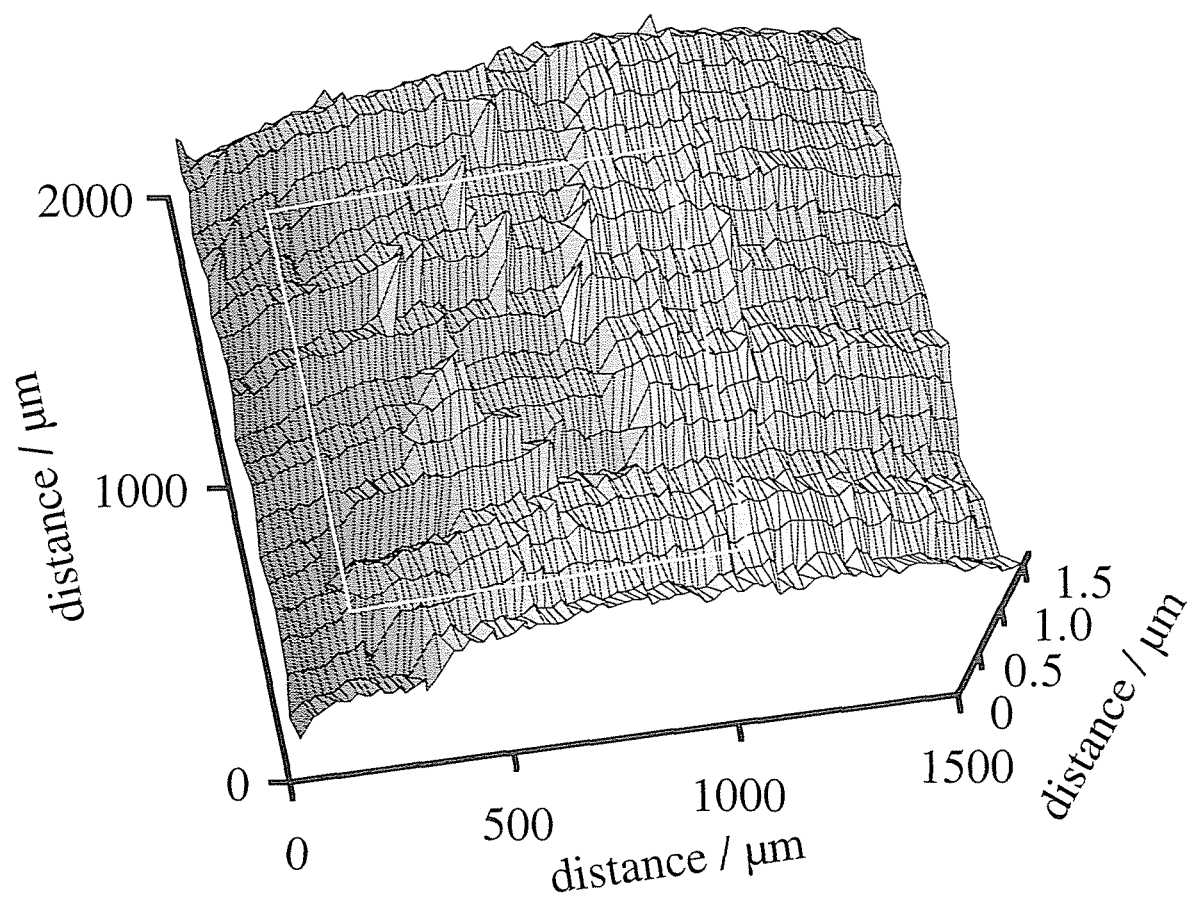


Fig. 5.3.9 Topographical image of the iron surface measured by a surface contracer.

6 Heterogeneous growth of anodic oxide film on a polycrystalline titanium electrode

6.1 Introduction

In Chapter 5, heterogeneity of passive film formed on iron electrode was evaluated using SECM. The probe current image had a distribution in reactivity of the redox ($\text{Fe}(\text{CN})_6^{3-}/\text{Fe}(\text{CN})_6^{4-}$) reaction which originated from the difference in film thickness, depending on substrate grain orientation. In case of passive film on iron, the film thickness is so thin that the redox reaction can proceed with an elastic tunneling of electrons. On the other hand, in case of thicker passive film such as anodic oxide film on titanium, it seems difficult that the redox reaction proceeds with a direct elastic tunneling of electrons because the film thickness is larger than the tunneling distance (< 3 nm). Therefore, the question rises whether the heterogeneity of thicker passive films can be evaluated from probe current image using the redox reaction.

Structure or thickness of oxide film on titanium also depends on substrate orientation. For example, Kozlowski et al (Kozlowski 1988, 1989) and Kudelka et al (Kudelka 1995, 1997) investigated heterogeneity of anodic oxide film formed on a polycrystalline titanium electrode in H_2SO_4 solution by various microscopic techniques such as photoelectrochemical microscopy and anisotropy micro-ellipsometry. Kozlowski et al reported that the non-uniform photocurrent response was attributed to heterogeneity in defect density of the film instead of that in film thickness. On the other hand, Kudelka et al, using micro electrochemistry and micro-ellipsometry, reported that higher photocurrent flowed on the titanium substrate grain with thinner oxide film and that the thinnest oxide film with the highest donor density was formed on the substrate grain with the highest package densities. Discrepancy between these results may be caused by differences in substrate crystallography and surface preparation. In any cases, it is necessary to examine whether heterogeneity of anodic oxide film on a polycrystalline titanium is caused by difference in film thickness, defective film structure, and/or substrate grain orientation.

In this chapter, SECM is applied to examine heterogeneity of anodic oxide film grown on a polycrystalline titanium electrode in deaerated pH 8.4 borate solution. Raman microprobe spectroscopy is also applied to support SECM results.

6.2 Experimental

6.2.1 Specimen preparation

A cross section of titanium rod (purity over 99.5%) with a 10 mm diameter was used as a specimen electrode. The electrode surface was electropolished in a mixed solution of methanol, 2-methoxyethanol, 2-ethoxyethanol, and perchloric acid in the volume ratio of 28 : 10 : 10 : 2 at 210 K. Afterward, the specimen electrode was anodically polarized at a constant potential of E_f for 3.6 ks in deaerated pH 8.4 borate solution to form an anodic oxide film.

6.2.2 SECM measurement

The SECM apparatus (type III in Table 4.3.1) was used for this experiment. After film formation, the electrolyte was changed to deaerated pH 8.4 borate solution containing $0.03 \text{ mol dm}^{-3} \text{ K}_4\text{Fe}(\text{CN})_6$ and a probe current image of the specimen electrode surface was measured under the following conditions:

- i) Distance separating probe and specimen electrodes was kept at about $5 \text{ }\mu\text{m}$.
- ii) The probe electrode was scanned stepwise to a distance of $1000 \text{ }\mu\text{m}$ at $5 \text{ }\mu\text{m}$ intervals of in the x direction and to a distance of 800 or $500 \text{ }\mu\text{m}$ at intervals of 10 or $20 \text{ }\mu\text{m}$ in the y direction.
- iii) Probe and specimen electrode potentials were held at $E_p = 1.2 \text{ V (SHE)}$ and $E_s = -0.4 \text{ V (SHE)}$, respectively, to oxidize $\text{Fe}(\text{CN})_6^{4-}$ on the probe electrode and to reduce again on the specimen electrode. The redox reaction of $\text{Fe}(\text{CN})_6^{3-/4-}$ was repeated between the probe and titanium electrodes with a positive feedback mode.
- iv) Probe current was recorded when the probe electrode scan was stopped at an interval of $5 \text{ }\mu\text{m}$ in the x direction.

6.2.3 Miscellaneous

Micro-areas of the electrode surface were characterized with a Raman microprobe spectrometer (JASCO, NRS-2000) having a $40 \text{ }\mu\text{m}$ diameter argon ion laser excitation beam (13 mW , wavelength = 514.5 nm). Back scattering light from the surface was detected with a CCD (Princeton Instr., LN/CCD-1100PF) and integrated 10 times.

6.3 Results and Discussion

6.3.1 Anodic polarization of a polycrystalline titanium electrode by successive potential step

Anodic polarization of a polycrystalline titanium electrode was performed, starting from 1 V (SHE) and with successive potential steps of 1 V or 2 V at an interval of 3.6 ks up to 10 V (SHE). Figure 6.3.1 shows time variation of anodic current density, i , during anodic polarization of the titanium electrode at the respective potential, E_f , in pH 8.4 borate solution. An almost linear relationship holds between $\log i$ and $\log t$ up to 6 V (SHE). At potentials higher than 6 V (SHE), however, the current decay deviates upward from the linear relationship. This deviation may be associated with other reactions such as oxygen evolution which would occur in parallel with film growth. Anodic current density, i_a , at 3.6 ks-anodic polarization is plotted versus potential, E_f , in Figure 6.3.2. It is seen that anodic current density increases significantly at potentials higher than 3 V (SHE).

6.3.2 SECM images of anodic oxide films on a polycrystalline titanium electrode

Figure 6.3.3 shows voltammograms of the titanium electrode measured in pH 8.4 borate solutions with and without $0.03 \text{ mol dm}^{-3} \text{ K}_3\text{Fe}(\text{CN})_6$ after anodic polarization at 6 V (SHE) for 3.6 ks in pH 8.4 borate solution. In solution with $\text{K}_3\text{Fe}(\text{CN})_6$, a significant cathodic current (e.g., $-2.8 \times 10^{-4} \text{ A cm}^{-2}$ at -0.6 V) flows corresponding to reduction of $\text{Fe}(\text{CN})_6^{3-}$ whereas a very small current (e.g., $-2.2 \times 10^{-6} \text{ A cm}^{-2}$ at -0.6 V) flows in solution without $\text{K}_3\text{Fe}(\text{CN})_6$. This indicates that reduction of film would be negligible compared to reduction of $\text{Fe}(\text{CN})_6^{3-}$ when the titanium electrode is polarized at -0.4 V (SHE) for SECM measurement.

Figure 6.3.4 shows typical probe current images of the titanium electrode surfaces measured in pH 8.4 borate solution containing $0.03 \text{ mol dm}^{-3} \text{ K}_4\text{Fe}(\text{CN})_6$ after 3.6 ks-anodic oxidation at each potential, E_f , in pH 8.4 borate solution. Probe current images reflect difference in reduction rates of $\text{Fe}(\text{CN})_6^{3-}$ at the local area of the titanium electrode surface located just below the probe electrode because the redox reaction of $\text{Fe}(\text{CN})_6^{3-}/\text{Fe}(\text{CN})_6^{4-}$ proceeds with a positive feedback mode between the probe and titanium electrodes.

Figure 6.3.5 shows the optical micrograph of the same area where the probe current image of Figure 6.3.4d was measured. Comparison of Figures 6.3.4d and 6.3.5 displays that the pattern in the probe current image coincides with the substrate grain shape in the optical micrograph.

Figure 6.3.6 shows a series of probe current profiles along the dashed line drawn in Figure 6.3.5 for the titanium electrode surfaces subjected to anodic oxidation at various potentials. Background current in the profiles decreases with increasing film formation potential, E_f , whereas current oscillation in the profiles increases conversely, becoming significant at potentials higher than 3 V (SHE). This indicates that heterogeneous growth of anodic oxide film,

depending on each substrate grain, becomes significant at potentials higher than 3 V (SHE).

6.3.3 *Laser Raman microprobe spectroscopy for surface characterization of anodic oxide films on substrate grains*

Laser Raman spectroscopy is a powerful tool for characterization of electrode surface layers. By using laser Raman spectroscopy, Ohtsuka et al investigated anodic oxide film structure formed on titanium in pH 6.9 phosphate solution (Ohtsuka 1986). They reported that an amorphous anodic oxide film grows at potentials lower than 4 V, whereas an anatase type of TiO_2 film grows at potentials higher than 4 V. On the other hand, a rutile type of TiO_2 film grows at potentials higher than 120 V in $1 \text{ mol dm}^{-3} \text{ H}_2\text{SO}_4$ solution (Arsov 1991).

Figure 6.3.7 shows Raman spectra of anodic oxide films formed on substrate grain, B, in Figure 6.3.5. Sharp peaks at 266.3 , 520.3 , and 587.3 cm^{-1} originate from other emission sources and not from the titanium surface. Raman shifts at 400 , 515 and 640 cm^{-1} marked with open circles in Figure 6.3.7 are assigned to an anatase type of TiO_2 (Ohtsuka 1986), whereas those at 232 , 447 and 612 cm^{-1} marked with solid circles are assigned to a rutile type of TiO_2 (Felske 1989). The broad Raman peak between 380 and 700 cm^{-1} emerges from the background at potentials higher than 3 V (SHE) and the peak area increases with increasing film formation potential, E_f . It is difficult to assign the anodic oxide film to either an anatase type or a rutile type from broad Raman spectra in Figure 6.3.7. However, it seems that anodic oxide film is an anatase type of TiO_2 with a low crystallinity because the film formation potential used in this experiment is up to 10 V (SHE) and a rutile type of TiO_2 film is not formed in this potential range (Arsov 1991).

Figure 6.3.8 shows the relation between Raman intensity at 608 cm^{-1} for grain B and average film thickness obtained ellipsometrically (Ohtsuka 1985). The almost linear relation implies that the anodic oxide film grows without changes of degree in grain crystallinity at potentials exceeding 3 V (SHE).

Figure 6.3.9 shows Raman spectra of anodic oxide films formed at 8 V (SHE) on grains, A, B and C in Figure 6.3.5. From comparison between Figures 6.3.5 and 6.3.9, the order of decrease in probe current between grains, A, B and C, appears to coincide with increased Raman intensity, indicating that probe current image heterogeneity is mainly ascribed to difference in thickness of anodic oxide films formed on substrate grains.

6.3.4 *Distribution of redox reaction reactivity on a polycrystalline titanium*

The probe current images indicated heterogeneous growth of anodic oxide film

depending on the substrate grains at potential higher than 3 V (SHE). During measurement of probe current images, the potential of the specimen electrode, E_s , was kept at -0.4 V (SHE), which was lower than the potential, E_f , at which the anodic oxide film was formed. If the flat-band potential of the anodic oxide film on titanium, E_{FB} , is less noble than $E_s = -0.4$ V (SHE), reduction of anodic oxide film would hardly occur as compared with that of $\text{Fe}(\text{CN})_6^{3-}$. Flat-band potentials, E_{FB} , of anodic oxide films on titanium have been measured so far in different pH solutions as shown in Table 6.3.1.

Table 6.3.1 Flat-band potential, E_{FB} , and band gap energy, ΔE_g , of the oxide film on titanium

Reference	E_{FB} / V (SHE)	ΔE_g / V	Solution	pH
Bolts 1976	-0.076-0.059 pH	3.0	0.5 M sulfate	2.5 ~ 13
Heusler 1977	0.303 -0.056 pH	-	0.1 M acetic-acetate	0.3 ~ 8
Tomkiewicz 1979	-0.236	-	0.1 M CH_3COOH	2.7
	-0.556	-	0.3 M phosphate	6.5
	-0.876	-	0.1 M NaOH	13
	-0.156	-	1 M Na_2SO_4	3
Gutierrez 1982	-0.156	-	1 M HClO_4	0.3
Schultze 1982	0.04	3.05	1 M HClO_4	0.3
Schultze 1983	0.04	-	1 M HClO_4	0.3
Memming 1983	-	3.2	-	1
Ohtsuka 1984	-	3.2	0.15 M borate	8.4
Azumi 1997	-0.50	-	0.15 M borate	8.4
Ohtsuka 1998	0.026 (RHE)	-	0.1 M H_2SO_4	0.7

If pH dependence (-0.059 V pH^{-1}) of E_{FB} is considered, the average value of E_{FB} corrected to pH 8.4 is -0.48 ± 0.02 V (SHE), which coincides with $E_{FB} = -0.50$ V (SHE) measured in pH 8.4 borate solution (Azumi 1997). Therefore, it is confirmed that E_{FB} is less noble than E_s and reduction of anodic oxide film hardly occurs at E_s . Probe current reflects the reduction rate of $\text{Fe}(\text{CN})_6^{3-}$ at the local area of the titanium electrode surface located just below the probe electrode. A series of anodic probe current images, therefore, indicates heterogeneous film growth on a polycrystalline titanium electrode, depending on substrate grain. Furthermore, even if film changes slightly, probe current would reflect difference in film properties at the film formation potential.

Anodic oxide film on titanium has n-type semiconductive properties with a band gap of 3.0-3.2 eV. It is known (Schultze 1975, 1978) that reduction of $\text{Fe}(\text{CN})_6^{3-}$ on a metal electrode covered with passive film proceeds with electron tunneling through the film. Ellipsometrical thickness (Ohtsuka 1985) of anodic oxide film formed on titanium at potentials higher than 4 V (SHE) is thicker than 10 nm. This value is too thick for direct elastic tunneling of electrons through the film, since probability of direct elastic tunneling, W , decreases exponentially with

film thickness, d_t , as formulated approximately by Equations 1.2.10 or 5.3.1. The value of W in Equation 5.3.1 is negligibly small for $d_t > 3$ nm. The direct elastic tunneling mechanism, therefore, is not operative in reduction of $\text{Fe}(\text{CN})_6^{3-}$ on the titanium electrode at -0.4 V (SHE). Another mechanism of electron transfer, therefore, has to be considered for reduction of $\text{Fe}(\text{CN})_6^{3-}$.

The following two mechanisms may be proposed as possibilities. The first one is a resonance tunneling of electrons via the donor level in anodic oxide film. Probability of two step resonance tunneling of electrons is given by Equation 1.2.12. In this case, cathodic current flowing through the titanium electrode should decrease with increase in film thickness, d_t , or with decrease in donor density, N_D . It has been reported (Heusler 1975) that the thinner anodic oxide film on titanium has the higher donor density. The second one is an indirect elastic tunneling of electrons in the film conduction band via the film space charge layer. In the latter case, thickness, d_{sc} , of the space charge layer directly influences indirect tunneling probability of electrons as discussed with Equation 1.2.13 (Memming 1983).

$$d_{sc} = \sqrt{\frac{2\epsilon\epsilon_0 kT}{N_D e^2}} \sqrt{\frac{e\Delta\epsilon}{kT} - 1} \quad [1.2.13]$$

Equation 1.2.13 indicates that d_{sc} decreases with increasing donor density, N_D , i.e., decreasing film thickness, d_t . Furthermore, decrease in d_{sc} implies increased probability of indirect tunneling of electrons in the conduction band via the space charge layer. Cathodic current passed through the titanium electrode, therefore, would increase with decreasing film thickness as far as the indirect tunneling mechanism is operative. Surface states of anodic oxide film may contribute to tunneling processes because the cathodic current peak at -0.35 V (SHE) in Figure 6.3.3 suggests presence of surface states which are presumably at an energy level lower by 0.15 eV than the conduction band edge of the film. At present, it is difficult to decide which mechanism, resonance tunneling or indirect tunneling, predominates in reduction of $\text{Fe}(\text{CN})_6^{3-}$ on the titanium electrode, although it seems that the indirect tunneling mechanism has an advantage of rapid and continuous transfer of electrons in the conduction band as compared with a discontinuous transfer of electrons between localized donor sites in resonance tunneling. Figure 6.3.10 illustrates schematically the charge transfer between titanium electrode with (a) thin or (b) thick anodic oxide film, $\text{Fe}(\text{CN})_6^{3-}/\text{Fe}(\text{CN})_6^{4-}$ redox system, and platinum probe electrode by using an electronic band model. The above discussion supports the concept that cathodic current resulting from reduction of $\text{Fe}(\text{CN})_6^{3-}$ on the titanium electrode increases with increasing donor density in the anodic oxide film, i.e., decreasing film thickness. Consequently, it is inferred that heterogeneity of probe current image mainly reflects difference in thickness of

the anodic oxide film formed on the titanium electrode, depending on substrate grains.

Kudelka et al (Kudelka 1995) have reported that the thinnest anodic oxide film with the highest donor density is formed on titanium substrate grains with highest package density, which is oriented to the basal (0001) index plane. On the other hand, the thickest oxide film with the lowest donor density is formed on substrate grains with the lowest package density, which is oriented to the (XXX0) index plane. Grains, A, B and C, in the optical micrograph of Figure 6.3.5 have relatively low probe current images as compared with neighbor grains. Grains, A, B and C, are probably oriented to the (XXX0) index plane with anisotropy. As shown in the optical micrograph in Figure 6.3.5, most grains have twin textures which may emerge on the basal (0001) index plane. As seen from comparison between the optical micrograph in Figure 6.3.5 and the probe current image in Figure 6.3.4d, grains with twin textures have relatively high probe current images corresponding to relatively thin anodic oxide film.

6.4 Conclusions

The following conclusions are drawn by applying SECM to anodic oxide film grown on a polycrystalline titanium electrode in pH 8.4 borate solution.

- i) The probe current image could detect heterogeneity of anodic oxide film, depending on substrate crystal grains.
- ii) This heterogeneity increased with increasing film formation potential, E_f . It became significant at potentials higher than 3 V (SHE).
- iii) Raman microprobe spectroscopy indicated that TiO_2 film (probably anatase type) with a low crystallinity forms at potentials higher than 3 V (SHE) and supported the concept that heterogeneity of probe current image is mainly ascribed to differences in thickness of passive films on substrate grains.
- iv) It was found from comparison between the optical micrograph and the probe current image that grains with twin textures have relatively thin anodic oxide films as compared with grains without twin textures.

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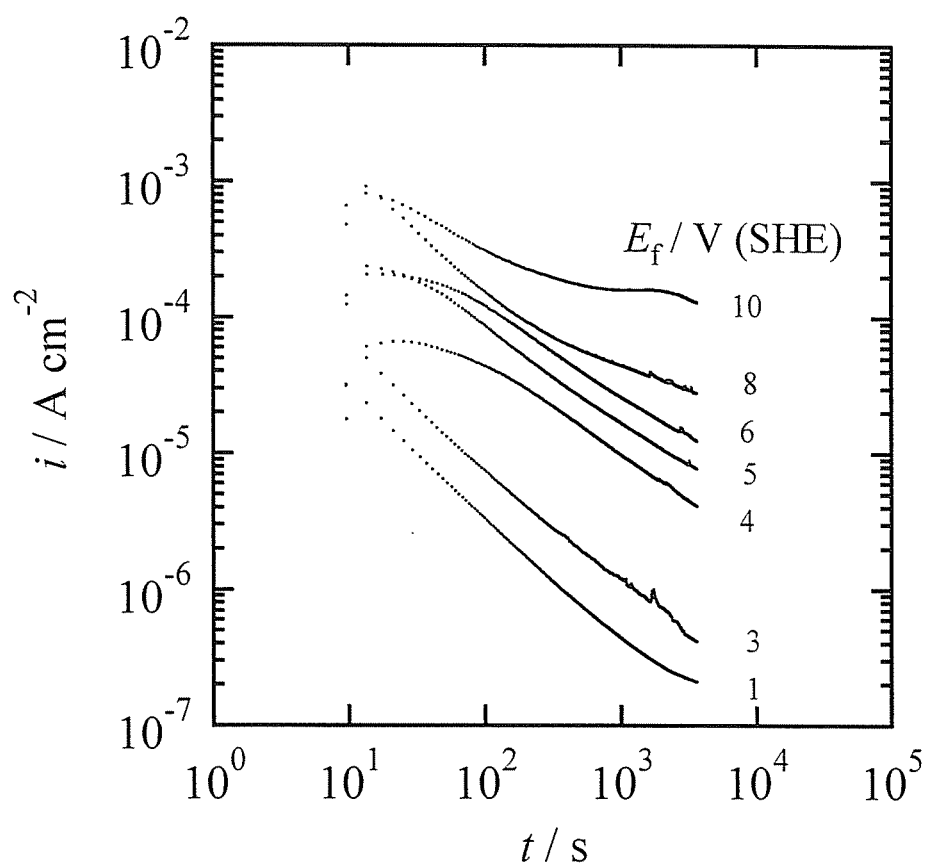


Fig. 6.3.1 Relation between logarithm of anodic current density, $\log i$, and logarithm of time, $\log t$, during anodic polarization at E_f by the successive potential steps for titanium electrode in pH 8.4 borate solution.

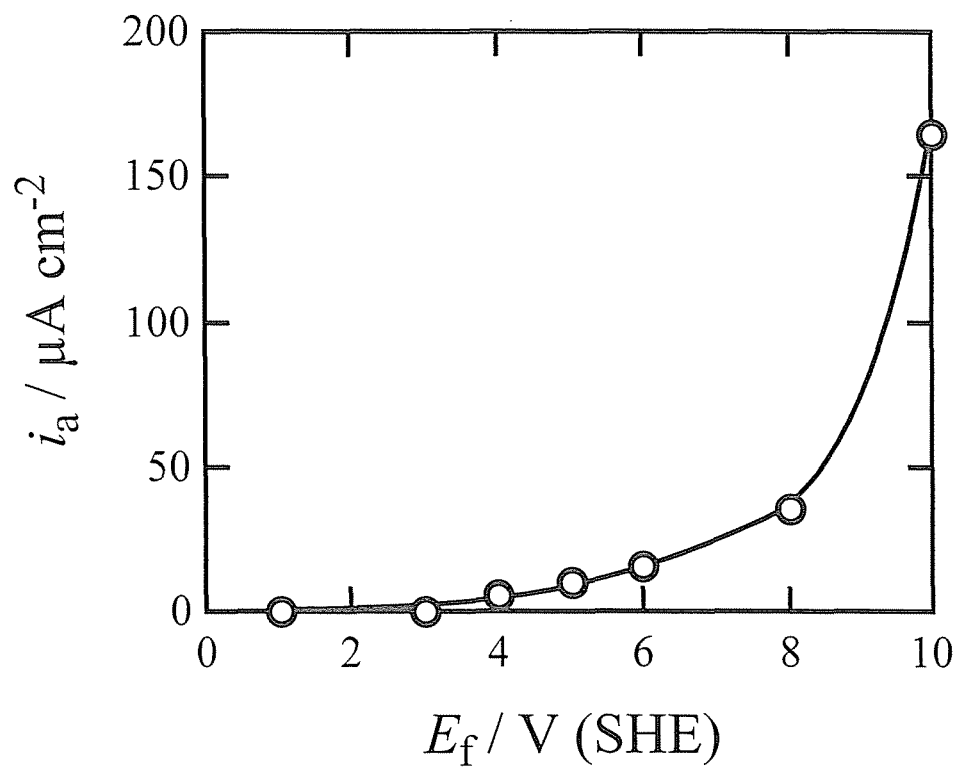


Fig. 6.3.2 Relation between anodic current density, i_a , at 3.6 ks-anodic polarization and potential, E_f , for titanium electrode in pH 8.4 borate solution.

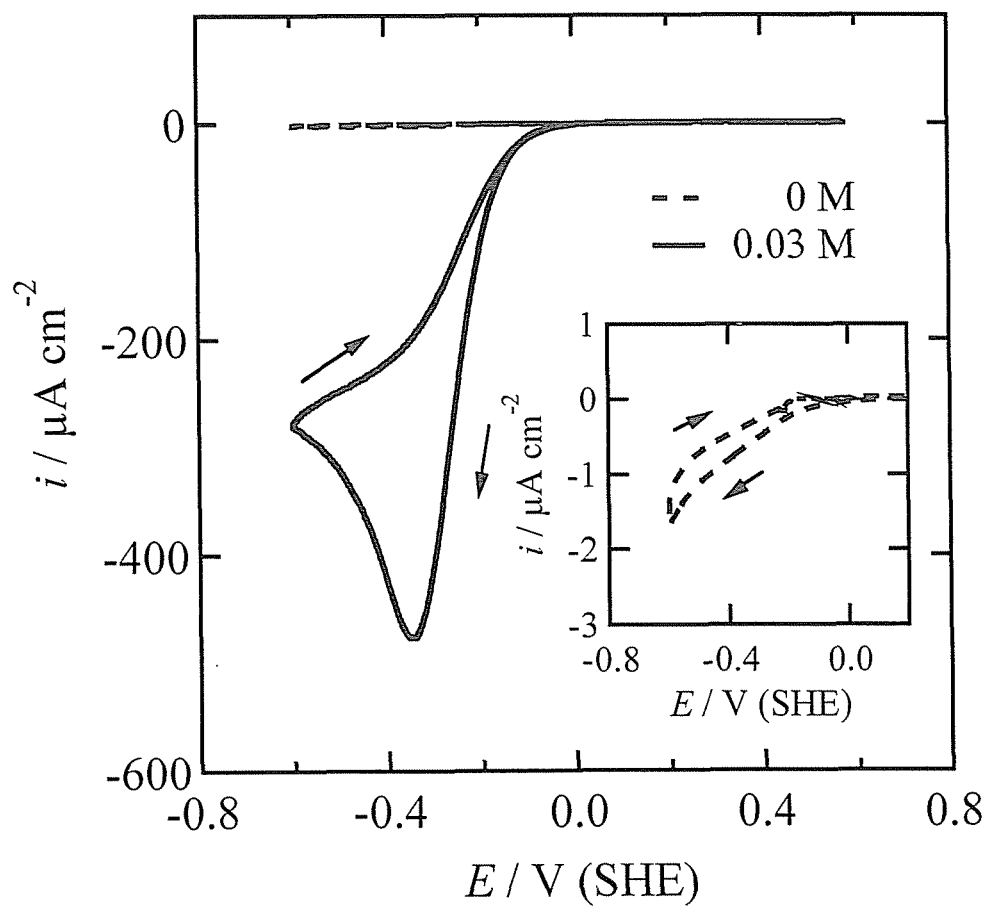


Fig. 6.3.3 Voltammogram of the titanium electrode measured in deaerated pH 8.4 borate solution containing $\text{K}_3\text{Fe(CN)}_6$ after anodic polarization at 6 V (SHE) for 3.6 ks in pH 8.4 borate solution.
Sweep rate was 2 mV s^{-1} .

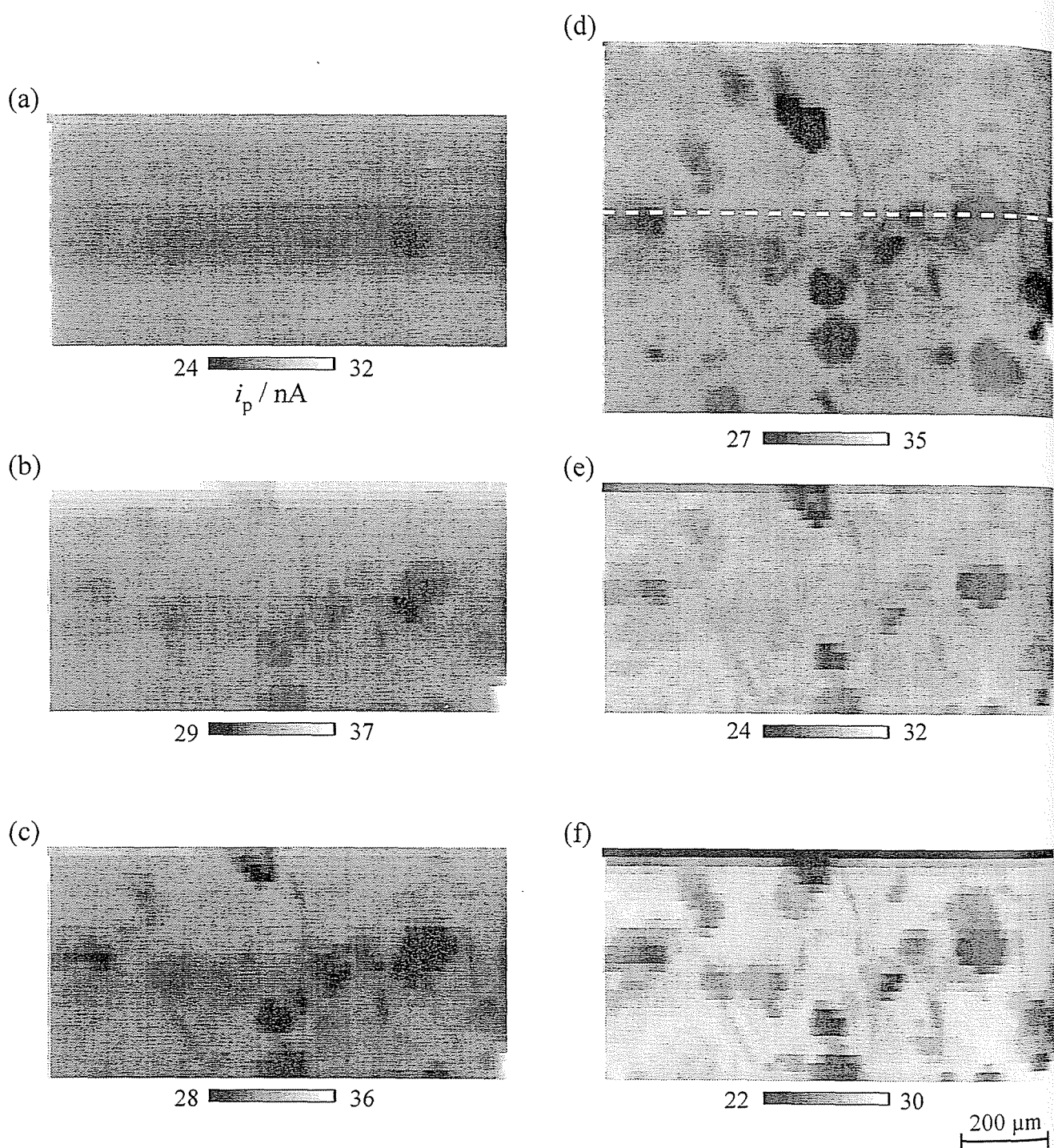


Fig. 6.3.4 Probe current images of the titanium electrode surfaces anodically oxidized at a) 1 V, b) 3 V, c) 4 V, d) 5 V, e) 6 V, and f) 8 V (SHE), respectively.

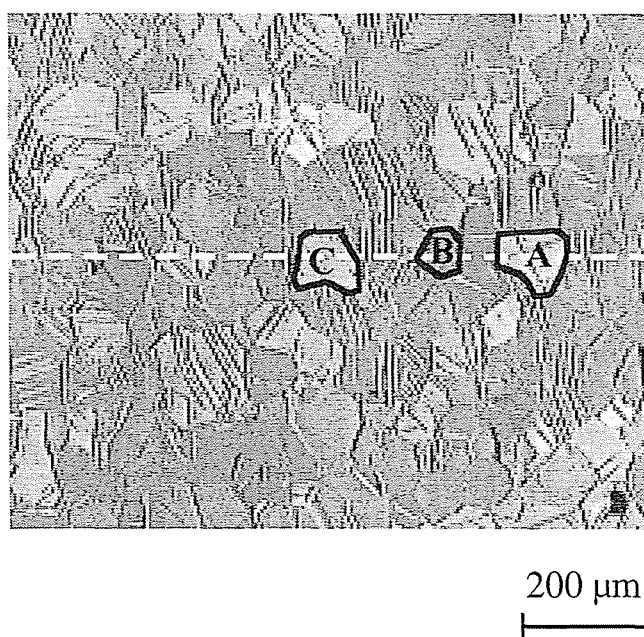


Fig. 6.3.5 Optical micrograph of the electrode surface area corresponding to the probe current image in Fig. 6.3.4d.

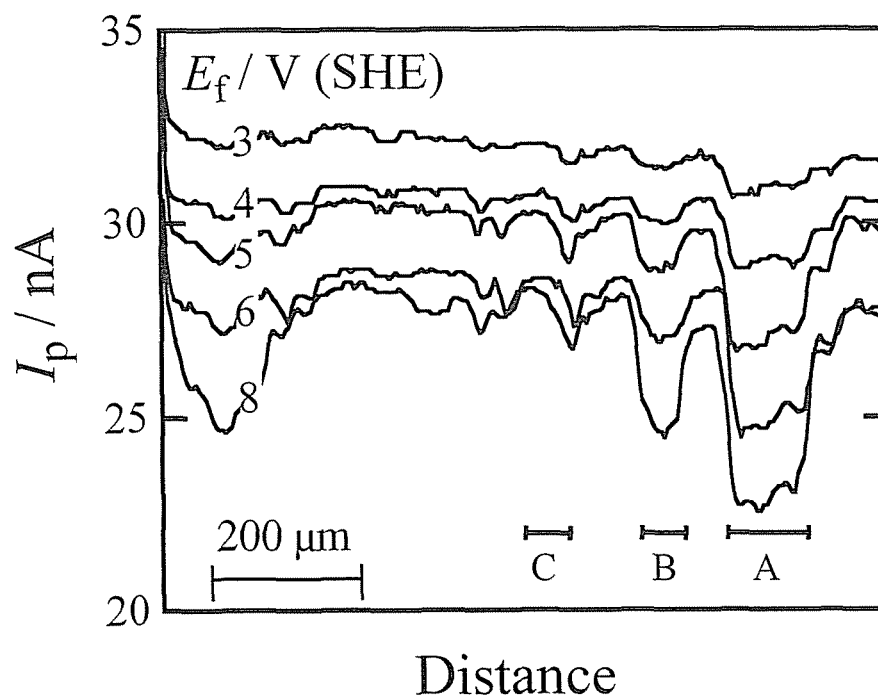


Fig. 6.3.6 Probe current profiles along the dashed line drawn in Fig. 6.3.5.

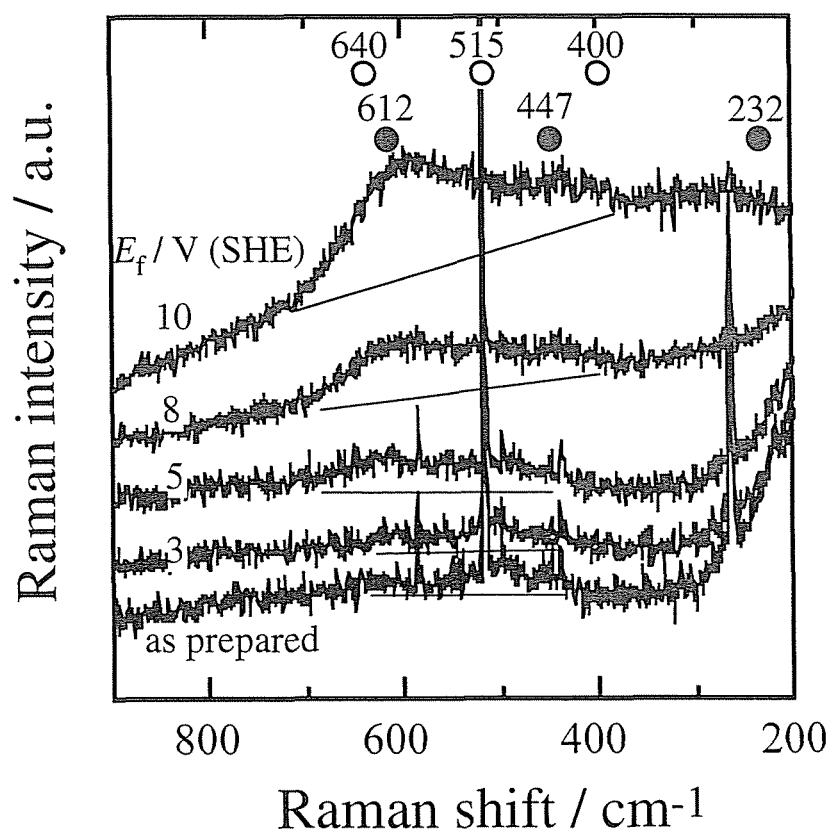


Fig. 6.3.7 Raman spectra of the anodic oxide film on the substrate grain B in Fig. 6.3.5. The Raman shifts of anatase type (Ohtsuka 1986) and rutile type (Felske 1989) of TiO_2 are marked with open and solid circles, respectively.

