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Jun-Seob LEE

Contents

Chapter 1 Preface

1.1	Stainless steel	1
1.1.1	Definition of stainless steel	1
1.1.2	Types of stainless steel	1
1.2	Passivity and passive film	3
1.2.1	Definition of passivity	3
1.2.2	Types of passive film	3
1.2.3	Formation and passive film and its composition	4
1.3	Passivity breakdown of stainless steel	6
1.3.1	Change in stability and removal of passive film	7
1.3.2	Removal of passive film	8
1.3.3	Initiation of localized corrosion	9
1.3.4	Repassivation or propagation of local corrosion	10
1.4	Previous investigations of localized corrosion of stainless steel	11
1.5	Sulfide inclusions in stainless steel	12
1.5.1	Effects of MnS inclusion on breakdown of passivity in stainless steel	12
1.6	Chloride ions and localized corrosion of stainless steel	13
1.7	Anion-generating system	14
1.8	Purpose of dissertation	14
	References	16

Chapter 2 Experimental setups and procedures

2.1	Preparation of electrodes	26
2.1.1	Liquid-phase ion gun (LPIG) microelectrode	26
2.1.2	Silver substrate electrode	26
2.1.3	pH and anion sensing microelectrode	26
2.1.4	Stainless steel substrate electrodes	27
2.1.4.1	Metallographic of stainless steels	27
2.1.5	Scanning electrochemical microscope (SECM) tip microelectrode	29
2.2	Characterization of SECM tip microelectrode	29
2.3	Set-ups of LPIG, pH, anion sensing electrode and SECM	30
2.3.1	LPIG setups	30
2.3.2	pH and anion sensing electrode setup	31
2.3.3	SECM steup	31
2.4	Chemicals and materials	31
2.5	Surface analysis	32
2.6	Summary	33
	References	34

Chapter 3	Anion-generating system	
3.1	Introduction	43
3.2	Experimental	44
3.2.1	Specimens preparation	44
3.2.2	Operation of the LPIG system	44
3.2.3	Surface characterization	45
3.2.4	Modeling parameters and conditions	45
3.3	Results	47
3.3.1	Electrochemical reaction of a silver microelectrode	47
3.3.2	Estimation of pH and $[\text{HS}^-]$	47
3.3.3	Electrochemistry of LPIG in alkaline solutions	48
3.3.4	Potentiostatic polarization of LPIG above an insulating surface	49
3.3.4.1	Geometrical dependences on generation behavior of anions released from LPIG	50
3.3.4.2	Geometrical dependences on concentration profiles of HS^- and OH^- potentiostatically generated from LPIG	50
3.3.5	Galvanostatic polarization of LPIG above an insulating surface	52
3.3.5.1	Geometrical dependences of concentration profiles of anions galvanostatically generated from the LPIG microelectrode	53
3.3.6	Polarization behaviors of LPIG above a conductive silver surface	54
3.3.6.1	Anodic polarization of silver substrate	54
3.3.6.2	Dependence of distance between LPIG and silver substrate on polarization behaviors of LPIG	55
3.3.6.3	Potential dependence of silver substrate on the polarization behaviors of LPIG	56
3.4	Potential of LPIG as a sulfide ion generation apparatus	57
3.5	Summary	58
References		59

Chapter 4	Effect of hydrogen sulfide ions (HS^-) on passive behavior of type 316L stainless steel	
4.1	Introduction	85
4.2	Experimental	86
4.2.1	Specimen preparation	86
4.2.2	Operation of the LPIG system	87
4.2.3	Impedance measurement	87
4.2.4	Mott-Schottky measurement	87
4.2.5	SECM measurement	88
4.2.6	Surface analysis	88
4.3	Results	89

4.3.1	Anodic polarization of type 316L stainless steel	89
4.3.2	Changes in electrode potentials of E_{LPIG} and $E_{316\text{L}}$ of the LPIG and stainless steel	89
4.3.3	Effect of HS^- on semiconductive properties of passive film formed on type 316L stainless steel	89
4.3.4	Surface analysis of passive film formed on 316L stainless steel	93
4.3.5	Effect of HS^- on a secondary passivity of type 316L stainless steel	95
4.3.6	Surface analysis of secondary passive film formed on 316L stainless steel	96
4.4	Discussion	97
4.5	Summary	100
References		101

Chapter 5 Evaluation of localized corrosion resistance of stainless steels

5.1	Introduction	122
5.2	Experimental	123
5.2.1	Specimens	123
5.2.2	Electrochemical experiments	123
5.2.3	LPIG set-up	124
5.2.4	Sensitivity of pH and $[\text{Cl}^-]$ set-up	124
5.2.5	Surface analyses	125
5.2.6	Modeling parameters and conditions	125
5.3	Results	126
5.3.1	Electrochemical reaction of a silver microelectrode	126
5.3.2	Anodic polarization of stainless steels	127
5.3.3	Current transients of LPIG and stainless steels during operation of LPIG	128
5.3.4	Estimation of pH and $[\text{Cl}^-]$ during the operation of LPIG	129
5.3.5	Pitting and repassivation potential of stainless steels	132
5.3.6	Evaluation of localized corrosion resistance parameters of stainless steels	133
5.3.7	Surface analyses of passive film on stainless steels	134
5.4	Discussion	134
5.5	Summary	136
References		137

Chapter 6	Conclusion	151
Appendix		154

Chapter 1 Preface

1.1 Stainless steel

1.1.1 Definition of stainless steel

Since the beginning of a research for chromium containing iron-based alloys by Faraday in the 1820s, the first commercialized stainless steel was fabricated in 1909 by German company Krupp. Stainless steel is defined with corrosion resistance steels containing of chromium from 11 wt% to 32 wt% and an iron content more than 50 wt%.[1] In order to meet different requirements of mechanical and corrosion resistive properties, there are various stainless steels with higher levels of corrosion resistance and mechanical properties.

1.1.2 Types of stainless steel

The various types of stainless steels are manufactured by controlling alloying elements to offer specific attributes in different environments. The main alloying elements of stainless steel are chromium and nickel. Constitutional diagrams are widely used to predict ferrite levels from the composition by comparing the effects of austenite and ferrite stabilizing elements. Figure 1.1 shows the Schaeffler diagrams that are the original methods of predicting a phase balance in stainless steel.[2] Austenite and ferrite stabilizing elements promote formation of austenite and ferrite phases, respectively. Chromium (Cr), molybdenum (Mo), tungsten (W), silicon (Si), titanium (Ti), aluminum (Al), and niobium (Nb) are ferrite stabilizing elements, while nickel (Ni), cobalt (Co), manganese (Mn), copper (Cu), carbon (C) and nitrogen (N) are austenite stabilizing elements.[3] The capacity of stabilization of each element to the each phase is varied. For example, when 1 wt% of Mo was added to 18 wt% Cr-8 wt% Ni stainless steel, Mo has an approximately twice stabilizing effect on ferrite phase compared with the case of adding the same 1 wt% of Cr. This is an experimental equivalent to quantify an equivalent coefficient. The equivalents show compositional equivalent areas in the Schaeffler diagrams where the austenite, ferrite, martensite and mixtures of these phases are present. The nickel and chromium equivalents are used x- and y-axes, respectively, of the Schaeffler diagram as follows:

$$\text{Ni (eq)} = \text{Ni wt\%} + (30\text{C wt\%}) + (0.5\text{Mn wt\%}) \quad [1.1]$$

$$\text{Cr (eq)} = \text{Cr wt\%} + \text{Mo wt\%} + (1.5\text{Si wt\%}) + (0.5\text{Nb wt\%}) \quad [1.2]$$

The types of stainless steel are generally classified into five groups: austenitic, ferritic, duplex, martensite and precipitation stainless steels depending on their microstructure at room temperature.

Austenitic stainless steels.— The austenitic stainless steels are characterized into types based on their alloying elements mainly with balanced Fe, 17-18 wt% Cr and 8-11 wt% Ni. The face-centered cubic (FCC) crystal structural of austenitic stainless steels are derived from the addition of Ni and Mn as substitution elements and N as an interstitial element in the FCC crystal structure.[4] Cr-Ni based austenitic stainless steels are classified into 300 series, while Cr-Mn-Ni austenitic stainless steels are based are classified into 200 series.[4] Austenitic stainless steels are the most widely used type of stainless steel because of their good formability and weld ability than ferritic and martensitic stainless steels. Austenitic stainless steels are normally susceptible to inter granular corrosion or localized corrosion with segregation or precipitation of carbides or nitrides at grain boundaries during or after heat treatment or welding.

Ferritic stainless steels.— Ferritic stainless steels are mainly characterized into types based on their alloying elements with balanced Fe, 11-30 wt% Cr, while they contain less or negligible Ni than austenitic stainless steels. Ferritic stainless steel have body-centered cubic crystal structures (BCC) and derived from the addition of Mo as substitution elements enhancing general and localized corrosion of ferritic stainless steels.[5] Ferritic stainless steels are the second most used type of stainless steel, because ferritic stainless steels are relatively lower in cost compared to austenitic steels due to the absence of nickel. Ferritic stainless steels are less corrosion resistive than austenitic stainless steels of the same content of chromium, while ferritic stainless steels are highly resistant to stress corrosion cracking than austenitic stainless steels.

Duplex stainless steels (DSSs).— Duplex stainless steels are bi-phased stainless steel with approximately similar volume fraction of austenite and ferrite, for improved mechanical strength and corrosion resistance. DSSs contain 21-27 wt% Cr, 4-7 wt% Ni and <4 wt% Mo additions.[6] In general, grade of DSSs is defined with pitting resistance equivalent ($PRE = \text{wt\% Cr} + (3.3 \text{ wt\% Mo} + 0.5 \text{ wt\% W}) + 16 \text{ wt\% N}$).[6] Lean duplex stainless steels have PRE value under 40, super duplex stainless steels have PRE value from 40 to 45.[7] Since DSSs have higher strength and superior resistance to stress corrosion cracking than austenitic and ferritic stainless steels, DSSs are used in extremely corrosive environments such as sour and acidic chloride conditions. However, DSSs are very susceptible to localized or inter granular corrosion when secondary phases are present in phase boundary between ferrite and austenite phase.