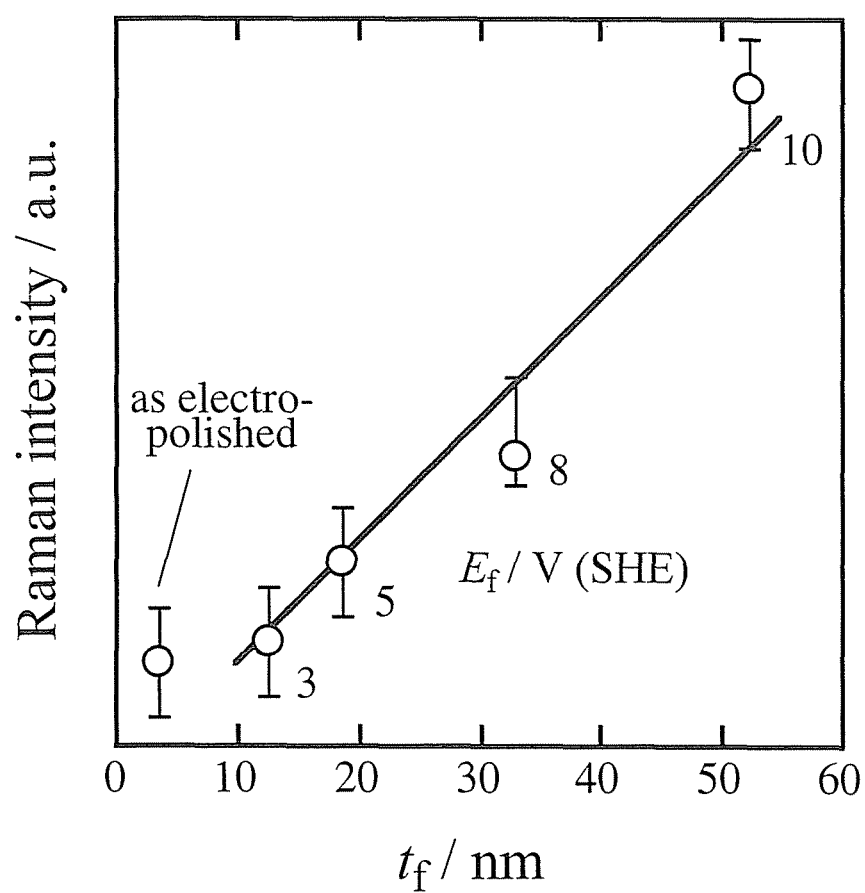


Fig. 6.3.8 Relation between Raman intensity of the grain B at 608 cm^{-1} and average film thickness, t_f , obtained ellipsometrically (Ohtsuka 1985).

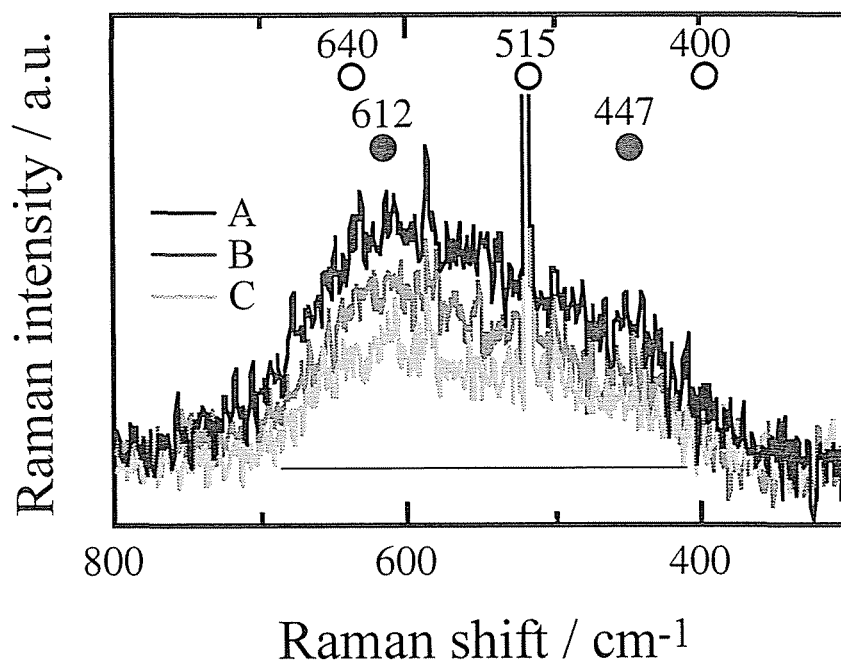


Fig. 6.3.9 Raman spectra of the anodic oxide films formed at 8 V (SHE) on the grains, A, B and C in Fig. 6.3.5. The Raman shifts of anatase type (Ohtsuka 1986) and rutile type (Fleske 1989) of TiO_2 are marked with open and solid circles, respectively.

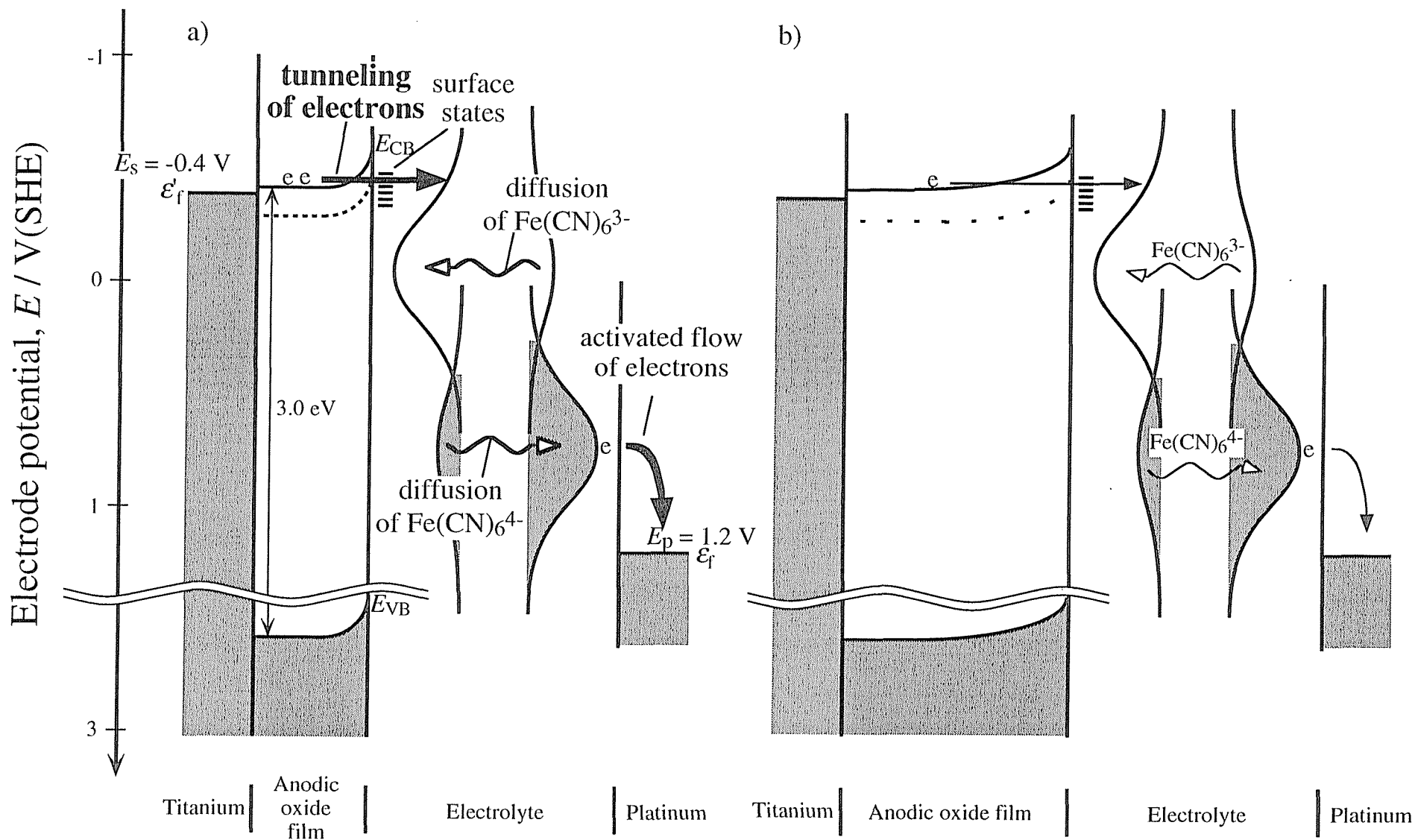


Fig. 6.3.10 Schematic illustration by an electronic band model for charge transfer between titanium electrode with a) thin or b) thick anodic oxide film, $\text{Fe(CN)}_6^{3-}/\text{Fe(CN)}_6^{4-}$ redox system and platinum probe electrode.

7 Oxygen evolution on a polycrystalline titanium during anodic oxidation

7.1 Introduction

For *in-situ* evaluation of electrochemical reactivities at local sites of a titanium electrode surface, SECM is powerful. In general, redox mediators such as $\text{Fe}(\text{CN})_6^{4-}$ or Br^- in solution are used for SECM measurements. $\text{Ru}(\text{NH}_3)_6^{3+}$ as a mediator was also used to investigate oxide films on titanium; it showed that oxide films have insulative properties (Wei 1995). Smyrl et al applied SECM to investigate initiation of pitting corrosion using Br_2/Br^- system (James 1989, Casillas 1993, 1994.1, 1994.2, Sukanto 1995). Basame et al investigated spatially-localized electrochemical reactivities of oxide films on titanium or tantalum by SECM (Basame 1995, 1998, 1999, 1999.2). The investigators used $\text{Fe}(\text{CN})_6^{4-}$, $\text{Ru}(\text{NH}_3)_6^{3+}$, Br^- , and I^- as mediators. Although these pioneer studies stressed SECM utility, the redox system added as a mediator in solution may alter oxide film electrochemical reactivities if the redox system adsorbs strongly on the film or reacts with the film.

In Chapter 6, SECM detected heterogeneity of anodic oxide film formed on a polycrystalline titanium electrode in pH 8.4 borate solution. Heterogeneous probe current images as well as those on a polycrystalline iron were dependent on substrate grains. They were mainly ascribed to differences in thickness of oxide films grown on substrate grains. This SECM measurement was carried out with TG/SC mode in pH 8.4 borate solution containing $0.03 \text{ mol dm}^{-3} \text{ K}_4\text{Fe}(\text{CN})_6$ as a mediator after anodic film formation in pH 8.4 borate solution. During measurement, the probe electrode potential was kept at $E_p = 1.2 \text{ V (SHE)}$ to generate $\text{Fe}(\text{CN})_6^{3-}$, while the titanium electrode was polarized at $E_s = -0.4 \text{ V (SHE)}$ to reduce to $\text{Fe}(\text{CN})_6^{4-}$. In this case, the titanium electrode potential was lower than that of film formation, E_f . These conditions are inevitable as far as SECM measurement is carried out in a solution containing $\text{K}_4\text{Fe}(\text{CN})_6$ as a mediator, although the oxide film may change to some extent. Therefore, it is the best to measure heterogeneity of oxide film as formed without alteration. Oxygen evolution is known to take place in parallel with anodic oxidation of metal and depends on anodic oxide film properties (Dyer 1978).

In this chapter, the probe current image corresponding to distribution of oxygen evolution was measured during anodic oxidation of titanium electrode in $0.1 \text{ mol dm}^{-3} \text{ H}_2\text{SO}_4$. It was compared with the conventional probe current image which was measured in pH 8.4 borate

solution containing $\text{K}_4\text{Fe}(\text{CN})_6$.

7.2 Experimental

7.2.1 Specimen preparation

The titanium specimen was similar to that in 6.2. Cross section of a titanium rod (purity above 99.5 %) with a 10 mm diameter was used as a specimen electrode. The electrode surface was finally electropolished as described in 6.2.1. Anodic polarization of the specimen electrode and SECM measurement were carried out simultaneously in deaerated $0.1 \text{ mol dm}^{-3} \text{H}_2\text{SO}_4$.

7.2.2 SECM measurements

The SECM apparatus (type III in Table 4.3.1) was used for this experiment. For a probe electrode, platinum micro-disk with a $10 \text{ }\mu\text{m}$ diameter embedded in a glass capillary tube was employed. In anodic polarization of the specimen electrode and SECM measurement, the specimen electrode was polarized at a constant potential, E_s , to form the anodic oxide film whereas the probe electrode was polarized at $E_p = 0.4 \text{ V (SHE)}$ to detect reduction current of oxygen evolved in parallel with film formation. A probe current image of the specimen electrode surface was measured under the following conditions:

- a) Distance between probe and specimen electrodes was kept at about $5 \text{ }\mu\text{m}$.
- b) The probe electrode was scanned over a surface area of $1000 \text{ }\mu\text{m} \times 800 \text{ }\mu\text{m}$ at $5 \text{ }\mu\text{m}$ intervals in the x direction and $10 \text{ }\mu\text{m}$ in the y direction.

After SECM measurement in $0.1 \text{ mol dm}^{-3} \text{H}_2\text{SO}_4$, the solution was changed to pH 8.4 borate solution containing $0.03 \text{ mol dm}^{-3} \text{K}_4\text{Fe}(\text{CN})_6$ to conduct conventional SECM measurement as reported in Chapter 6. In conventional SECM measurement, probe and specimen electrode potentials were held at $E_p = 1.2 \text{ V (SHE)}$ and $E_s = -0.4 \text{ V (SHE)}$, respectively.

7.3 Results and Discussion

7.3.1 Detection of oxygen with the probe electrode

Figure 7.3.1 shows the cyclic voltammogram (CV) of the probe electrode in $0.1 \text{ mol dm}^{-3} \text{H}_2\text{SO}_4$. Probe current in the solution aerated with oxygen and air shifts to cathodic current

direction at potentials lower than 0.7 V (SHE) as compared with those in solutions deaerated with purified argon gas. This indicates that oxygen dissolved in the solution is reduced on the probe electrode. Figure 7.3.2 shows the CV of the probe electrode located above the titanium electrode surface in deaerated 0.1 mol dm⁻³ H₂SO₄. When the titanium electrode was oxidized anodically at 5.0 V (SHE), the probe current at potentials lower than 0.7 V (SHE) shifts to the cathodic current direction as compared with that in the case when the titanium electrode was in an open circuit. This indicates that oxygen evolves on the titanium electrode and that the probe electrode can detect oxygen.

As conferred in 1.2.5, total anodic current, i_{total} , consists of the formation current of anodic oxide film, i_{oxide} , the dissolution current of titanium, i_{dis} , the charging current of the electric double layer, i_{charge} , the current of the electron transfer reaction, i_{etr} , and oxygen evolution, i_{oxygen} .

$$i_{\text{net}} = i_{\text{dis}} + i_{\text{oxide}} + i_{\text{charge}} + i_{\text{oxygen}} \quad [7.3.1]$$

At the steady state, i_{charge} is negligibly small. According to the potential-pH diagram shown in Figure 1.2.2, titanyl ions, TiO²⁺, are stable as dissolved species in acid solution in the potential range between 0 V and 2.1 V (SHE). Therefore, Ti(IV) ions, even if dissolved from the titanium electrode, can not be detected with any probe electrode polarized in the same potential range. If titanium dissolves as Ti(VI) ions, the CVs of the probe electrode in Figure 7.3.2 should move down the cathodic current direction as a whole since cathodic reaction of Ti(IV) ions occurs on the probe electrode. On the other hand, anodic polarization of titanium would provide decrease in solution pH near the titanium electrode surface due to formation of oxide film or oxygen evolution.



Decrease in solution pH shifts hydrogen evolution potential in the positive direction. When the probe electrode is polarized at a certain potential between hydrogen evolution potential ($E = -0.059 \text{ V pH}^{-1}$) and 0.7 V (SHE), oxygen can be detected with the probe electrode. The probe electrode, therefore, is polarized at 0.4 V (SHE) to detect oxygen evolved from the titanium electrode.

7.3.2 Probe current image of oxygen distribution

Figure 7.3.3 shows transients of current density, i_s , of the titanium specimen electrode at 4.0 V (SHE) and of current, I_p , of the probe electrode at 0.4 V (SHE) in 0.1 mol dm⁻³ H₂SO₄ during SECM measurement in the SG/TC mode. Probe current attains a steady state with some

fluctuations, which reflect difference in oxygen evolution depending on the specimen surface position during scanning of probe electrode. Figure 7.3.4a shows the probe current image of the titanium electrode obtained from SECM experiment in Figure 7.3.3. Cathodic current flowing through the probe electrode due to oxygen reduction reflects anodic oxide film properties on the local area of the titanium electrode surface just below the probe electrode. Several white spots observed in Figure 7.3.4a show that surface sites where oxygen evolution occurs preferentially are distributed heterogeneously. On the other hand, when the titanium electrode was polarized at 1.0 V (SHE), the probe current image was homogeneous because no oxygen evolution took place on the titanium electrode. The large transient of probe current at the initial stage of SECM measurement (see location of $y = 0\text{--}100\text{ }\mu\text{m}$ at the bottom of Figure 7.3.4a) corresponds to the large specimen current transient, indicating that oxygen evolution reaction on the titanium electrode proceeds significantly at the initial stage of anodic oxidation. Figure 7.3.4b shows the probe current image measured by conventional SECM in pH 8.4 borate solution containing $0.03\text{ mol dm}^{-3}\text{ K}_4\text{Fe}(\text{CN})_6$ after the experiment of Figure 7.3.4a. Probe current profiles along dashed lines drawn in Figure 7.3.4a and 7.3.4b, are shown in Figure 7.3.4c. It is clear that heterogeneity of probe current image in Figure 7.3.4a coincides completely with that in Figure 7.3.4b. The heterogeneity of probe current image also coincides with the patch pattern in the optical micrograph of the specimen surface as shown in Figure 7.3.4d. Height difference between grains along dashed lines measured by laser microscopy was less than $0.13\text{ }\mu\text{m}$, which was too small to influence significantly the probe current intensity. In general, the positive feedback mode of SECM measurement is feasible to detect surface roughness for an insulative specimen. However, the probe current image in the positive feedback mode was not heterogeneous which was measured for an open circuit of the specimen electrode in pH 8.4 borate solution containing $0.03\text{ mol dm}^{-3}\text{ K}_4\text{Fe}(\text{CN})_6$. Therefore, the surface roughness of titanium electrode surface would not influence probe current images.

The probe current image of anodic oxide film as formed in $0.1\text{ mol dm}^{-3}\text{ H}_2\text{SO}_4$ was in good agreement with that measured in $\text{Fe}(\text{CN})_6^{3-}/\text{Fe}(\text{CN})_6^{4-}$ redox system after anodic oxidation in $0.1\text{ mol dm}^{-3}\text{ H}_2\text{SO}_4$. In Chapter 6, the probe current image of anodic oxide film on titanium was measured by using $\text{Fe}(\text{CN})_6^{4-}$ redox system as a mediator. Dependence of the probe current image on the substrate grain was explained in terms of difference in thickness of anodic oxide film on each substrate grain, i.e., higher probe current for substrate grain covered with thinner oxide film. Good coincidence of two probe current images in Figures 7.3.4a and 7.3.4b indicates that oxygen evolution also takes place preferentially on the substrate grain covered with thinner oxide film in H_2SO_4 . These results are supported by Kudelka et al (Kudelka 1995) who reported

correlation between oxygen evolution and thickness of anodic oxide film on polycrystalline titanium. Particularly that study noted that oxygen evolution proceeds preferentially on substrate grain (i.e., (0001) index plane) covered with thinner film with higher donor density rather than the substrate grain (i.e., xxx0) index plane) covered with thicker film with lower donor density.

7.3.3 *Dependence of oxygen evolution image on polarization potential*

Thickness of oxide film on titanium increases with increasing anodic potential (Ohtsuka 1985). In 6.3.2, it was reported that heterogeneity of film thickness changed with anodic potential. Here, dependence of heterogeneity of oxygen evolution on anodic potential was examined for comparison. Figures 7.3.5a-i show normalized probe current, I_p/I_s , images of the titanium electrode polarized at $E_s = 2.0$ to 10 V (SHE) with successive potential steps by 1.0 V in 0.1 mol dm⁻³ H₂SO₄ solution. Current, I_s , flowing through the titanium specimen electrode increased with increasing anodic potential. Average probe electrode current during SECM imaging also increased with increasing anodic potential. Therefore, normalized probe current images in Figures 7.3.5a-i divided by each specimen electrode current would give some evaluation criteria for different current efficiencies of oxygen evolution. During each probe current imaging of the titanium electrode at potentials up to 3.0 V (SHE), the normalized probe current increased with scanning time of probe electrode, indicating that current efficiency of oxygen evolution increases concomitant with film growth. On the other hand, normalized probe current decreased fairly with scanning time of the probe electrode when the titanium electrode was polarized at potentials higher than 7.0 V (SHE), indicating decrease in current efficiency of oxygen evolution. Raman spectroscopic study (Ohtsuka 1986) showed that an amorphous anodic oxide film on titanium grows up to 4 V, whereas an anatase type of TiO₂ film starts to form at 4 V. Furthermore, steady state-anodic current density of titanium in 0.1 mol dm⁻³ H₂SO₄ solution increased at potentials higher than 3 V (Ohtsuka 1985). This increase in anodic current density may result from anodic dissolution of titanium through defective film and contribute to decrease in current efficiency of oxygen evolution. Decrease in the current efficiency of oxygen evolution would be the reason why heterogeneous probe current images are not observed at potentials higher than 7.0 V (SHE).

Figure 7.3.5j shows the conventional probe current image measured in pH 8.4 borate solution containing 0.03 mol dm⁻³ Fe(CN)₆⁴⁻ solution after experiments of Figures 7.3.5a-i were performed. Moreover, the optical micrograph of the same area where SECM measurements were carried out is shown in Figure 7.3.5k. Heterogeneity of both probe current images of oxygen evolution and of the redox reaction coincides with metallographic heterogeneity

observed by optical micrograph. Figure 7.3.6 shows probe current profiles along dashed lines drawn in Figures 7.3.5a-j. The marks, A, B, ..., and F in Figure 6.3.6 show position of the probe electrode line scan, whereas numbers, 2, 3, ..., and 10 represent anodic oxidation potential of the titanium electrode. It is apparent that changes in probe current depend on position of the line scan and anodic potential. Figure 7.3.7 shows probe current at each position normalized with that at position B as a function of anodic oxidation potential. Positions are classified into the following 3 types:

- i) oxygen evolution is relatively poor, independent of potential, corresponding to the area where thicker oxide films form (at positions, D and F).
- ii) oxygen evolution is relatively active, dependent on potential, corresponding to the area where the thinner oxide films form (at positions of A and E).
- iii) position, C, classified as type i) at potentials less than 4.0 V, but as type ii) at 4.0 V (SHE), indicating that oxygen evolution becomes active at 4.0 V (SHE).

This means that the structure changes in oxide film from amorphous to anatase at 4.0 V (SHE) contribute to passage of ionic charges through the film.

7.3.4 *Oxygen evolution on breakdown sites of anodic oxide film*

Average thickness of the anodic oxide film on titanium, obtained ellipsometrically (Ohtsuka 1985), increases rapidly at potentials higher than 7 V. This rapid increase in film thickness may be attributed to creation of lattice defects which increase ionic leakage current. Figure 7.3.8a shows the current transient of the titanium electrode during polarization at 10 V (SHE) in 0.1 mol dm⁻³ H₂SO₄. After rapid increase at the initial stage, current decreases exponentially. After about 1200 s, however, current increases gradually and attains a steady value. It seems that anodic oxide film is partly broken down due to increase in compressive film stress after 1200 s, and the repair and breakdown are repeated. The SECM measurements were carried out during polarization. Figure 7.3.8b shows probe current profiles at the time period represented by the numbers in Figure 7.3.8a. Average probe current in the profile reaches a minimum at about 1200 s. Shapes of probe current profiles are similar up to 1200 s. After about 1200 s, however, shapes change with increasing specimen current at positions shown with arrow marks in Figure 7.3.8b. Figure 7.3.8c shows the optical micrograph of the same area where the probe electrode was scanned. Positions shown with arrow marks which correspond to active sites of oxygen evolution are located on needle like grains. These grains may be twins orientated to the {1012} index plane (JIM 1990), which are formed easily due to shear stress during mechanical processing. Seo and Ueno have reported, by a laser-bending beam method (Seo

2000), that compressive stress is accumulated in the oxide film on titanium during anodic oxidation. It is expected that oxide films formed on twin grains are easily broken down due to accumulated compressive stress.

7.4 Conclusions

Without additives as a mediator, SECM was applied to a polycrystalline titanium electrode during anodic oxidation in $0.1 \text{ mol dm}^{-3} \text{ H}_2\text{SO}_4$. The probe current image was measured by detecting oxygen evolved in parallel with formation of anodic oxide film on titanium. The probe current image corresponding to oxygen evolution distribution was compared with the conventional probe current image which was measured in pH 8.4 borate solution containing $\text{K}_4\text{Fe}(\text{CN})_6$ as a mediator. Both probe current images gave good coincidence, particularly at the point that anodic oxide film depends on the substrate crystal grain. Good coincidence of probe current images implies that oxygen evolution takes place preferentially on the substrate grain covered with thinner oxide film. Moreover, it is suggested that anodic oxide films on twin grains are easily broken down and become active sites of oxygen evolution. From these results, it is inferred that oxygen reduction current measurement with the probe electrode is useful as an *in-situ* method without any additives as a mediator for evaluating metal surface heterogeneity during anodic oxidation.

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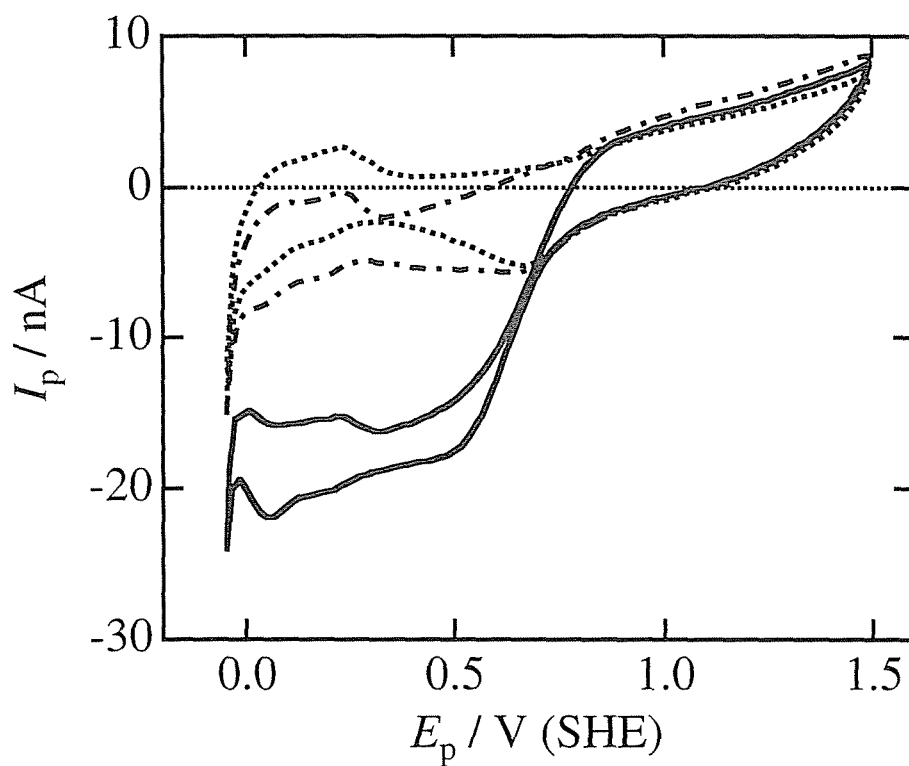


Fig. 7.3.1 Cyclic voltammogram (CV) of the probe electrode in $0.1 \text{ mol dm}^{-3} \text{ H}_2\text{SO}_4$ which was deaerated with purified argon (.....), aerated with air (-.-.), or aerated with oxygen (—). The potential sweep rate was 100 mV s^{-1} .

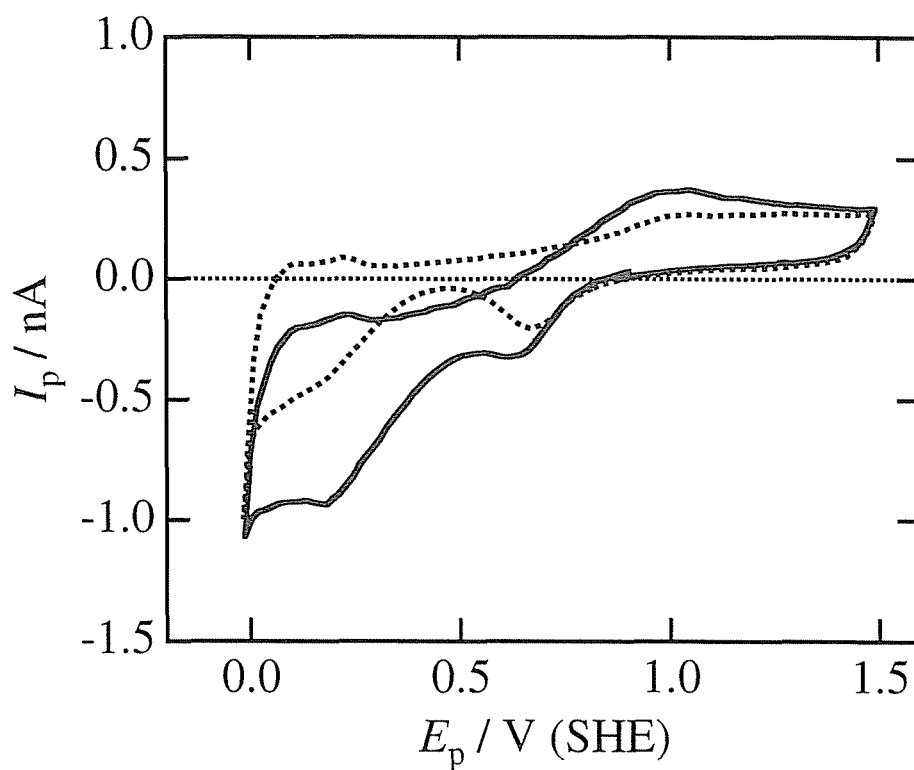


Fig. 7.3.2 CV of the probe electrode located above the titanium electrode surface in deaerated $0.1 \text{ mol dm}^{-3} \text{ H}_2\text{SO}_4$. The titanium electrode was in an open circuit (.....) or anodically oxidized at 5.0 V (SHE) (—). The CV was measured after the titanium electrode became steady state. The potential sweep rate was 100 mV s^{-1} .

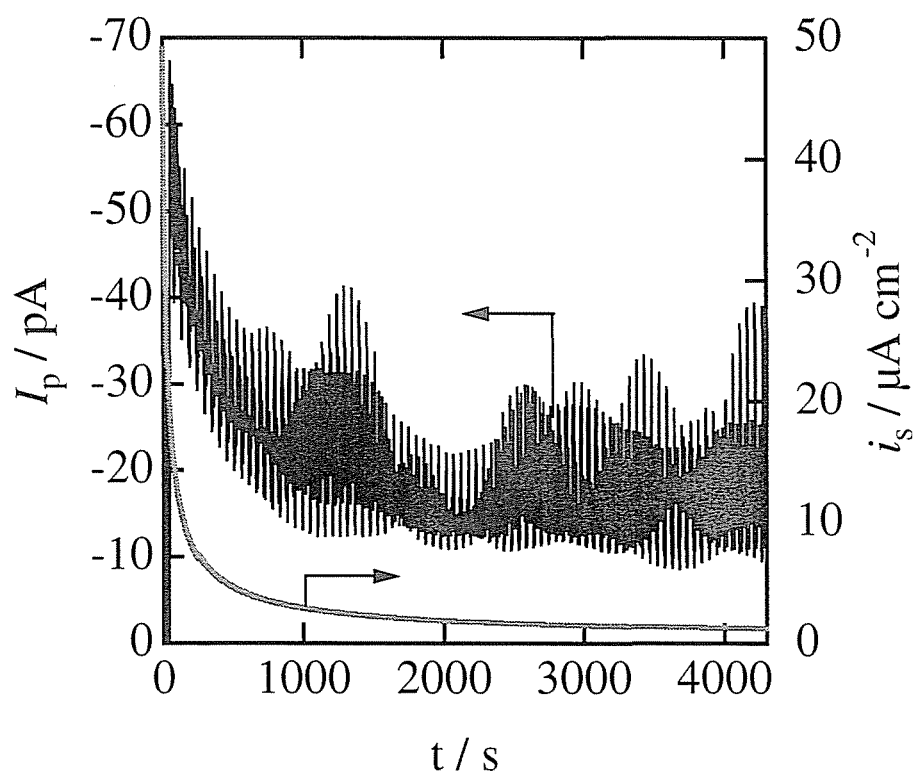


Fig. 7.3.3 Transients of current density, i_s , of the titanium specimen electrode at 4.0 V (SHE) and of current, I_p , of the probe electrode in 0.1 mol dm^{-3} H_2SO_4 during SECM measurement in the SG/TC mode.

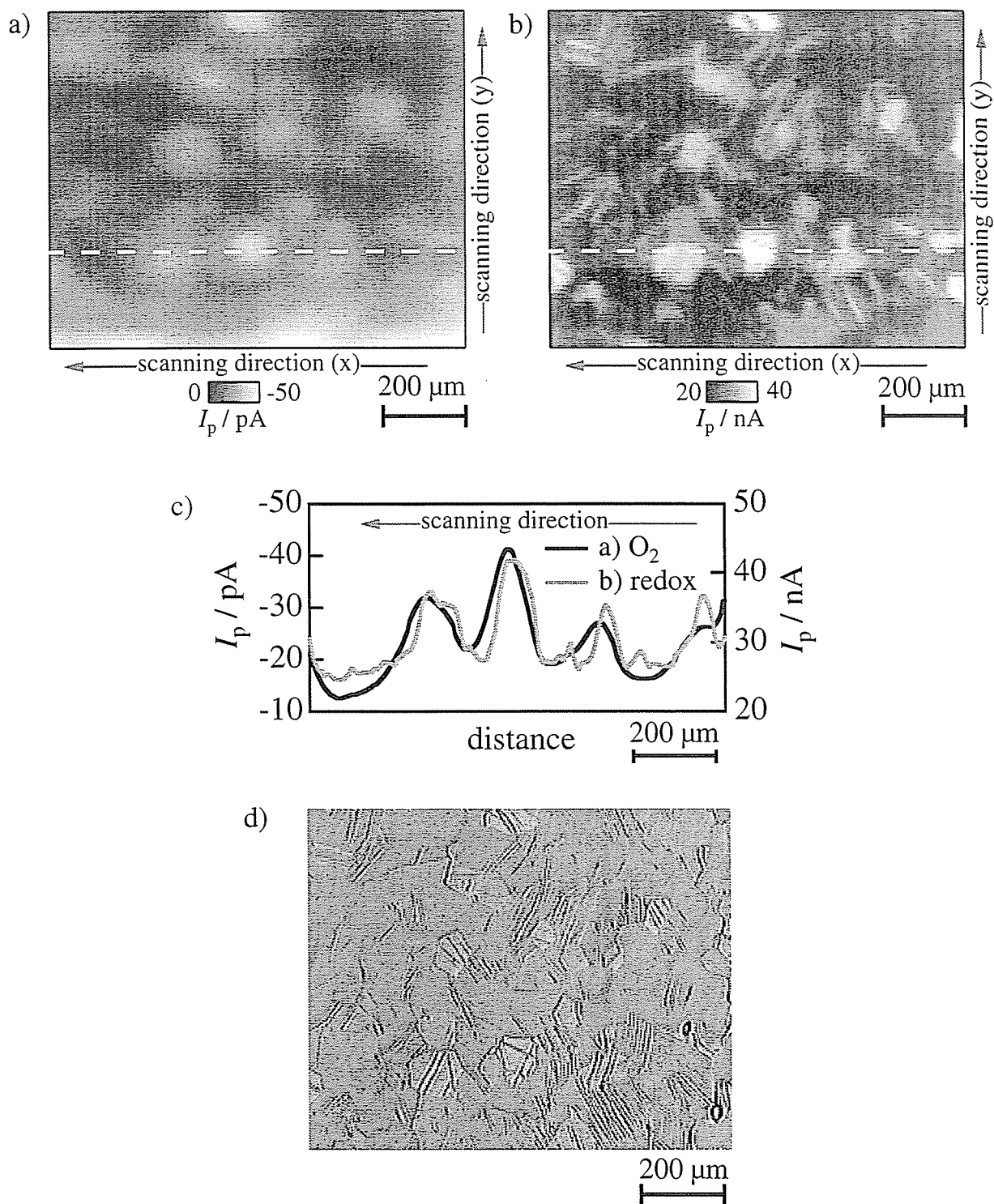


Fig. 7.3.4 a) Probe current image of the titanium electrode during anodic polarization at 4.0 V (SHE) in $0.1 \text{ mol dm}^{-3} \text{ H}_2\text{SO}_4$. The probe electrode was polarized at 0.4 V (SHE).
b) Probe current image measured by conventional SECM in pH 8.4 borate solution containing $0.03 \text{ mol dm}^{-3} \text{ K}_4\text{Fe}(\text{CN})_6$ after the experiment of Fig. 7.3.4a
c) Probe current profiles along the dashed lines drawn in Fig. 7.3.4a and 7.3.4b.
d) Optical micrograph of the titanium electrode surface where the SECM experiment was performed.

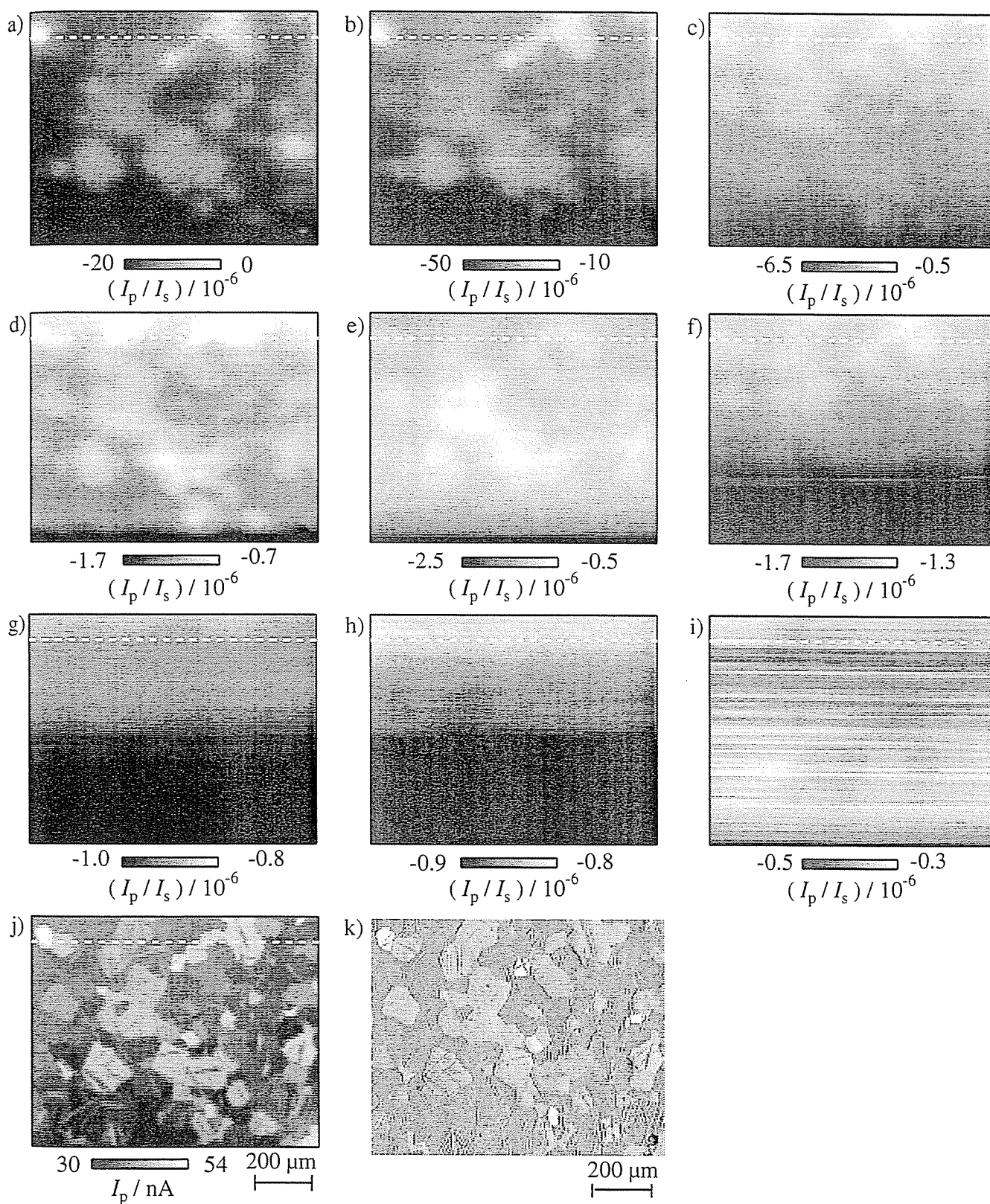


Fig. 7.3.5 a-i) Normalized probe current images of the titanium electrode polarized at $E_s = 2.0$ to 10 V (SHE) with successive potential steps by 1.0 V in $0.1 \text{ mol dm}^{-3} \text{ H}_2\text{SO}_4$ solution.
 j) Probe current image of the titanium electrode measured in pH 8.4 borate solution containing $0.03 \text{ mol dm}^{-3} \text{ K}_4\text{Fe}(\text{CN})_6$ after the experiments of Fig. 7.3.5a-i.
 k) Optical micrograph of the local area of titanium electrode surface where the probe electrode was scanned.