Martensitic stainless steels.— Martensitic stainless steels have a similar microstructure to ferritic stainless steels of BCC structure with 11-18 wt% chromium containing, while they have high mechanical strength due to high carbon content from 0.15 wt% to 1.2 wt% by heat treatment. The martensitic stainless steels are iron-chromium based steels without containing nickel, while molybdenum can be added in the stainless steels.[5]

Optimum corrosion resistance of martensitic stainless steels is strongly affected by heat treatment such as hardened and tempered conditions. In general, martensitic stainless steels are less resistant to various corrosions than austenitic and ferritic stainless steels of the same chromium content.

Precipitation hardened stainless steels (PHs).— Most of PHs contain Ni from 7 wt% to 26 wt% which prevents martensite transformation. Precipitation hardened stainless steels can be strengthened heat treatment. They can be either austenitic or martensitic in the heat treatment condition. As the low carbon content compared to martensitic stainless steels, the strengthening mechanism is not different from that of martensitic stainless steels. PHs contain approximately <1% of a Ti and/or Al which makes fine precipitates in order to increase in strength.[5,6] Corrosion resistance of PHs is strongly dependent on heat treatment condition. In room temperature of aqueous chloride solutions, PHs are susceptible to localized corrosion, while PHs are highly resistant to stress corrosion cracking after solution heat treated at 550°C or higher.

1.2 Passivity and passive film

1.2.1 Definition of passivity

Corrosion of metal is dependent on a free energy difference between the metal itself and a specific environment. Noble metals such as platinum and gold are rarely corroded in an acidic solution, while iron that is relatively less active than platinum and gold is easily corroded in an acid solution by producing hydrogen gas. However, when iron is exposed to a concentrated nitric acid solution, the iron resists corrosion after some time of hydrogen generation.[8] The sudden decrease of corrosion of metals during anodic polarization is also observed in acidic or neutral solutions.[9] The loss of chemical reactivity experienced by certain metals under particular conditions is called “passivity”. [10] Certain passivated metals become chemically quasi-inert by forming a passive film. Pourbaix suggested a thermodynamically stable state of metal and dissolved metal ions and oxides with respect to their electrode potentials and pH[11]. Figure 1.2 shows the Pourbaix diagram, a potential-pH diagram of iron in an aqueous solution at 298 K.[11] The diagram designates the lowest free energy of metal or oxides in an area of each electrode potential and pH. The passivity of metal inhibits the active dissolution of metals by forming passive film, which limits ionic conductivity between a metal surface and electrolytes.

1.2.2 Types of passive film

Although most passive film consists of oxide on a metal, it does not always

exist in an oxide state. Passive film on metal could be classified into chemical passive film and mechanical passive film. A chemical passive film is an oxide film that results from the formation of a metal oxide- or other chemical species of passive film- that separates metal, as a diffusion barrier layer of a reaction product, from a corrosive environment.[12] Uhlig et al. suggested that the electrode potential of metals is moved in a positive potential direction by generating a protective, thin (10 – 30 Å), insoluble, and invisible layer on the metal surface.[13] The other chemical passive film was a chemically adsorbed layer of oxygen that covered a metal surface by replacing molecules of the adsorbed water.[14] The adsorbed layer decreases the anodic dissolution rate due to hydration of metal ions. The adsorbed oxygen increases anodic overvoltage and decreases the exchange current density of the metal dissolution reaction. In this case, it is difficult for the passive film to act as a diffusion barrier. However, the mechanical passive film is produced by a film that is slightly thicker than the chemical passive films that have a porous salt layer.[13] The mechanical passive film also acts as a barrier layer of reaction products against corrosive environments. Figure 1.3 shows five types of passive films, based on the following chemical and mechanical passive films:

- 1) Mono- or multi-layer of oxygen or other chemical species of adsorbed on metal surfaces
- 2) Three-dimensional barrier layer of oxide film
- 3) Barrier layer with a less protective layer
(i.e. passive film formed on cobalt in a neutral aqueous solution)
- 4) Barrier layer covered with a hydrated deposition layer
(i.e. passive film formed on iron in a neutral aqueous solution)
- 5) Barrier layer covered with a porous layer of the same composition
(i.e. anodized aluminum oxide film formed from acidic solutions)

In this dissertation, a passive film of stainless steels is formed by anodic potentiostatic polarization; consequently, passive films are thought to be present as a barrier layer inhibition of anions transfer between the electrolyte and metal substrate that is related to the types 2, 3 or 4.

1.2.3 Formation and composition of passive film

Various researchers have studied the formation of passive film on iron-based metals or alloys. Uhlig proposed that passive film is formed by an adsorption of monolayer oxygen on a metal surface by an oxidation of hydroxide ions.[15]



However, Evans and Nagayama suggested that the formation of passive film is related to the presence of a continuous thin layer of cubic iron oxide.[16,17] Figure 1.4 shows a schematic anodic polarization curve of pure iron in an acidic solution. At a potential higher than active-to-passive transition potential E_{a-p} , the current density of a pure iron electrode drastically decreases, indicating that the passive film formation is becoming more dominant than the dissolution of metal elements on the pure iron surface. The drastic decrease of the current density at the potential range from E_{a-p} to the primary passive potential E_{pp} is a sign of passive film formation on a stainless steel surface. Frankenthal revealed that the decrease of current density at the potential range from E_{a-p} to E_{pp} is due to the local presence of an oxygen monolayer on an iron surface. He also suggested that the decrease of the current density is due to the selective adsorption of oxygen on high surface active sites such as kink sites.[18] After some time has passed for anodic polarization or higher applied potential on a pure iron electrode, the pure iron surface is finally covered with a three-dimensional continuous oxide film of cubic iron oxide. An ellipsometric technique from Kruger revealed this oxide film that forms on pure iron.[19] The growth of the oxide film obeys a logarithmic rate law, and the thickness of the oxide film is dependent on an applied potential on a pure iron electrode.[19] Nagayama et al. also revealed the similar growth process of a pure iron surface in a pH 8.4 borate buffer solution, by using a cathodic reduction of the passive film formed on the pure iron surface.[17]

The passive film of iron in an aqueous solution is classified into a three-dimensional oxide film. Many researchers agree that a passive film formed on an iron surface has a bi-layer structure with a thickness ranging from 10 Å to 30 Å. [17-19] The inner Fe_3O_4 layer on an iron surface and the inner Fe_3O_4 layer are connected with the outermost $\gamma\text{-Fe}_2\text{O}_3$ layer in the passive film. Those of inner and outermost oxides have a face-centered cubic structure with a lattice parameter of 8.3 Å and 8.4 Å for $\gamma\text{-Fe}_2\text{O}_3$ and Fe_3O_4 , respectively.[20] Nagayama et al. suggested that there is a non-uniform distribution of iron cations and oxygen anions in the oxide film that is formed on iron.[17] They revealed that the outermost layer of the passive film is depleted by iron cations, because of a valence state of iron cations that is higher in the outermost layer than it is in the innermost layer. Meanwhile, Pryor suggested that there is a defect concentration distribution in the homogeneous $\gamma\text{-Fe}_2\text{O}_3$ layer on the iron surface.[21] The higher donor levels of metal cations are in the innermost layer of the passive film, while the higher acceptor levels are in the outermost layer. Electro-neutrality is maintained by the negative electrons and positive holes in the outermost and innermost layers of the passive film, respectively. This charge distribution in the passive film makes it possible to form a thin passive film with relatively large lattice parameters of the iron oxides.

The formation of passive film on stainless steel has an elemental enrichment in the passive film. Generally, there are two suggestions for understanding the enrichment of alloying elements during passive film formation. One is the selective dissolution of iron during passive film formation, and the other is oxygen adsorption on chromium to enrich alloying elements during passive film formation. When stainless steel is exposed to an acid

solution, a massive loss of the oxides and the metal substrates due to the selective dissolution of iron in stainless steel enriches chromium in the passive film. In alkaline solution, however, the selective dissolution of iron is difficult on stainless steel. Therefore, the outermost layer of the passive film becomes enriched in iron oxides.[22,23] Landolt confirmed the selective dissolution of iron and the enrichment of iron oxides on the outermost layer of the passive film on stainless steel in an acidic solution and an alkaline solution, respectively, by using an electrochemical quartz crystal microbalance (EQCM).[22] The enrichment of chromium in a passive film by the chemical adsorption of oxygen on chromium is related to the preferential adsorption of oxygen on metallic chromium, leading at first to the selective oxidation of the chromium. The cation gradients of iron and chromium are due to the faster diffusion of iron cations through the growth of a passive film. Therefore, the outermost layer of passive film becomes enriched in iron oxides, while chromium oxides are concentrated near the metal-passive film interface.[22,23] Olsson and Calinski confirmed the enrichment of iron oxide at the outermost passive film of Fe-Cr alloys, examined by X-ray photoelectron spectroscopy (XPS) and ion-scattering spectroscopy (ISS).[24, 25] The enrichment of alloying elements iron or chromium in simple Fe-Cr stainless steel meets for understanding composition distributions of iron and chromium oxides. However, these approaches are not in agreement with the distribution of other alloying elements in the passive film of stainless steel such as nickel, molybdenum, tungsten, and copper. Olefjord confirmed that chromium, nickel, and molybdenum are enriched in the outermost layer of the passive film on Fe-Cr-Ni-Mo stainless steel in an acidic solution.[26] An XPS analysis of Fe-Cr-Ni-Mo stainless steel in a neutral solution showed that there is a depletion of chromium in the inner region, followed by an enrichment of the central region of the passive films; the outermost layer is enriched in hydroxyl groups. [27] The formation, growth, and composition of the passive film are not yet completely understood; consequently, many corrosion researchers are interested in further study of the formation mechanism of passive film on stainless steel.

1.3 Passivity breakdown of stainless steel

A passive film effectively protects stainless steel against direct exposure to a corrosive environment. Stainless steel's resistance to corrosion is dependent on the stability of the passive film in an exposure environment. The degradation of passive film is associated with the instability of the local or entire passive film, leading to the exposure of the stainless steel bare metal surface. When passive film forms on a stainless steel brake in a corrosive environment, the degradation process of passive film comprise the following sequence of events (Figure 1.5):

- 1) Passive film formation
- 2) Change in the stability of the passive film
- 3) Removal of the passive film at local sites

- 4) Initiation of localized corrosion
- 5) Recovery of its passivity at the initiation sites of localized corrosion
- 6) Propagation of localized corrosion at the initiation sites of localized corrosion

The stability change and the removal of passive film are related to the degradation processes of passive film before the initiation of localized corrosion. The localized corrosion processes are related to the degradation processes of passive film after the initiation of localized corrosion.

1.3.1 Stability change and removal of passive film

The stability of passive film is dependent on the electrode potential of stainless steel, the solution temperature,[28,29] the pH,[30] and the concentration of aggressive anions in the exposure solution.[31] In an anodic polarization curve of stainless steel in an aqueous solution without the presence of aggressive anions, stable passive film can be formed in a passive region,[32] while passive film does not sustain its stability, and degradation of passive film occurs at a low or high potential of the active region or the transpassive region. Pallotta et al. revealed showed that the temperature dependence on the stability of passive film correlates with the defect generation during the oxidation of chromium cations by surrounding water molecules.[28] Moreover, the increase in solution temperature produces a thicker and more crystalline passive film, which becomes more stable than it would have been if it were formed in a lower solution temperature. Ferreira et al. also confirmed that an increase in the temperature of the solution for passive film formation affects the thickness of the passive film and the doping densities.[29]

The pH solution also affects the stability of passive film. Carmezim et al. investigated the electrochemical behavior of passive films in pH solutions from acidic to alkaline solutions, and revealed that doping densities in passive film increased when the pH solution decreased. The films were enriched in iron cations, whereas chromium cations decreased with a decrease in the pH solution.[30]

The presence of aggressive anions also makes passive film instable and eventually results in a localized corrosion on stainless steel.[35-39] Although a conclusive analysis of the chloride content of passive film is quite difficult to achieve due to the thin nature of passive film, various researchers have made suggestions concerning the effects of aggressive anions on the defect generation in the passive film.[33,34] The degradation models of passive film have been discussed using three main models concerning the presence of aggressive anions.[40] The adsorption model[41,42] is associated with the adsorption of aggressive anions on the passive film. The adsorbed anions transfer metal cations to the electrolyte by forming a metal cation complex on the film. As a result, the passive film is defective; eventually, it is thinned and removed. According to the penetration model,[43,44] the depassivation of metal is due to the transfer of aggressive anions through the passive film

to the metal surface. The adsorbed and/or contaminated anions introduce higher ionic conductive paths through the film, leading to a rapid release and removal of metal cations. The passive film breakdown model [45,46] is related to the mechanical breakdown of the film. The adsorption of aggressive anions on the passive film reduces surface tension, resulting in a mechanical breakdown. As a result, the stability change in passive film in the presence of aggressive anions is primarily based on the adsorption of aggressive anions onto passive film.

The adsorption of an anion is associated with its polarizability when it is adsorbed on metal cations.[47] Polarizability (deformability) shows a degree of polarization that occurs when ions or molecules experience a strong electric field.[47] When an ion is placed in a strong electric field, its electron shells (charge clouds) deform. The net shift in the internal charge produces a dipole, consisting of effectively separated positive and negative charges. The dipole produces an opposite electric field in order to cancel the electric field affecting it. At this point, the ion is considered polarized. Table 1.1 gives values for the polarizability of some ions, estimated from molar refractions.[47] Polarizability increases with ionic size (principle quantum number, n_p) and decreases with effective nuclear charge.[47] Therefore, the polarizability of sulfur ion is large ($n_p = 3$), and that of halides (I^- , Br^- and Cl^- for $n_p = 5, 4$ and 3 , respectively) is smaller; their effective nuclear charges are also smaller than that of sulfur ions. The value of polarizability indicates how an anion deforms when adsorbed as solvating ligands onto a cation or in the double layer of a metal electrode. Consequently, it is expected that the deformable anion's electron charge cloud is ready to overlap that of a metal cation. The higher the polarizability of the anion, the stronger the adsorption of the anion onto cations of a metal surface. Although there have been many investigations of the localized corrosion of stainless steel with a concentration of aggressive anions, there is still lack of clarity concerning the stability change of passive film in the presence of an infinitesimal amount of aggressive anions, because it is difficult to obtain information from *ex-situ* or macro-scale analyses.

Table 1.1 Polarizability of some anions[47]

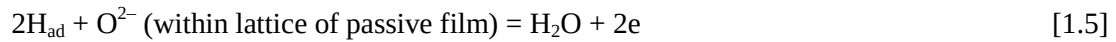
Ion	Polarizability / $\text{mm}^2 \text{mol}^{-1}$
S^{2-} , Sulfide	2200
I^- , Iodide	1910
HS^- , Hydrogen sulfide	1330
Br^- , Bromide	1250
Cl^- , Chloride	890
O^{2-} , Oxide	770
OH^- , Hydroxide	490
F^- , Fluoride	260

1.3.2 Removal of passive film

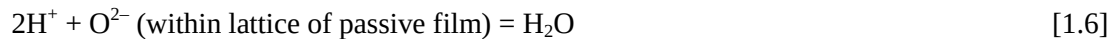
Without aggressive anions, the passive film of stainless steel is protective and chemically inert in specific environments, such as neutral or alkaline solutions.[48-50] However, when passive film is exposed to an acidic solution, reductive dissolution can be originated by chemical and/or electrochemical dissolution. This dissolution of passive film is associated with the electrical properties of passive film, as well as the composition of stainless steel substrate. For example, when the semi-conductive passive film passes electrons from the film to electrolytes, the protons in the acidic solution can be reduced to hydrogen:



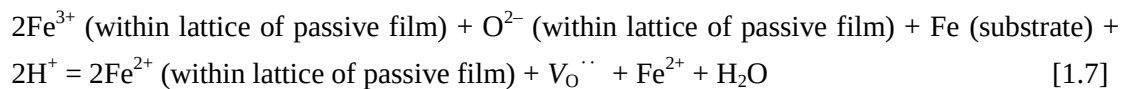
The above reaction accompanies the following oxidation reaction of an oxygen anion being moved from the lattice of passive film to an electrolyte:



Therefore, the overall reaction is as follows:



The above reactions spontaneously occur with a negative value of chemical free energy change. These reactions also satisfy the vacancies or high lattice energy of oxygen anions in passive film.[51] The removal of oxygen anions is accelerated by the high mobility of protons in the passive film lattice.[52] Moreover, removing oxygen anions also promotes the number of cations in the passive film lattice, such as Fe^{2+} or Cr^{3+} . [51,52]



The reductive dissolution of Fe(III) oxide involves the combination of the reduction of hydrogen and the production of oxygen vacancies in passive film in order to form either hydroxyl ions or water molecules, which pass into the solution. The Fe^{3+} ion is removed directly to the solution as Fe^{2+} , or reduced to Fe^{2+} in the passive film.

1.3.3 Initiation of localized corrosion

The localized corrosion of stainless steel is described as a corrosion event at a local site on a stainless steel surface, comprising the local dissolution of a bare stainless steel surface after the removal of passive film. When aggressive anions such as chloride ions are

present in an aqueous solution, it is possible that localized corrosion will begin. Crevice corrosion, a type of localized corrosion, arises from differential aeration within a narrow crevice gap with a small anodic area and a large cathodic area in a solution containing chloride ions. The occluded narrow crevice rapidly consumes oxygen in the gap and accumulates metal cations, because of the reduction of oxygen and the oxidation of the stainless steel:



The hydrolysis reaction of the dissolved metal cations produces protons in the crevice:



Chloride ions accumulate in the crevice in order to maintain charge valence where the concentration of protons is high. Finally, the accumulated chloride ions increase the solution resistance, which in turn increases the IR drop between the local anode and cathode areas near the local sites. The high IR drop shifts the local electrode potential to a negative direction of the active region. The local sites are actively dissolved, and crevice corrosion initiates. Pitting corrosion, another type of localized corrosion, is associated with a generation of “pit” on a metal surface. Pit is defined as a hole with a surface diameter that is smaller than that of its depth. The pitting corrosion of stainless steel occurs on a stainless steel bare surface after the local removal of passive film.

1.3.4 Repassivation or propagation of localized corrosion

After the initiation of localized corrosion at a local site on stainless steel, it is possible to recover its passivity. When there is a sufficient current for concentrating metal cations in order to form oxide or hydroxide flows to the initiation of localized corrosion sites, the local electrode potential shifts from an active region to the primary passivation potential E_{pp} , indicating that the passivation is progressing in the local sites. A current sufficient for concentrating metal cations or hydroxide ions in order to form oxide or hydroxide, is necessary for recovering passivity in the local sites. The increase of the anodic current in the local sites or a decrease in the limiting current for oxide or hydroxide layer formation makes it possible to recover its passivity in the local sites. However, if the local site cannot be repassivated, the localized corrosion of stainless steel might propagate. The destroyed localized corrosion site, containing a pit inside, sustains a small anode with a large cathode area outside the occluded pit. The large cathode area and small anode area increase the anodic reaction rate in the pit, lowering the pH and the accumulation of chloride ions. A combination of chloride ions and acidic solution prevents repassivation. The local pH value of the

propagated pit inside measured between -0.1 and 0.3 . [53,54] The increase in the rate of dissolution at anodic sites increases the migration of chloride ions, resulting in a generation of HCl with an autocatalytic propagation of the pit:



These electrochemical and chemical processes continue until the surface of stainless steel is perforated. In general, the repassivation in the localized corrosion site occurs at a potential below E_p , while the propagation of localized corrosion is dominant above E_p . Knowledge of cyclic potentiodynamic polarization is important for understanding the localized corrosion of stainless steel; however, this measurement is not the only parameter for understanding localized corrosion due to its various shortcomings. One of the limitations of this measurement is the occurrence of many propagations before the reversing of the anodic scan direction, because E_r or E_p can be changed according to the extent of localized corrosion during the anodic polarization. [55] Additional information and more comprehensive research are necessary for more thoroughly understanding the localized corrosion of stainless steel.