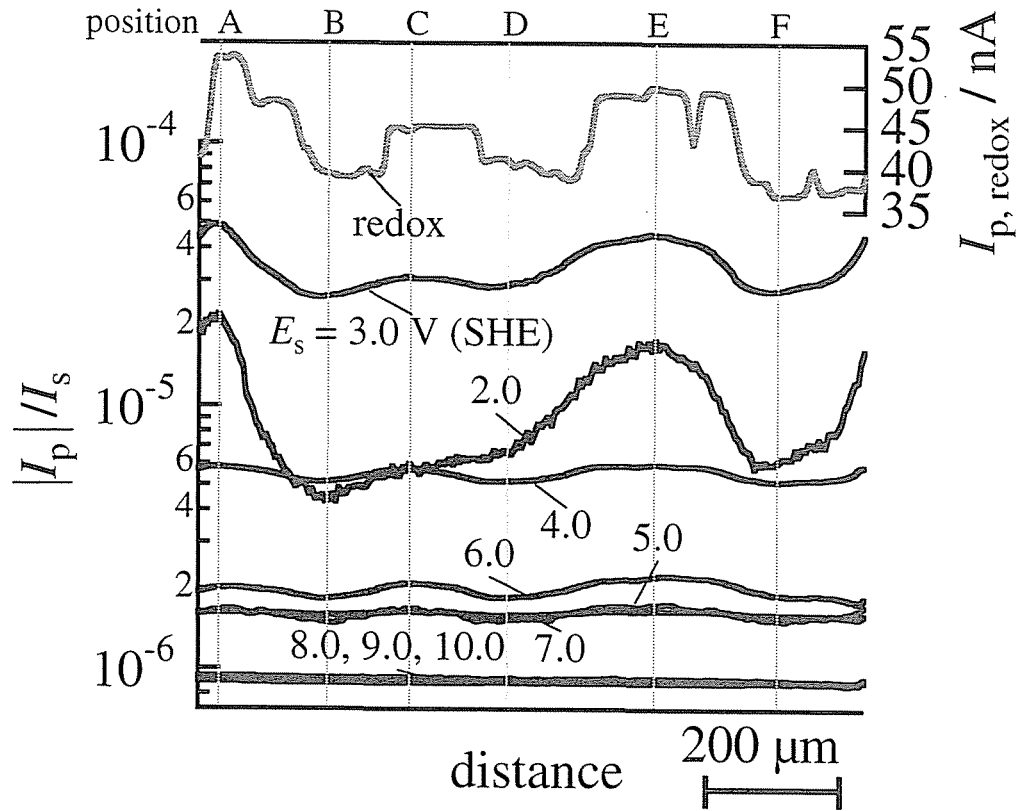


Fig. 7.3.6 Probe current profiles along the dashed line drawn in Fig. 7.3.5a-j. The marks, A, B, ..., F indicate the position of the line scan of probe electrode, whereas the numbers, 2, 3, ..., 10 represent anodic oxidation potential of the titanium electrode.

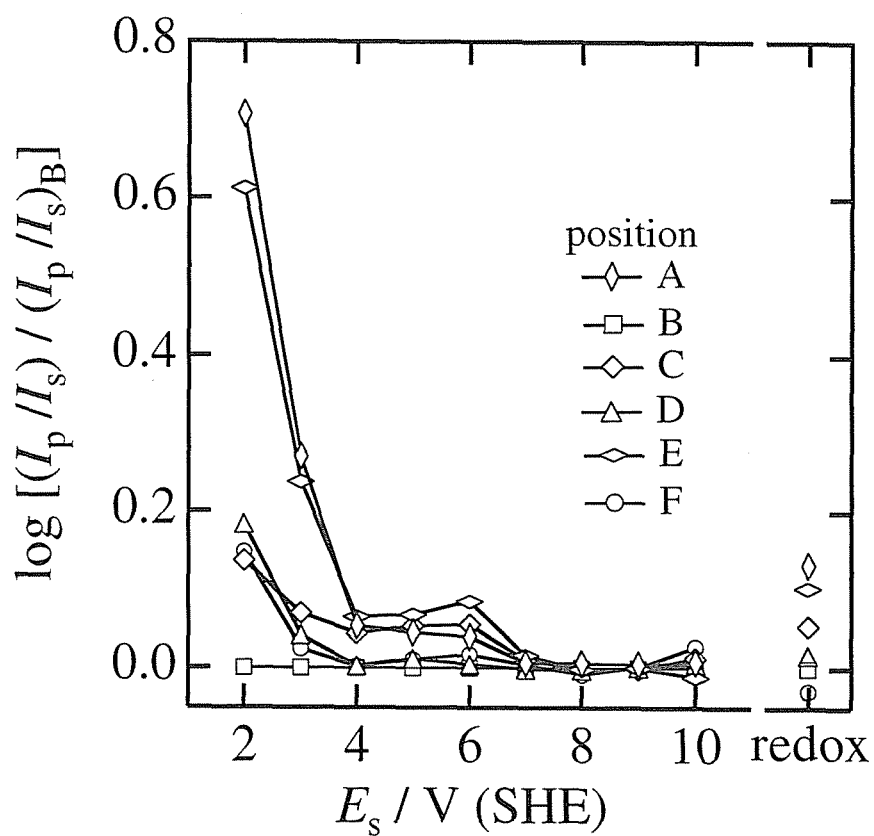


Fig. 7.3.7 The probe current at each position normalized with that at position B as a function of anodic oxidation potential, E_f .

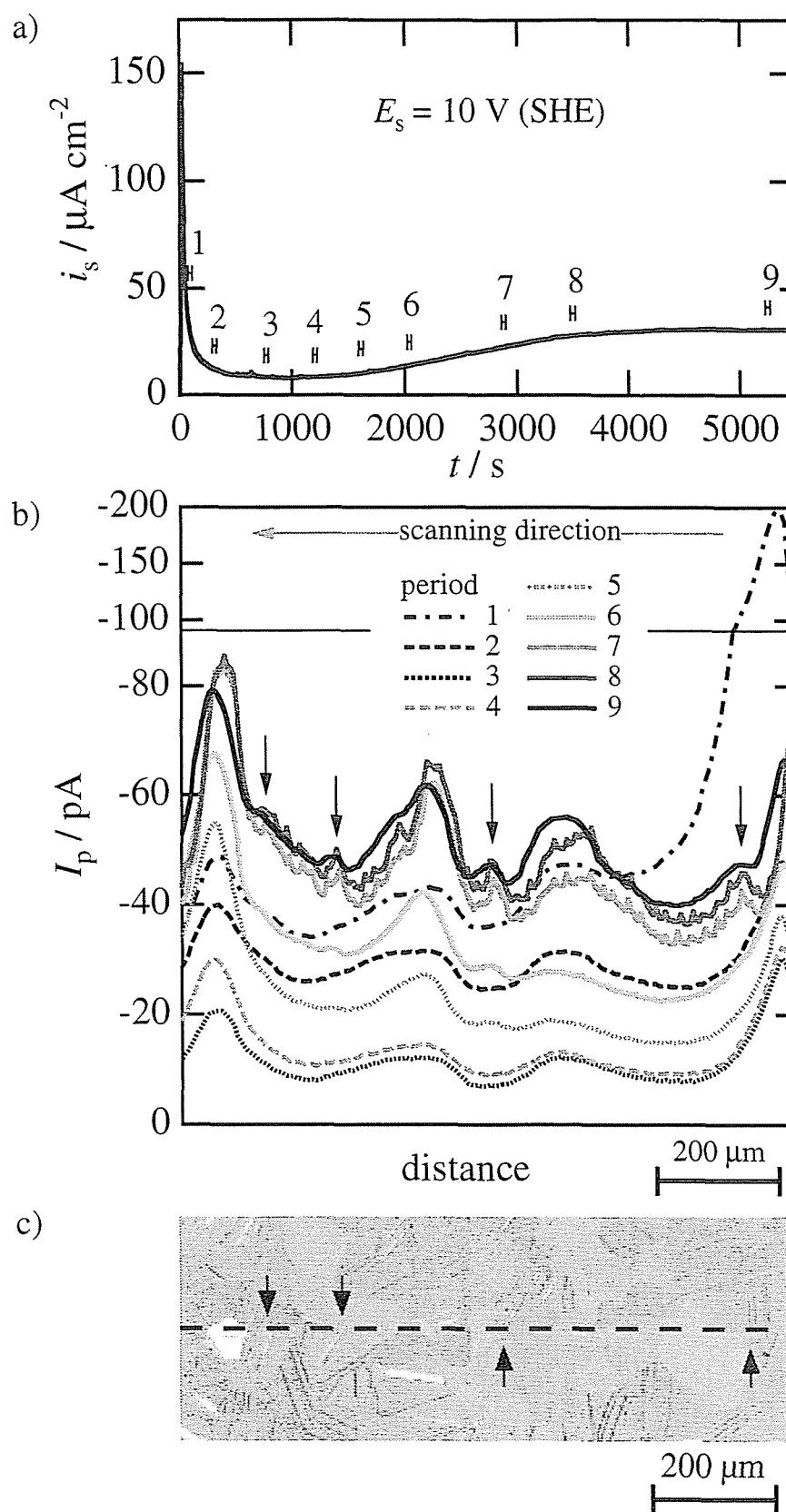


Fig. 7.3.8 a) Current transient of the titanium electrode during polarization at 10 V (SHE) in 0.1 mol dm⁻³ H₂SO₄.
 b) Probe current profiles at the time period represented by the numbers.
 c) Optical micrograph of the same area where the probe electrode was scanned.

8 Distribution of ferrous or ferric ions dissolved from a polycrystalline iron electrode

8.1 Introduction

Anodic dissolution of iron has been investigated and discussed by many researchers. Among them, dissolution mechanisms proposed for active dissolution by Bockris (Bockris 1961) and Heusler (Heusler 1958) are well known. Benzekri (Benzekri 1989, 1990) and Tsuru (Tsuru 1986, 1991) investigated presence of an adsorption intermediate during dissolution of iron in sulfuric acid media by using an rotating ring disc electrode (RRDE) and a channel flow double electrode (CFDE), respectively, to explain a consecutive dissolution mechanism by Bockris. In all mechanisms proposed, it is assumed that dissolution proceeds uniformly over the whole surface. Schweickert has claimed (Schweickert 1980) that surface active sites, such as kink sites, decide which mechanism is operative. This means that local site dissolution kinetics are important for evaluation of dissolution mechanism. The dissolution rate should be distributed for a polycrystalline iron electrode consisting of grains with different orientations. However, no study on distribution of dissolution rate for a polycrystalline iron has been reported so far.

The SECM is one of the most useful and powerful techniques for *in-situ* measurement of lateral distribution of electroactive species above an electrode surface. Chapters 5 and 6 indicated that SECM could measure heterogeneity of passive films on iron and titanium, depending on substrate grains. Film heterogeneity was ascribed mainly to difference in thickness of passive films grown on substrate grains. In Chapter 5, especially, it was found that passive film formed on the iron {100} plane was thicker than that on the iron {110} or {111} plane.

In this chapter, measurement of probe current image is attempted to evaluate dissolution distribution of ferrous or ferric ions from a polycrystalline iron electrode during anodic polarization in pH 2.3 sulfate solution.

8.2 Experimental

8.2.1 Specimen preparation

A polycrystalline iron plate (5 mm x 5 mm x 1.5 mm) with a purity above 99.99% annealed at 873 K in vacuum was mainly employed for experiments. An iron wire (1 mm ϕ) with purity above 99.95% was also employed. These iron electrodes were embedded into an epoxy resin except for surface areas (0.25 cm^2 and $7.9 \times 10^{-3} \text{ cm}^2$, respectively) exposed to solution, and set into the SECM electrochemical cell. The iron surface was mechanically polished with α -alumina abrasives down to $0.05 \text{ }\mu\text{m}$. Furthermore, the surface was chemically etched in ethanol containing 10 vol.% nitric acid for 15 s to make substrate crystal grains distinctive prior to measurement of probe current images with SECM. After the iron specimen was cathodically reduced at a constant current density of $5 \text{ }\mu\text{A cm}^{-2}$ in deaerated pH 6.5 borate solution to remove an air-formed film, the iron specimen was anodically polarized in acidic sodium sulfate solution (total concentration of SO_4^{2-} and HSO_4^- was 0.1 mol dm^{-3} ; pH was adjusted to 2.3 by addition of H_2SO_4).

8.2.2 Preparation of GRC probe electrode

A mechanical pencil lead with a diameter of 0.3 mm described in 4.4 was etched to a smaller size with a gas flame and embedded into a glass tube using an epoxy resin. The tip of the glass tube was cut and its cross section was mechanically polished with a diamond whetstone (#5000) on a turntable to prepare a disk microelectrode. The microelectrode surface was cleaned and stabilized by using cyclic voltammetry in $0.1 \text{ mol dm}^{-3} \text{ H}_2\text{SO}_4$ in the potential region between hydrogen and oxygen evolutions until the voltammogram achieved a steady state.

8.2.3 SECM measurements

The SECM apparatus (type III in Table 4.3.1) was used for this experiment. The microelectrode, acting as an SECM probe electrode in 8.2.2, was located above the iron electrode surface. Probe and specimen electrode potentials were independently controlled with a bipotentiostat. The probe current image or profile was measured to evaluate lateral distribution of electroactive species generated from the specimen electrode surface. Two different modes were used for SECM measurements. First, SECM measurement in TG/SC mode was carried out in pH 8.4 borate containing $0.03 \text{ mol dm}^{-3} \text{ Fe(CN)}_6^{4-}$ with a probe electrode which was composed of platinum wire with a diameter of $10 \text{ }\mu\text{m}$. Before SECM measurement, passive film was potentiostatically formed on the iron electrode surface at 1.0 V for 3600 s in pH 8.4 borate solution. The probe current image was measured under the following conditions:

i) Distance between probe and specimen electrodes was kept at about $5 \text{ }\mu\text{m}$ using the relation

between probe current and distance reported in 5.3.1.

- ii) The probe electrode was scanned stepwise to a distance of 1250 μm at 5 μm intervals in the x direction and a distance of 500 μm at a 10 μm interval in the y direction.
- iii) The probe electrode was polarized at $E_p = 1.2$ V (SHE) to oxidize $\text{Fe}(\text{CN})_6^{4-}$ while the specimen electrode was polarized at $E_s = 0.1$ V (SHE) to reduce $\text{Fe}(\text{CN})_6^{3-}$. In the second, SECM measurement in SG/TC mode was carried out with the carbon microelectrode as a probe electrode in pH 2.3 sulfate solution.

The probe current profile was measured under the following conditions:

- i) Distance between probe and specimen electrodes was kept at about 5 μm .
- ii) The probe electrode was scanned stepwise to a distance of 1500 μm at 5 μm intervals only in the x direction.
- iii) The probe electrode was polarized at $E_p = 1.2$ V (SHE) to detect ferrous ion or at $E_p = -0.2$ V (SHE) to detect ferric ion while the iron electrode was polarized at -0.1 V (SHE).

8.3 Results and Discussion

8.3.1 Detection of ferrous or ferric ions using a carbon microelectrode

The potential window of a carbon electrode in the low potential region is wide compared with that of a platinum or gold electrode in aqueous solution. Aoki reported (Aoki 1989) that a carbon microelectrode prepared from graphite reinforcement carbon (GRC), which was commercially available as a lead of a mechanical pencil, had a good performance for micro-electrochemical detection. Although the GRC microelectrode had an electric capacity of 25-30 $\mu\text{F cm}^{-2}$ (Aoki 1989), it showed a high reproducibility and stability for an electrochemical reaction in solutions containing ferric or ferrous species. Furthermore, the GRC microelectrode has good electric conductivity and no electric contacts such as a silver paint are needed for the GRC. Thus, a GRC microelectrode was chosen as a probe electrode.

Figure 8.3.1 shows the CV of a carbon microelectrode in 0.1 mol dm^{-3} KCl solution containing 0.01 mol dm^{-3} $\text{K}_3\text{Fe}(\text{CN})_6$ and 0.01 mol dm^{-3} $\text{K}_4\text{Fe}(\text{CN})_6$. Diffusion-limiting current, I_{limit} , for redox reactions is given by Equation 2.2.13. Using $D_{\text{ferricyanide}} = 7.63 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$ and $D_{\text{ferrocyanide}} = 6.50 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$ for diffusion coefficients of $\text{Fe}(\text{CN})_6^{3-}$ and $\text{Fe}(\text{CN})_6^{4-}$, respectively (Adams 1969), microelectrode diameter estimated from I_{limit} in Figure 8.3.1 was 17 μm .

Figure 8.3.2 shows CV of the carbon microelectrode in 0.1 mol dm^{-3} H_2SO_4 which was deaerated with bubbling argon gas, aerated with bubbling air, or aerated with bubbling pure

oxygen. Diffusion-limiting current for reduction of dissolved oxygen in solution was observed at potentials lower than -0.2 V (SHE), indicating that the microelectrode cannot detect dissolved oxygen at potentials higher than -0.2 V (SHE).

Figure 8.3.3a shows the CV of the carbon microelectrode in 0.1 mol dm⁻³ H₂SO₄ containing 10⁻³ mol dm⁻³ ferrous ion. Diffusion-limiting current for oxidation of ferrous ion was observed at potentials higher than 0.8 V. On the other hand, diffusion-limiting current for reduction of ferric ion was observed at potentials lower than 0.5 V as seen from the CV of the carbon microelectrode in 0.1 mol dm⁻³ HCl containing 10⁻³ mol dm⁻³ ferric ion in Figure 8.3.3b.

When the carbon microelectrode was polarized at 1.2 V in 0.1 mol dm⁻³ H₂SO₄ with various ferrous ion concentrations, c_{ferrous} , anodic current for ferrous ion oxidation decreases exponentially with time and attains a steady value after several seconds as shown in Figure 8.3.4a. Figure 8.3.4b shows the linear relation between c_{ferrous} and anodic current at 300 s, i. e., limiting current, which is given by the following.

$$I_{\text{limit}} = 1.40 \times 10^{-6} [\text{A dm}^3 \text{ mol}^{-1}] c_{\text{ferrous}} + 4.02 \times 10^{-10} [\text{A}] \quad [8.3.1]$$

Diffusion coefficient of ferrous ion in 0.1 mol dm⁻³ H₂SO₄ calculated from the shape in Figure 8.3.4b by using Equation 8.3.1 was $D_{\text{ferrous}} = 4.27 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$, which was close to the reported value, $D_{\text{ferrous}} = 5.3 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$, in 1 mol dm⁻³ H₂SO₄ (Adams 1969). On the other hand, when the carbon microelectrode was polarized at -0.2 V (SHE) in 0.1 mol dm⁻³ HCl with various ferric ion concentrations, c_{ferric} , cathodic current for reduction of ferric ion also decreases exponentially with time and attains a steady value after several seconds as shown in Figure 8.3.5a. Figure 8.3.5b shows the linear relation between c_{ferric} and current at 300 s, which is formularized by:

$$I_{\text{limit}} = -1.11 \times 10^{-6} [\text{A dm}^3 \text{ mol}^{-1}] c_{\text{ferric}} . \quad [8.3.2]$$

The calculated diffusion coefficient of ferric ion in 0.1 mol dm⁻³ HCl was $D_{\text{ferric}} = 3.38 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$, which was consistent with the reported value, $D_{\text{ferric}} = 4.7 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$, in 1 mol dm⁻³ HCl (Adams 1969). These results indicate that the carbon microelectrode composed of GRC is available as a probe to detect ferrous and ferric ions in acidic solutions.

8.3.2 Anodic dissolution of iron as ferrous or ferric species

Figures 8.3.6a-d show respective CV of the iron electrode in active and passive regions in deaerated pH 2.3 sulfate solution, probe currents, $I_{\text{p,ferrous}}$, at $E_p = 1.2 \text{ V (SHE)}$ and, $I_{\text{p,ferric}}$, at $E_p = -0.2 \text{ V (SHE)}$, and $E_{\text{p,OC}}$ in an open circuit as a function of iron electrode potential, E_s . Distance between iron and probe electrodes was kept at 75 μm with an optical microscope. It is seen that both probe currents in Figures 8.3.6b and c dramatically change with iron electrode

polarization potential. The probe electrode polarized at 1.2 V (SHE) could detect mainly ferrous ions dissolved from the iron electrode. Anodic probe current increases with anodic potential sweep of the iron electrode in the active potential region (stage I), corresponding to increase in active-dissolution current of the iron electrode. This means that ferrous species dissolved from the iron electrode and diffused to the probe electrode surface are mainly detected by the probe electrode, although hydrogen may also be generated from the iron electrode at potentials lower than -0.13 V (SHE). Anodic probe current, however, decreases in spite of that the anodic current of the iron electrode increases further with anodic potential sweep (stage II). In this stage, the open circuit potential of the probe electrode as shown in Figure 8.3.6d shifts to the positive direction due to enrichment of ferrous ions in the narrow space between iron and probe electrodes which would form a salt film such as FeSO_4 (Bartlett 1952, Heusler 1973, Beck 1982). If a large iR drop is present in the salt film, the probe electrode potential likely changes to the negative direction even if the probe electrode potential referred to an $\text{Ag}/\text{AgCl}/\text{sat-KCl}$ electrode is kept constant. Therefore, decrease in anodic probe current, i.e., difficulties in detecting ferrous ions, may result from a significant shift of potential of the probe electrode due to the large iR drop in the salt film. On the other hand, when the iron electrode is passivated, potential of the probe electrode recovers immediately to the normal state and the anodic probe current increases because the salt film dissolves and the large iR drop disappears. Changes in anodic probe current in stage II cannot be explained without assumption of the presence of salt film. The probe current decreases gradually after passivation since ferrous ion diffuses out from the narrow space between iron and probe electrodes (stage III). When the passivated iron electrode becomes active in the cathodic potential sweep from 1.8 V (SHE), the potential of the probe electrode shifts again to the negative direction and detection of ferrous ion becomes difficult. As the active-dissolution current decreases, however, potential of the probe electrode is restored to detect ferrous ion (stage IV).

Figure 8.3.6c supports that the probe electrode polarized at -0.2 V (SHE) can detect ferric species dissolved from the iron electrode in the active region. At stage II, cathodic probe current increases with anodic potential sweep of the iron electrode, indicating that iron dissolves as ferric ion in the active region although the dissolved amount of ferric ion is slight as compared with that of ferrous ion. However, a large spike of the probe current from cathodic to anodic at the active/passive transition is observed, which is also ascribed to negative potential shift of the probe electrode due to the large iR drop and followed by restoration of the probe electrode due to passivation of the iron electrode. Moreover, at stage V corresponding to the trans-passive region of the iron electrode, the cathodic probe current increases again, indicating

that iron dissolves as ferric ions in the trans-passive region (Heusler 1973, Franck 1952). In the cathodic potential sweep of the passivated iron electrode from 1.8 V to 0 V (SHE) (stages VI and VII), the probe current spike in the cathodic direction is observed when the iron electrode becomes active, which can be explained in the same manner described above.

Figure 8.3.7 shows the ratio, I_p/I_s , as a function of time when the potential of the iron electrode was changed stepwise from E_s to 1.2 V (SHE), while the probe electrode potential was kept at 1.2 V (SHE). In case where E_s is located in the active-dissolution region ($E_s = -0.2$ V to 0.4 V (SHE)), the ratio, I_p/I_s , after the potential step at 1 ks increases rapidly, passing through a maximum, and then decreases gradually. On the other hand, in case where E_s is located in the passive region ($E_s = 0.6$ V and 0.8 V (SHE)), the ratio, I_p/I_s , does not change significantly. As described before, assuming that the salt film is formed in the active region due to accumulation of ferrous ion in the narrow space between probe and iron electrodes, the probe electrode could not detect ferrous ion in the active region because the probe electrode potential shifts to the negative direction due to the large iR drop in the salt film. After potential of the iron electrode was changed stepwise to 1.2 V, the probe electrode could detect ferrous ions due to restoration of potential to the normal state as far as ferrous ion is present in the narrow space. Gradual decrease in I_p/I_s after passing through the maximum may be associated with consumption of ferrous ions in the narrow space or diffusion of ferrous ions from the narrow space. It should be remarked in this work that presence of the salt film prior to passivation of the iron was first supported by SECM.

8.3.3 *Imaging distribution of anodic dissolution at a polycrystalline iron electrode surface*

Figure 8.3.8a shows the probe current image measured after the iron electrode surface with distinctive crystal grains was passivated at 1.0 V (SHE) for 3.6 ks in pH 8.4 borate solution. To obtain the probe current image in TG/SC mode, iron and probe electrodes were polarized at -0.1 V and 1.2 V (SHE), respectively, in pH 8.4 borate solution containing 0.03 mol dm^{-3} $\text{K}_4\text{Fe}(\text{CN})_6$. Figure 8.3.8b is an optical micrograph of the same surface region where the probe current image was measured. From comparison between Figures 8.3.8a and b, shapes of patch patterns on the probe current image are seen to coincide completely with shapes of crystal grains on the iron surface. It was reported in Chapter 5 that distribution of probe current in Figure 8.3.8a is caused by difference in thickness of the passive film, depending upon grain orientation of the iron substrate. On the iron {100} plane, thicker film forms as compared with other iron planes {110} or {111}. After cathodic reduction of passive film on the iron electrode, the iron electrode was polarized at -0.1 V (SHE) in pH 2.3 sulfate solution. Simultaneously,

SECM line-scans in SG/TC mode were carried out. The carbon microelectrode with a diameter of 6.9 μm was polarized at 1.2 V (SHE) and scanned repeatedly above the iron electrode surface at a distance of about 5 μm along the dashed line drawn in Figure 8.3.8a. After 300 s, as seen in Figure 8.3.8c, active-dissolution current of the iron electrode became a steady state while probe current oscillated significantly, depending on the scanning position of the probe electrode. Probe current oscillation indicates that dissolution rates of ferrous species are distributed. Figure 8.3.8d shows time dependence of probe current profiles. Oscillation in probe current has a good reproducibility and attains a steady state. This indicates that the dissolution rate of ferrous ions at a steady state depends on position of the iron electrode surface. Lateral resolution of the current profile is in the order of several hundred micrometers, although probe current oscillates about 30% at a maximum. Furthermore, it is clear from comparison of Figures 8.3.8a and d that concentration of ferrous species dissolved from the substrate grain which is covered with thinner film in the passive region is higher than that from the substrate grain which is covered with thicker film in the passive region. These relationships indicate that the active dissolution rate from substrate grain with thicker film formed in the passive region, is relatively lower than that from substrate grain with thinner film in the passive region. Seo and Chiba (Seo 2001?) confirmed from polarization curves in pH 8.4 borate solution that the active-dissolution current of the iron {110} plane was larger than that of the iron {100} plane, which strongly supports present results. Correlation between active-dissolution current or passive film thickness and crystal orientation of substrate iron has not been well established. Surface atomic density of the iron {110} plane is 1.41 times as much as that of the iron {100} plane, which may be reflected on difference in active dissolution currents between iron {100} and {110} planes. On the other hand, Toney, et al (Toney 1993) and Davenport, et al (Davenport 2000) reported that thicker passive film oriented to (100) grows on the iron (001) plane, while thinner passive film oriented to (111) grows on the iron (110) plane. The epitaxial relationship between passive film and substrate iron would influence film thickness.

8.4 Conclusions

The SECM was applied to evaluate dissolution distribution of ferrous or ferric ion from a polycrystalline iron electrode in deaerated pH 2.3 sulfate solution. The following conclusions were drawn.

- i) Ferrous or ferric ion could be detected with a probe microelectrode composed of graphite

reinforcement carbon.

- ii) Dissolution of ferrous and ferric ions in the active region was successfully monitored. However, once the salt film such a FeSO_4 was formed due to accumulation of ferrous ion in the narrow space between probe and iron electrodes, detection of ferrous or ferric ion became difficult because potential of the probe electrode shifted to the negative direction due to the large iR drop in the salt film. On the other hand, it was confirmed that ferric ions dissolved from the iron electrode in the trans-passive region.
- iii) Dissolution distribution of ferrous ion from a polycrystalline iron electrode in the active region, depending on substrate grains, was measured by SECM probe current profile. The active-dissolution rate of ferrous ions from the substrate grain with thicker film formed in the passive region was less than that from the substrate grain with thinner film formed in the passive region.

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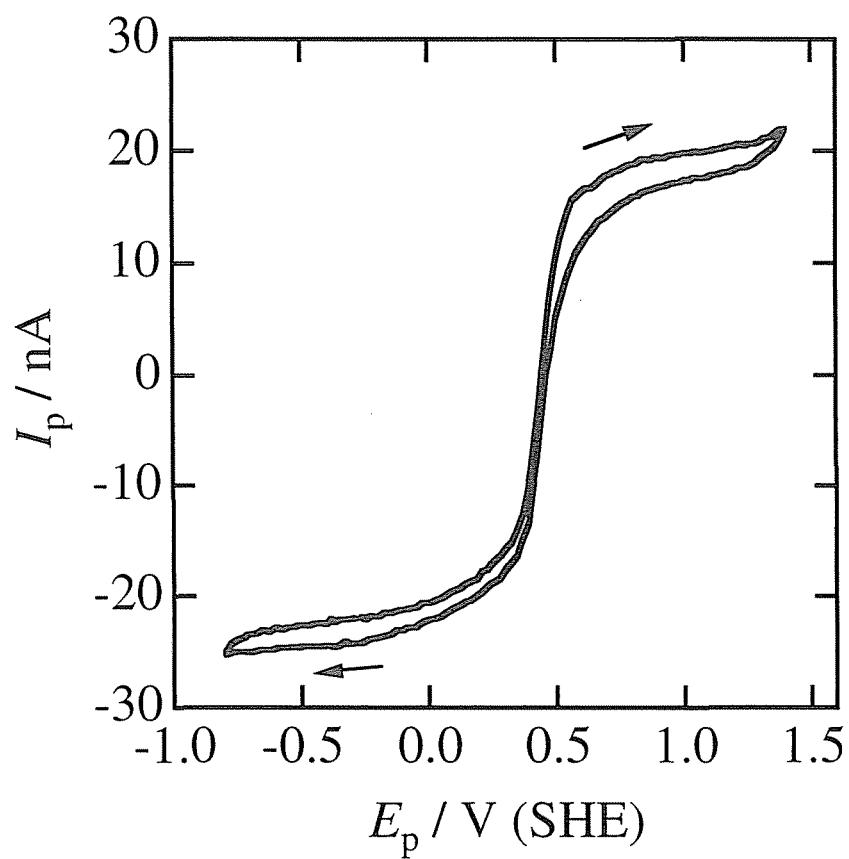


Fig. 8.3.1 CV of a carbon microelectrode in deaerated 0.1 mol dm^{-3} KCl solution containing 0.01 mol dm^{-3} $\text{K}_3\text{Fe}(\text{CN})_6$ and 0.01 mol dm^{-3} $\text{K}_4\text{Fe}(\text{CN})_6$.
The potential sweep rate was 100 mV s^{-1} .

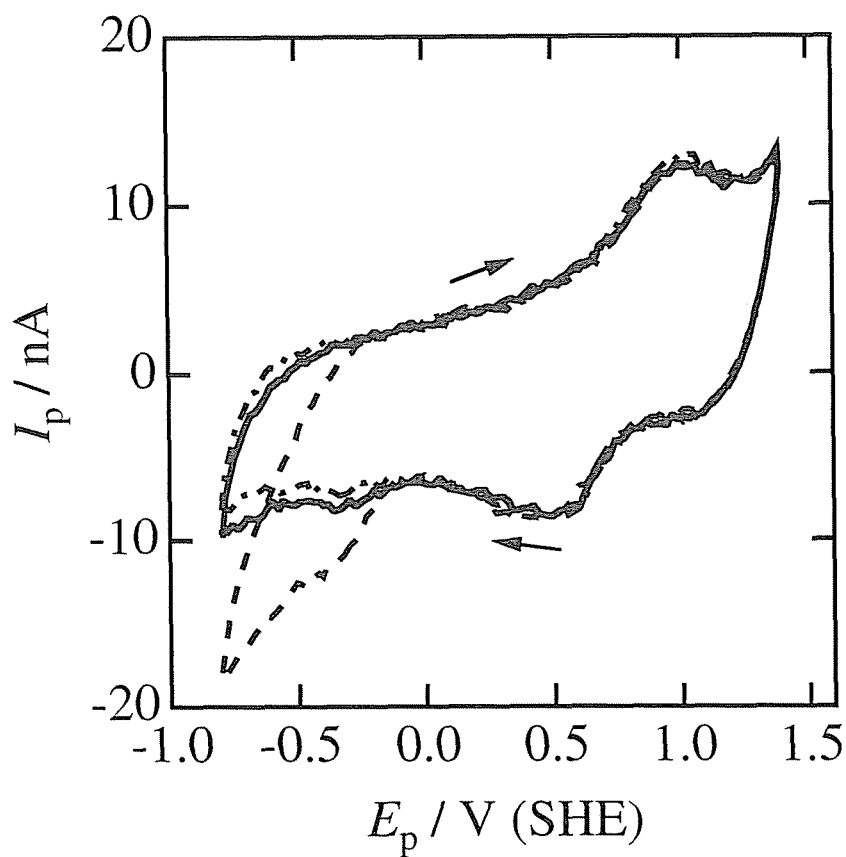


Fig. 8.3.2 CV of the carbon microelectrode with a diameter of $17 \mu\text{m}$ in $0.1 \text{ mol dm}^{-3} \text{H}_2\text{SO}_4$ deaerated with bubbling argon gas (---), aerated with bubbling air (—), or aerated with bubbling pure oxygen (- · - ·).

The potential sweep rate was 100 mV s^{-1} .

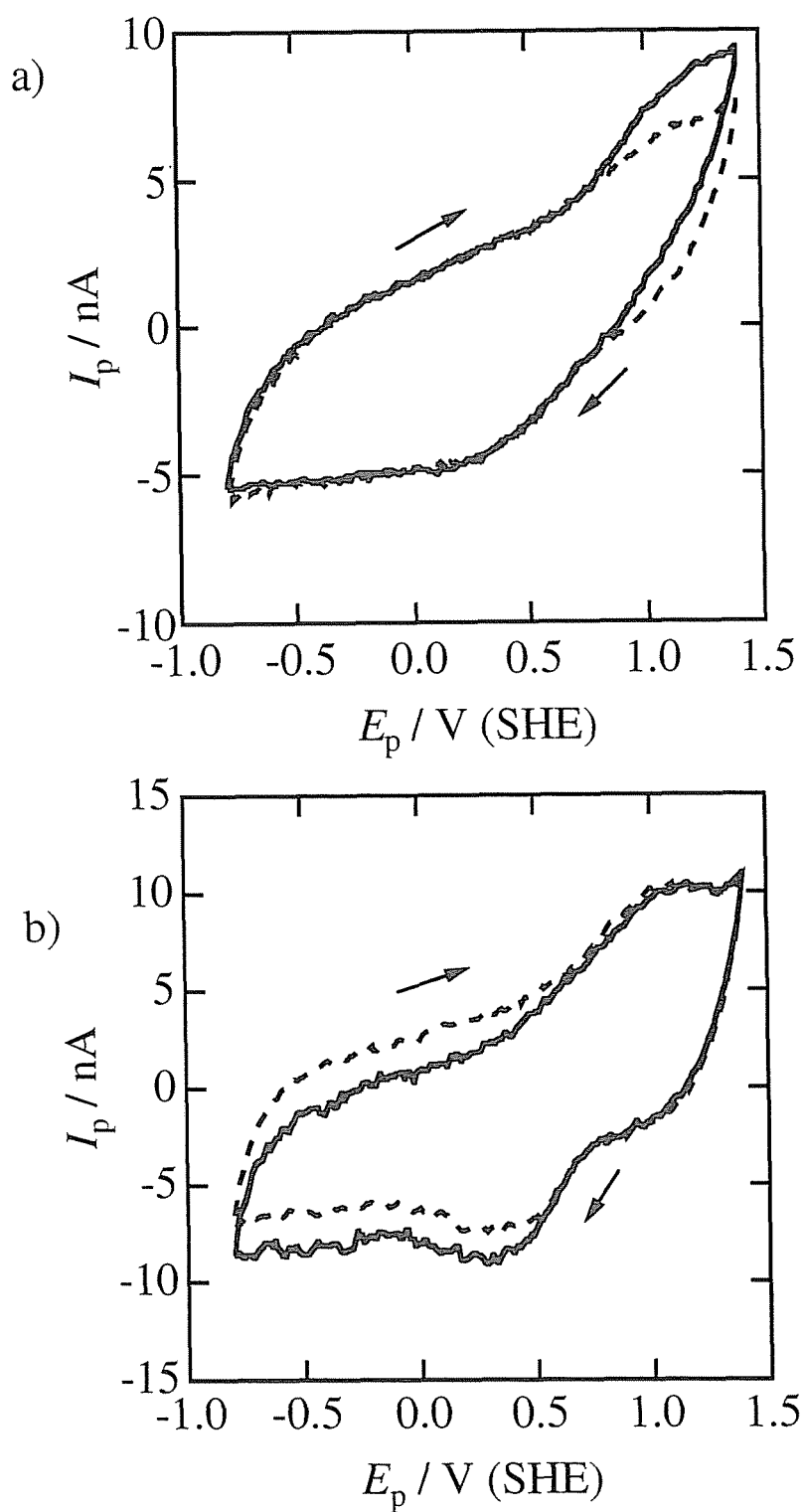


Fig. 8.3.3 a) CV of the carbon microelectrode in deaerated 0.1 mol dm⁻³ H₂SO₄ (---) or in deaerated 0.1 mol dm⁻³ H₂SO₄ containing 10⁻³ mol dm⁻³ ferrous ion (—). b) CV of the carbon microelectrode in deaerated 0.1 mol dm⁻³ HCl (---) or in deaerated 0.1 mol dm⁻³ HCl containing 10⁻³ mol dm⁻³ ferric ion (—). The potential sweep rate is 100 mV s⁻¹.

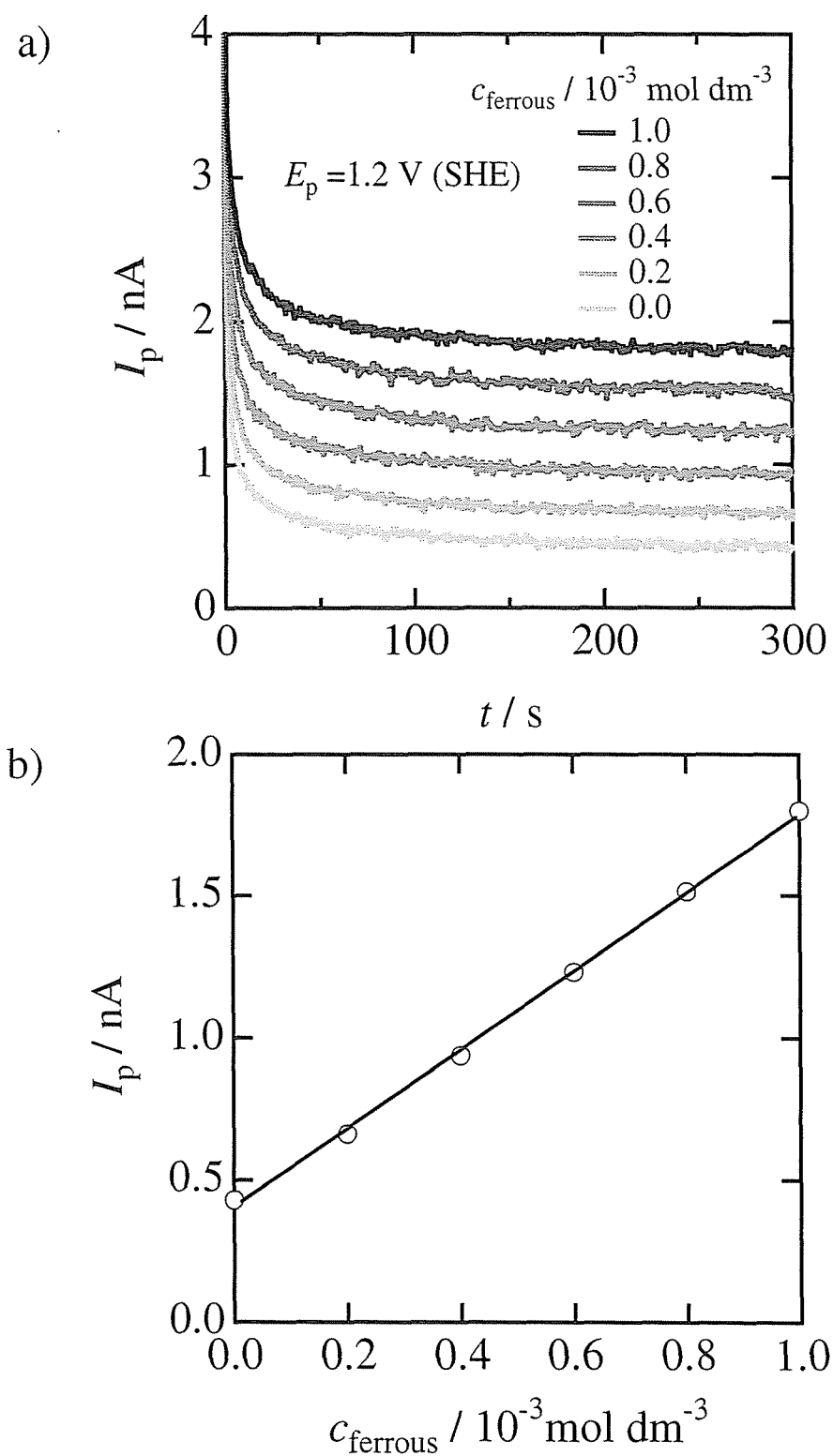


Fig. 8.3.4 a) Transients of current flowing through the carbon microelectrode polarized at 1.2 V (SHE) in deaerated $0.1 \text{ mol dm}^{-3} \text{ H}_2\text{SO}_4$ with various concentrations of ferrous ion, c_{ferrous} .
b) Relation between c_{ferrous} and anodic current at 300 s.

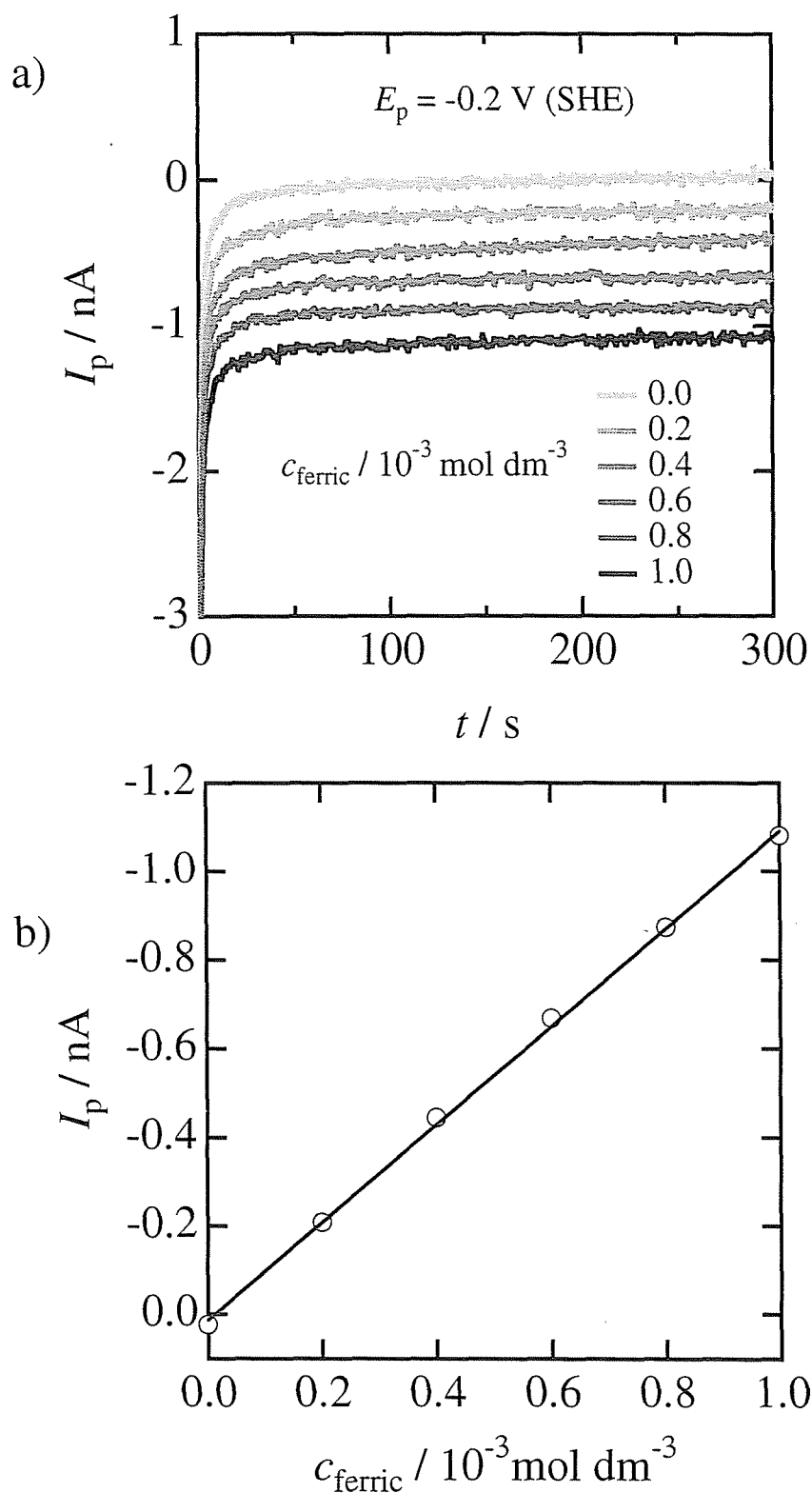


Fig. 8.3.5 a) Transients of current flowing through the carbon microelectrode polarized at -0.2 V (SHE) in deaerated $0.1 \text{ mol dm}^{-3} \text{ HCl}$ with various concentrations of ferric ion, c_{ferric} .
b) Relation between c_{ferric} and cathodic current at 300 s.

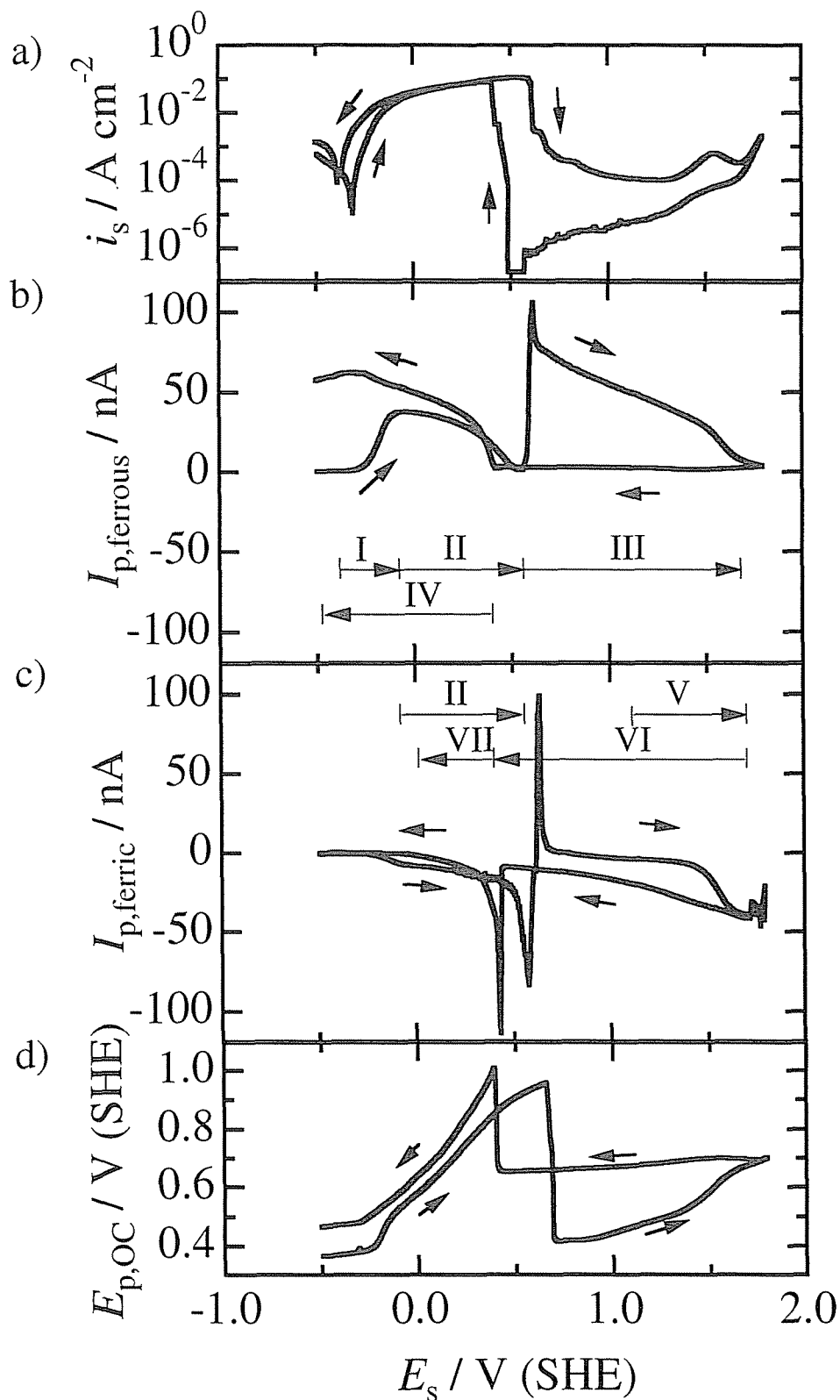


Fig. 8.3.6 a) CV of the iron electrode with a diameter of 1 mm in deaerated pH 2.3 sulfate solution. The potential sweep rate was 10 mV s^{-1} .
 b) and c) Probe currents, $I_{p,\text{ferrous}}$ and $I_{p,\text{ferric}}$, as a function of polarization potential of the iron electrode, E_s , when the probe electrode was polarized at 1.2 V and -0.2 V (SHE), respectively. The distance between probe and iron electrodes was kept at $75 \mu\text{m}$.
 d) Potential of the probe electrode in an open circuit, $E_{p,\text{OC}}$, as a function of polarization potential of the iron electrode, E_s .

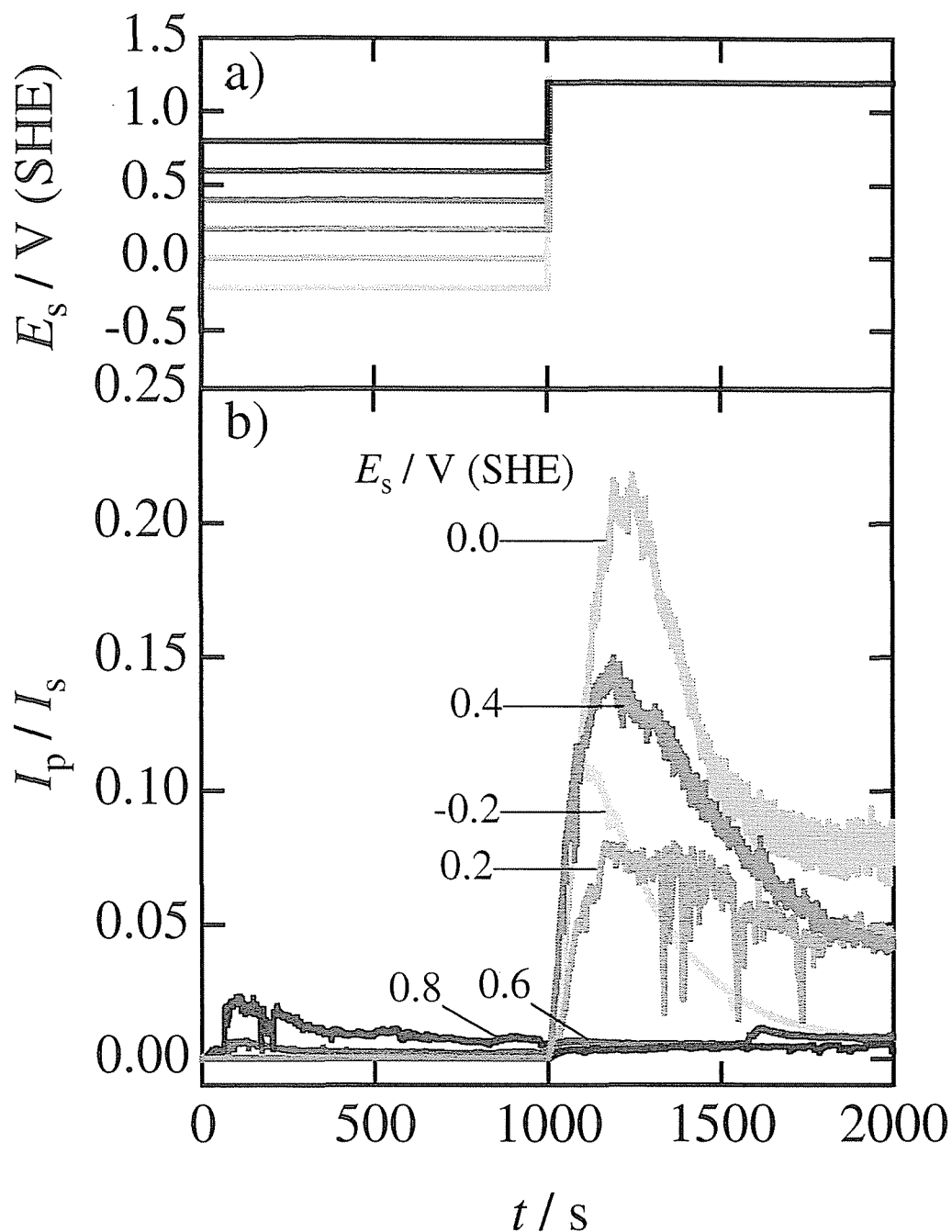


Fig. 8.3.7 Current ratio, I_p/I_s , as a function of time when the potential of the iron electrode was changed stepwise from E_s to 1.2 V (SHE) in deaerated pH 2.3 sulfate solution, while the potential of the probe electrode was kept at 1.2 V (SHE). The distance between probe and iron electrodes was kept at 75 μm .

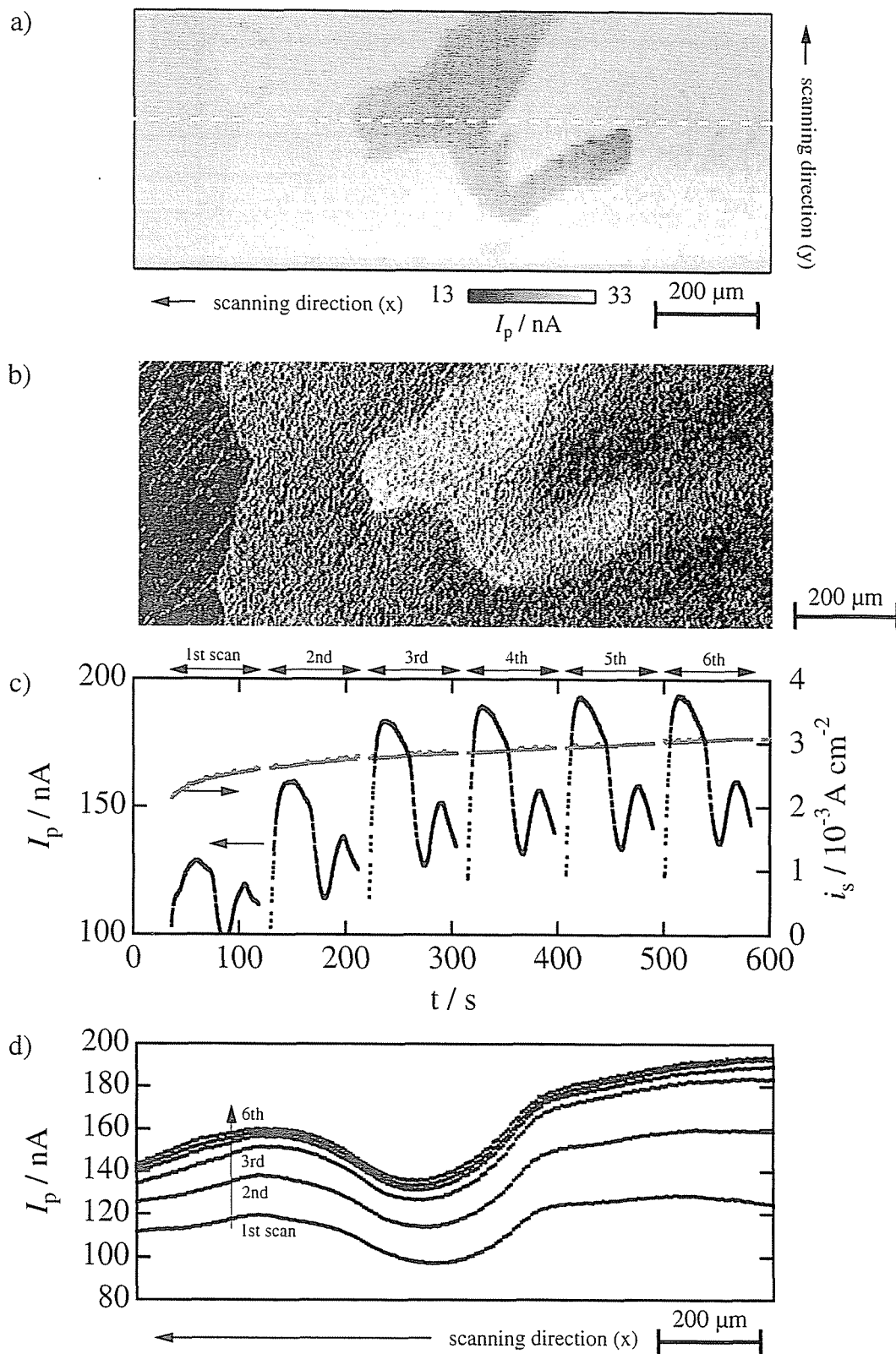


Fig. 8.3.8 a) Probe current image in TG/SC mode measured after the iron electrode surface with distinctive crystal grains was passivated at 1.0 V (SHE) for 3.6 ks in pH 8.4 borate solution. For measurement of the probe current image, the platinum probe electrode with a diameter of $10 \mu\text{m}$ and the iron electrode were polarized at 1.2 V and 0.1 V (SHE), respectively, in pH 8.4 borate solution containing $0.03 \text{ mol dm}^{-3} \text{ K}_4\text{Fe}(\text{CN})_6$. Distance between probe and iron electrodes was kept at about $5 \mu\text{m}$. b) Optical micrograph of the same surface region where the probe current image was measured. c) Polarization curves of the carbon probe microelectrode with a diameter of $6.9 \mu\text{m}$ and the iron electrode. The probe and iron electrodes were polarized at 1.2 V and -0.1 V (SHE), respectively, in deaerated pH 2.3 sulfate solution (in SG/TC mode). The probe electrode was scanned repeatedly above the iron electrode surface at a distance of about $5 \mu\text{m}$ along the dashed line drawn in Fig. 8.3.8a. d) A part of probe current profile corresponding to the dashed line at each scan in the measurement of Fig. 8.3.8c.

9 **Detection of hydrogen generated from a single crystal magnetite coupled galvanically with carbon steel**

9.1 Introduction

Thermodynamics reveals that most metals corrode in earth's environment. Material lifetime is considered to be the time period when functions of materials degrade to critical levels due to corrosion. If materials corrode uniformly, lifetime can be estimated easily from measurement of average corrosion rate in the environment of use. However, it is very difficult to estimate lifetime in cases where materials corrode locally.

In general, carbon steel is subjected to relatively uniform corrosion in the active region. In Japan, therefore, carbon steel is one promising candidate for an over-pack in which nuclear wastes are preserved for long periods of over one thousand year (JNC DI 1999). The over-pack, surrounded with bentonite clay as a buffer material, should be located deep underground and free from oxygen.

It has been recently claimed (Kojima 1997, 1998) that magnetite, which may be regarded as a corrosion product of iron, accelerates corrosion of carbon steel through a galvanic coupling. If corrosion of carbon steel is accelerated with magnetite, both hydrogen evolution and reduction of magnetite itself have to be considered as cathodic reactions of magnetite coupled with anodic reactions of carbon steel.

The amount of hydrogen generated on magnetite in acidic solutions could be detected by gas chromatography (Haruna 1999) and differential pressure gauges (Watanabe 1999). On the other hand, detection of hydrogen in neutral solutions presents difficulties because only a trace of hydrogen is generated on magnetite. It is known that scanning electrochemical microscopy (SECM) is powerful for investigation of electrochemical activity at the local site of the electrode surface. In this chapter, hydrogen generation from a single crystal magnetite coupled with a carbon steel electrode was first investigated using an SECM probe electrode.

9.2 Experimental

9.2.1 *Specimen preparation*

Blocks (5 mm x 5 mm x 2 mm) of carbon steel and single crystal magnetite {100} plane were employed. Their compositions are shown in Table 9.2.1.

Table 9.2.1 Chemical compositions of magnetite and carbon steel (mass%)

Magnetite	Mg 0.04	Al 0.02	Ti 0.07	V 0.30		Fe bal.
Carbon steel (SM400B)	C 0.14	Si 0.19	Mn 1.02	P 0.011	S 0.001	Fe bal.

After embedding into epoxy resin, the surface of each block with a surface area of 25 mm² was mechanically polished with α -alumina abrasives to 3 μ m. Furthermore, platinum plate (5 mm x 5 mm x 0.5 mm) with a purity of 99.99%, the surface of which was prepared as described above, was used as a standard material for hydrogen generation.

9.2.2 Measurement of coupling current

Figure 9.2.1 shows a block diagram of apparatus used for galvanic coupling current measurement. Coupling current flowing from the magnetite to the carbon steel was measured with a zero shunt ammeter (Hokuto Denko Co., HM-104) in deaerated 0.1 mol dm⁻³ Na₂SO₄ solution of pH 5.8. Coupling or uncoupling was controlled with a relay (Omron, G5V-2) driven by a computer.

A platinum microdisk electrode with a diameter of 100 μ m was mainly employed as a probe for hydrogen detection. Figure 9.2.2 shows a block diagram of apparatus used for hydrogen detection. The probe electrode was held above the magnetite or platinum specimen electrode at a distance of 200 μ m. In deaerated solutions, the probe electrode was polarized cyclically or at a constant potential while the specimen electrode was galvanostatically polarized or coupled with the carbon steel electrode.

To evaluate distribution of hydrogen generated on a model electrode system of carbon steel and magnetite shown in Figures 9.2.3a and b, SECM imaging was carried out with the apparatus of type III in Table 4.3.1. A platinum microelectrode with a diameter of 10 μ m was employed as a probe electrode for SECM imaging. Probe current images of the specimen electrode surface were measured in two different solutions: (a) deaerated pH 8.4 borate solution containing 0.03 mol dm⁻³ K₄Fe(CN)₆ and (b) deaerated 0.1 mol dm⁻³ Na₂SO₄ solution of pH 3.3 (adjusted by H₂SO₄). Moreover, the following conditions were adopted:

- i) distance between probe and specimen electrodes was maintained at about 5 μ m.
- ii) the probe electrode was scanned stepwise to a distance of 2500 μ m at 5 μ m intervals in the *x* direction and to a distance of 500 μ m at 10 μ m intervals in the *y* direction in solution (a), though no scan in the *y* direction was done for solution (b).
- iii) the probe electrode was polarized at $E_p = 1.2$ V (SHE) while the magnetite and carbon steel

of the model system were uncoupled in solution (a). On the other hand, in solution (b), the probe electrode was polarized at $E_p = 0.3$ V (SHE) while magnetite and carbon steel were coupled or uncoupled.

9.3 Results and Discussion

9.3.1 *Coupling current flowed between single crystal magnetite and carbon steel*

Figure 9.3.1 shows time variation of coupling current passed between single crystal magnetite and carbon steel in deaerated pH 5.8 sulfate solution. Current flowed from magnetite to carbon steel and attained a steady state after 18 ks. This steady state current of $5 \mu\text{A cm}^{-2}$ was several tens of times higher than the corrosion current ($0.1\text{-}0.2 \mu\text{A cm}^{-2}$) of carbon steel in deaerated pH 5.8 sulfate solution.

Figure 9.3.2 shows the cathodic polarization curve of a single crystal magnetite electrode in pH 5.8 sulfate solution. Each electrode potential was measured at 600 s after each current step. Electrode potential shifts linearly with increasing cathodic polarization current up to $10 \mu\text{A cm}^{-2}$. In the current region higher than $10 \mu\text{A cm}^{-2}$, however, potential shifts exponentially with increasing current, corresponding to hydrogen generation on the magnetite electrode. After cathodic polarization, rest potential of the magnetite shifts to about -0.52 V (SHE). This negative shift of rest potential may be caused by reduction of the magnetite surface to an iron oxide with lower valency or metallic iron during cathodic polarization. On the other hand, the magnetite potential during galvanic coupling in pH 5.8 sulfate solution was -0.47 V (SHE) at which reduction of the magnetite itself takes place in parallel with hydrogen generation as described later.

9.3.2 *Detection of hydrogen generated from magnetite electrode during galvanic coupling with carbon steel electrode*

Figure 9.3.3 shows the CV of the platinum microelectrode which was located above the platinum or magnetite surface cathodically polarized under different galvanostatic conditions in deaerated pH 5.8 sulfate solution. Over the whole potential region, microelectrode current shifts to the anodic direction with increasing specimen galvanostatic current, indicating that the microelectrode oxidizes some reaction products, e.g., hydrogen diffused from the specimen electrode. If potential of the microelectrode is set to a constant potential at which any other electrochemical reactions cannot take place except for hydrogen reduction, hydrogen can

be detected using the microelectrode. According to the potential-pH diagram of iron in aqueous solution at 298 K shown in Figure 1.2.1, Fe^{2+} ions, the concentration of which is less than $10^{-4} \text{ mol dm}^{-3}$, are thermodynamically stable in the potential region between -0.15 V and -0.45 V (SHE) in solutions with pH lower than 6.5.

Figure 9.3.4 shows transients of the normalized probe current, $\Delta I_p (= \Delta I_p(i_s) - \Delta I_p(0))$, when the probe microelectrode polarized at -0.15 V (SHE) was located above the platinum or magnetite surface cathodically polarized at i_s in deaerated pH 5.8 sulfate solution. During cathodic polarization of the specimen, anodic current flows through the probe electrode due to anodic oxidation of hydrogen generated from the specimen. Probe current increases with increasing $|i_s|$. Figure 9.3.5 shows the relation between specimen current, $|i_s|$, and normalized probe current, ΔI_p , in the steady state. Since current efficiency for hydrogen generation on the platinum surface is 100%, the ratio of the probe currents, $\Delta I_p(\text{above the magnetite})/\Delta I_p(\text{above the platinum})$, corresponds to current efficiency for hydrogen generation on the magnetite electrode. Current efficiency for hydrogen generation on the magnetite is estimated to be about 50% from the slope ratio of the two lines in Figure 9.3.5.

Figure 9.3.6 shows transients of coupling current flowed from the magnetite to the carbon steel during galvanic coupling and of probe current when the probe electrode located above the magnetite electrode was polarized at -0.15 V (SHE) in deaerated pH 5.8 sulfate solution. It is seen from Figure 9.3.6 that the normalized probe electrode current, ΔI_p , is 1.5 nA at the coupling current of $i_{\text{couple}} = 5 \mu\text{A cm}^{-2}$ in the steady state. Assuming that $i_{\text{couple}} = 5 \mu\text{A cm}^{-2}$ is equivalent to i_s in Figure 9.3.5, $\Delta I_p = 2.5 \text{ nA}$ is obtained as a normalized probe current from Figure 9.3.5. This discrepancy of ΔI_p may arise from difference in electrode potential of magnetite between galvanic coupling and galvanostatic polarization. However, if large fluctuation in experimental data of ΔI_p for the magnetite is considered, it can be inferred that current efficiency of hydrogen generation on the magnetite during galvanic coupling with the carbon steel is about 50%.

9.3.3 *Distribution of hydrogen generated from the magnetite during galvanic coupling with the carbon steel*

Figure 9.3.7a is a schematic top view of model electrode system for the SECM measurement, which is composed of single crystal magnetite and carbon steel. Figure 9.3.7b shows the probe current image of the model system measured when the probe electrode was polarized at 1.2 V (SHE) in deaerated pH 8.4 borate solution containing $0.03 \text{ mol dm}^{-3} \text{ K}_4\text{Fe(CN)}_6$ under uncoupled condition of magnetite and carbon steel. The probe electrode,

polarized at 1.2 V (SHE), can oxidize Fe(CN)_6^{4-} to Fe(CN)_6^{3-} , which is reduced on the magnetite or carbon steel surface in the open circuit. If Fe(CN)_6^{3-} reduction takes place easily on the magnetite or carbon steel surface, the $\text{Fe(CN)}_6^{3-}/\text{Fe(CN)}_6^{4-}$ redox reaction occurs repeatedly between the probe electrode and the magnetite or carbon steel, i.e., positive feedback is operative. The line of the highest probe current is observed at the edge of the magnetite facing the carbon steel. High activity for reduction of Fe(CN)_6^{3-} at the edge of the magnetite may result from high mechanical damage due to mechanical polishing for surface preparation. Except for this anomalous probe current at the edge of the magnetite, probe currents above the magnetite and carbon steel surfaces are relatively high as compared with probe current above the epoxy resin, indicating that reduction of Fe(CN)_6^{3-} takes place easily on both magnetite and carbon steel surfaces. Moreover, current above the magnetite is higher than that above the carbon steel. This means that Fe(CN)_6^{3-} reduction takes place more easily on the magnetite than the carbon steel. An air-formed oxide film on the carbon steel surface may suppress Fe(CN)_6^{3-} reduction. Particularly, heterogeneity in the probe current image is observed above the magnetite surface, which may result from fluctuation in chemical composition of the magnetite surface because electrochemical activity such as reduction of Fe(CN)_6^{3-} is strongly influenced by chemical composition of oxide (Schultze 1986). In any case, location of magnetite and carbon steel electrodes in Figure 10a could be confirmed by probe current imaging as shown in Figure 9.3.7b.

Figure 9.3.7c shows probe current profiles along the dashed line drawn in Figure 9.3.7b. The probe electrode was polarized at 0.3 V (SHE) while the carbon steel electrode was coupled or uncoupled with the magnetite electrode in deaerated pH 3.3 sulfate solution. Since hydrogen is oxidized to protons on the probe electrode at 0.3 V (SHE), the degree of hydrogen generation can be evaluated from probe current. Probe current at each position corresponds to concentration of hydrogen generated from the specimen surface. During uncoupling, the probe current is high on the carbon steel electrode compared to the epoxy resin or magnetite electrode. The same current profiles were obtained after 1 ks-uncoupling. On the other hand, during coupling, the probe current profile above the magnetite shifts to the anodic direction with time and attains a steady state after 4 ks-coupling. Anodic shift in probe current profiles indicates that hydrogen generation is induced on the magnetite due to coupling. In contrast, the probe current profile above the carbon steel during coupling is not significantly different from that during uncoupling. Significant change in the probe current profile above the magnetite during coupling compared to that above the carbon steel indicates that galvanic corrosion of carbon steel is controlled by the cathodic reaction of the magnetite. In spite of the poor resolution of the probe

current profile of about several hundred micrometers in the SG/TC mode of SECM, oscillation of probe current profile above the magnetite assigned with arrows in Figure 9.3.7c correlates with heterogeneity in probe current image in Figure 9.3.7b. This correlation suggests that electrochemical activity of hydrogen generation on the magnetite surface depends on local chemical composition.

9.4 Conclusions

Galvanic coupling with the single crystal magnetite accelerated carbon steel corrosion in deaerated pH 5.8 sulfate solution. Acceleration was due to both reduction of water, i.e. hydrogen generation on the magnetite and reduction of the magnetite itself. From measurement of the probe current above the magnetite or carbon steel, it was deduced that current efficiency for hydrogen generation on the magnetite during galvanic coupling with the carbon steel was about 50%. Moreover, the probe current profile revealed that hydrogen generation was significantly promoted on the magnetite electrode during galvanic coupling in deaerated pH 3.3 sulfate solution.

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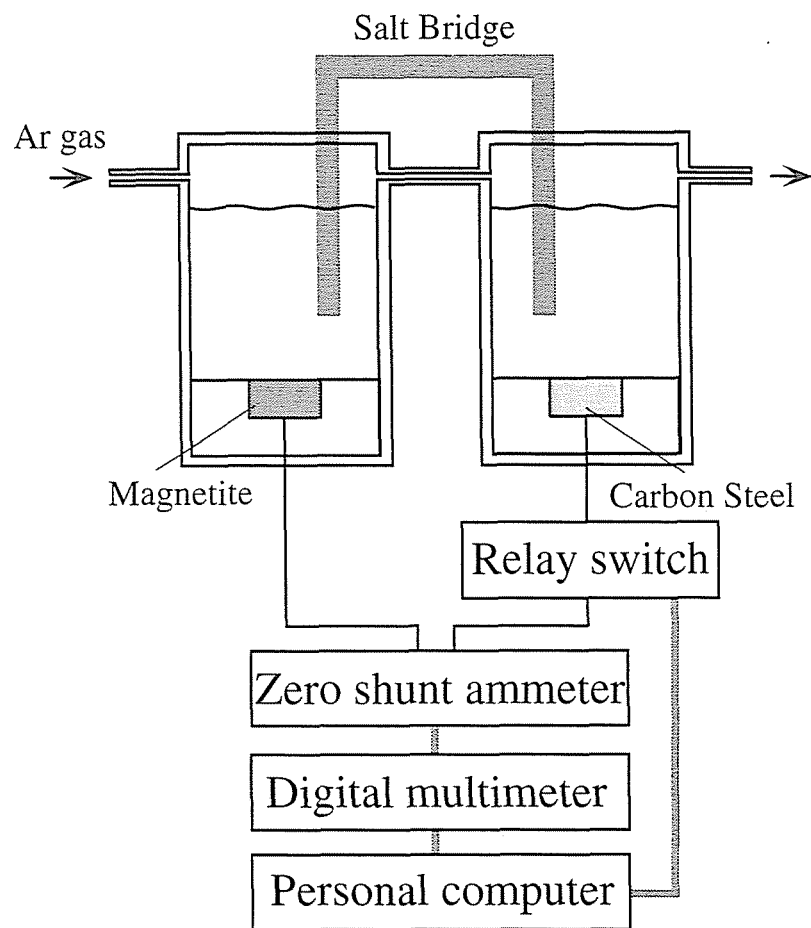


Fig. 9.2.1 Schematic diagram of the apparatus used for measurement of coupling current.

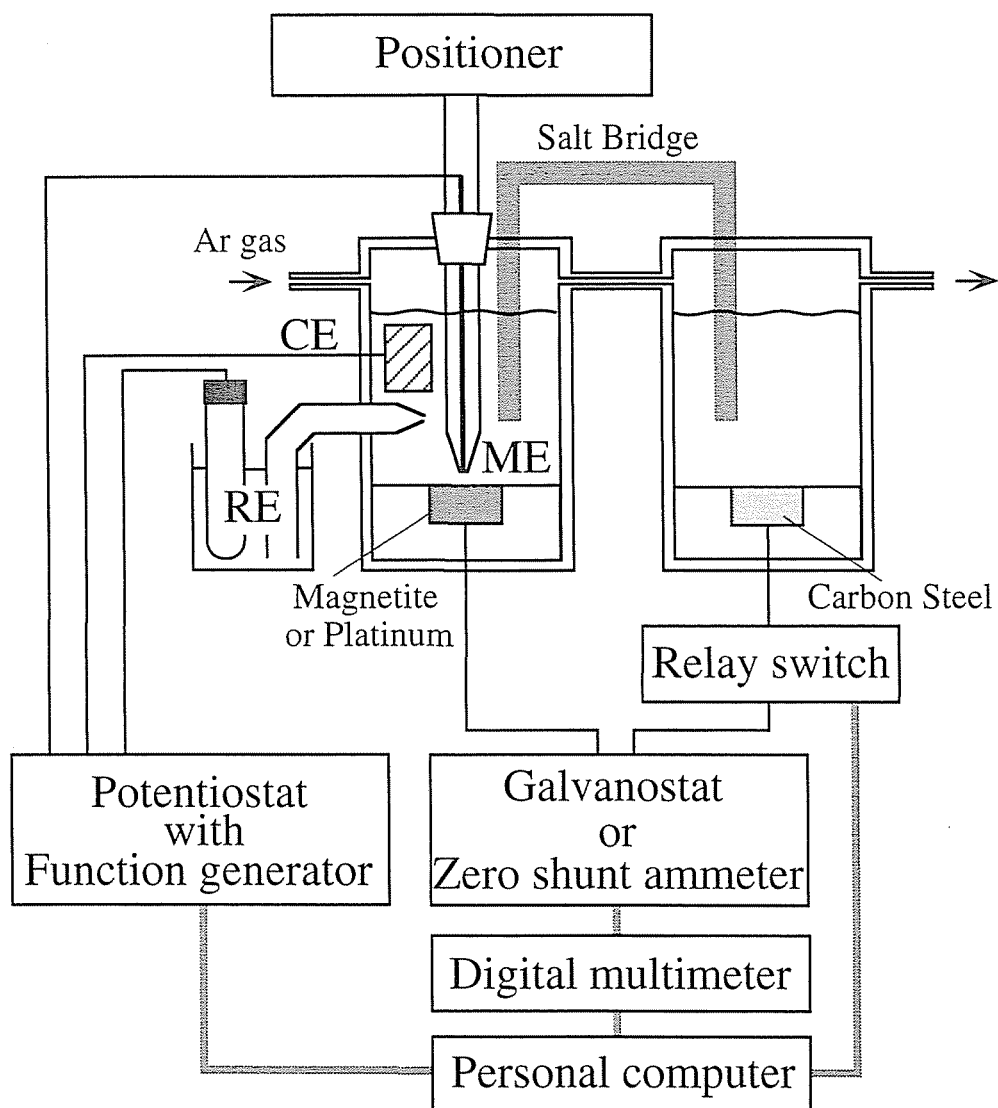


Fig. 9.2.2 Schematic diagram of apparatus used for voltammetry of microelectrode.