1.4 Previous investigations of the localized corrosion of stainless steel

A number of studies have been conducted in order to better understand the localized corrosion of stainless steels. Table 1.2 shows various factors related to localized corrosion initiation or propagation in various types of stainless steels.

Table 1.2 Localized corrosion initiation or propagation factors on stainless steels

Type of stainless steel	Localized corrosion factor	References
Austenitic	Inclusion	56
	Precipitates (carbide)	57
	Chloride	58
	Solution Temperature	59
	pH	60
Ferritic	Inclusion	61
	Precipitates (carbide)	62
	Chloride	63
	Temperature	64
	pH	65
Martensitic	Chloride	66
	Temperature	67

Duplex	Inclusion	68
	Secondary phase	69
	Chloride	70
	Temperature	71
	pH	72
Precipitation hardened	Precipitates (carbide)	73
	Chloride	74

The majority of researchers agree that localized corrosion of stainless steel begins at local sites of defective passive film or at heterogeneous sites on stainless steel substrate, which are inclusions or precipitates of stainless steel in solutions containing chloride ions. The localized corrosion of stainless steels is susceptible to aggressive anions at sites of sulfide inclusions in chloride-containing aqueous solutions. Although there are many factors involved in the occurrence of localized corrosion in stainless steel, a localized corrosion process is closely related to local chemical and/or electrochemical reactions at sulfide inclusion and initiation and/or propagation of localized corrosion by chloride ions. However, the detailed information concerning the contemplated localized corrosion process of the stability change of passive film, and the initiation or propagation of localized corrosion, have not yet been clarified in research concerning this issue, as described later on.

1.5 Sulfide inclusions in stainless steel

Carbon (C), silicon (Si), phosphorous (P), sulfur (S), and manganese (Mn) are the five main alloying elements of iron-based alloys. Although the iron is balanced by elements of stainless steel, these five elements must be contained. During the solidification of stainless steel from ca. 1500°C, elemental sulfur forms manganese sulfide (MnS), which has a higher melting point of over 1600°C, before the solidification of stainless steel phases. Consequently, the presence of MnS is inevitable in stainless steel. Table 1.3 shows the physical properties of MnS.

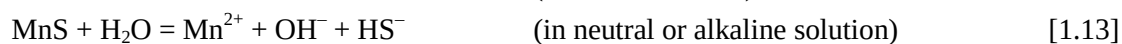
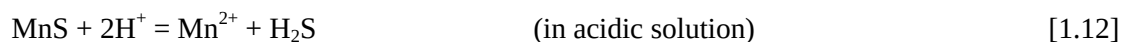
Table 1.3 Typical data for manganese sulfide (MnS) [75]

Molar mass / g mol ⁻¹	Density / g cm ⁻³	Melting point / °C	Solubility in water (18°C) / ppm	Crystal structure	Coordination geometry
87.00	3.990	1610	4.700	Cubic	Mn ²⁺ (Octahedral) S ²⁻ (Octahedral)

1.5.1 Effects of MnS inclusion on breakdown of passivity in stainless steel

MnS inclusion is well known as an initiation site of breakdown of passivity in stainless steel, and many researchers have investigated breakdown of passivity near MnS inclusion. Those of researchers focused on electrochemical and/or chemical reactions of MnS release S species such as SO_4^{2-} , HSO_3^- , $\text{S}_2\text{O}_3^{2-}$, S and S^{2-} . Most of the researchers have concluded that the released S species change the composition of the local solution contiguous to the inclusion, and the presence of aggressive S species result in the initiation of pitting corrosion in stainless steel. [76-79] However, they did not consider the primal S species released from MnS inclusion. The effect of the primal S species on localized corrosion has never been studied.

It is considerable that electrochemical or chemical reaction of MnS at the first time of exposure in aqueous solution is a clue for understanding the primal S species from MnS. When MnS is exposed in an aqueous solution, a small amount of MnS on stainless steel surface dissolves because its solubility in water is 4.7 ppm at 18°C (Table 1.3) as follows:



Furthermore, the dissociations of H_2S and HS^- in aqueous solutions are as follows:



The values of pK_a for Eqs. 1.14 and 1.15 are 7.05 and 19.0, respectively, at 25°C.[80] The dissociation of HS^- is negligibly small and H_2S generates mainly protons during its dissociation. Thus, the primary dissolution reaction of MnS shortly increases pH of the local solution near the MnS. Figure 1.7 represents a potential-pH diagram for the stable equilibrium of the water-sulfur system at 25°C. [81] The chemicals are considered as seven forms in the system: H_2S , HS^- , S^{2-} , S^0 , HSO_4^- , SO_4^{2-} and $\text{S}_2\text{O}_8^{2-}$. Although HS^- is stable in an alkaline solution with an active potential range under $-0.6 V_{\text{SHE}}$, the presence of HS^- can affect some electrochemical and/or chemical reactions on stainless steel.

1.6 Chloride ions and the localized corrosion of stainless steel

Stainless steel is susceptible to localized corrosion when it is exposed to solutions containing chloride ions. If stainless steel is uniformly corroded, it is easy to estimate its lifetime; however, this is difficult to accomplish in cases where localized corrosion occurs on stainless steel. Consequently, researchers have used many different electrochemical methods to try to better understand localized corrosion on stainless steels. Although conventional electrochemical methods have provided some localized corrosion

parameters, the localized corrosion of stainless steel should be comprehensively studied within the localized corrosion parameters obtained by conventional electrochemical methods. Since localized corrosion is a competitive reaction with repassivation and a propagation of localized corrosion, additional kinetic parameters are necessary for elucidating the initiation and/or a propagation of localized corrosion.

1.7 Anion-generating system

It is well known that localized corrosion of stainless steel is initiated and/or propagated in a presence of aggressive anions such as chloride and sulfide ions. During localized corrosion on stainless steel, concentration distribution of chloride ion at localized corrosion sites does not uniform. Concentration of aggressive anions should be changed and in a non-steady state condition in the occluded cell of the localized corrosion sites. Therefore, local generation of aggressive anions such as chloride ions on metal surface has been attempted. Heurtault et al. injected acidic chloride solution on 316L stainless steel surface.[82] The solution releasing system is difficult to control the amount of released chloride ions as well as protons on metal surface. Casillas et al. reported electrochemical generation of bromide ions at an active site of passive film on titanium surface.[83] Wipf suggested to generate chloride ion through electrochemical reaction of trichloro acetic acid, and applied to pit initiation or propagation on stainless steel surface.[84] Fushimi et al. proposed a chloride ion generation technique, which is called as liquid-phase ion gun (LPIG), and applied to local breakdown of iron surface.[85] This technique is based on a use of microelectrode, a type of scanning electrochemical microscopy (SECM), which is effective for controlling the release of infinitesimal anions to a local space in the solution. The LPIG is a useful for controlling the generation of chloride ions. Application of the LPIG to release aggressive anions such as sulfide and chloride ions on stainless steel can be expected to elucidate the mechanism and/or kinetics of depassivation of the stainless steel surface.

1.8 Purpose of dissertation

Localized corrosion of stainless steel initiates or propagates from a manganese sulfide (MnS) inclusion in an aqueous solution containing chloride ions. Moreover, localized corrosion of stainless steel is dependent on the degradation behavior of passive film near a MnS inclusion. The passive film of stainless steel does not exist on MnS, and passive film near MnS inclusion degrades by the S species released from MnS. The S species afterwards initiates or propagates localized corrosion near the MnS inclusion. Various types of S species have been discussed for initiation or propagation of localized corrosion in stainless steels.[76-79] Most researchers agree that MnS releases various S species by its electrochemical and/or chemical reactions, and that those S species finally lead to the

initiation or propagation of localized corrosion in stainless steel. Before the progression of localized corrosion on stainless steel, the steps of the degradation process of passive film occurs in the same order as that of the stability change of passive film, the removal of the passive film, and the initiation or propagation of localized corrosion in stainless steel substrate. Therefore, the initial degradation process of passive film is related to the stability change of passive film. The role of the S species associated with stability-change in passive film has not been clarified due to lack of information for the primal S species and HS^- , released to from the MnS inclusion. It is vital to clarify the stability change of passive film in the primal S species and the HS^- , in order to elucidate the degradation of passive film formed on stainless steel near MnS. Localized corrosion initiation and/or a propagation reaction are closely related to chloride ions. Several studies have proposed localized corrosion parameters related to pitting corrosion by using various electrochemical techniques. These methods are useful for investigating the localized corrosion behavior of stainless steels in solutions containing chloride ions. However, it is difficult to investigate certain kinds of localized corrosion of stainless steel (such as pitting corrosion) using only one electrochemical method, because every method has shortcomings in dealing with localized corrosion. Consequently, it is necessary to develop other electrochemical-based techniques in order to obtain more detailed, accurate information concerning the localized corrosion of stainless steel. Since sulfide and chloride ions affect the complicated process of the degradation of passive film and localized corrosion on stainless steel, it is necessary to investigate the role of each anion in the degradation of passive film-especially the influences of sulfide and chloride ions on the stability of passive film and the initiation and/or propagation of localized corrosion, respectively. The microelectrode technique of generating a chloride anion system, liquid-phase ion gun (LPIG), is a powerful technique for controlling a release of chloride ions into a local area in an aqueous solution. This technique has been used to investigate local breakdown behavior on iron, stainless steel, and copper surfaces.[82,85,86] The development of LPIG techniques such as the sulfide ions generation system would be a useful technique for investigating the degradation of passive film formed on stainless steel. In this dissertation, the LPIG system is developed in order to generate aggressive anions, and it was applied to the degradation of passive film on stainless steels. This dissertation consists of six chapters. The present chapter, Chapter 1, provides the dissertation objectives and the reported background knowledge concerning stainless steel, passivity, degradation of passive film, and localized corrosion. Chapter 2 introduces the methodologies for using the equipment discussed in this dissertation. Chapters 3-5 cover the development and application of LPIG, and Chapter 3 deals with the development of the LPIG system as a sulfide ions generator and its application on a silver surface. Chapter 4 investigates the passivity of type 316L stainless steel in the presence of hydrogen sulfide ions. Chapter 5 evaluates localized corrosion resistance parameters obtained by using the chloride ions generation LPIG system, and discusses other localized corrosion parameters obtained from conventional electrochemical methods. Finally, Chapter 6 is a conclusion of this dissertation.