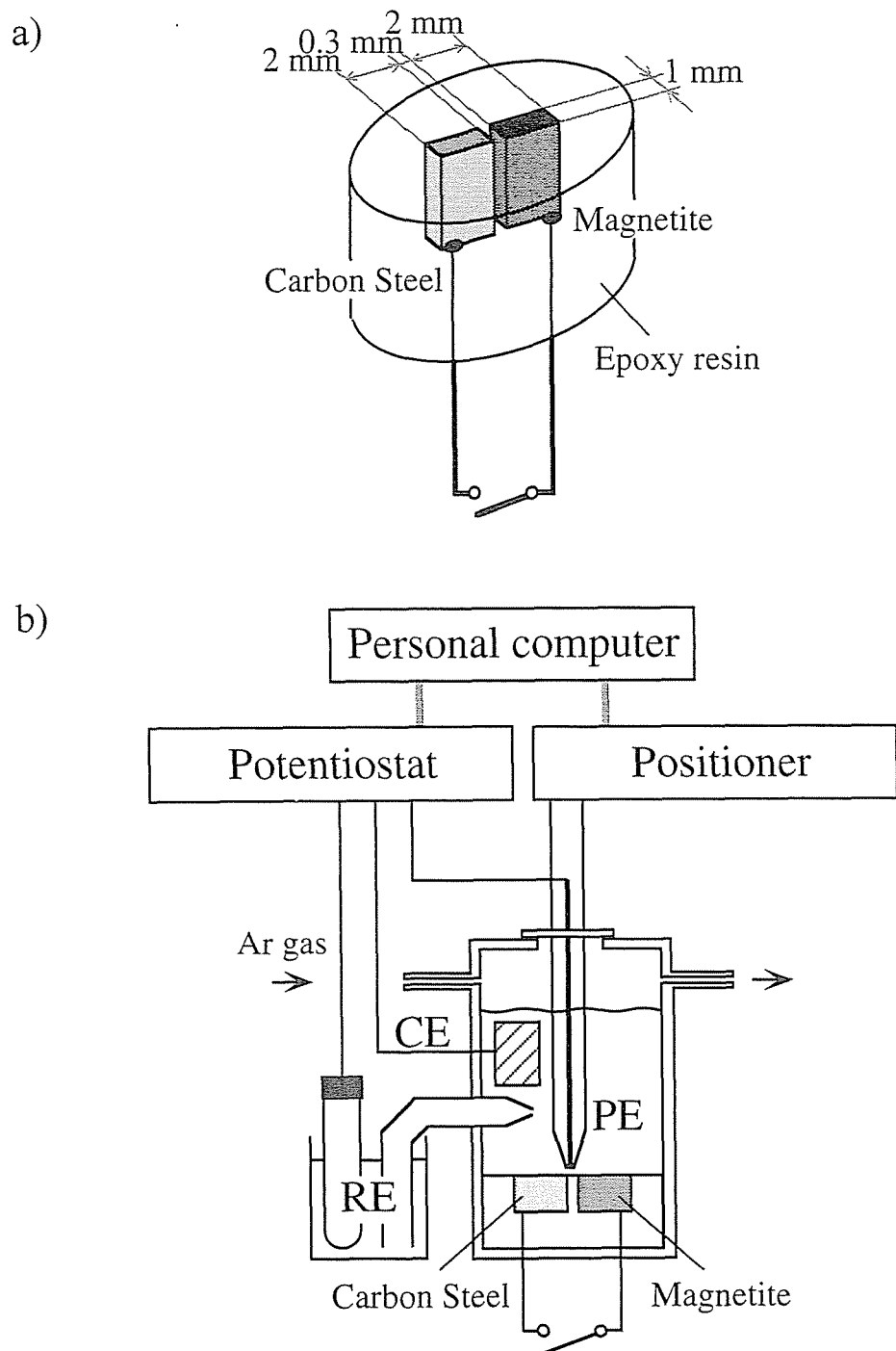


Fig. 9.2.3 Schematic diagram of a) the model electrode system and b) the apparatus used for SECM measurement.

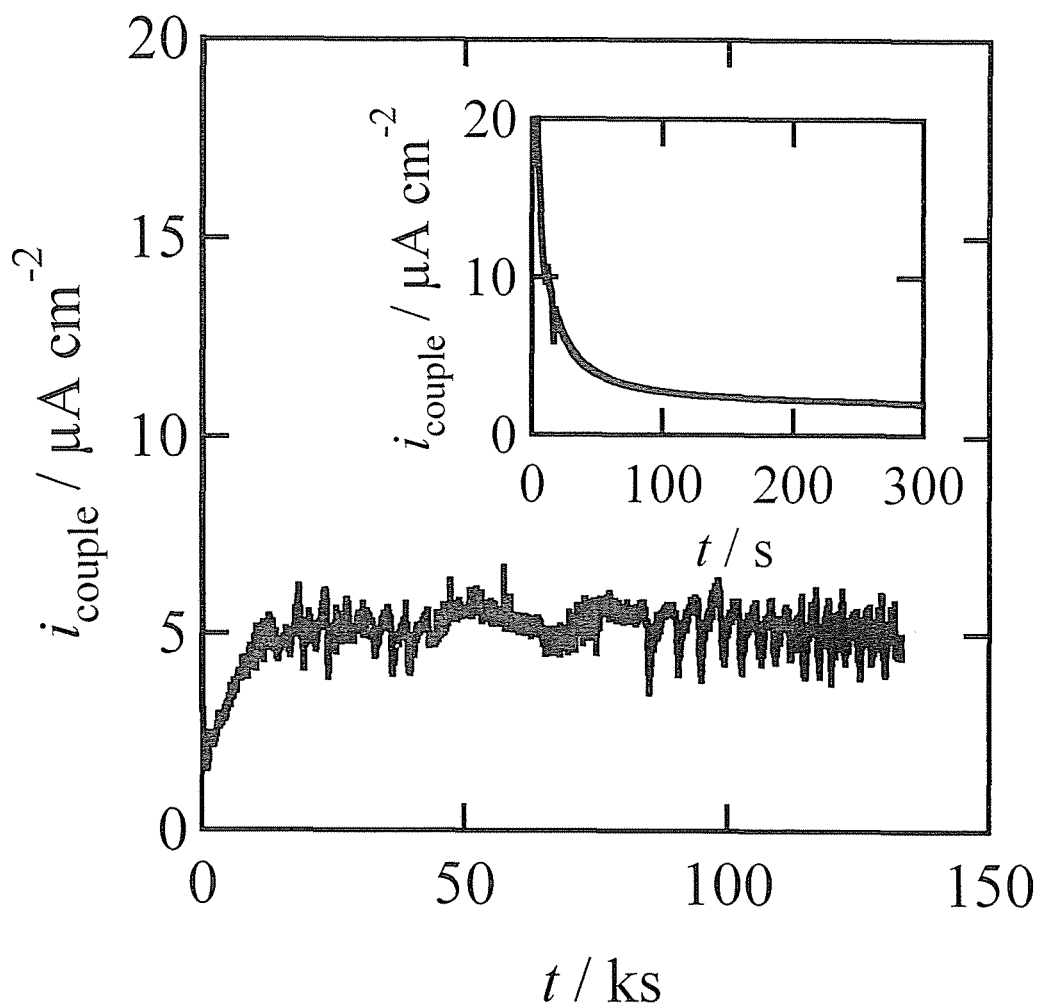


Fig. 9.3.1 Time-variation of coupling current, i_{couple} , passed from the single crystal magnetite to the carbon steel in $0.1 \text{ mol dm}^{-3} \text{ Na}_2\text{SO}_4$ solution of pH 5.8.

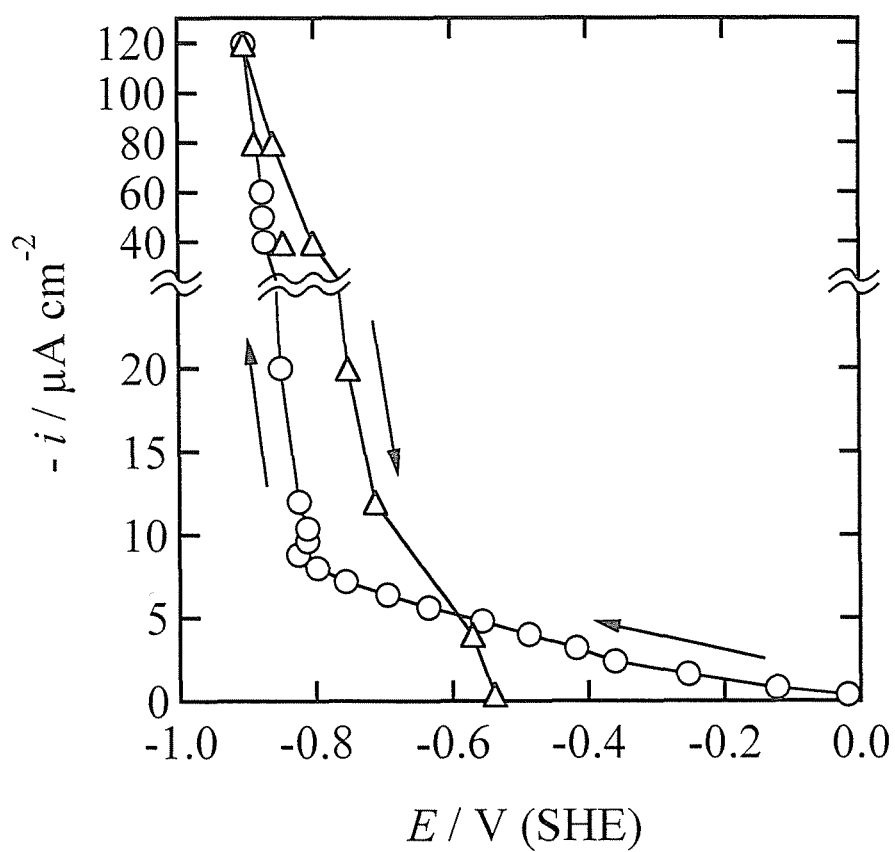


Fig. 9.3.2 Polarization curve of the single crystal magnetite measured in $0.1 \text{ mol dm}^{-3} \text{ Na}_2\text{SO}_4$ solution of pH 5.8 by a galvanostatic current step in the cathodic direction followed by anodic direction.

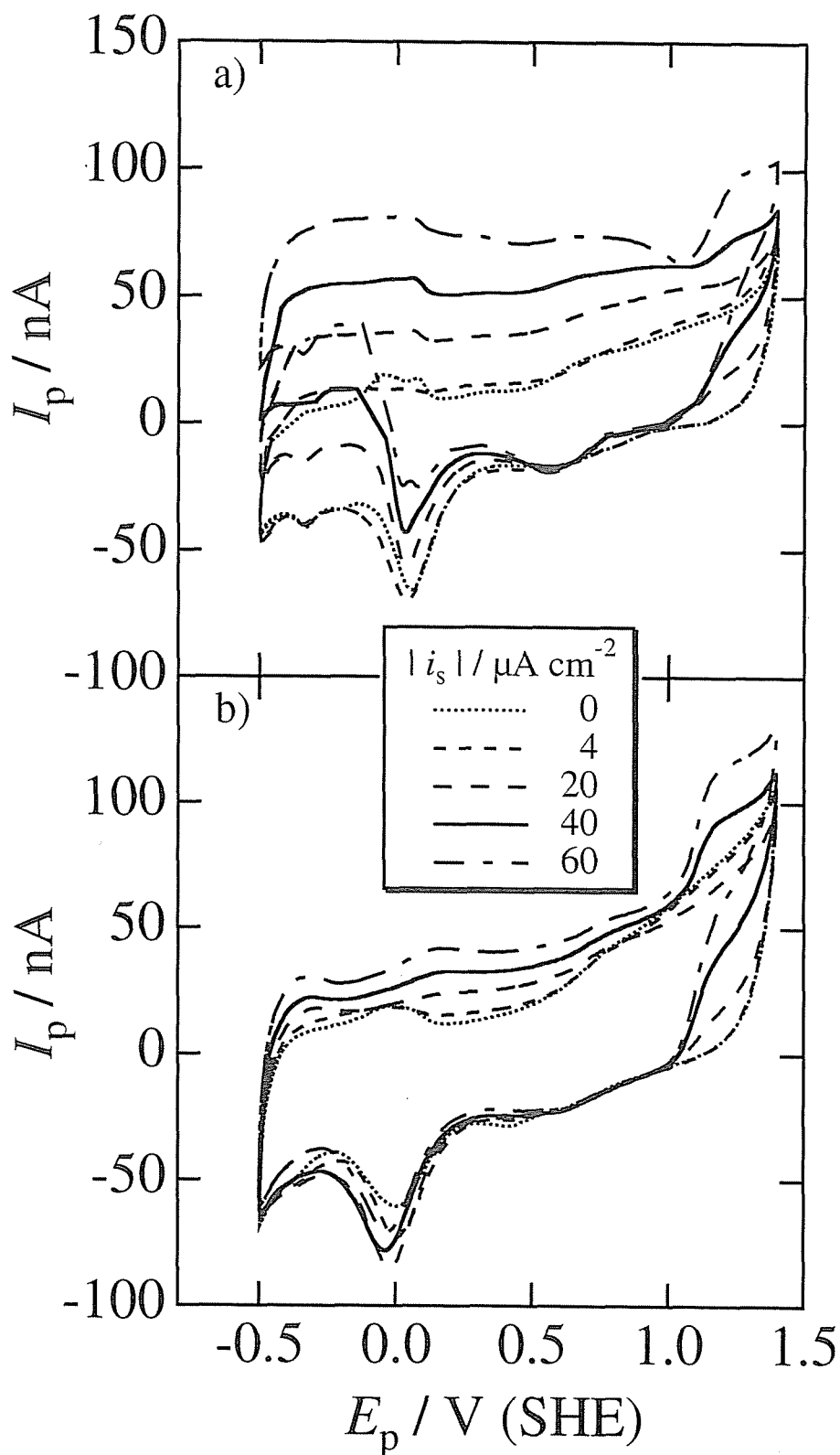


Fig. 9.3.3 Cyclic voltammogram of the probe electrode located above the specimen electrode in $0.1 \text{ mol dm}^{-3} \text{ Na}_2\text{SO}_4$ solution of pH 5.8. a) Platinum or b) magnetite electrode was cathodically polarized at galvanostatic conditions of $i_s = 0 \sim -60 \mu\text{A cm}^{-2}$. Potential sweep rate was 100 mV s^{-1} .

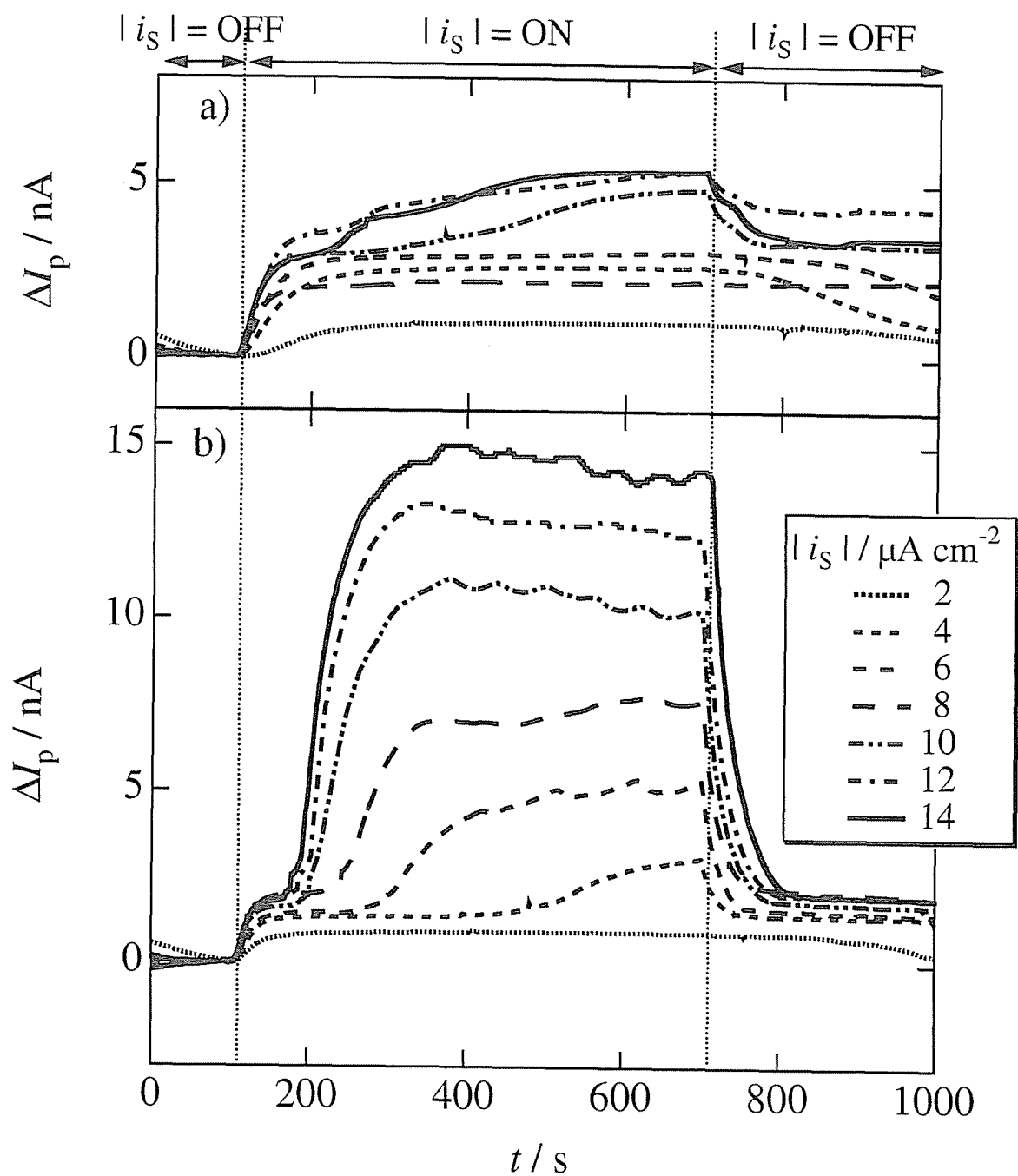


Fig. 9.3.4 Time-variation of the normalized probe electrode current, ΔI_p , in $0.1 \text{ mol dm}^{-3} \text{ Na}_2\text{SO}_4$ solution of pH 5.8. The probe electrode polarized at -0.15 V (SHE) was located above a) magnetite or b) platinum electrode cathodically polarized at $|i_s|$. $\Delta I_p = \Delta I_p(i_s) - \Delta I_p(0)$

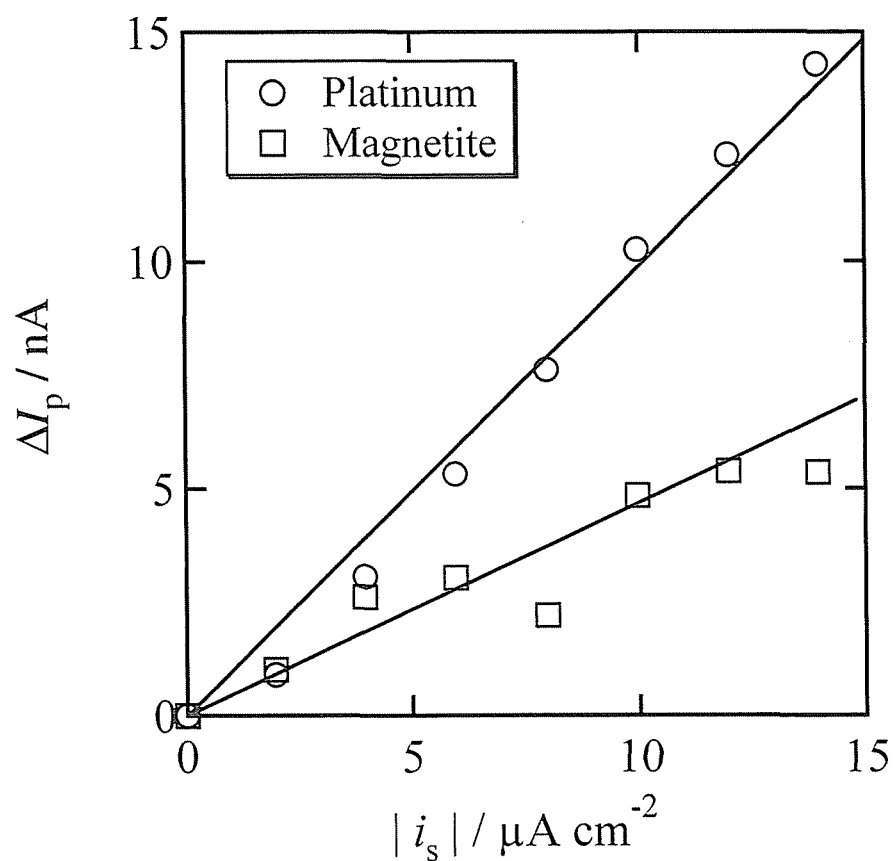


Fig. 9.3.5 Relation between platinum or magnetite electrode current, $|i_s|$, and normalized probe electrode current, ΔI_p , in 0.1 mol dm⁻³ Na₂SO₄ solution of pH 5.8. $\Delta I_p = \Delta I_p(i_s) - \Delta I_p(0)$

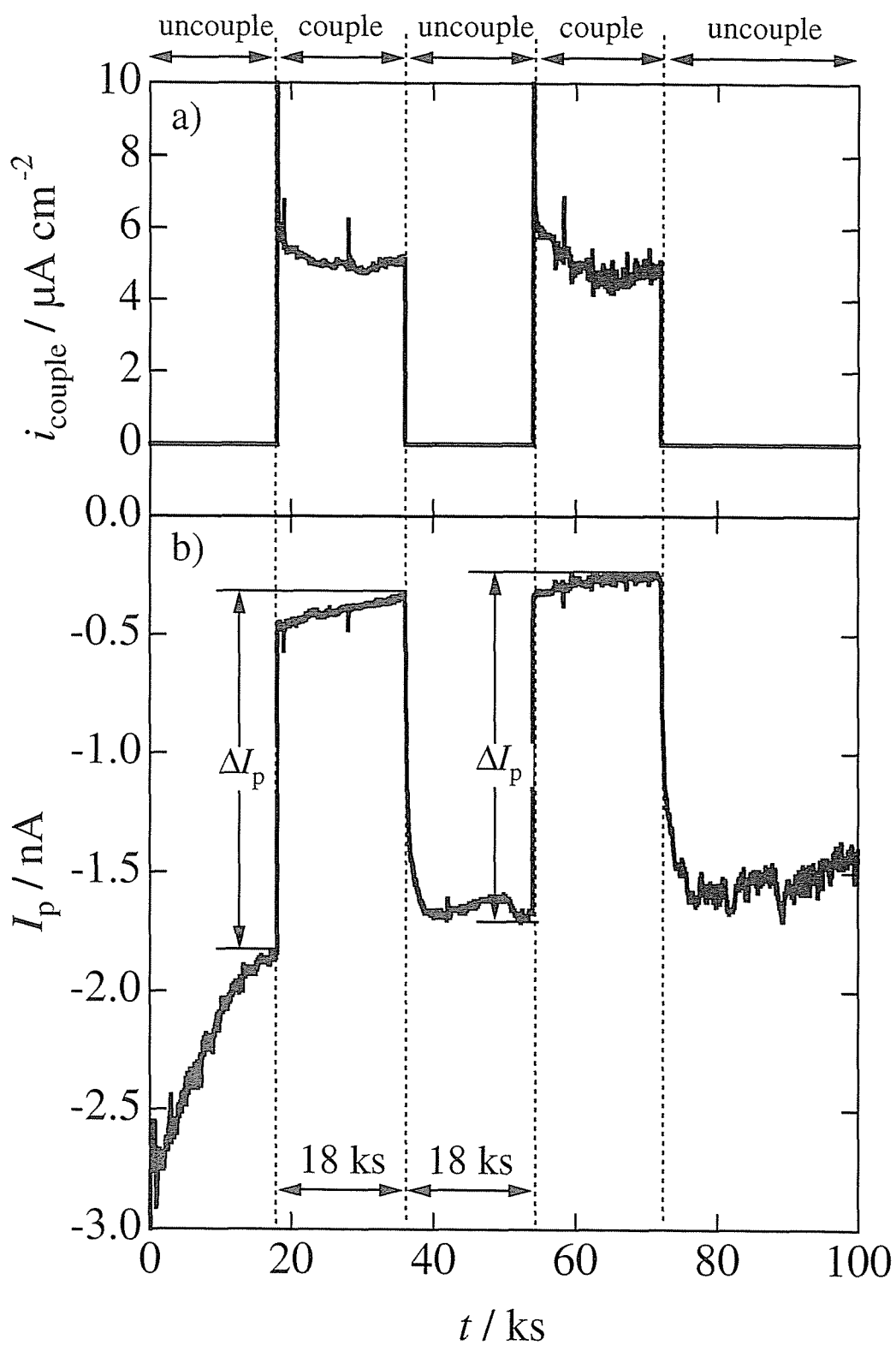


Fig. 9.3.6 Time-variation of a) coupling current, i_{couple} , passed from the magnetite to the carbon steel and b) probe electrode current, I_p , in $0.1 \text{ mol dm}^{-3} \text{ Na}_2\text{SO}_4$ solution of pH 5.8.
 $\Delta I_p = \Delta I_p(i_s) - \Delta I_p(0)$

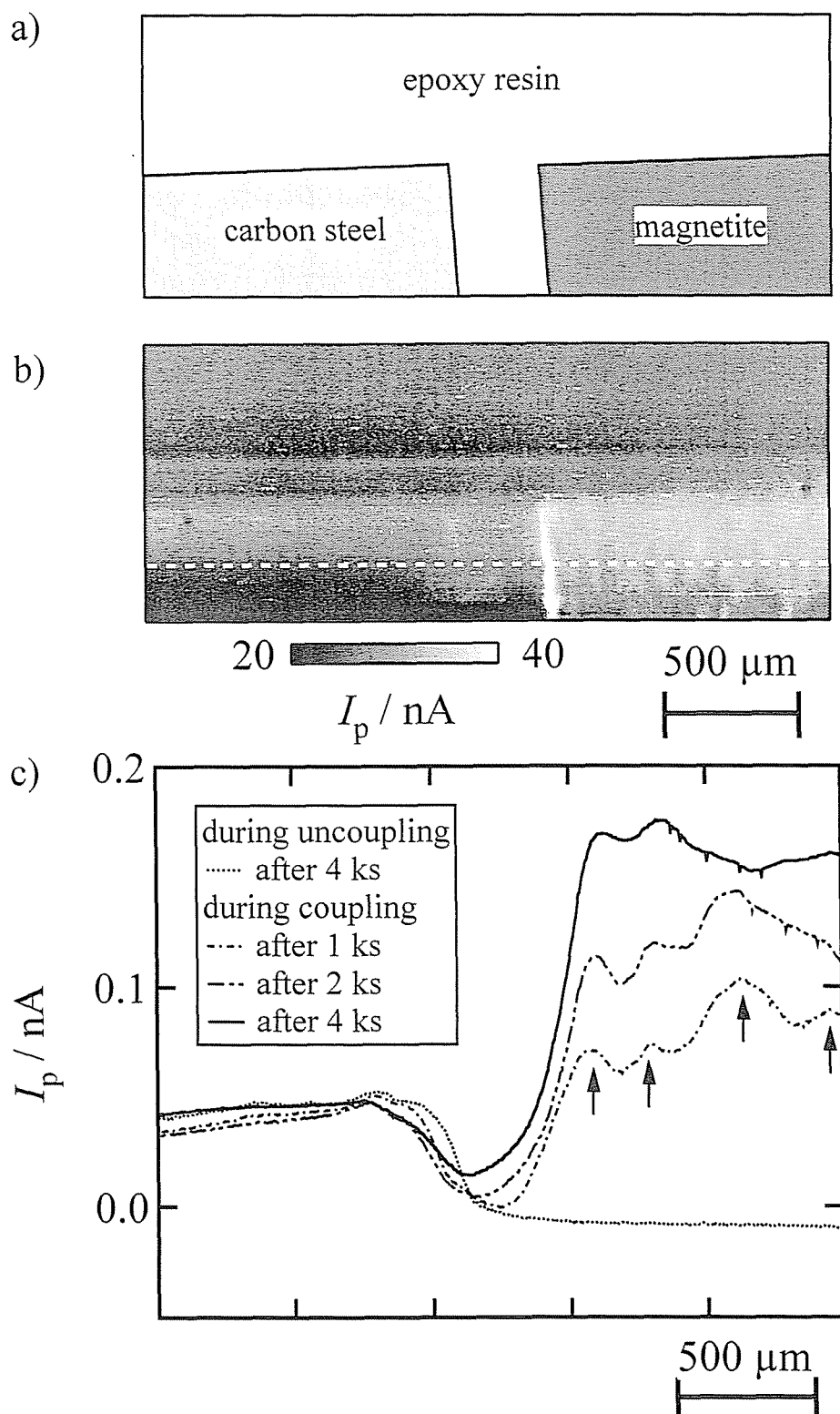


Fig. 9.3.7

a) Schematic top view of the model electrode system for SECM measurement.
 b) Probe current image of the model electrode surfaces in the open circuit measured when the probe electrode was polarized at 1.2 V (SHE) in pH 8.4 borate solution containing $0.03 \text{ mol dm}^{-3} \text{Fe(CN)}_6^{4-}$.
 c) Probe current profiles along the dashed line drawn in Fig. 10b. The probe electrode was polarized at 0.3 V (SHE) while the carbon steel was coupled or uncoupled with the magnetite in $0.1 \text{ mol dm}^{-3} \text{Na}_2\text{SO}_4$ solution of pH 3.3.

10 Liquid-Phase Ion Gun (LPIG)

10.1 Introduction

It is well known that pitting corrosion is initiated in presence of aggressive anions such as Cl^- ions in solutions. The pit initiation is directly associated with local breakdown of passive film due to aggressive anions. Therefore, evaluation of electrochemical reactivities at a specified site of passive films is important to understand pitting precursor processes because local breakdown would start at the most active or defective sites of passive film. However, direct measurement of precursor processes has not been reported due to difficulties in specifying location and in following its evolution. This explains why initiation of pitting is still not clear.

To evaluate distribution in electrochemical reactivity on electrode surfaces, SECM is very useful. In Chapters 5 and 6, SECM was applied to evaluate heterogeneity of passive film formed on iron and titanium. Chapters 7 and 8 demonstrate that SECM was appropriate to observe distribution of oxygen evolved from titanium and dissolution distribution of iron. Moreover, hydrogen generated from single crystal magnetite during galvanic coupling with carbon steel was carried out with an SECM probe electrode in Chapter 9. Incidentally, SECM is also powerful to induce electrochemical reactions on electrode surfaces locally because the SECM probe electrode can be used as a drilling-bit for surface fabrication with any new reactions as described in 3.4.3. In the field of corrosion, Wipf et al employed a solution containing trichloroacetic acid and locally generated chloride ions at a probe electrode of SECM to investigate local breakdown of passive films on stainless steel (Wipf 1994) and iron (Still 1997). Local generation of aggressive anions is effective to study precursor processes of pitting corrosion because location of precursor sites can be specified.

In this chapter, a state of the art technique, so-called 'liquid-phase ion gun' (LPIG) is developed to investigate local breakdown of passive film. This LPIG is a microelectrode consisting of a silver microelectrode covered with silver chloride which can generate Cl^- ions by cathodic polarization in any solution. Here, LPIG is applied on a passivated iron electrode in borate solution to investigate the local breakdown of passive film.

10.2 Experimental

10.2.1 Preparation of LPIG

Silver wire (purity over 99.9%) with a diameter of 180 μm was embedded into a glass tube using an epoxy glue. The glass tube tip was cut and the cross section was mechanically polished with a diamond whetstone (#5000) on a turntable to prepare a silver disk microelectrode. The CV of the microelectrode was measured in the potential range between -0.1 V and 0.5 V (SHE) at a sweep rate of 10 mV s^{-1} in 1 mol dm^{-3} HCl solution. After the steady state CV was obtained, the microelectrode was anodically polarized at 0.4 V (SHE) in 1 mol dm^{-3} HCl solution to form a silver chloride film. Silver chloride film thickness was controlled by electric charge, Q_f , flowing during anodic polarization. Figure 10.2.1 shows optical micrographs of the tip surface covered with silver chloride.

10.2.2 Specimen preparation

A polycrystalline iron plate with purity above 99.99% and surface area of 0.25 cm^2 was employed for experiments. The iron surface was mechanically polished with α -alumina abrasives down to a size of 0.05 μm . After the iron surface was cathodically reduced at a constant current density of 5 $\mu\text{A cm}^{-2}$ in deaerated pH 6.5 borate solution to remove an air-formed film, the passive film was potentiostatically formed on the surface at a certain potential, E_f , for a certain period, t_f , in a renewed deaerated pH 6.5, 7.2 or 8.4 borate solution.

10.2.3 Operation of LPIG

For local generation of Cl^- , the LPIG microelectrode was located above the passivated iron electrode surface and acted as an SECM probe electrode. Distance between the microelectrode and the passivated iron electrode was maintained at 75 μm with an optical microscope. Potentials of probe and specimen electrodes were independently controlled with a bipotentiostat using the SECM apparatus described in 4.3. Microelectrode potential, E_{ME} , was changed stepwise from 0.5 V to -0.1 V (SHE) to generate Cl^- ions, whereas potential of the specimen electrode was kept at a constant potential, $E_{\text{IE,LPIG}}$, during Cl^- generation.

10.2.4 Miscellaneous

To evaluate distribution of electrochemical reactivity over the specimen electrode surface, SECM measurement in TG/SC mode was carried out under the same experimental conditions described in 5.3. The disk-shaped microelectrode composed of a platinum wire with a 10 μm diameter was employed as a probe electrode of SECM. After the electrolyte was changed to deaerated pH 8.4 borate solution containing 0.03 mol dm^{-3} $\text{K}_4\text{Fe}(\text{CN})_6$, a probe current image of the specimen electrode surface was measured under the following conditions:

- i) Distance between probe and specimen electrodes was kept at about 5 μm .
- ii) The probe electrode was scanned stepwise to distances of 500 μm with 5 μm intervals in the x direction and with 10 μm intervals in the y direction.
- iii) Probe and specimen electrodes were polarized at $E_p = 1.2 \text{ V}$ and $E_s = 0.1 \text{ V}$ (SHE), respectively.

10.3 Results and Discussion

10.3.1 Silver/silver chloride microelectrode and generation of chloride ions

Since the solubility product of silver chloride is very small (1.56×10^{-10} at 298 K), the amount of Cl^- ions dissolved from the microelectrode during natural immersion in aqueous solution may be negligibly small. On the other hand, if the microelectrode is cathodically polarized, a significant amount of Cl^- ions can be generated rapidly. Figure 10.3.1 shows the CV of a silver disk microelectrode with a 180 μm diameter in 1 mol dm^{-3} HCl solution. After cycling several times, the CV attained a steady state. The anodic current peak at about 0.28 V (SHE) and the cathodic current peak at about 0.10 V (SHE) correspond to formation and reduction of silver chloride, respectively, as described by the following equation.



Therefore, after anodic polarization at potentials higher than 0.28 V (SHE) in HCl solution, the microelectrode can generate Cl^- ions with cathodic polarization at potentials lower than 0.1 V (SHE). Furthermore, electric charges corresponding to areas of anodic and cathodic current peaks were 5.3 and 5.4 mC, respectively, indicating that formation and reduction reactions of silver chloride are reversible.

When a silver disk microelectrode was polarized at 0.4 V (SHE) in 1 mol dm^{-3} HCl solution, anodic current decreased exponentially and attained a steady value after several minutes. The anodic electric charge, Q_f , flowing during anodic polarization would correspond to the amount of silver chloride formed on a silver microelectrode as a forward reaction of Equation 10.3.1. On the other hand, the backward reaction of Equation 10.3.1 with generation of Cl^- takes place when a silver/silver chloride microelectrode is cathodically polarized. The amount of Cl^- ions generated from the microelectrode, Δn , can be estimated from the cathodic electric charge, Q_g , consumed by the microelectrode as follows.

$$\Delta n = \eta \frac{Q_g}{F}, \quad [10.3.2]$$

where η is the current efficiency for chloride ion generation and F is the Faraday constant. Figure 10.3.2 shows time variation of current, I , passed through the microelectrode and electric charge, Q_g , consumed by the microelectrode when potential of the microelectrode was changed stepwise from 0.5 V to -0.1 V (SHE) in pH 6.5 borate solution after anodic polarization at 0.4 V (SHE) in 1 mol dm⁻³ HCl solution. Separate experiments under identical experimental conditions were performed to determine η using silver/silver chloride electrodes with large and different surface areas. The value of η was determined from the linear relation between Q_g and weight loss of silver/silver chloride electrode with large surface area due to cathodic potential step from 0.5 V to -0.1 V (SHE). The value of η thus determined was 0.95 ± 0.05 . The amount of Cl⁻ ions generated from the microelectrode in Figure 10.3.2, $\Delta n = 1.15 \times 10^{-8}$ mol, was calculated by taking into consideration $\eta = 0.95$.

When a silver/silver chloride microelectrode was polarized potentiostatically at -0.1 V (SHE) in deaerated pH 6.5 borate solution, the relation between the anodic electric charge, Q_f , for silver chloride formation and cathodic charge, $|Q_g|$, for Cl⁻ generation indicates a good linear correlation as shown in Figure 10.3.3.

$$|Q_g| = 0.996 Q_f + 1.68 \times 10^{-4} \text{ [C]} \quad [10.3.3]$$

Therefore, the amount of Cl⁻ generated from the microelectrode can be estimated from Q_f , although a constant charge in the right side of Equation 10.3.3 may be due to reduction of oxygen dissolved in the solution.

Figure 10.3.4a shows current transients of LPIG microelectrode, I_{ME} , on which silver chloride was formed by flowing the anodic electric charge, $Q_f = 5$ mC, in borate solutions of pH 6.5-9.3. The LPIG current is accelerated by solution pH, implying that generation of Cl⁻ in solutions of lower pH is relatively slow. This pH dependence of LPIG current can be explained from the relation between the maximum LPIG current, $I_{ME,max}$, and conductivity of solution, κ , shown in Figure 10.3.4b, that is, $I_{ME,max}$ is controlled by iR drop in solutions, which leads the apparent pH dependence. The relation between $I_{ME,max}$ and κ is given by

$$I_{ME,max} = -1.76 \times 10^{-4} \text{ [A]} (\kappa / [\text{S m}^{-1}])^{0.480}. \quad [10.3.4]$$

Concentration of Cl⁻ generated from a silver/silver chloride microelectrode located above the specimen surface may be calculated from the relevant time-dependent diffusion equation appropriate to SECM geometry as described in 3.3.1. However, calculation is very complicated in case where the microelectrode embedded in a semi-infinite insulating plane faces the specimen electrode and the amount of Cl⁻ generated from the microelectrode is not infinite. Moreover, it is still questionable whether the calculated value can be confirmed with the experimental one. Local concentration of Cl⁻, c_{Cl^-} , in a narrow space between microelectrode

and specimen electrode may be estimated from potential difference between two silver/silver chloride reference electrodes immersed in bulk and spatially limited HCl solutions with different chloride activities, a_1 and a_2 . Potential difference, $\Delta\phi$, between both reference electrodes is given by the following equation (Hanai 1968),

$$\Delta\phi = -2t_+ \frac{RT}{F} \ln\left(\frac{a_2}{a_1}\right), \quad [10.3.5]$$

where t_+ is the transport number of H^+ . Figure 10.3.5b shows $\Delta\phi$ transients between silver/silver chloride reference microelectrodes with a 100 μm diameter, which were located, respectively, just below and far from the LPIG microelectrode tip in deaerated $10^{-3} \text{ mol dm}^{-3}$ HCl solution. During generation of Cl^- as shown in Figure 10.3.5a, $\Delta\phi$ depends on LPIG current, $|I_{ME}|$. At the maximum LPIG current, the value of a_2 calculated using the transport number (MacInnes 1961), $t_+ = 0.8216$, is about 1 mol dm^{-3} of Cl^- , as shown in Figure 10.3.5c. Furthermore, a_2 increases exponentially with increasing $|I_{ME}|$ for Cl^- generation, as shown in Figure 10.3.6. After consumption of silver chloride on the LPIG microelectrode, however, $\Delta\phi$ decreases gradually in contrast to the abrupt drop in $|I_{ME}|$, suggesting that diffusion of Cl^- from the narrow space between LPIG microelectrode and specimen electrode is relatively slow. In any case, concentration of Cl^- , c_{Cl^-} , near the specimen electrode surface in various solutions would be roughly estimated from $|I_{ME}|$ and Equation 10.3.4.