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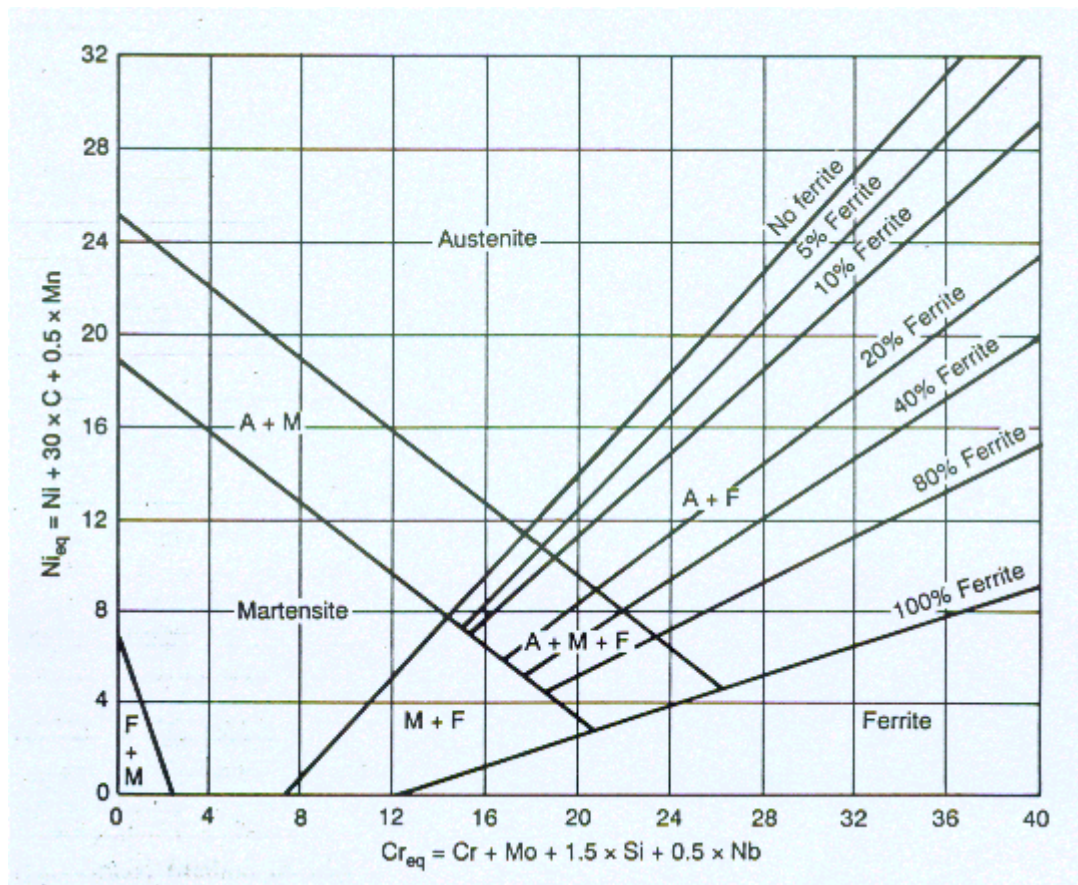


Fig. 1.1

Schaeffler diagrams.

Cr equivalent = Cr wt% + Mo wt% + (1.5Si wt%)
+ (0.5Nb wt%),

Ni equivalent = Ni wt% + (30C wt%) + (0.5Mn wt%).

F=ferrite phase, A=austenite phase, M=martensite phase.

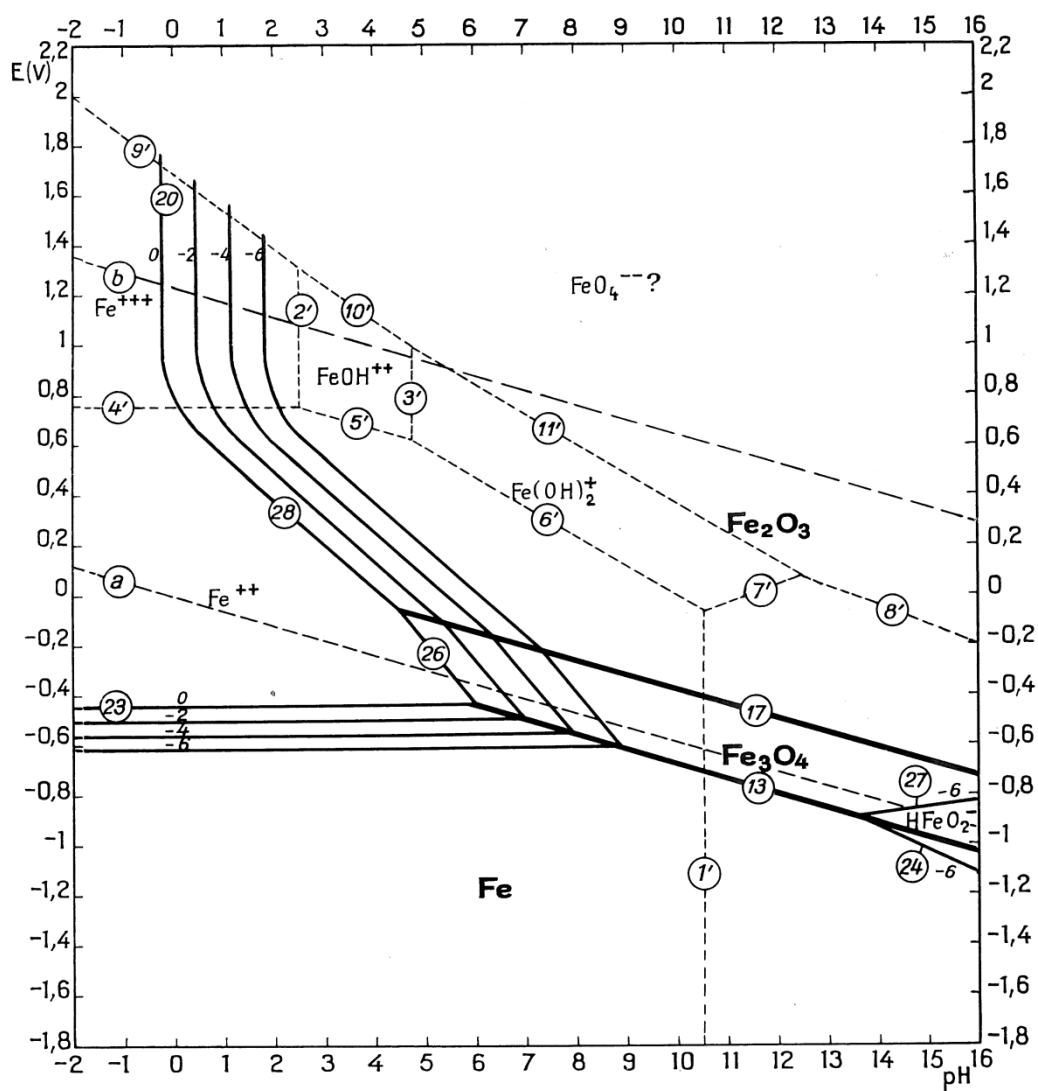


Fig. 1.2

Potential-pH diagram for Fe-H₂O system at 298 K. The concentrations of soluble species are $1 \times 10^{-6} \text{ mol kg}^{-1} (\text{H}_2\text{O})$. [11]

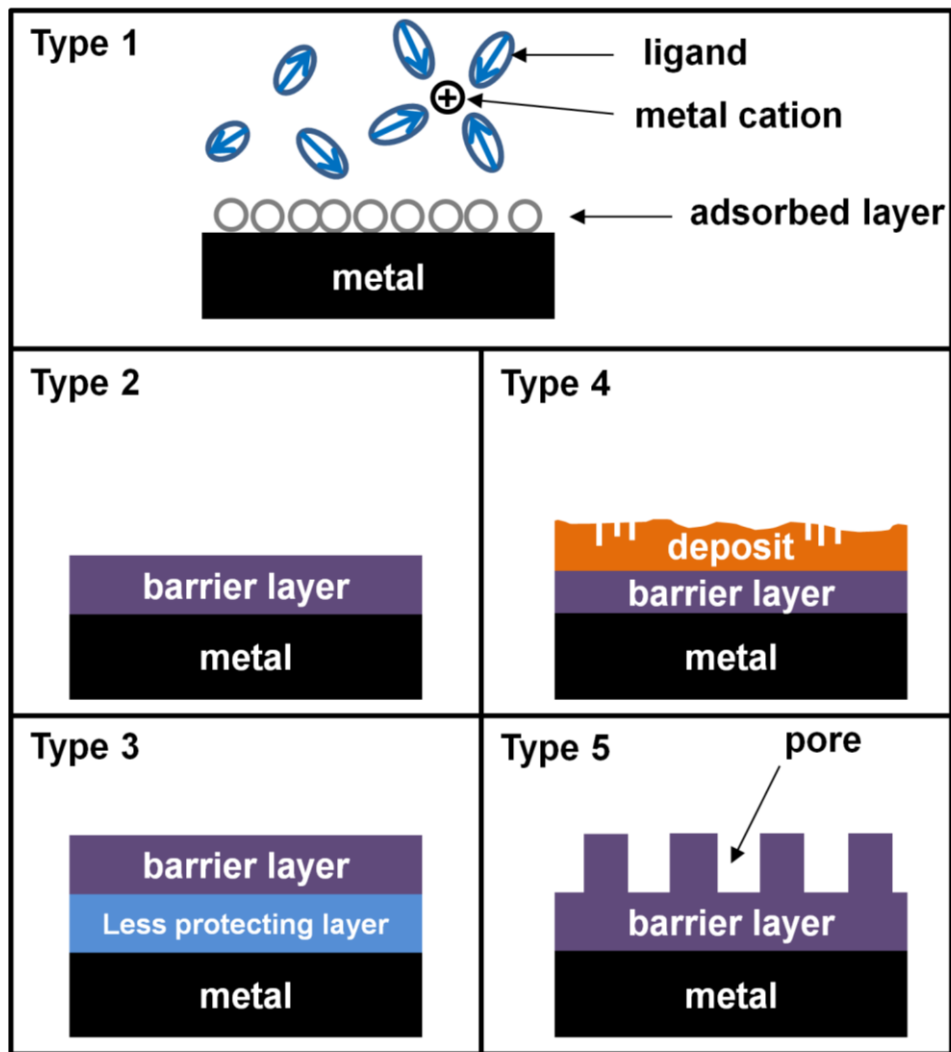


Fig. 1.3 Schematic illustration of typical five types of passive film.

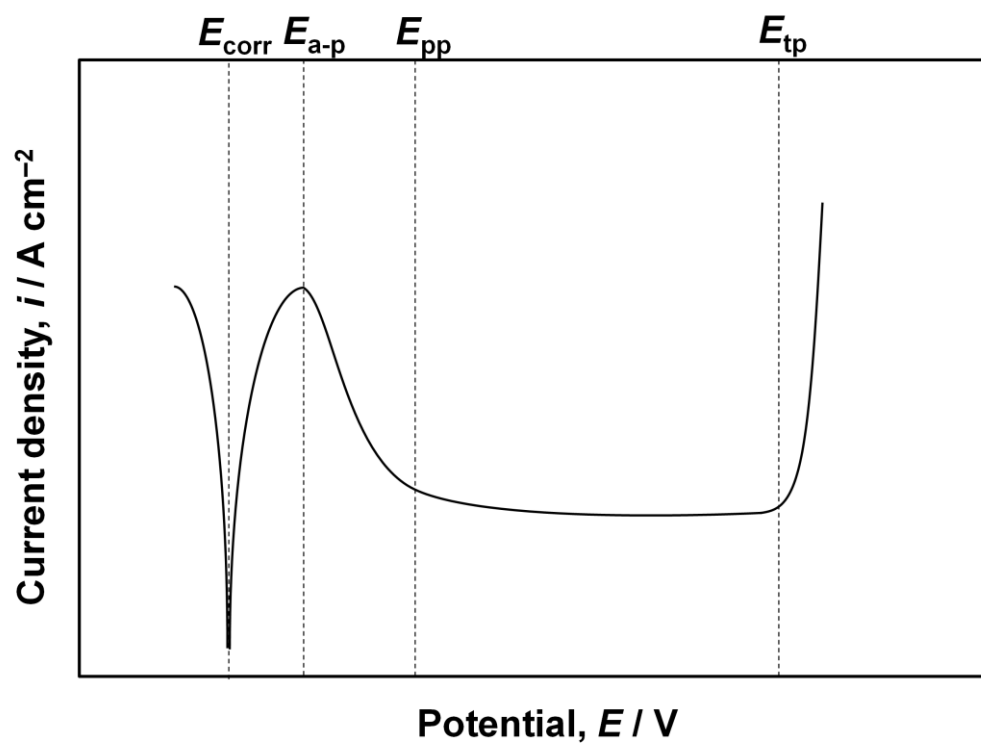


Fig. 1.4

Schematic diagram of potentiodynamic polarization curve of stainless steel in an acidic solution.

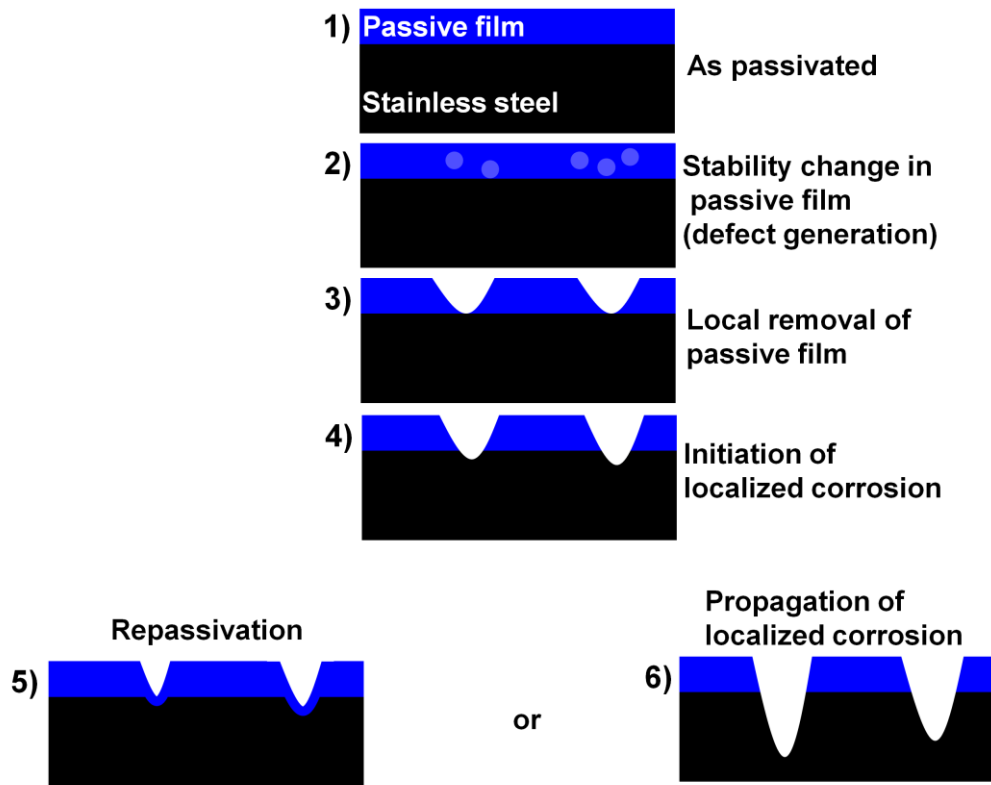


Fig. 1.5

Schematic diagrams for process of degradation of passive film and localized corrosion; (1) as formed passive film on stainless steel, (2) stability-change in passive film by generating defect levels, (3) local removing of passive film, (4) local dissolution of stainless steel bare surface exposure after the removing of passive film (initiation of localized corrosion), (5) repassivation of the localized corrosion and (6) propagation of localized corrosion.

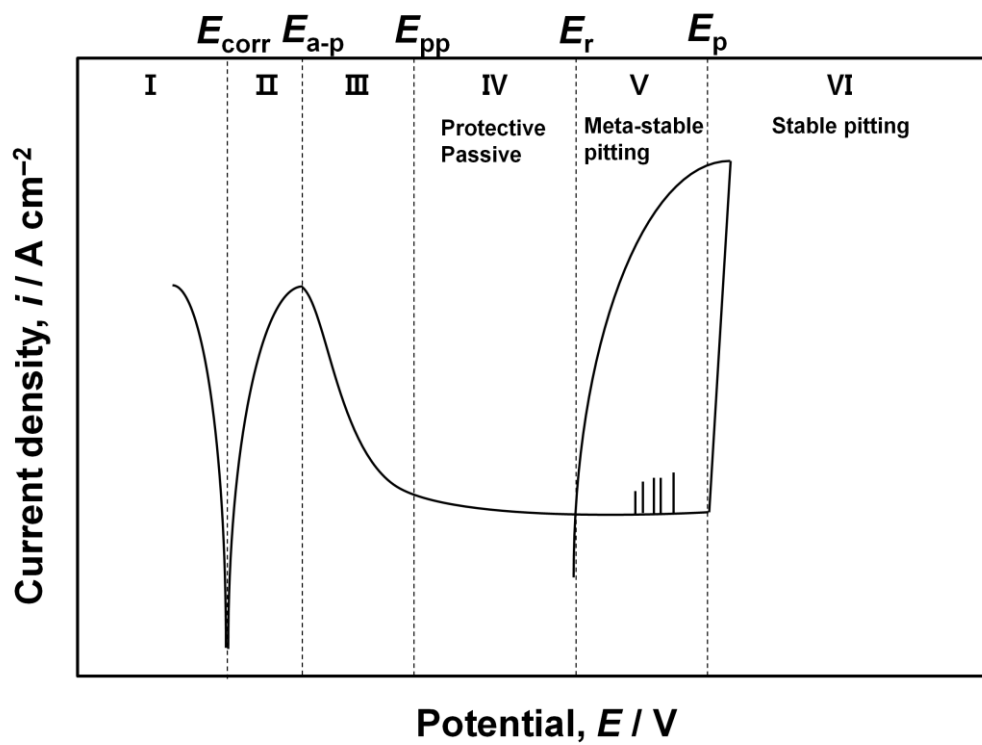


Fig. 1.6

Schematic diagram of potentiodynamic polarization curve of stainless steel in an acidic chloride solution.