10.3.2 LPIG microelectrode as a detector of ferric ions

A bare silver surface appears on the microelectrode as a result of complete generation of Cl^- ions. Reduction of ferric ions on the silver microelectrode at -0.1 V (SHE) was examined by adding a small amount of $FeCl_3$ to pH 6.5 borate solution. Figure 10.3.7a shows time variation of current flowing through the microelectrode at -0.1 V (SHE) when $FeCl_3$ is successively added to pH 6.5 borate solution at 1 ks intervals. Cathodic current reached the steady state at several hundred seconds after each addition. Steady state current increases linearly with increasing concentration of $FeCl_3$ in solution as shown in Figure 10.3.7b. This indicates that the silver microelectrode at -0.1 V (SHE) straightforwardly reduces ferric ions to ferrous ions and the steady state current corresponds to the limiting current. When a redox reaction of mediator takes place on a microelectrode, the limiting current, I_{limit} , passed through the microelectrode can be formalized from Equation 2.2.16 as the following:

$$I_{limit} = 4\gamma nFDc^*a, \quad [10.3.6]$$

where γ ($= f(\tau^2, \rho_i)$) is the correction coefficient for influence of insulation geometry on the current at the microelectrode which was embedded in a semi-infinite insulating sheath.

According to Shoup (Shoup 1984), the value of γ is given as a function of $\rho_i = a/r^*$ where r^* is radius of finite insulating plane of microelectrode tip (= thickness of an insulating sheath + a). In the case of a microelectrode embedded in an infinite insulating sheath, γ is unity. In this experiment, ρ_i was about 0.8 because $a = 90 \mu\text{m}$ and $r^* = 115 \mu\text{m}$ as shown in Figure 10.2.1b. The value of $\gamma = 1.2$ was finally obtained at from the relation between γ and ρ_i of Figure 2.2.1. The diffusion coefficient of ferric ions, therefore, can be calculated from the linear slope in Figure 10.3.7b by using Equation 10.3.6. The diffusion coefficient of ferric ions thus calculated is $D_{\text{ferric}} = 4.4 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$, which is consistent with that ($D_{\text{ferric}} = 3.0 \sim 5.5 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$) reported so far (Adams 1969). The linear trace in Figure 10.3.7b indicates that the silver microelectrode is useful for detecting ferric ions. On the other hand, no cathodic current flowed through the silver microelectrode at -0.1 V (SHE) , when the microelectrode was located above the iron electrode subjected to active dissolution in pH 6.5 borate solution, indicating that ferrous ions could not be reduced to metallic iron on the silver microelectrode at -0.1 V (SHE) .

10.3.3 Local breakdown of passive film on iron due to chloride ions generated from the LPIG microelectrode

The silver/silver chloride microelectrode was located about $75 \mu\text{m}$ above the iron electrode passivated at 1.2 V (SHE) in borate solution in order to examine local breakdown of passive film due to local generation of Cl^- ions from the microelectrode. Figure 10.3.8 shows current transients of the microelectrode and iron electrode both prior to and after the potential step of the microelectrode from 0.5 V to -0.1 V (SHE) for local generation of Cl^- ions. Anodic current of the iron electrode increases rapidly via induction period after increase in cathodic current of the microelectrode due to generation of Cl^- ions. Simultaneously, microelectrode cathodic current increases rapidly in response to rapid anodic current increase in the iron electrode. The iron electrode was subjected to an open circuit immediately after the rapid increase in anodic current and then washed with doubly distilled water to examine the iron surface with an optical microscope. As depicted in Figure 10.3.9, a corrosion pit with a $100 \mu\text{m}$ diameter and a $5 \mu\text{m}$ depth was observed on the local area of iron surface just below the microelectrode. Presence of the corrosion pit proved that local breakdown of passive film was induced by Cl^- ions generated from the silver/silver chloride microelectrode.

Figure 10.3.10a shows current transients of the microelectrode and the iron electrodes passivated at $E_f = 0.2 \text{ V}$, 0.7 V , and 1.2 V (SHE) , respectively. After every experiment, a corrosion pit was observed at the local area of the iron surface below the microelectrode. Integration of current with time provides electric charges, Q_c and Q_a , consumed by the

microelectrode and passivated iron electrode, respectively. In Figure 10.3.10b, Q_a were plotted versus Q_c . Figure 10.3.10b illustrates that electrochemical interaction between the microelectrode and iron electrode leading to local breakdown is classified into three domains. Details of each domain are schematically illustrated in Figure 10.3.11.

In domain I, Cl^- ions are generated from the microelectrode by cathodic polarization,



and are enriched in the narrow space between the microelectrode and iron electrode due to spatial restriction for diffusion, whereas the iron electrode maintains complete passivity. Therefore, Q_a is very small in spite of increase in Q_c .

In domain II, enriched Cl^- ions would promote dissolution of passive film as ferric ions into solution. The driving force promoting dissolution may be formation of thermodynamically stable iron-chloride complex ions such as FeCl^{2+} (Seo 1975). Ferric ions once dissolved from the passive film diffuse to the microelectrode and then are reduced to ferrous ions on the microelectrode. Ferrous ions thus produced on the microelectrode diffuse to the iron electrode and are oxidized again to ferric ions on the iron electrode as far as the passive film is present on iron. This means that a positive feedback mechanism of ferric and ferrous ions via chloride ions is operative between the microelectrode and iron electrode. As passive film thins due to enriched chloride ions, values of Q_a and Q_c increase simultaneously. The ratio of Q_a/Q_c in domain II is nearly unity, irrespective of potential, E_t , or film thickness, d_t , strongly supporting the positive feedback mechanism described above. Furthermore, confirmation of the positive feedback mechanism has been made by the following separate experiment. The platinum electrode with a surface area of 0.25 cm^2 was used in place of the iron electrode. Distance between the platinum electrode and iron electrode polarized at 1.2 V and -0.1 V (SHE), respectively, in pH 6.5 borate solution was kept at $75 \text{ }\mu\text{m}$. Figure 10.3.12a shows current transients at the microelectrode and iron electrode after addition of a small amount of FeCl_3 to the solution. Both current transients behave in a similar way, although they decay exponentially with time. These exponential current decays may be ascribed to rapid decrease in electrochemical oxidation rate of ferrous ions on the platinum electrode probably due to formation of surface oxide film such as $\gamma\text{-FeOOH}$ (Seo 1992). Nevertheless, as shown in Figure 10.3.12b, the ratio of electric charge consumed by the platinum electrode, Q_a to that by the microelectrode, Q_c is unity, indicating that the positive feedback system is operative between the platinum electrode and microelectrode.

In domain III, a bare surface emerges on the local area of the iron electrode just below the microelectrode due to dissolution of passive film as ferrous ion from the local bare surface

since it is subjected to active dissolution.



Although dissolved ferrous ions diffuse to the microelectrode, the microelectrode at -0.1 V (SHE) can not reduce ferrous ions to metallic iron. Moreover, no ferric ions are produced on the iron surface subjected to active dissolution. Therefore, positive feedback of ferric and ferrous ions between the microelectrode and iron electrode diminishes and finally disappears in domain III, corresponding to negligibly small cathodic current at the microelectrode. Continuous anodic current flow at the iron electrode implies continuous growth of the corrosion pit in depth after complete dissolution of passive film due to chloride ions generated from the microelectrode.

In Figure 10.3.10, the time period or the electric charge of domain I increases with increasing formation potential of passive film, i.e., film thickness, indicating that the thinner passive film dissolves earlier as ferric ions by the less amount of chloride ions. In contrast, the time period or electric charge of the domain II decreases with increasing film formation potential. This means that the dissolution rate, i.e., the breakdown rate of passive film, increases with increasing film formation potential once dissolution starts. In the case of the iron electrode passivated at 0.2 V (SHE), both cathodic and anodic current peaks of the microelectrode and the iron electrode were significantly large compared with the case of the iron electrode passivated at 0.7 V or 1.2 V (SHE). The slow dissolution rate of thin passive film, therefore, gives rise to increase in turnover of the positive feedback of ferric and ferrous ions between the microelectrode and iron electrode. In domain III, for the iron electrode passivated at a low potential such as 0.2 V (SHE), dissolution current of ferrous ions from the bare iron surface finally decreases to zero due to repassivation of the corrosion pit. On the other hand, for the iron electrode passivated at a high potential such as 0.7 V or 1.2 V (SHE), dissolution current of ferrous ions does not decrease and the corrosion pit grows continuously due to high driving force of active dissolution at high potential. Increase in dissolution current of ferrous ions with increasing film formation potential in domain III can be explained in terms of the increase in the driving force of active dissolution, i.e., increase in potential difference between the bare iron surface and solution.

Present results obtained using the silver/silver chloride microelectrode as a probe electrode of SECM is consistent with those obtained by Heusler and Fischer (Heuster 1976) who employed a RRDE for study on precursor process of pitting corrosion of iron. Compared with the RRDE method, use of LPIG has the advantage of specifying a local area of the electrode surface where breakdown of passive film or precursor process of pitting takes place.

10.3.4 *Inducing local breakdown of passive film due to chloride ions*

A number of models have been proposed to explain breakdown of passive film in Cl^- containing solutions as described in 1.3.1. Among them, several are briefly summarized as follows. Formation of chloride-nuclei at the film surface and their growth into the film may result in pitting initiation (Okada 1984). If a small amount of Cl^- adsorbs around a cation in the film to form a high-energy complex which will easily dissolve into solution (Hoar 1967.1), the film is locally thinned and finally is broken down. Incorporation of Cl^- ions into the film and migration through the film to the metal/film interface may cause film breakdown (McBee 1974). In chemico-mechanical theory (Hoar 1967.2), adsorption of Cl^- onto the film/solution interface may lead to a peptization due to mutual repulsion between adsorbed charged species, and induce cracks in the film due to sufficiently high repulsive forces. Furthermore, if film pressure exceeds some critical value due to decrease in surface tension by adsorption of Cl^- , the film may be broken down (Sato 1971). On the other hand, according to the point-defect model (Lin 1981), incorporation of Cl^- into an oxygen-vacant site at the film/solution interface may provide increase in concentration of cation vacancy, which moves to the metal/film interface to form voids and finally induce film breakdown. Moreover, adsorption or incorporation of Cl^- may introduce electron acceptor levels in the band gap of the film matrix, by which potential distribution across metal/film/solution interfaces is changed or a redox reaction via passive film is promoted (Sato 1982). As summarized above, passive film properties should be deteriorated due to contact with Cl^- ions. Local enrichment of Cl^- ions on the passivated iron surface is feasible to introduce defective structure in passive film and promote formation of iron-chloride complex ions such as FeCl_2^+ , which are thermodynamically stable (Seo 1975).

In order to induce local breakdown of passive film due to Cl^- generated from the microelectrode, the LPIG microelectrode was located above the iron specimen electrode surface passivated at 0.7 V (SHE) in pH 6.5 borate solution. Figure 10.3.13 shows typical current transients of the microelectrode and the specimen electrode after the potential step of the microelectrode from 0.5 to -0.1 V (SHE) for generation of Cl^- . In 10.3.3, electrochemical interaction between the microelectrode and specimen electrode has been classified into three domains. Among them, domain I should be directly connected with initiation of passive film breakdown.

To analyze the features of iron electrode surface in domain I, SECM observations were carried out with the iron electrode passivated at 0.7 V (SHE) for 1800 s in pH 6.5 borate solution. Figure 10.3.14b shows the probe current image of the passivated iron surface above which Cl^- ions up to about 0.1 mol dm^{-3} (roughly estimated from 10.3.1) were generated prior to

domain II as shown in Figure 10.3.14a. Probe current responds to the rate of $\text{Fe}(\text{CN})_6^{3-}/\text{Fe}(\text{CN})_6^{4-}$ redox reaction on the passive film which proceeds with an electron tunneling through the film between the solution and substrate metal as discussed in 5.3. This electron tunneling process depends on thickness and electronic properties of passive film. The flat probe current image in Figure 10.3.14b means that film on the iron electrode located just below the LPIG microelectrode suffers no damage by Cl^- generated from the microelectrode or is recovered to the passive state. On the other hand, Figure 10.3.15b shows the probe current image of the iron electrode surface when generation of Cl^- was ceased at the entry of domain II as shown in Figure 10.3.15a. The site with a high current intensity at the center of the image corresponds to the damaged area of the film, e.g., thinner and/or defective film, caused by Cl^- generated from the microelectrode. There is no doubt that the local breakdown site of passive film in domain II is located just below the microelectrode from which Cl^- ions are generated. Therefore domain I can be assigned as an induction period for local breakdown of passive film.

10.3.5 Induction period, critical concentration of chloride ions, and increase in current of iron electrode during local breakdown initiation

Anodic current, I_{IE} , flowing through the passivated iron electrode during LPIG operation can be explained from Equation 1.2.4.

$$I_{\text{IE}} = I_{\text{oxide}} + I_{\text{dis}} + I_{\text{etr}} + I_{\text{charge}} \quad [10.3.9]$$

At the film/solution interface, partial currents, I_{oxide} and I_{dis} , are equal to rates of the following charge transfer reactions.



They are controlled by potential-difference, $\Delta\phi_{\text{f/s}}$, at the film/solution interface,

$$I_{\text{oxide}} = I_{0,\text{oxide}} \exp\left(\frac{\alpha_{\text{oxide}} n_{\text{oxide}} F}{RT} \Delta\phi_{\text{f/s}}\right), \quad [10.3.12]$$

$$I_{\text{dis}} = I_{0,\text{dis}} \exp\left(\frac{\alpha_{\text{dis}} n_{\text{dis}} F}{RT} \Delta\phi_{\text{f/s}}\right), \quad [10.3.13]$$

where $I_{0,\text{oxide}}$ and $I_{0,\text{dis}}$ are exchange currents of oxide growth and dissolution, respectively, α is the transfer coefficient, and n is the charge number. At steady state, I_{oxide} becomes zero. Since I_{charge} is flowed only at the early stage of polarization, there is no contribution of I_{charge} to I_{IE} after film formation. No oxygen evolution generally takes place as a side reaction in the passive potential region. In domain II, however, oxidation of ferrous ions which diffuse from the LPIG microelectrode can occur as a side reaction when the film is sufficiently damaged for the

electron transfer reaction to proceed easily through the film. Reduction of ferric ions to ferrous ions at the microelectrode and oxidation of ferrous ions to ferric ions at the specimen electrode are repeated, i.e., positive feedback is operative, indicating that I_{etr} is almost equivalent to I_{IE} ($I_{\text{etr}} \gg I_{\text{oxide}} + I_{\text{dis}}$). In either case, Equation 10.3.9 is deformed as follows.

$$I_{\text{IE}} = I_{\text{oxide}} + I_{\text{dis}} + I_{\text{etr}} \quad [10.3.14]$$

When a small amount of Cl^- is generated from the LPIG microelectrode above the passivated iron electrode surface, concentration of Cl^- , c_{Cl^-} , at the film surface could be roughly estimated from breakdown current, $|I_{\text{ME,BD}}|$, flowing through the microelectrode. The time period, t_{BD} , of domain I is defined with the induction period for initiation of local breakdown of the passive film as shown in Figure 10.3.13. In domain I, as Cl^- ions are generated, the iron electrode current increases slightly until initiation of local breakdown. The increment in the current of the iron electrode, $\Delta I_{\text{IE,BD}}$, is connected with generation of Cl^- . It is also given as follows.

$$\Delta I_{\text{IE,BD}} = \Delta I_{\text{oxide}} + \Delta I_{\text{dis}} + \Delta I_{\text{etr}} \quad [10.3.15]$$

Local deterioration of the film due to Cl^- ions decreases the potential difference in the film and increases the potential difference, $\Delta\phi_{\text{f/s}}$, at the film/solution interface. Then the passivity-maintaining current increases by $\Delta I_{\text{oxide}} + \Delta I_{\text{dis}}$ although film deterioration may also influence ΔI_{etr} to some extent. Local deterioration of the film continues up to the critical level at which the film dissolves rapidly as ferric ions, and then positive feedback of ferric/ferrous ions predominate. Thus, values of t_{BD} , $|I_{\text{ME,BD}}|$, and $\Delta I_{\text{IE,BD}}$ were investigated as a function of time or potential of film formation.

Figure 10.3.16 shows relation between t_{BD} , $|I_{\text{ME,BD}}|$ or $\Delta I_{\text{IE,BD}}$, and film formation time, t_{f} , for iron electrodes passivated at 0.7 V (SHE) in pH 6.5, 7.2, and 8.4 borate solutions. In spite of large scatters in experimental data, t_{BD} increases with increasing t_{f} as shown in Figure 10.3.16a, suggesting that the aged film is less susceptible to initiation of local breakdown. Furthermore, t_{BD} increases with increasing solution pH at the same value of t_{f} . On the other hand, the value of $|I_{\text{ME,BD}}|$ is almost independent of t_{f} except for the initial stage but increases linearly with increasing solution pH as shown in inset of Figure 10.3.16b. Each value of $|I_{\text{ME,BD}}|$ was identical with limiting current of the LPIG microelectrode obtained when the LPIG microelectrode was scanned above the glass specimen surface in a separate experiment. These indicate that concentration of Cl^- , c_{Cl^-} , in the narrow space is sufficiently high for initiation of local breakdown in the same pH solution. Moreover, $\Delta I_{\text{IE,BD}}$ keeps almost constant or decreases slightly with increasing t_{f} , indicating that critical film properties just before initiation of local breakdown are similar. In contrast, t_{BD} is so highly sensitive to t_{f} that t_{BD} is a time period

required for properties of passive films attaining to the critical level just before initiation of local breakdown. The aging effect implies that the structure of passive film on iron changes to be less defective with time because the less defective structure of passive film would prolong initiation of local breakdown due to generation of Cl^- . It is known that passive film on iron has n-type semiconductive properties, and that donor density of the film decreases exponentially with time, t_f (Azumi 1987). Furthermore, increase in passive film thickness due to aging contributes to increase in t_{BD} since the passive film usually grows obeying the inverse-logarithmic law (Moshtev 1967).

It is also well known that thickness of passive film on iron increases linearly with increasing film formation potential, E_f (Sato 1974). To clarify the influence of film thickness on initiation of local breakdown, a series of experiments was carried out at different potentials, E_f and $E_{\text{IE,LPIG}}$, of the iron electrode. Figure 10.3.17a shows the relation between t_{BD} and film formation potential, E_f , when $E_{\text{IE,LPIG}}$ of the iron electrode during operation of LPIG was kept at E_f . In spite of large scatters in experimental data of Figure 10.3.17a, the value of t_{BD} increases slightly with increasing E_f , indicating that thicker film gives the longer induction period. However, t_{BD} decreases with increasing $E_{\text{IE,LPIG}}$ in case of $E_f = 1.0$ V (SHE) and $E_{\text{IE,LPIG}} = 0.4$ - 1.0 V (SHE) as shown in Figure 10.3.18a. At $E_{\text{IE,LPIG}} \leq E_f = 1.0$ V (SHE), the average electric field in the film (potential difference in film divided by film thickness) decreases with increasing difference, $\Delta E = E_f - E_{\text{IE,LPIG}}$, since the flat-band potential of passive film on iron, E_{FB} , is located at -0.05 V (SHE) in pH 6.5 borate solution (Azumi 1987) and film thickness remains constant at $E_{\text{IE,LPIG}} > E_{\text{FB}}$. Therefore, it is suggested that average electric field in the passive film influences t_{BD} . Figure 10.3.19a shows relation between t_{BD} and E_f in case where E_f is higher than $E_{\text{IE,LPIG}} = 0.7$ V (SHE). The slope in Figure 10.3.19a is steeper than that in Figure 10.3.17a, indicating that the average electric field in the film influences t_{BD} as well as total film thickness or defective structure. On the other hand, LPIG current, $|I_{\text{ME,BD}}|$, just before breakdown initiation increases with increasing E_f as shown in Figure 10.3.17b, indicating less susceptibility of thicker film. $|I_{\text{ME,BD}}|$ decreases with increasing $E_{\text{IE,LPIG}}$ as shown in Figure 10.3.18b, implying that $|I_{\text{ME,BD}}|$ is influenced by average electric field. In general, the logarithm of concentration of Cl^- is inversely proportional to pitting potential (Vetter 1970, Heusler 1976). Experimental results in Figure 10.3.18b are similar to this. However, $|I_{\text{ME,BD}}|$ is not influenced significantly by film thickness, defective structure or average electric field as shown in Figure 10.3.19b. This contradiction suggests that concentration of Cl^- , $c_{\text{Cl}^-, \text{BD}}$, just before initiation of local breakdown seems sufficient for film breakdown as remarked previously. In contrast, $\Delta I_{\text{IE,BD}}$ increases exponentially with average electric field in the film as shown in Figure 10.3.18c or 10.3.19c

although $\Delta I_{IE,BD}$ decreases with increasing film thickness as shown in Figure 10.3.17c. This implies that increase in passivity maintaining current of the iron electrode is caused by changes in semiconductive properties of film such as potential distribution and donor density due to generation of Cl^- .

From these experimental results, it is deduced that the higher electric field in film is more feasible for initiating breakdown and thus leads to shorter t_{BD} . At the same film thickness, t_{BD} and $\Delta I_{IE,BD}$ depend on electric field strength. However, in case where the average electric field in the film is almost identical, t_{BD} and $\Delta I_{IE,BD}$ are independent of film thickness. Ionic current throughout the film, i_{ion} , is accelerated by electric field in the film as follows (Cabrera 1949, Fehlner 1986).

$$i_{ion} = i_{ion,0} \exp\left(\frac{aqF}{RT} \Delta V\right), \quad [10.3.16]$$

where a is half the distance separating two adjacent equilibrium ion sites in the film, q is magnitude of charge on ion, and ΔV is strength of electric field as introduced in Equation 1.2.6. The term $i_{ion,0}$ contains concentration of ion vacancy in the film which is increased by adsorption of Cl^- . It is notable that $\Delta I_{IE,BD}$ is reflected on the degree in deterioration of film which sustains passivity. When the degree of film deterioration attains the critical level, film dissolution proceeds significantly as ferric ions and then positive feedback predominates between the LPIG and iron electrodes.

10.3.6 Substrate dependence of local breakdown initiation

In this study, the iron specimen was mechanically polished with alumina abrasives and then the air-formed film on the specimen was removed by cathodic reduction in pH 6.5 borate solution before passivation. However, mechanical polishing gives a mechanically damaged layer, i.e., a bibly layer, on the iron surface. It is well accepted that passive films formed on the bibly layer are usually amorphous. On the other hand, more crystalline films are formed on iron surfaces which are chemically etched to remove the bibly layer. Moreover, crystal structure and thickness of passive films depend on substrate grain orientation as discussed in 5.3. An electron transfer reaction of redox species takes place more feasibly on the iron {110} or {111} grain with thinner passive film than on the {100} grain with thicker passive film. Here, dependence of local breakdown initiation on substrate grain was investigated by using iron electrode which was etched chemically to make crystal grains distinctive and then passivated.

A galvanostatic generation of Cl^- has the merit of constant concentration of Cl^- , c_{Cl^-} , during LPIG operation. Figure 10.3.20 shows typical transients of potential, E_{ME} , of the LPIG

microelectrode (50 μm diameter) and of current, I_{IE} , passed through the iron electrode after the current step of the microelectrode from 0.1 nA to $-8 \mu\text{A}$ in pH 6.5 borate solution. The iron electrode was passivated at 0.7 V (SHE) for 1800 s in pH 6.5 borate solution after chemical etching. Orientation of substrate grains was confirmed by an etch-pit method as described in 5.2.3. After the cathodic current step, E_{ME} tends to hover about 0.15 V (SHE) due to generation of Cl^- but shifts to the anodic direction when I_{IE} increases rapidly, i.e., local breakdown is initiated. The induction period, t_{BD} , depends on the substrate grain whereas $\Delta I_{\text{IE,BD}}$ had less dependence of substrate grain. Induction period, t_{BD} , becomes longer in the order of grains $\{110\} < \{111\} < \{100\}$ which is the same as the order of film thickness evaluated previously in 5.3. It is clear that local breakdown is initiated with shorter time for the thinner film. This is also consistent with the least protective film on the Armco iron $\{110\}$ plane reported (Kruger 1959).

10.4 Conclusions

A silver/silver chloride microelectrode which acts as an SECM probe electrode was developed as a liquid-phase ion gun (LPIG) to induce local breakdown of passive film on metal. The LPIG microelectrode was applied to induce a local breakdown of passive film formed on iron in deaerated borate solution. The following conclusions were drawn.

- i) Local generation of Cl^- ions due to a cathodic polarization of the microelectrode could succeed in inducing local breakdown of passive film on iron just below the microelectrode.
- ii) From current transients of the microelectrode and the iron electrode during LPIG operation, it was found that breakdown processes were classified into the following three domains:

In domain I, Cl^- ions are generated from the microelectrode and are enriched in the narrow space between microelectrode and specimen electrode, whereas passive film on the specimen electrode remains stable. The time period of this domain corresponds to the induction period for local breakdown and passive film composition or structure attained a critical level just before local breakdown initiation.

In domain II, enriched Cl^- promotes dissolution of passive film as ferric ions. Reduction of ferric ions to ferrous ions at the microelectrode and oxidation of ferrous ions to ferric ions at the specimen electrode are repeated (positive feedback) as long as passive film is present on iron. In this domain, passive film dissolved into ferric ions and thinned.

In domain III, a bare surface emerges on the local area of the iron electrode from which ferrous ions dissolve and a corrosion pit grows. The dissolution rate of ferrous ions increased with

increasing film formation potential. A corrosion pit grew continuously at high potential, while repassivation of the pit took place at low potential.

- iii) Concentration of Cl^- in the narrow space between the microelectrode and specimen electrode was estimated to be about 1 mol dm^{-3} , which was sufficient for initiation of local breakdown.
- iv) The induction period increased with film formation time due to the aging effect of the film. The higher electric field in the passive film shortened the induction period and increased passivity-maintaining current.
- v) Local breakdown of passive film depended on substrate grain orientation. Passive film formed on substrate grain oriented to $\{100\}$ was the most protective against local breakdown as compared with those on grains oriented to $\{111\}$ and $\{110\}$. Grain orientation dependence was explained in terms of difference in thickness or defective structure of film grown on each grain.

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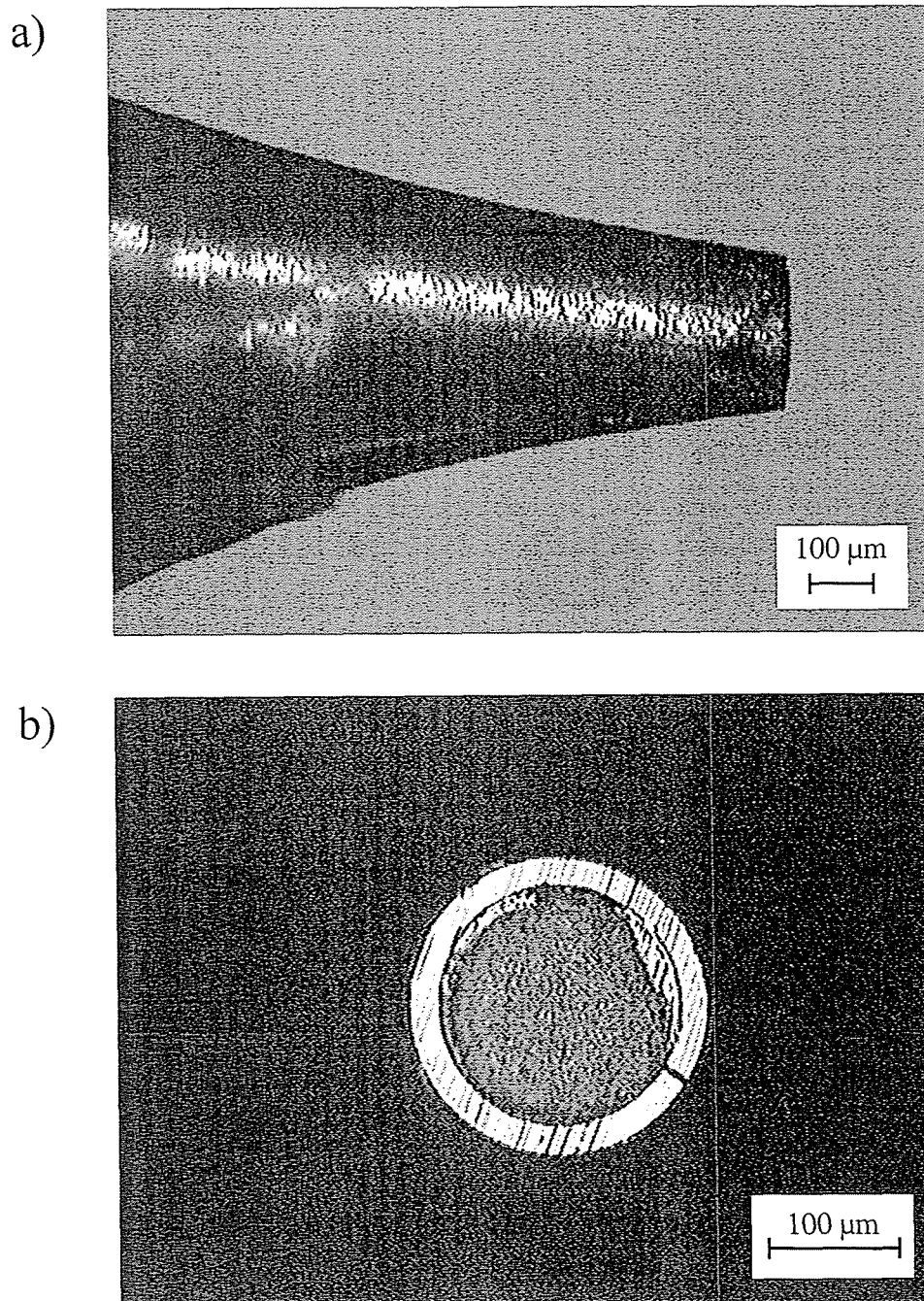


Fig. 10.2.1 Optical micrographs of the tip surface of the silver/silver chloride microelectrode with a diameter of 180 μm .
a) side view. b) top view.

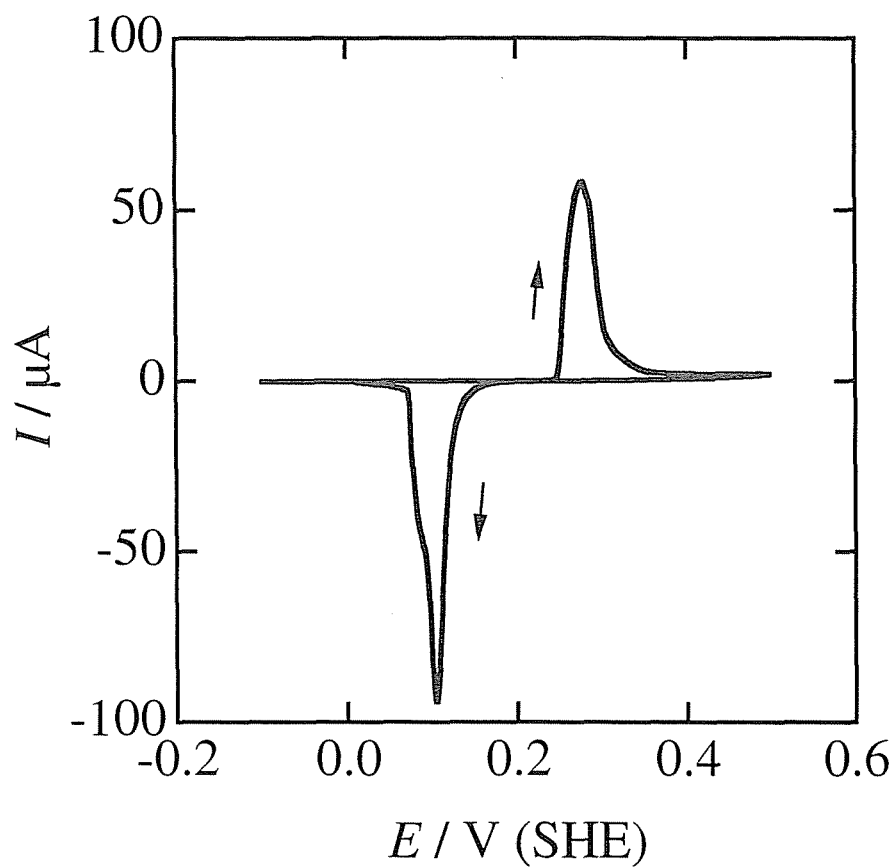


Fig. 10.3.1 Cyclic voltammogram of the microelectrode composed of a silver disk with a diameter of $180\text{ }\mu\text{m}$ in 1 mol dm^{-3} HCl solution.

Potential sweep rate was 10 mV s^{-1} .

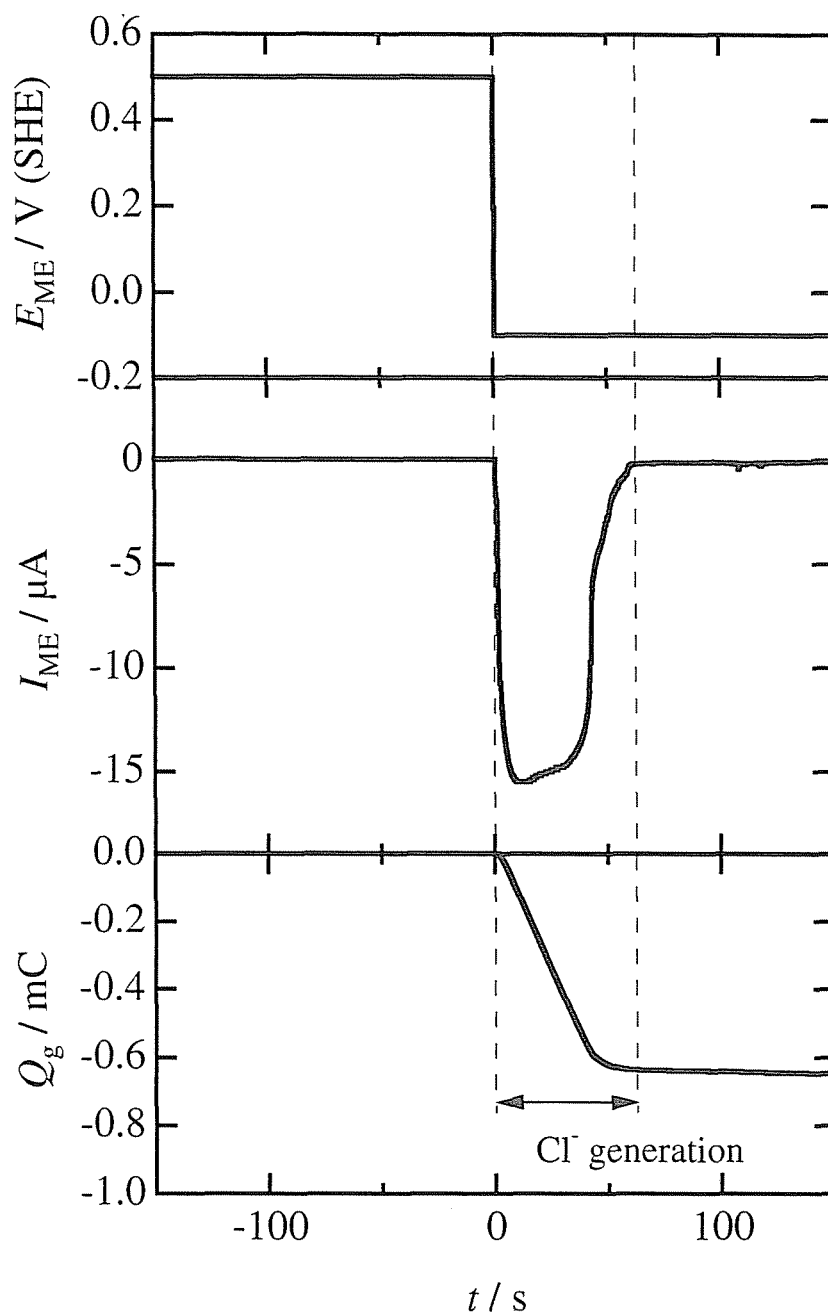


Fig. 10.3.2 Time variation of current, I_{ME} , passed through the microelectrode and the electric charge, Q_g , consumed on the microelectrode, when microelectrode potential, E_{ME} , was changed stepwise from 0.5 V to -0.1 V (SHE) in deaerated pH 6.5 borate solution after anodic polarization at 0.4 V (SHE) for 1.8 ks in 1 mol dm⁻³ HCl solution.

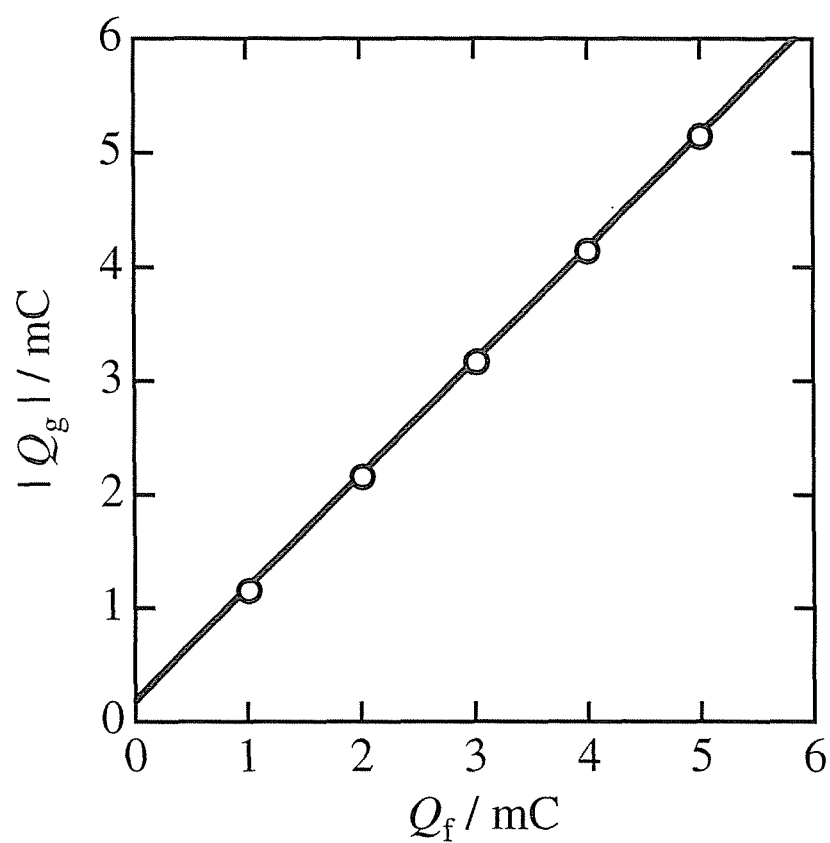


Fig. 10.3.3 Relation between anodic charge, Q_f , required for silver chloride formation and cathodic charge, $|Q_g|$, required for exhaustive generation of Cl^- .

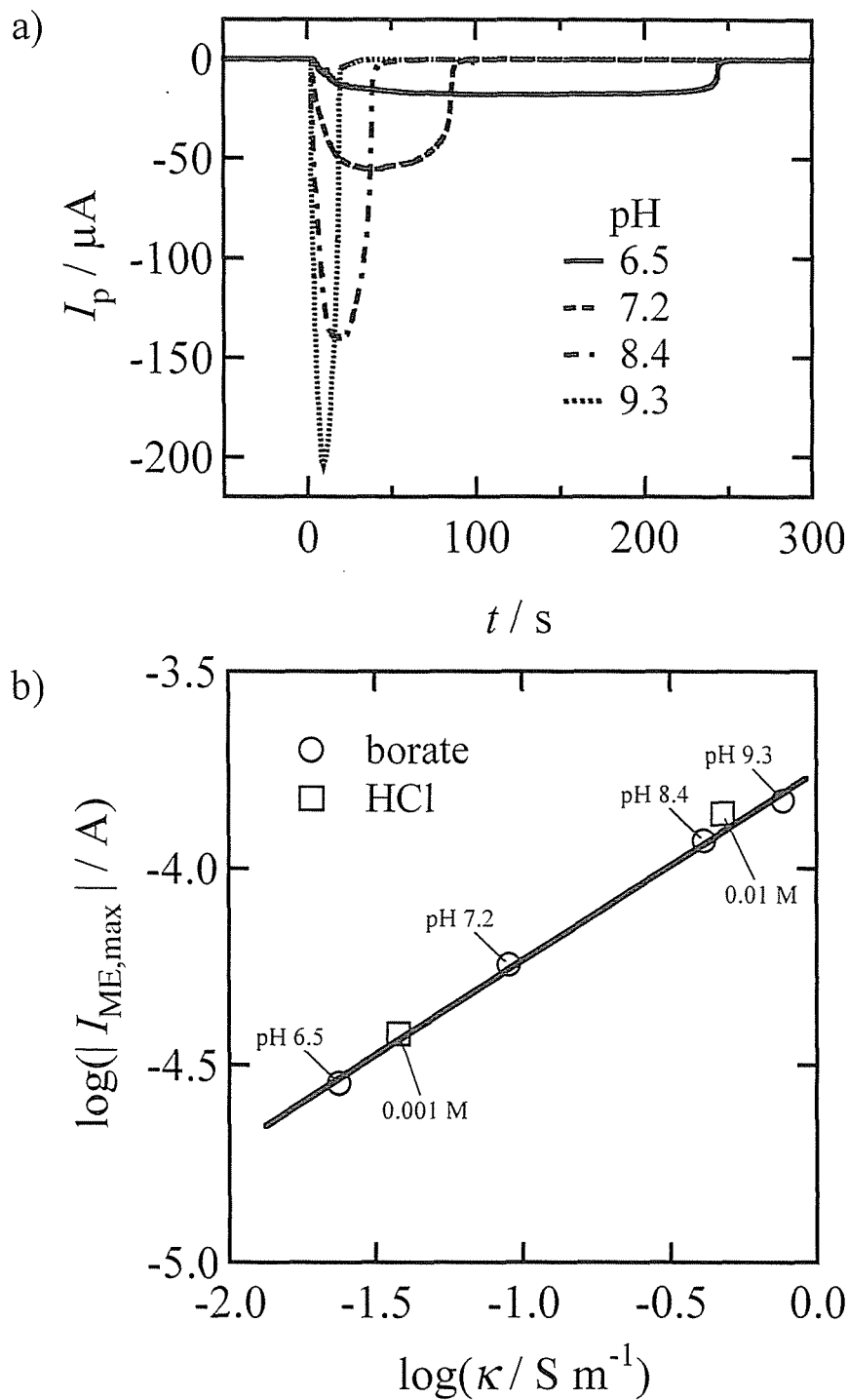


Fig. 10.3.4 a) Current transients of LPIG microelectrode, I_{ME} , after potential step of microelectrode from 0.5 V to -0.1 V (SHE) in deaerated borate solutions.
b) Relation between the maximum LPIG current, $I_{\text{ME,max}}$, and solution conductivity, κ .

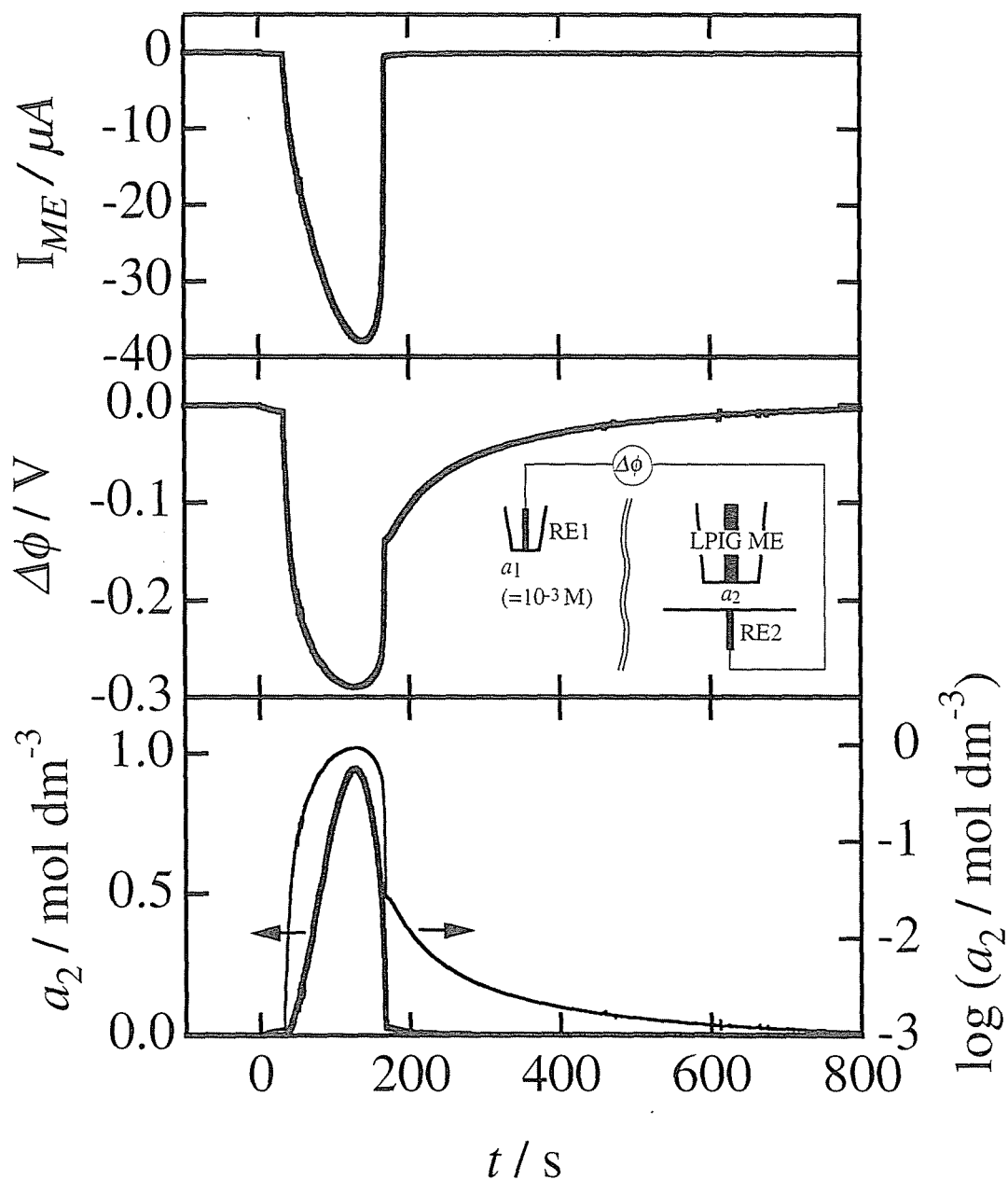


Fig. 10.3.5 a) Current transient of LPIG microelectrode, I_{ME} , after potential step of microelectrode from 0.5 V to -0.1 V (SHE) in deaerated 10^{-3} mol dm $^{-3}$ HCl solution. b) Transient of potential difference, $\Delta\phi$, between a pair of Ag/AgCl reference microelectrodes which were faced to and away from the LPIG microelectrode tip, respectively. The distance between LPIG and the reference microelectrode facing LPIG was kept at 75 μ m.

c) Transient of activity of Cl^- , a_2 , at the surface of the reference microelectrode facing the LPIG.

Activity of Cl^- , a_2 , was calculated from Eq. 10.3.5.

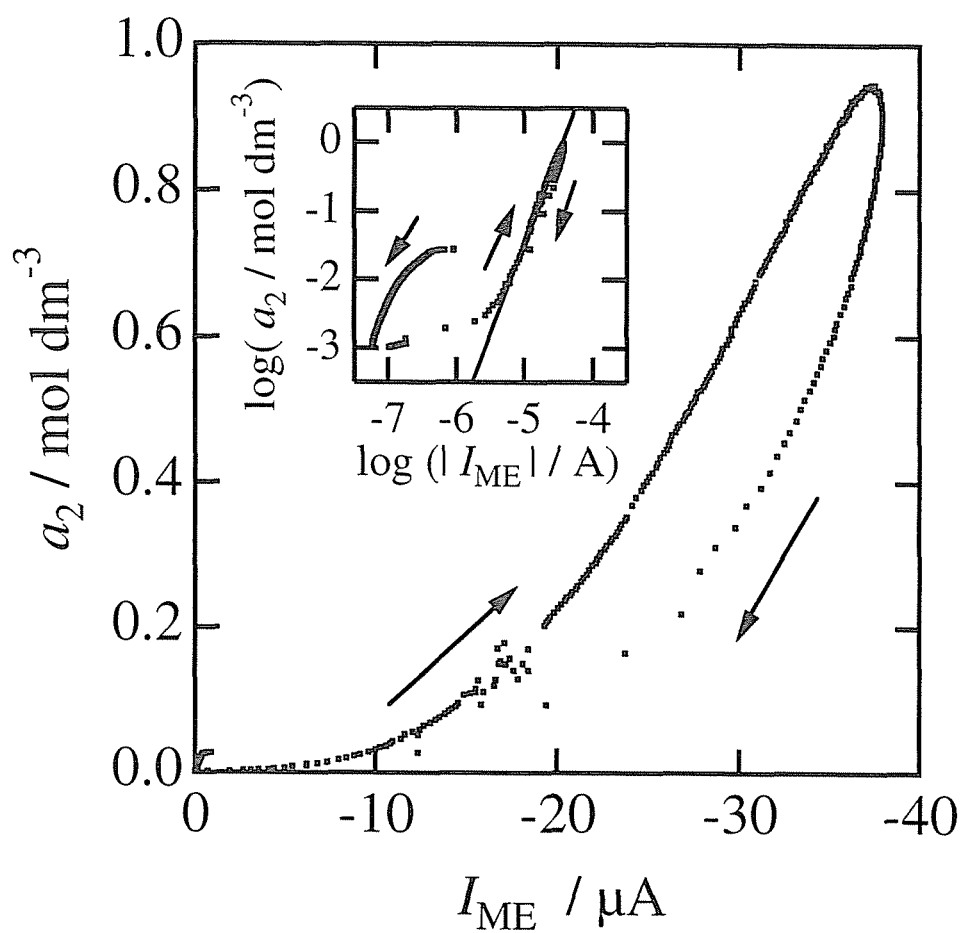


Fig. 10.3.6 Relation between LPIG current, I_{ME} , and activity of Cl^- , a_2 .

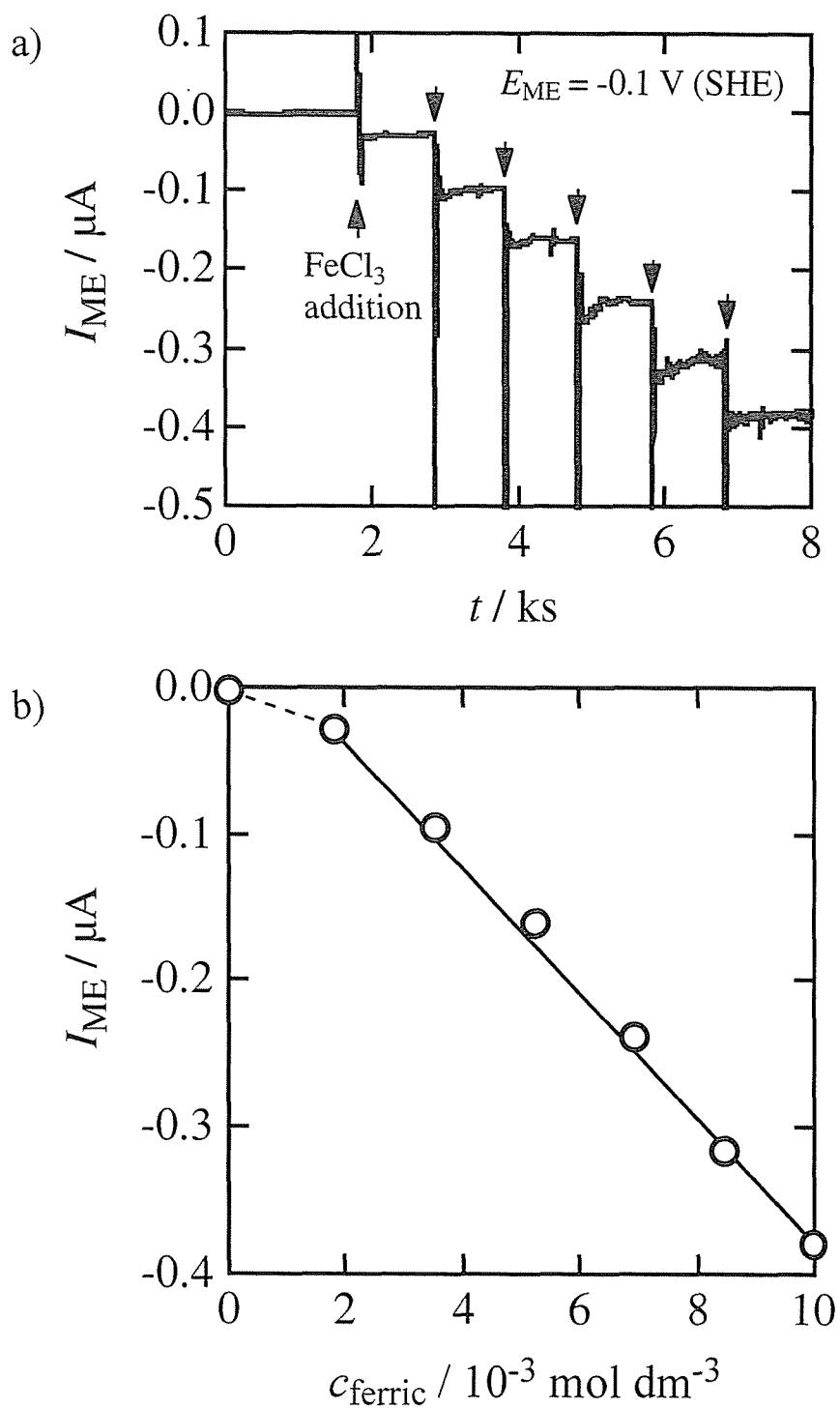


Fig. 10.3.7 a) Time variation of current, I , flowing through the micro-electrode at $-0.1 V (SHE)$ when a small amount of $FeCl_3$ is successively added to pH 6.5 borate solution. b) Relation between the plateau current and concentration of $FeCl_3$, c_{ferric} , in pH 6.5 borate solution.

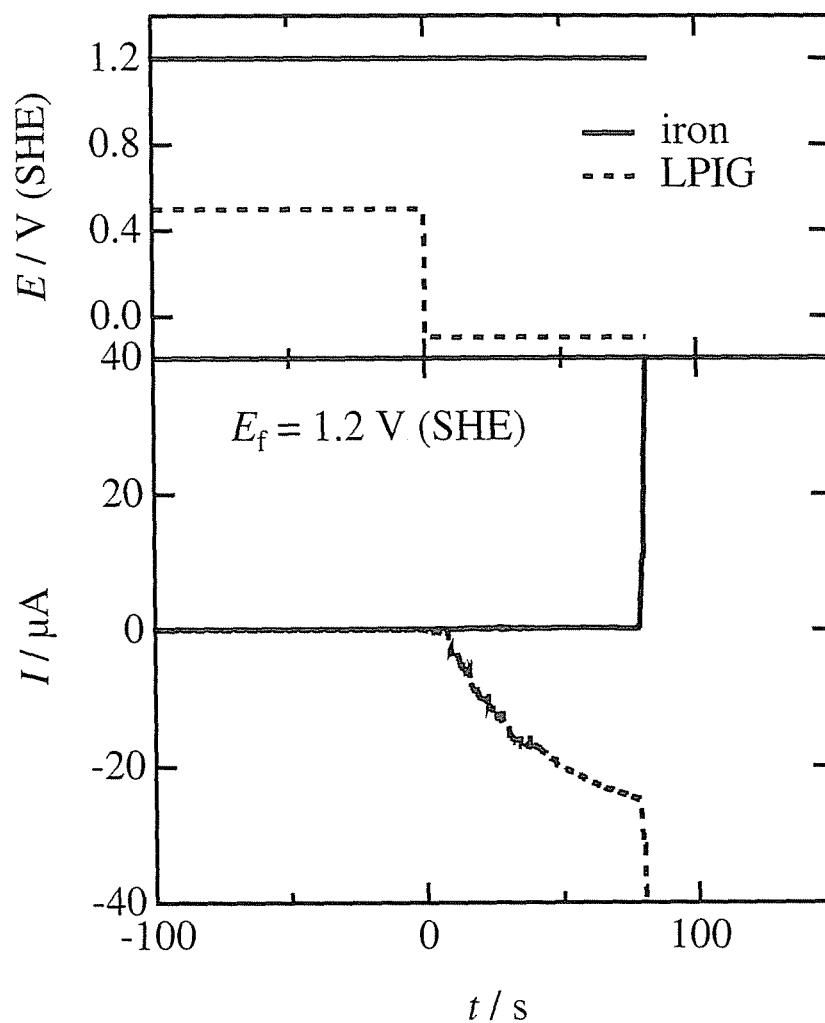


Fig. 10.3.8 Time variation of current, I , passed through the passivated iron electrode or LPIG microelectrode in deaerated pH 6.5 borate solution when microelectrode potential was changed stepwise from 0.5 V to -0.1 V (SHE). Passivation of the iron electrode was performed with anodic polarization at 1.2 V (SHE) for 1.8 ks in deaerated pH 6.5 borate solution. Distance between the iron electrode and the microelectrode was kept at 75 μm .

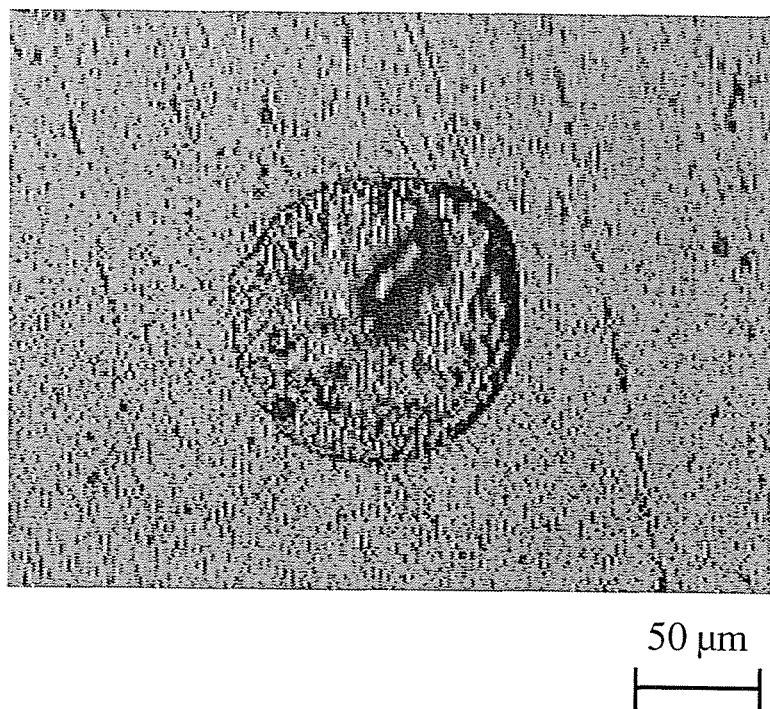


Fig. 10.3.9 Optical micrograph of a typical pit grown on the iron surface after local breakdown of the passive film due to chloride ions generated from the microelectrode.

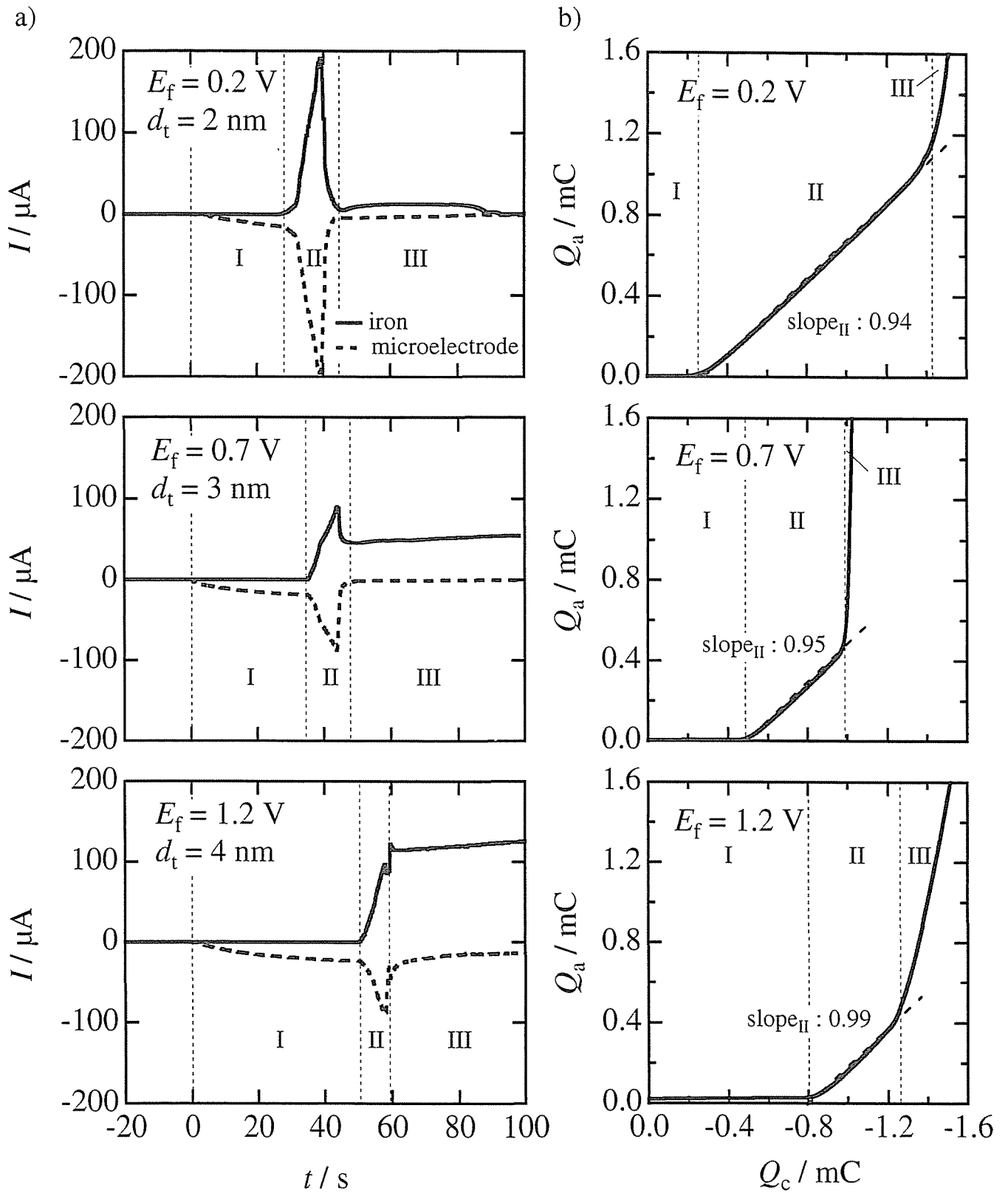


Fig. 10.3.10 a) Current transients at the passivated iron electrode and the microelectrode in deaerated pH 6.5 borate solution after potential step of the microelectrode from 0.5 V to -0.1 V (SHE). The potential of the iron electrode was kept at E_f . The thickness of passive film, d_t , was employed from Azumi 1985.

b) Relation between the electric charge consumed by the microelectrode, Q_c , and the passivated iron electrode, Q_a .

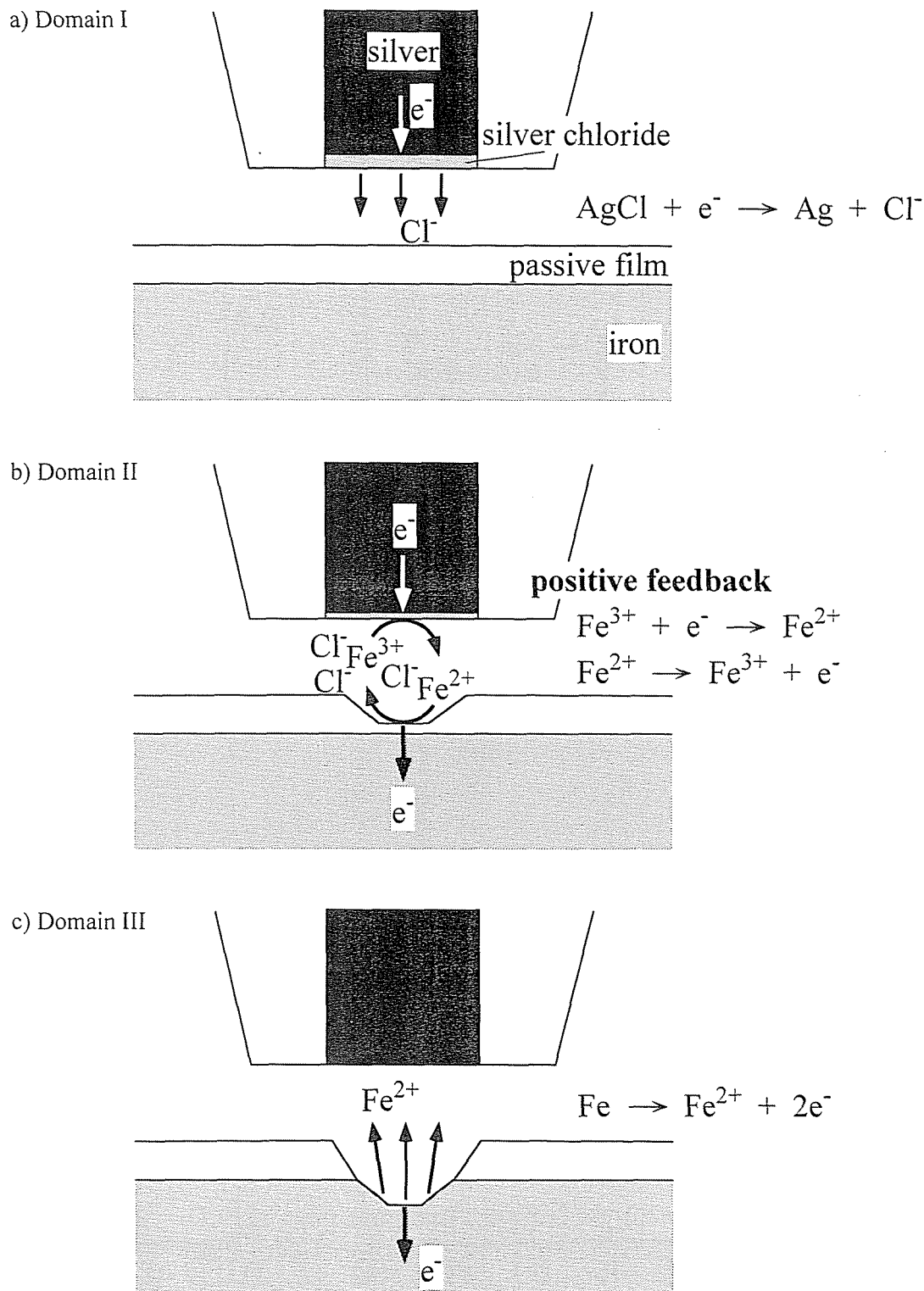


Fig. 10.3.11 Illustration for the local breakdown processes of the passive film on iron by LPIG.

a) Domain I: A small amount of Cl^- ions is generated from the microelectrode while the passive film on iron electrode remains stable.

b) Domain II: Enriched Cl^- ions attack the passive film. The film dissolves as ferric ions. Furthermore, positive feedback takes place between the microelectrode and the iron electrode.

c) Domain III: A bare surface emerges on the local area of the iron electrode surface, from which ferrous ions dissolve and the corrosion pit grows.

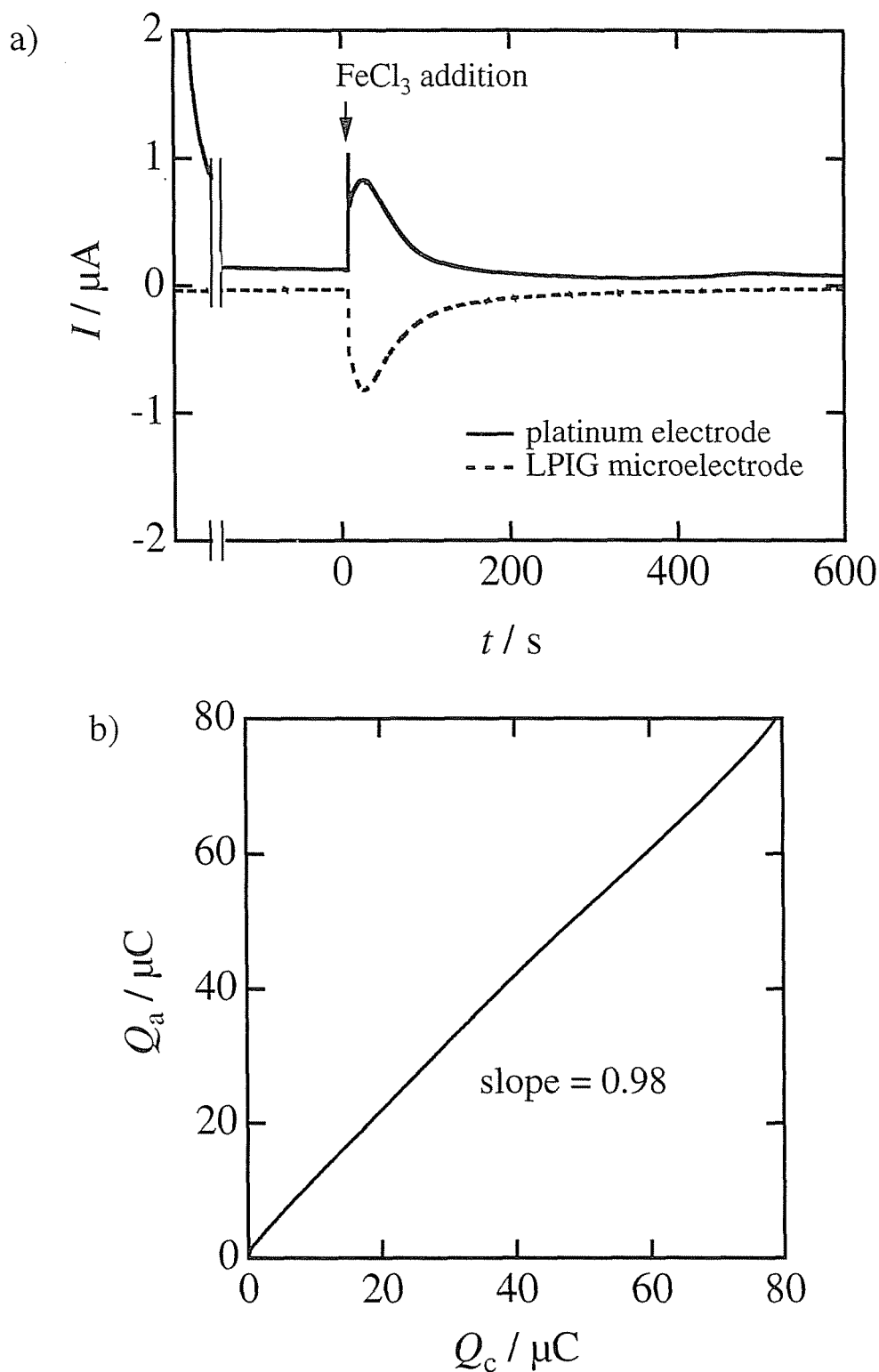


Fig. 10.3.12 a) Time variation of the current, I , flowed through the platinum electrode with a surface area of 0.25 cm^2 or the microelectrode when FeCl_3 of 1.3 mol dm^{-3} is added to pH 6.5 borate solution. The platinum electrode and the microelectrode were polarized at 1.2 V and -0.1 V (SHE), respectively. The distance between the platinum electrode and the microelectrode was kept at $75 \mu\text{m}$. b) Relation between the electric charges consumed by the microelectrode, Q_c , and the platinum electrode, Q_a .

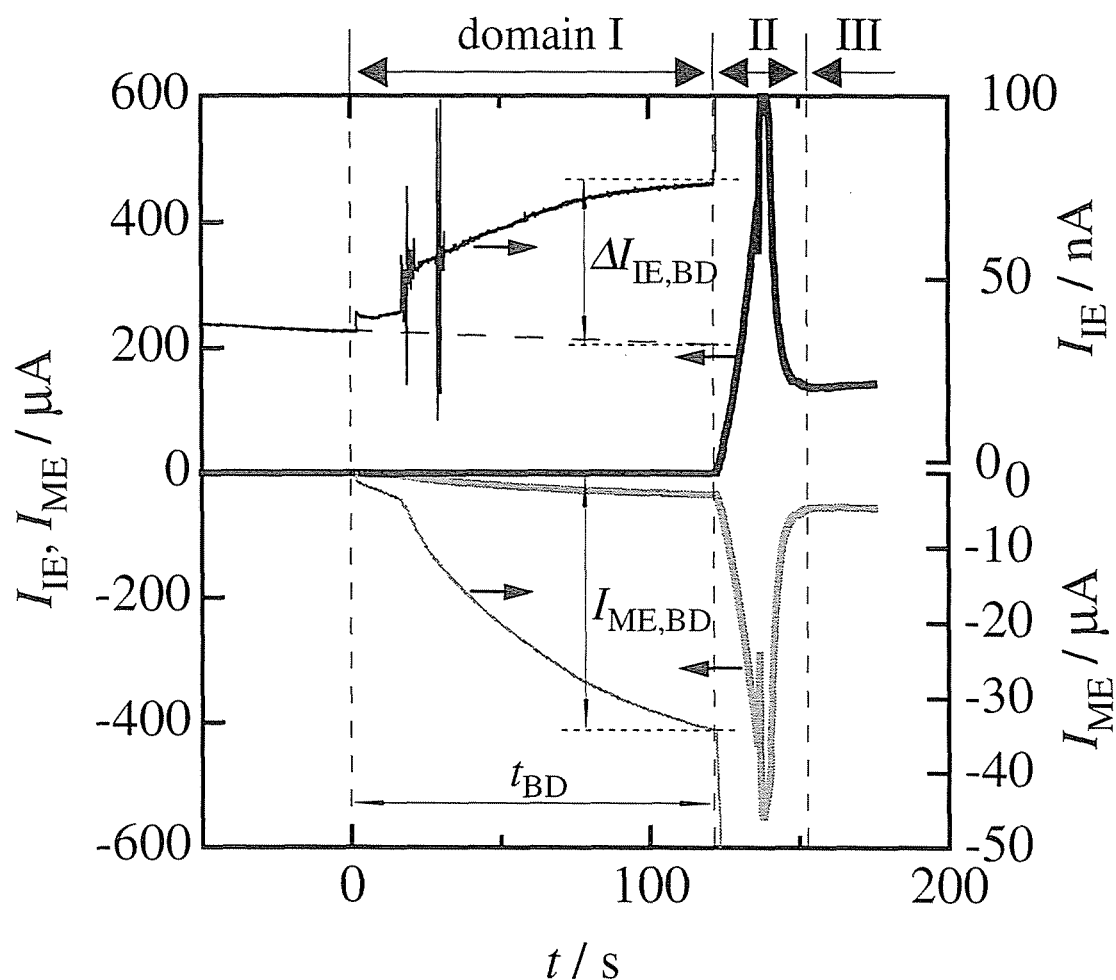


Fig. 10.3.13 Current transients of microelectrode, I_{ME} , and iron electrode, I_{IE} , after potential step of the microelectrode from 0.5 V to -0.1 V (SHE) whereas the iron electrode was polarized at 0.7 V (SHE) in deaerated pH 6.5 borate solution.

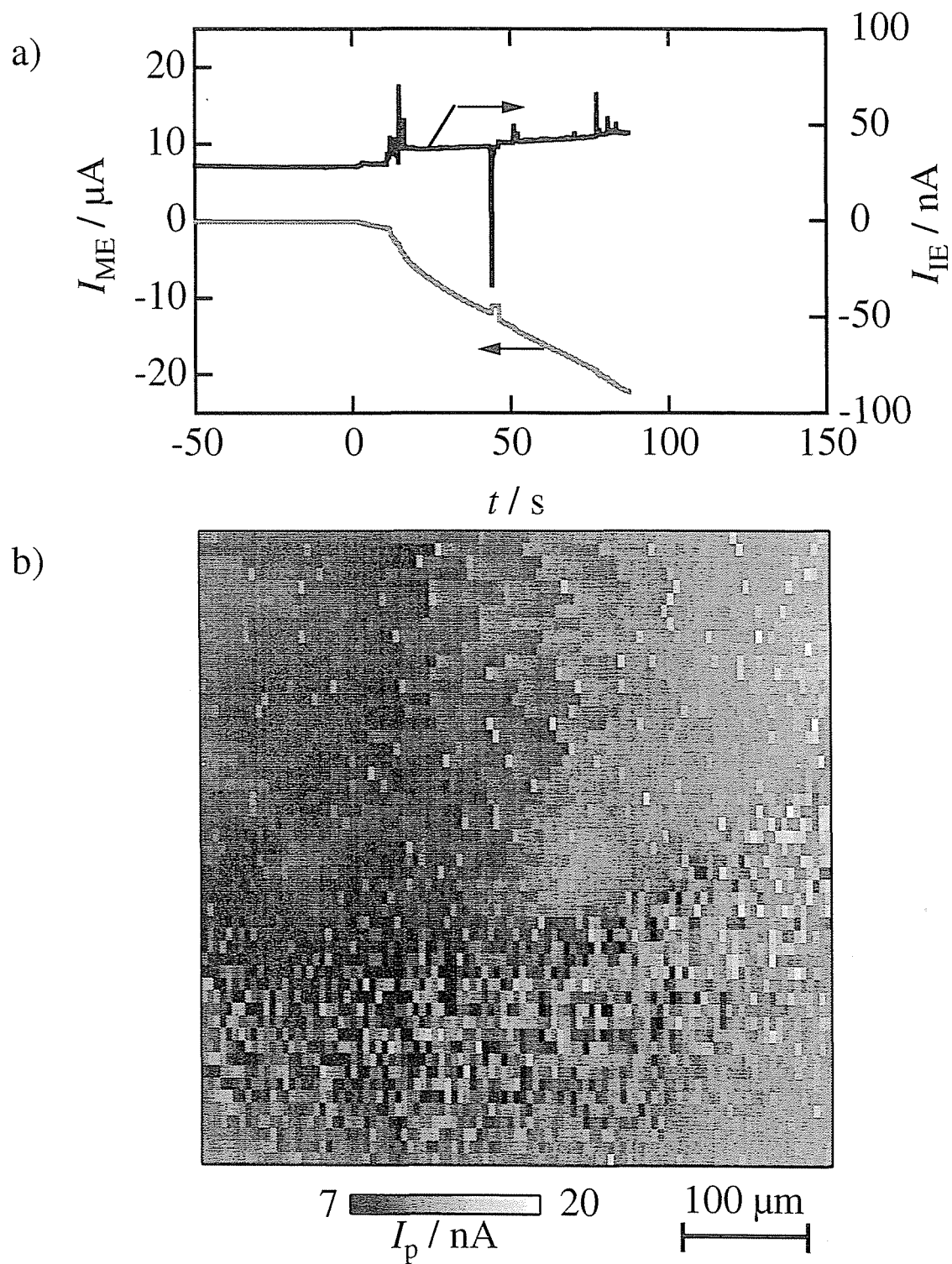


Fig. 10.3.14 a) Current transients of microelectrode, I_{ME} , and of iron electrode, I_{IE} , in domain I prior to domain II.
b) SECM image of the iron electrode surface in domain I prior to domain II.