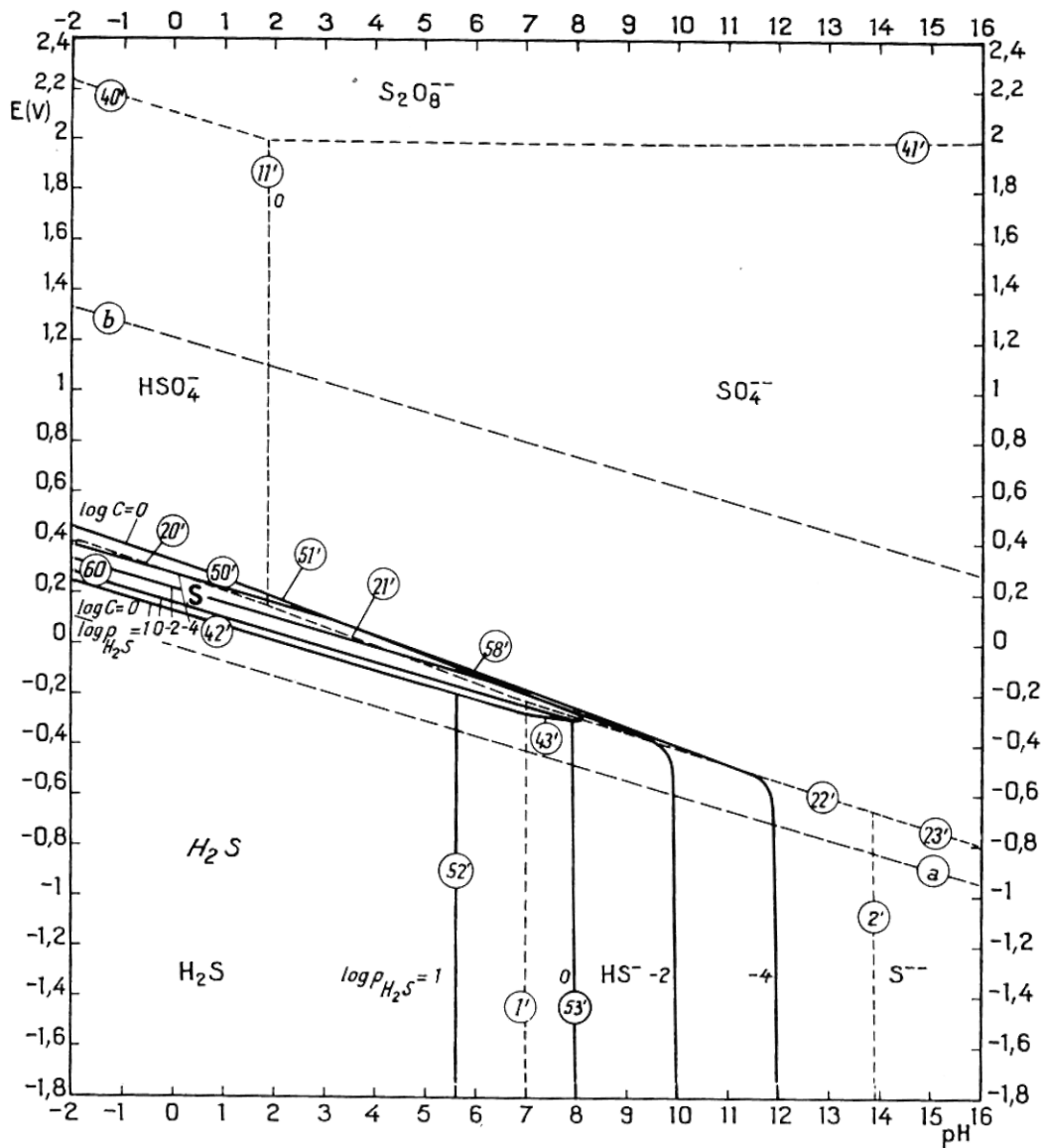


Fig. 1.7

Potential - pH diagram for S-H₂O system at 298 K. The concentrations of soluble species are $1 \times 10^{-6} \text{ mol kg}^{-1} (\text{H}_2\text{O})$. [81]

Chapter 2 Experimental set-ups and procedures

2.1 Preparation of electrodes

2.1.1 Liquid-phase ion gun (LPIG) microelectrode

A silver wire (AG-401385, Nilaco) with a purity of 99.99% and a diameter of 500 μm was embedded in a glass capillary (#1-000-1000, Drummond Scientific Company) with an outer diameter of 1 mm using an epoxy resin (Epofix resin 40200030, Struers). The cross section of the silver-glass capillary tip was used as a silver microelectrode after mechanical polishing with SiC papers down to 4000 grit and rinsing with distilled water. Figure 2.1 shows an optical microscopic image of the tip of the fabricated silver microelectrode. After grinding the silver microelectrode, the microelectrode was polarized at 0.3 V_{RHE} (reversible hydrogen electrode potential) in 0.1 mol dm^{-3} Na_2S solution (pH 13.4) until the electric charge of 10 mC, $Q_{\text{LPIG,charge}}$, was consumed in order to forming silver sulfide layer on the silver microelectrode. The electrode potential was converted in to reversible hydrogen electrode potential as follow:

$$V_{\text{RHE}} = V_{\text{SSE}} - 0.197 - 0.05916\text{pH} \quad [2.1]$$

On the other hand, the silver microelectrode was polarized at 0.3 V_{SSE} (silver/ silver chloride electrode potential saturated in KCl) in 0.1 mol dm^{-3} NaCl solution (pH 5.8) until the electric charge of 10 mC, $Q_{\text{LPIG,charge}}$, was consumed in order to forming silver chloride layer on the silver microelectrode.

2.1.2 Silver substrate electrode

A silver plate (AG-403518, Nilaco) with a purity of 99.98% and a surface area of 0.80 cm^2 was prepared as a substrate electrode. The silver substrate was mounted in an epoxy resin mechanically ground with SiC papers down to 800 grit and then rinsed with distilled water.

2.1.3 pH and anion concentration sensing microelectrodes

Tungsten wire (W-461167, Nilaco) with a purity of 99.95% and silver wire (AG-401167, Nilaco) with a purity of 99.99%, both with diameters of 100 μm , were embedded in resin (64708865, Heraeus Kulzer) with a diameter of 25 mm as a substrate for estimating pH and anions concentration released from LPIG microelectrodes (sulfide ions or

chloride ions), respectively. The microelectrodes were mechanically ground with SiC paper down to 4000 grit and then rinsed with distilled water.

2.1.4 Stainless steel substrate electrodes

Four types of stainless steel were used. The first was type 316L stainless steel (782560, Nilaco) for investigating passivity behavior in a solution that contained sulfide ions. The other three types of stainless steel were prepared as substrate electrodes in order to evaluate localized corrosion resistance in solutions that contained chloride ions. They were types 430, 304 and 443 stainless steels (supplied from JFE Steel Corp.). The chemical compositions of the stainless steels that were used in this dissertation are shown in Table 2.1.

Table 2.1 Chemical compositions of stainless steels that were used in this dissertation

Type	Chemical composition (wt.%)							
	Cr	Ni	Mo	Ti	Cu	C	N	Fe
316L	16-18	10-14	2.0-3.0	-	-	<0.03	<0.10	Bal.
430	16	-	-	-	-	0.05	0.03	Bal.
304	18	8.0	-	-	-	0.05	0.03	Bal.
443	21	-	-	0.3	0.4	0.01	0.01	Bal.

2.1.4.1 Metallography of stainless steels

Specimen preparation.— Stainless steels were embedded in resin with a diameter of 25 mm. The electrodes were mechanically ground with SiC paper down to 4000 grit, polished with a colloidal silica, with a grain size of approximately 0.04 μm (OP-S 40700001, Struers). The specimens were electrochemically etched in a 10 wt.% oxalic acid aqueous solution for platinum counter electrode and specimen anode connected to a battery-driven signal source (SS7012, HIOKI) at 10 V for 1 to 10 min according to ASTM E 407-07[1] and then rinsed with ethanol and distilled water. The microstructural characterization was made by scanning electron microscopy (SEM).

Surface morphology of stainless steels.— Figure 2.2 shows SEM images of the surface of stainless steel specimens after electrolytic etching. After the etching, the grain boundaries are attacked and appeared as bright lines in the microstructure. The stainless steel surfaces are polycrystalline materials. Twin boundaries are seen only in Figures 2.2a and 2.2c because of their crystal structure as face-centered cubic structure, while Fig. 2.2a for type 316L stainless steel shows many twin boundaries due to its plastic deformation during a fabrication process (extrusion molding method). The body-centered cubic structure of ferritic

stainless steel does not contain twin boundaries. The pit-like corroded surface of Figure 2.2d is due to the relatively greater susceptibility to attack by oxalic acid with its small content of chromium in type 430 of stainless steel than that of the other stainless steels.

Determination of the grain-size of stainless steels.— Grain size and average grain diameters of the stainless steels can be determined by the ASTM E 112-96 standard test methods for determining average grain size with the lineal intercept method [2]. The grain size is specified by the number n_g in the expression:

$$N_g = 2^{(n_g - 1)} \quad [2.2]$$

where N_g is the number of grains per square inch (in an area of $1 \text{ in}^2 = 0.0645 \text{ mm}^2$), when the sample is examined at a magnification of $\times 100$. The grains cut by the circumference of the circle are taken to be as one-half of the number. Generally, a material with a higher n_g value is classified as fine-grained. The grain size numbers obtained for the stainless steels are shown in Table 2.2. Stainless steel of type 316L has a finer grain than the other stainless steels types.