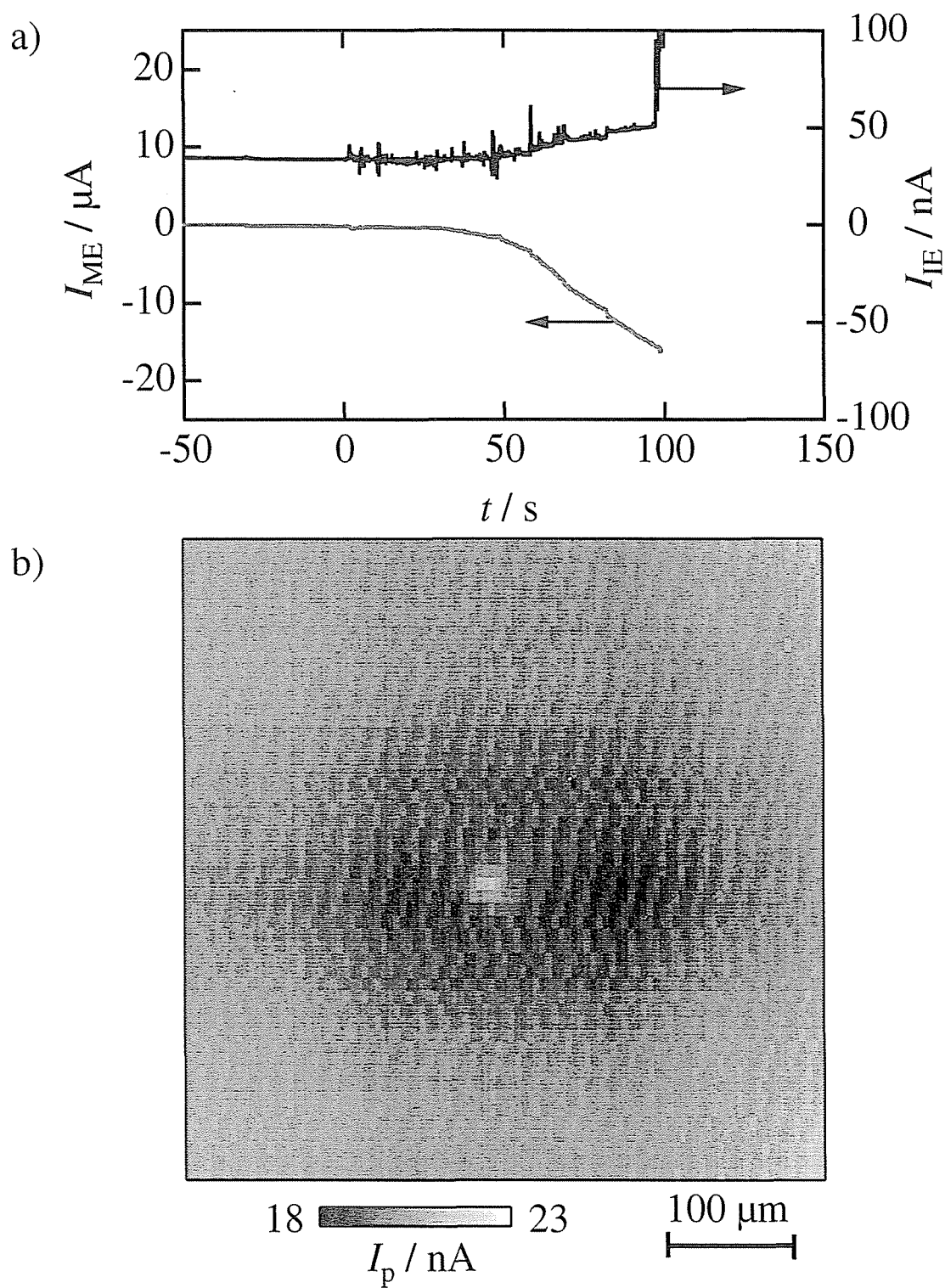


Fig. 10.3.15 a) Current transients of microelectrode, I_{ME} , and of iron electrode, I_{IE} , in domain II.
b) SECM image of the iron electrode surface in domain II.

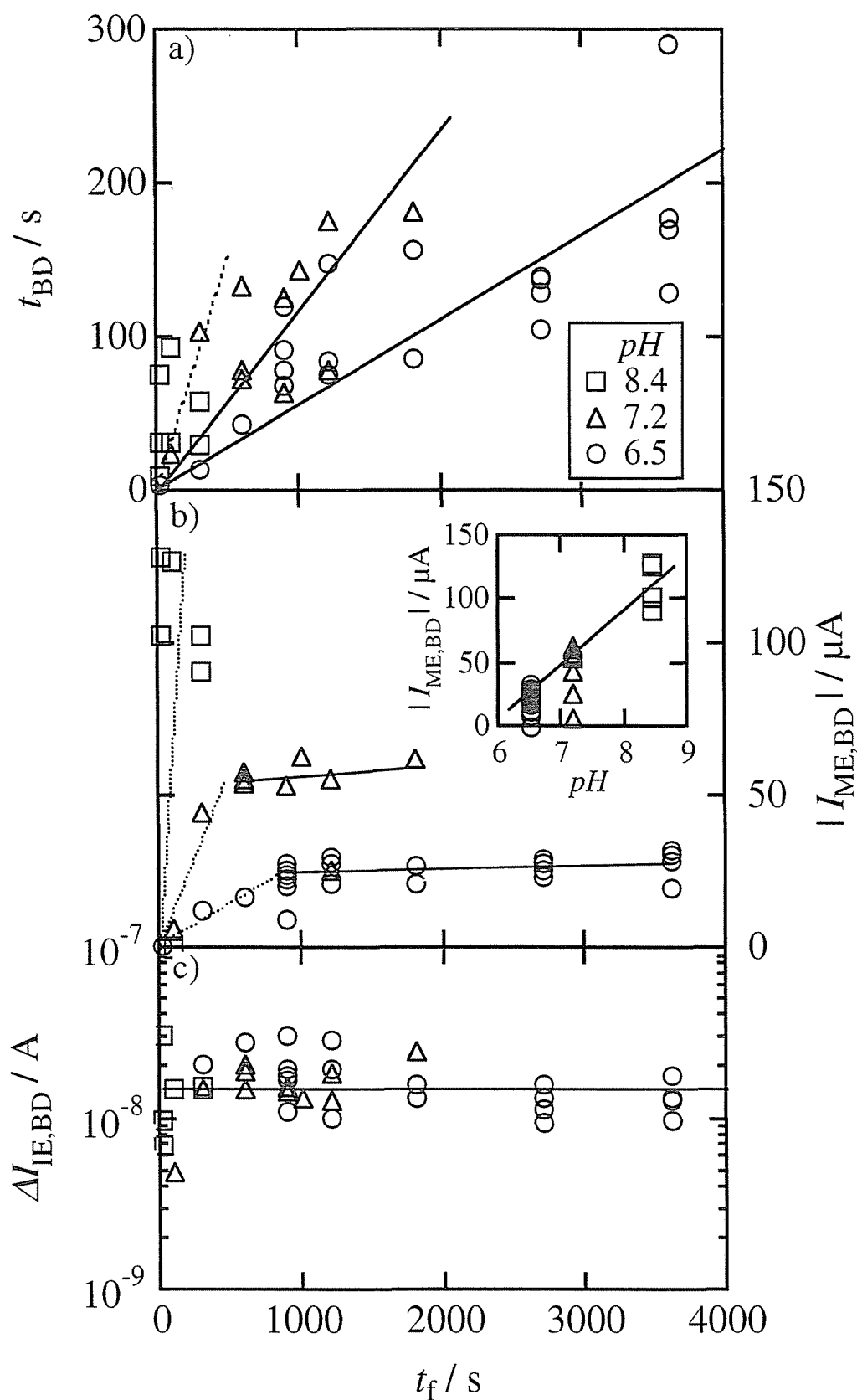
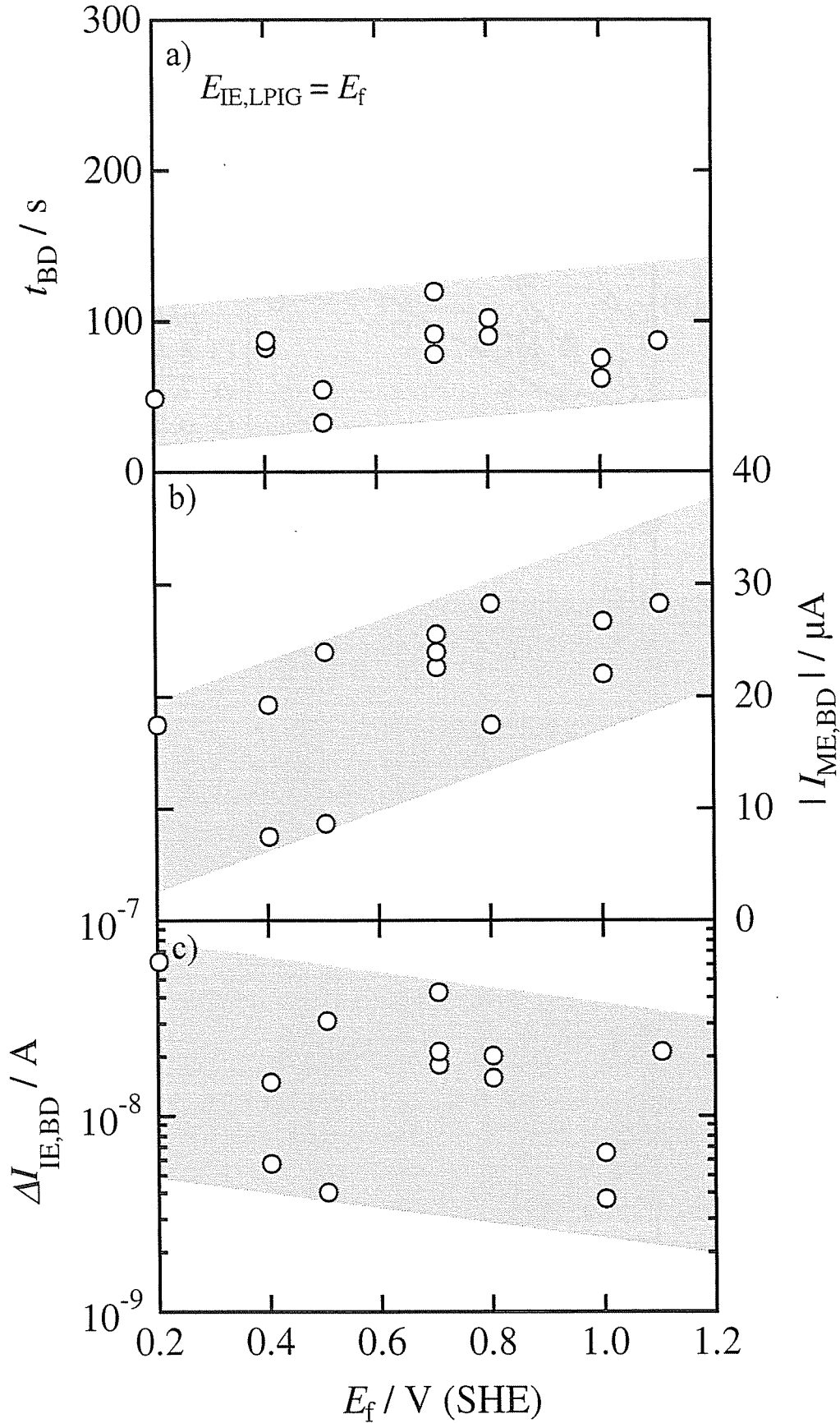
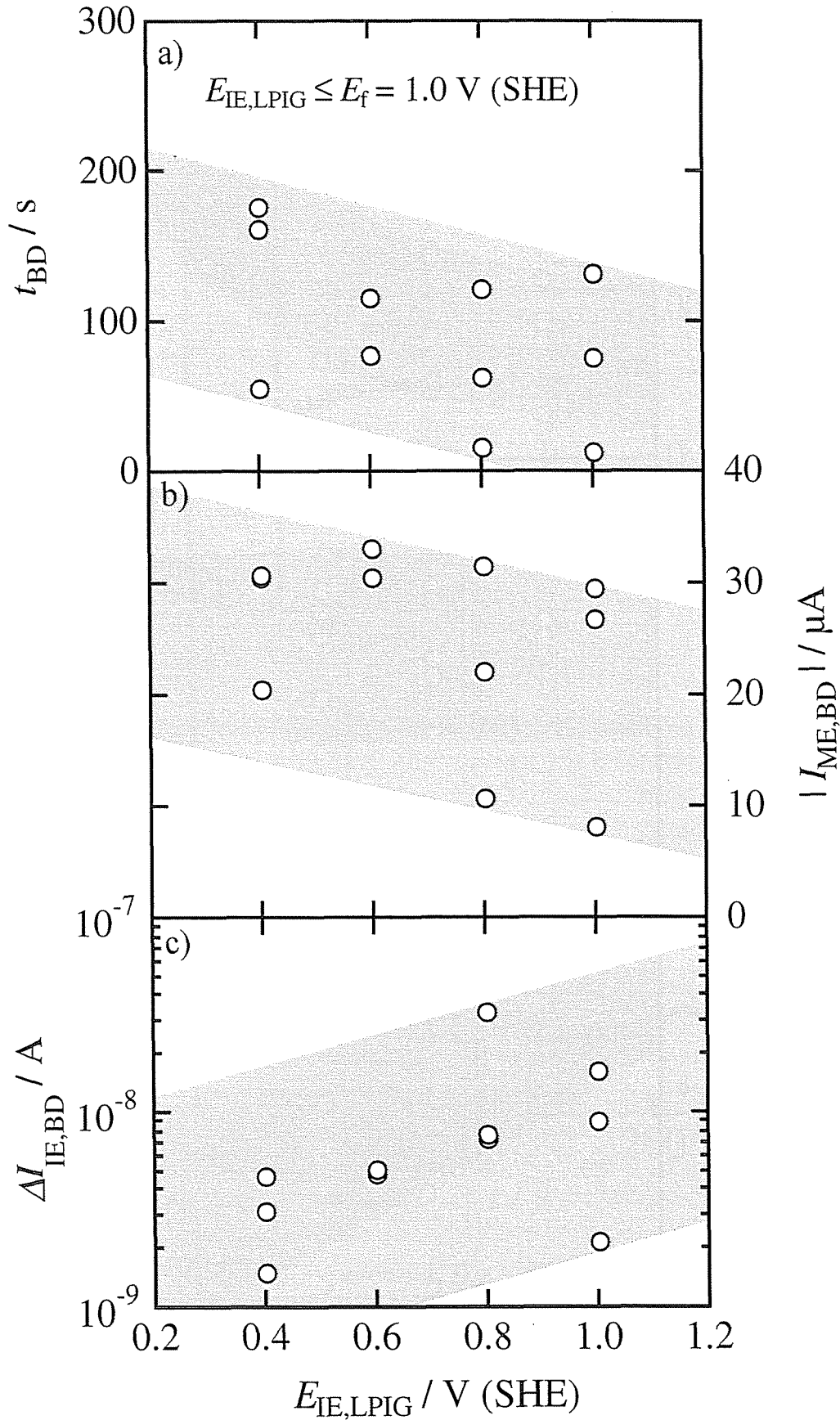


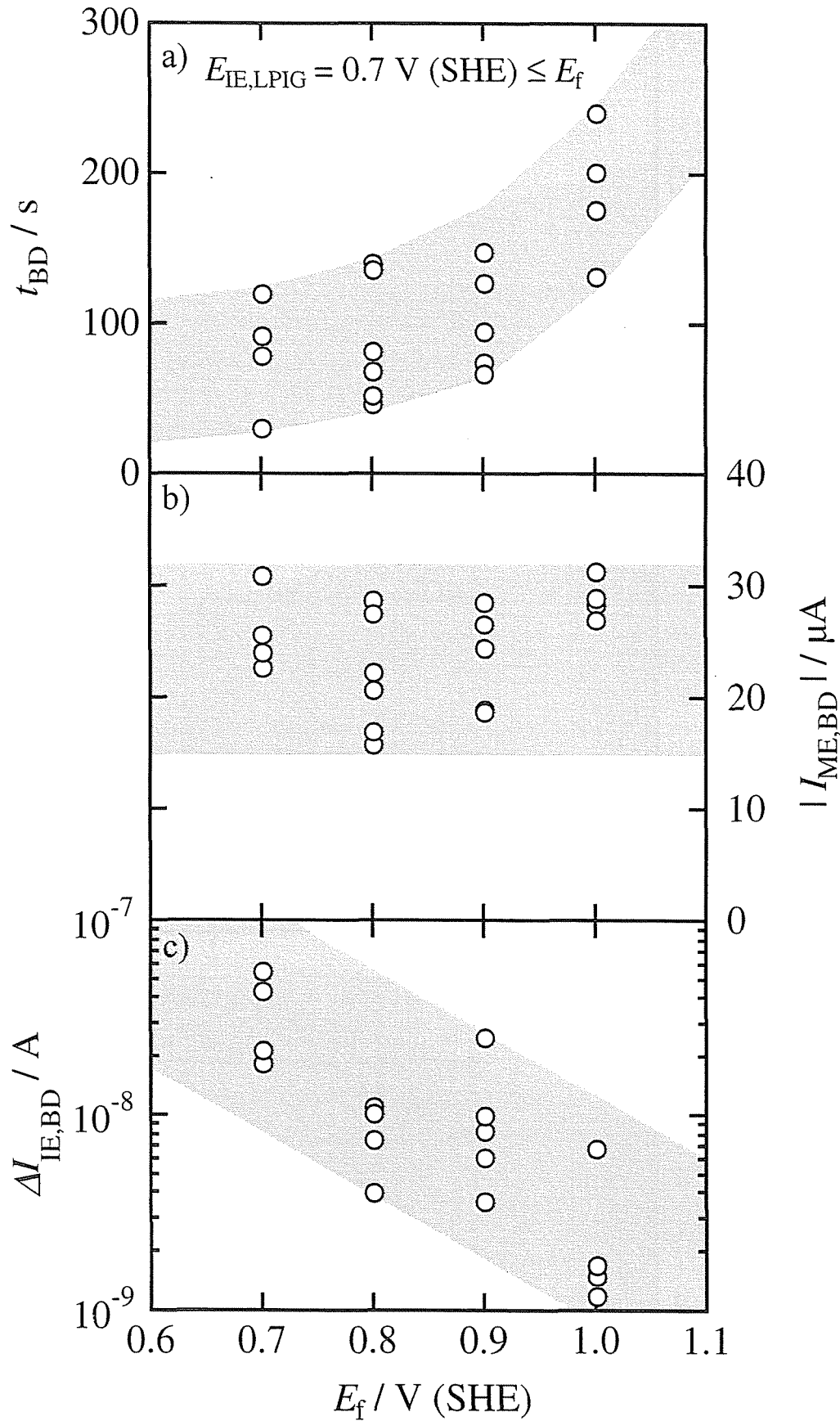
Fig. 10.3.16 a) Relation between induction period, t_{BD} , for initiation of local breakdown and film formation time, t_f , in pH 6.5, 7.2 and 8.4 borate solutions.
b) Relation between LPIG current, $|I_{ME,BD}|$, at initiation of local breakdown and t_f
c) Relation between change in current of iron electrode current, $\Delta I_{IE,BD}$, and t_f
The passive films were formed on iron at 0.7 V (SHE) for t_f in pH 6.5, 7.2 and 8.4 borate solutions, respectively. The iron electrode potential, $E_{IE,LPIG}$, was kept 0.7 V (SHE) during generation of Cl^- .



- 10.3.17 a) Relation between induction period, t_{BD} , for initiation of local breakdown and film formation potential, E_f in pH 6.5 borate solution.
 b) Relation between LPIG current, $|I_{\text{ME,BD}}|$, at initiation of local breakdown and E_f .
 c) Relation between change in iron electrode current, $\Delta I_{\text{IE,BD}}$, and E_f .
 The iron electrode was passivated at E_f for 900 s in pH 6.5 borate solution. Iron electrode potential, $E_{\text{IE,LPIG}}$, was kept at E_f during operation of the LPIG.



3.10.18 a) Relation between induction period, t_{BD} , for initiation of local breakdown and potential of the iron electrode, $E_{IE,LPIG}$, during operation of the LPIG in pH 6.5 borate solution.
b) Relation between LPIG current, $|I_{ME,BD}|$, at initiation of local breakdown and $E_{IE,LPIG}$.
c) Relation between change in iron electrode current, $\Delta I_{IE,BD}$, and $E_{IE,LPIG}$.
The passive film was formed on the iron electrode at $E_f = 1.0 \text{ V (SHE)}$ for 900 s in pH 6.5 borate solution, whereas the iron electrode potential, $E_{IE,LPIG}$, was kept at 0.4 V to 1.0 V (SHE) during operation of LPIG.



- 10.3.19 a) Relation between induction period, t_{BD} , for initiation of the local breakdown and film formation potential, E_f , in pH 6.5 borate solution.
- b) Relation between LPIG current, $|I_{\text{ME,BD}}|$, at initiation of the local breakdown and E_f .
- c) Relation between change in the current of the iron electrode, $\Delta I_{\text{IE,BD}}$, and E_f .
- The passive film was formed at the potential, E_f , higher than 0.7 V (SHE). The potential of the iron electrode, $E_{\text{IE,LPIG}}$, was kept at 0.7 V (SHE) during operation of the LPIG, for 900 s in pH 6.5 borate solution.

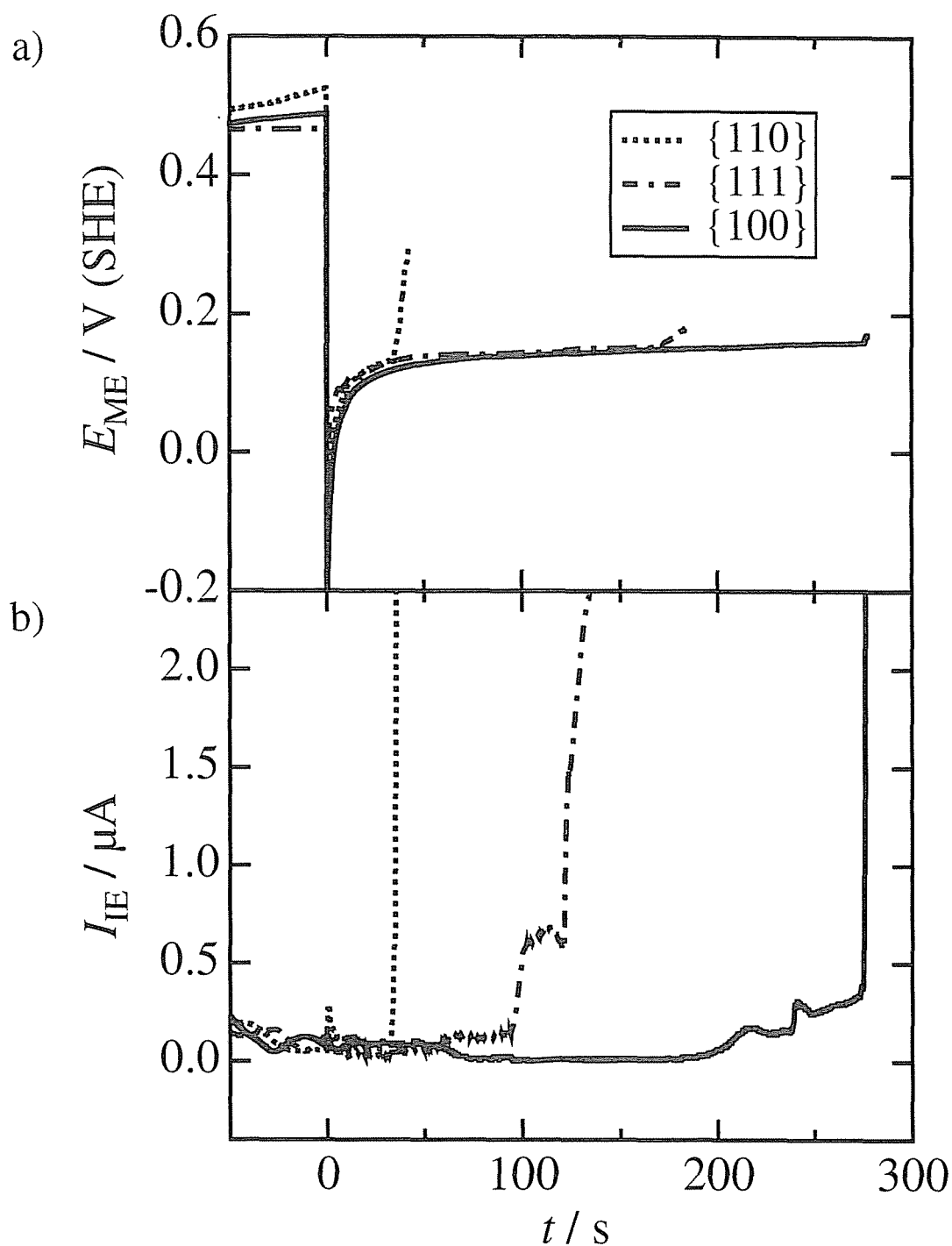


Fig. 10.3.20 Transients of a) potential, E_{ME} , of the LPIG microelectrode with a diameter of 50 μm and b) current passed through the iron electrode, I_{IE} , after current step of the microelectrode from 0.1 nA to -8 μA for galvanostatic Cl^- generation in pH 6.5 borate solution. The iron electrode was passivated at 0.7 V (SHE) for 1800 s in pH 6.5 borate solution after chemical etching. The LPIG was operated on each iron grain oriented to $\{110\}$, $\{111\}$, or $\{100\}$ plane at distance of about 40 μm between the LPIG and iron electrode.

11 Summary

In this thesis, scanning electrochemical microscopy (SECM) has been applied to the field of corrosion. Particularly, distributions of surface reactions on iron and titanium with relation to localized corrosion were investigated in wide potential regions of hydrogen evolution, active dissolution, passivity, trans-passivity and oxygen evolution using SECM. In addition to them, hydrogen evolution was also observed by SECM. Furthermore, a new technology, the so-called 'liquid-phase ion gun (LPIG)', which can generate Cl^- ions locally to induce passive film breakdown, was developed to pursue local breakdown of passive film. Besides, precursor process of breakdown of passive film on iron was focused with LPIG.

Chapters 1-3 were devoted to fundamental concepts throughout the thesis. Chapter 1 provided briefly reported knowledge concerning passivity, passive film and its breakdown, and localized corrosion. The purpose of this thesis was also described. Chapters 2 and 3 deal with methodologies of microelectrodes and SECM, respectively.

Instrumentation for developed SECM apparatus and public experimental procedures were covered in Chapter 4. Basic configurations and specifications of SECM and preparation of microelectrodes were also illustrated in this chapter.

Chapters 5-10 described practical aspects. Among them, SECM was employed for imaging distribution of electrochemical reactions on iron and titanium surfaces and inducing local breakdown of passive film formed on iron. In Chapter 5, SECM was applied to evaluate differences in thickness of passive film formed on iron in deaerated pH 8.4 borate solution containing $\text{Fe}(\text{CN})_6^{4-}$ as a mediator. The following conclusions were drawn:

- i) Difference in thickness of passive films formed on iron could be evaluated from both currents passed through a probe electrode on which $\text{Fe}(\text{CN})_6^{4-}$ was oxidized to $\text{Fe}(\text{CN})_6^{3-}$, and through an iron electrode on which $\text{Fe}(\text{CN})_6^{3-}$ diffused from the probe electrode and was reduced to $\text{Fe}(\text{CN})_6^{4-}$.
- ii) Lateral resolution of the probe current image was twice the diameter of the employed probe electrode.
- iii) The probe current image of the passive film on a polycrystalline iron showed heterogeneity. Shapes of patch patterns on the probe current image coincided completely with shapes of crystal grains on the substrate iron surface.
- iv) Probe current passed above the grain surface oriented to $\{100\}$ plane was less than that above the grain surface oriented to $\{110\}$ or $\{111\}$ plane.

- v) Grain orientation dependence of the probe current was ascribed to difference in thickness of passive films formed on crystal grains.

In Chapter 6, the following things were clarified by applying SECM to the anodic oxide film grown on a polycrystalline titanium electrode in pH 8.4 borate solution.

- i) The probe current image could detect heterogeneity of anodic oxide film, depending on substrate crystal grains.
- ii) This heterogeneity increased with increasing film formation potential. It became significant at potentials higher than 3 V (SHE).
- iii) Raman microprobe spectroscopy indicated that TiO₂ film (probably anatase type) with a low crystallinity forms at potentials higher than 3 V (SHE) - supporting the assertion that heterogeneity in the probe current image is ascribed mainly to difference in thickness of passive films on substrate grains.
- iv) Comparison between the optical micrograph and the probe current image demonstrated that grains with twin textures have relatively thin anodic oxide films as compared with grains without twin textures.

In Chapter 7, SECM without use of mediator was applied to a polycrystalline titanium electrode during anodic oxidation in 0.1 mol dm⁻³ H₂SO₄. The probe current electrode could detect oxygen evolved in parallel with formation of anodic oxide film on titanium. The following conclusions were drawn:

- i) From comparison between the probe current image corresponding to distribution of oxygen evolution and the conventional probe current image, which was measured in pH 8.4 borate solution containing K₄Fe(CN)₆ as a mediator, both probe current images gave good coincidence; particularly in the point that the anodic oxide film depends on the substrate crystal grain.
- ii) Good coincidence of probe current images implied that oxygen evolution took place preferentially on the substrate grain covered with the thinner oxide film. Moreover, it was suggested that anodic oxide films on twin grains were easily broken down and become active sites of oxygen evolution.
- iii) These results implied that measurement of oxygen reduction current with the probe electrode was useful as an *in-situ* method without addition of mediator for evaluating the heterogeneity of metal surface during anodic oxidation.

In Chapter 8, SECM was applied to evaluate dissolution distribution of ferrous or ferric ion from a polycrystalline iron electrode in a deaerated pH 2.3 sulfate solution. The following results were obtained:

- i) Ferrous or ferric ion could be detected with a probe microelectrode composed of graphite reinforcement carbon.
- ii) Dissolution of ferrous and ferric ions in the active region was successfully monitored. However, once the salt film such as FeSO_4 was formed due to accumulation of ferrous ion in the narrow space between probe and iron electrodes, detection of ferrous or ferric ion became difficult because the probe electrode potential shifted in the negative direction due to the large iR drop in the salt film. On the other hand, it was confirmed that ferric ion dissolved from the iron electrode in the trans-passive region.
- iii) Dissolution distribution of ferrous ion from a polycrystalline iron electrode in the active region, depending on the substrate grains, was measured by SECM probe current profile. The active-dissolution rate of ferrous ion from the substrate grains, on which the thicker film was formed in the passive region, was less than that from the substrate grains on which the thinner film was formed in the passive region.

In Chapter 9, SECM was applied for *in-situ* detection of hydrogen generated from a single crystal magnetite during galvanic coupling with a carbon steel. The following things were clarified:

- i) Galvanic coupling with the magnetite accelerated the carbon steel corrosion in deaerated pH 5.8 sulfate solution. Acceleration was not only due to water reduction, that is, generation of hydrogen on the magnetite but also due to reduction of the magnetite itself.
- ii) It was deduced from measurement of the probe current above the magnetite or carbon steel that current efficiency for hydrogen generation on the magnetite during galvanic coupling with the carbon steel was about 50%.
- iii) The probe current profile revealed that hydrogen generation was significantly promoted on the magnetite electrode during galvanic coupling in deaerated pH 3.3 sulfate solution.

In Chapter 10, a silver/silver chloride microelectrode, which acts as a probe electrode of SECM, was developed as a liquid-phase ion gun (LPIG) to induce local breakdown of passive film on metal. The LPIG microelectrode was applied to induce local breakdown of passive film formed on iron in deaerated borate solutions. The following considerations were drawn:

- i) Local generation of Cl^- ions due to cathodic polarization of the microelectrode succeeded in inducing local breakdown of passive film on iron just below the microelectrode.
- ii) From current transients of the microelectrode and iron electrode during LPIG operation, it was found that breakdown processes could be classified into the following three domains:

In domain I, Cl^- ions are generated from the microelectrode and are enriched in the narrow

space between the microelectrode and specimen electrode, whereas the passive film still remains on the specimen electrode. The time period of this domain corresponds to the induction period for local breakdown, and the composition or structure of the passive film attained to a critical level just before initiation of the local breakdown.

In domain II, enriched Cl^- promotes dissolution of passive film as ferric ions. Reduction of ferric ions to ferrous ions at the microelectrode and oxidation of ferrous ions to ferric ions at the specimen electrode are repeated (positive feedback) as long as the passive film is present on iron. In this domain, the passive film is dissolved to ferric ions and thus become thin.

In domain III, a bare surface emerges on the local area of the iron electrode from which ferrous ions dissolve and a corrosion pit grows. The dissolution rate of ferrous ions increases with increasing film formation potential. A corrosion pit grows continuously at high potentials, while pit repassivation takes place at low potentials.

- iii) Concentration of Cl^- in the narrow space between the microelectrode and specimen electrode was estimated to be about 1 mol dm^{-3} which was sufficient for initiation of local breakdown.
- iv) The induction period increased with film formation time due to aging of the film. The higher electric field in the passive film shortened the induction period and increased the passivity-maintaining current.
- v) Local breakdown of the passive film depended on the substrate grain-orientation. The passive film formed on the substrate grain oriented to $\{100\}$ was the most protective against local breakdown as compared with those on grains oriented to $\{111\}$ and $\{110\}$. Grain-orientation dependence was explained in terms of difference in thickness or defective structure of the film grown on each grain.

In summary, it is concluded that SECM is useful in evaluating distribution of electrochemical reactions proceeding on the electrode surface such as corrosion reaction, redox reaction on passive film and so on. In active-dissolution, passive, and oxygen-evolution regions, heterogeneity of probe current images could catch clearly distribution of the respective electrochemical reaction over the specimen surface. They were dependent on the substrate crystallographic orientation. Particularly, on iron in the passive region, the redox reaction of $\text{Fe}(\text{CN})_6^{3-}/\text{Fe}(\text{CN})_6^{4-}$ proceeded more easily on passive film formed on the grain with high packing density than that on grain with low packing density. It is mainly due to difference in film thickness. Moreover, LPIG was developed as a state of art technique to investigate local breakdown of passive film. Application of LPIG to passive film formed on iron revealed details of its local breakdown process.

Appendix

Symbols used in the thesis

A	$[m^2]$	surface area
A_j	$[m^2]$	surface area of the element, j
a	$[m]$	radius of microelectrode
C_d	$[F]$	capacitance of double layer
c	$[mol\ m^{-3}]$	concentration of diffusing species
c^*	$[mol\ m^{-3}]$	concentration at bulk
c_j	$[mol\ m^{-3}]$	concentration in the volume element, j
D	$[m^2\ s^{-1}]$	diffusion coefficient of diffusing species
d	$[m]$	distance between microelectrode and specimen surface
d_b	$[m]$	barrier thickness for tunneling of electrons
(dd_t/dE)	$[m\ V^{-1}]$	formation factor of oxide film
d_0	$[m]$	initial thickness of oxide film
d_{SC}	$[m]$	thickness of space-charge layer
d_t	$[m]$	film thickness
E	$[V]$	electrode potential
E^0	$[V]$	formal potential
E_{CB}	$[V]$	conduction band potential
E_{BD}	$[V]$	breakdown potential
E_{FB}	$[V]$	flat-band potential
E_{pit}	$[V]$	pitting potential
E_{RP}	$[V]$	repassivation potential
E_{VB}	$[V]$	valence band potential
E_f	$[V]$	film formation potential
$E_{IE,LPIG}$	$[V]$	potential of iron electrode during operation of the LPIG
E_{ME}	$[V]$	potential of LPIG microelectrode
E_{OX}	$[V]$	equilibrium potential of oxide electrode
E_p	$[V]$	potential of probe electrode
E_s	$[V]$	potential of specimen electrode
e	$[C]$	elementary electric charge, $e = 1.602 \times 10^{-19}\ C$
$erf(x)$		error function
		$erf(x) \equiv \frac{2}{\sqrt{\pi}} \int_0^x e^{-y^2} dy = \frac{2}{\sqrt{\pi}} \left(x - \frac{x^3}{3} + \frac{x^5}{5 \cdot 2!} - \frac{x^7}{7 \cdot 3!} + \frac{x^9}{9 \cdot 4!} - \dots \right)$
$erfc(x)$		complementary error function, $erfc(x) \equiv 1 - erf(x)$
F	$[C\ mol^{-1}]$	Faraday constant, $F = 96485\ C\ mol^{-1}$
h	$[J\ s]$	Planck constant, $h = 6.626 \times 10^{-34}\ J\ s$
I	$[A]$	current
I_{limit}	$[A]$	diffusion-limited current
I_p	$[A]$	current flowed through probe electrode
I_s	$[A]$	current flowed through specimen electrode
I_{charge}	$[A]$	current for charging of electric double layer
I_{dis}	$[A]$	dissolution current
I_{etr}	$[A]$	current of electron transfer reaction
I_{ME}	$[A]$	current flowed through LPIG microelectrode
$I_{ME,BD}$	$[A]$	I_{ME} just before initiation of film breakdown
I_{oxide}	$[A]$	current of oxide formation
I_{oxygen}	$[A]$	current of oxygen evolution
I_{total}	$[A]$	total current during anodic polarization
i	$[A\ m^{-2}]$	current density
i_a	$[A\ m^{-2}]$	anodic current density at 3.6 ks-anodic polarization

i_s	[A m ⁻²]	current density of specimen electrode
i_{total}	[A m ⁻²]	total current density during anodic oxidation
J	[-]	given volume element
j	[mol m ⁻² s ⁻¹]	diffusion flux
k	[J K ⁻¹]	Boltzmann constant, $k = 1.381 \times 10^{-23}$ J K ⁻¹
k	[m V ⁻¹]	film formation factor
k^0	[m ³ s ⁻¹]	standard rate constant
k_b	[m ³ s ⁻¹]	rate constants for oxidation
k_f	[m ³ s ⁻¹]	rate constants for reduction
$L_{D,\text{eff}}$	[m]	effective Debye length
M	[kg mol ⁻¹]	molecular weight
m_e	[kg]	effective mass of electron, $m_e = 9.109 \times 10^{-31}$ kg
N_D	[m ⁻³]	donor density
q	[C]	charge
Q_f	[C]	charge consumed for formation of silver chloride on LPIG microelectrode
Q_g	[C]	charge consumed for exhaustive generation of Cl ⁻ from LPIG microelectrode
R	[Ω]	solution resistance
r	[m]	radial coordinate
r_s	[m]	radius of specimen electrode
r^*	[m]	radius of finite insulating plane of microelectrode tip (= a + thickness of insulating sheath of microelectrode tip)
T	[K]	temperature
t	[s]	time
t_{BD}	[s]	induction period for film breakdown
t_+	[-]	transference number of cations
v_j	[m ³]	volume of the element, j
W	[-]	probability of electron tunneling
x	[m]	coordinate normal to the plane of electrode
z	[-]	number of electrons
α	[-]	transfer coefficient
γ	[-]	correction coefficient for influence of insulation geometry on current at microelectrode
$\Delta I_{\text{IE,BD}}$	[A]	increment in iron electrode current during domain I
Δn	[mol]	amount of Cl ⁻ ions generated from LPIG microelectrode
ΔV	[V m ⁻¹]	field strength in film
ΔX	[-]	difference of electronegativity
$\Delta \epsilon$	[eV]	energy barrier of height for electron tunneling
$\Delta \epsilon_g$	[eV]	band gap energy
$\Delta \phi$	[V]	potential difference
$\Delta \phi_{\text{f/s}}$	[V]	potential-difference at film/solution interface
δ	[m]	thickness of diffusion layer
ϵ	[eV]	energy level
ϵ	[-]	dielectric permittivity of oxide
ϵ_0	[C N ⁻¹ m ⁻²]	dielectric permittivity of oxide in vacuum
ϵ_{CB}	[eV]	energy level of conduction band edge
ϵ_r	[eV]	step energy level of resonance electron tunneling
η	[-]	current efficiency for generation of Cl ⁻ ions
κ	[Ω ⁻¹ m ⁻¹]	solution conductivity

ρ	[kg m ⁻³]	density of oxide film
ρ_i	[-]	insulating coordinate, $\rho_i = \frac{a}{r^*}$
ρ_s	[Ω m]	solution resistivity
τ	[-]	$\tau = \frac{2\sqrt{Dt}}{a}$
ξ	[-]	roughness factor,
$\hbar$	[J s]	$\hbar = \frac{h}{2\pi}$
∇^2	[-]	Laplacian diffusion operator