Table 2.2 **ASTM grain size number of the stainless steels used**

Type	ASTM grain size number, n_g
316L	9.86 ± 0.03
430	9.07 ± 0.03
304	9.11 ± 0.05
443	9.07 ± 0.01

Other approach to determining the grain size of stainless steels is by drawing a line in the photomicrograph, and counting the number of grain-boundary intercepts, N_l , along the line. This method offers an advantage to the ASTM grain size that does not offer direct information of the actual grain size. The mean intercept is given as [1]:

$$l = \frac{SL}{N_l M} \quad [2.3]$$

where S is a constant ($S = 1.5$ for typical microstructure), L is the length of the line and M is the magnification in the photomicrograph of the stainless steels. The mean lineal intercept l refers to the actual grain size. The grain sizes of stainless steels are shown in Table 2.3.

Table 2.3 Grain size of the stainless steels as determined by lineal intercept method

Type	Mean lineal intercept l , μm
316L	13.1 ± 1.50
430	22.6 ± 1.37
304	22.2 ± 3.21
443	22.6 ± 1.14

It is clear that type 316L stainless steel has 58% finer grains than type 430, 304 or 443 stainless, whereas type 430, 304 and 443 stainless have similar sizes of grains. Thus, it is believed that the effect of grain size on localized corrosion of 403, 304 and 443 stainless steels is negligible.

2.1.5 Scanning electrochemical microscope (SECM) tip microelectrode

A platinum wire (PT-351095, Nilaco) with a purity of 99.98% and a diameter of 30 μm was thermally sealed into a glass capillary (#1-000-1000, Drummond Scientific Company) and was used as a tip microelectrode of SECM. The tip of the probe electrode was mechanically polished with a diamond whetstone (#5000) on a turntable (Narishige Co., EG-400) and then rinsed with distilled water.

2.2 Characterization of SECM tip microelectrode

The platinum microelectrode is characterized before operating SECM measurements. Figure 2.3 shows typical cyclic voltammogram (CV) of tip electrode measured in deaerated pH 8.4 borate solution containing $1 \times 10^{-3} \text{ mol dm}^{-3}$ hydroxymethylferrocene (ferrocenemethanol, FcMeOH) when the platinum tip electrode with a diameter of 30 μm is ca. 2 cm far from the substrate surface. The cyclic voltammogram shows a sigmoid shape with a limiting current, $I_{t, \text{lim.}} = 4.01 \text{ nA}$, at potentials above 0.4 V_{SSE} . This limiting current is in a good agreement with that theoretically calculated for a microdisc electrode with a hemispherical diffusion layer. The theoretical limiting current, $I_{t, \text{lim. th.}}$ can be described as follows:[3]

$$I_{t, \text{lim. th.}} = 4nFDC_{\text{Fc}}a \quad [2.2]$$

where n is number of electrons participating in redox reaction from FcMeOH^+ to FcMeOH , and F is the Faraday constant, D is diffusion coefficient $7.0 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$, [4] and C_{Fc} is concentration of mediator FcMeOH, respectively. a is radius of tip electrode. The tip electrode current, I_t , changes depending on electronic properties of substrate electrode surface

because of a limitation of diffusion.[5,6] The value of I_t decreases above insulating substrate surface when the tip electrode approaches to the substrate electrode within a distance of a length of diffusion layer, because the reduction of FcMeOH^+ is difficult to occur on the insulating surface. Since it is difficult to supply FcMeOH from the outside of the tip electrode, the tip electrode is subjected to flowing small tip current compared to that flow in bulk solution. On the other hand, the value of I_t increases above an electronic conductor surface when the tip electrode approaches to the substrate electrode within a distance of a length of diffusion layer, because the reduction of FcMeOH^+ easily progresses on the conductor surface. Since it is easy to supply FcMeOH from the outside of the tip electrode, the tip electrode is subjected to flowing large tip current compared to that flow in bulk solution.

2.3 Set-ups of LPIG, pH, anion sensing electrodes and SECM

In all experimental set-ups of the LPIG microelectrode, pH, anion sensing electrodes and SECM, an electrochemical cell of an acrylic cell of 100 cm³ in volume with the LPIG microelectrode for working electrode, a platinum counter electrode and an Ag/AgCl/sat. KCl reference electrode was used. Moreover, an optical microscope with a resolution of ca. 5 μm and types of x-y-z stepping motor stage (SGSP20-35, Sigma Koki) with an incremental motion of 0.1 μm were used to control the distance between the LPIG microelectrode and substrate electrodes.

2.3.1 LPIG set-ups

Two different types of LPIG set-up were used for generating aggressive anions. The one type of LPIG was applied for generating sulfide ions, while the other type of LPIG was used for generating chloride ions. The sulfide or chloride ions were generated by reducing silver sulfide or silver chloride layers, respectively, formed on silver microelectrode (section 2.1.1). In order to forming silver sulfide or silver chloride layer on silver microelectrode, silver microelectrode was polarized at 0.3 V_{RHE} or 0.3 V_{SSE} in 0.1 mol dm⁻³ Na₂S solution (pH 13.4) or 0.1 mol dm⁻³ NaCl (pH 5.8), respectively, until the electric charge of 10 mC, $Q_{\text{LPIG.charge}}$, was consumed.

The silver sulfide layer was potentiostatically or galvanostatically polarized in pH 8.4 boric-borate buffer solution in order to generate sulfide ions on substrates. Figure 2.4 shows schematic illustrations of the experimental set-ups for generating sulfide ions by potentiostatic polarization of LPIG. The LPIG microelectrode was located in the vicinity of the silver substrate electrode with an interelectrode distance of 125 μm . The system used a bipotentiostat (HAL-1512 mM2, Hokuto Denko), which independently controls the potentials of the LPIG microelectrode and the silver substrate electrode as independent working electrodes. Figure 2.5 shows the other LPIG set-up used for generating sulfide ions by

galvanostatic polarization. In this case, the LPIG microelectrode and stainless steel substrate electrode are independently controlled. The LPIG microelectrode, a working electrode, is connected to a battery-driven current source (SS7012, HIOKI), and the potential of the LPIG microelectrode was measured by an electrometer (R8240, Advantest) against the reference electrode. On the other hand, the substrate electrode was controlled as the other working electrode using a potentiostat (SP-150, Biologic). This LPIG set-up has two working electrodes, LPIG and substrate, which are separately connected to a current source and a potentiostat, respectively.

The chloride generation system is shown in Figure 2.6. The silver chloride layer covered with silver microelectrode and substrate electrode were used as two working electrodes with an interelectrode distance of 75 μm . The bipotentiostat independently controlled potentials of the LPIG microelectrode and the substrate electrode.

2.3.2 pH and anion sensing electrode set-up

Figure 2.7 shows set-up used for estimating solution pH and/or concentration of sulfide or chloride ions. The LPIG microelectrode was connected to the current source and an electrometer with counter and reference electrodes for generating sulfide or chloride ions. The LPIG microelectrode was galvanostatically or potentiostatically polarized using the battery-driven current source or bipotentiostat, respectively. The substrate tungsten and silver microelectrodes were connected to two electrometers in order to monitor their electrode potentials against the reference electrode during generation of sulfide or chloride ions from LPIG microelectrode.

2.3.3 SECM set-up

The set-up of SECM consists of the platinum (Pt) tip microelectrode specimen substrate electrode connected to the bipotentiostat and polarized independently for the stainless substrate electrode potential for a tip generation/substrate collection (TG/SC) mode. Simultaneously, the tip microelectrode was scanned in an area of 3000 μm square with an interelectrode distance of 20 μm . Figure 2.8 shows the SECM set-up used in this dissertation.

2.4 Chemicals and materials

Chemicals and pure metals used in this dissertation are listed in Tables 2.2 and 2.3, respectively. Chemicals with super-purified grade and Milli-Q water were used for all aqueous solutions at room temperature.

Table 2.4 Chemicals used in this dissertation

Chemicals	Chemical -maker	Assay / %	Usage
agar	KC*	-	Salt bridge
boric acid/ H_3BO_3	KC	99.5	pH 8.4 standard solution and electrolyte solution
disodium phosphate/ Na_2HPO_4	TOADKK	99.5	pH 6.9 standard solution
hydroxymethylferrocene/ $\text{C}_{11}\text{H}_{12}\text{FeO}$	TCI**	95.0	SECM mediator
monopotassium phosphate/ KH_2PO_4	TOADKK	99.5	pH 6.9 standard solution
oxalic acid/ HOOCCOOH	KC	99.5	etchant
potassium chloride/ KCl	KC	99.5	Salt bridge and saturation for AgCl reference electrode
potassium hydrogen phthalate/ $\text{C}_6\text{H}_4(\text{COOK})(\text{COOH})$	TOADKK	99.5	pH 4.0 standard solution
sodium chloride/ NaCl	KC	99.5	LPIG formation
sodium hydroxide/ NaOH	KC	97.0	pH 10.0 solution
sodium sulfide nonahydrate/ $\text{Na}_2\text{S}\cdot 9\text{H}_2\text{O}$	KC	95.0	LPIG formation
sodium sulfate/ NaSO_4	KC	99.0	Electrolyte solution
sodium tetra borate decahydrate/ $\text{Na}_2\text{B}_4\text{O}_7\cdot 10\text{H}_2\text{O}$	KC	99.5	pH 8.4 standard solution and electrolyte solution
sulfuric acid/ H_2SO_4	KC	96.0	pH 0.9 solution and electrolyte solution
*KC	Kanto Chemical Co. Inc.		
**TCI	Tokyo Chemical Industry		

Table 2.5 Pure metals used in this dissertation

Materials	Assay	Usage
silver wire	99.9%	LPIG fabrication
silver plate	99.9%	silver substrate electrode
platinum	99.98%	counter electrode

2.5 Surface analyses

The specimen surfaces were characterized by using X-ray ediffraction technique (XRD), scanning electron microscopy (SEM), transmission electron microscopy

(TEM), Auger electron spectroscopy (AES), X-ray photoelectron spectroscopy (XPS) and Raman spectroscopy. The specifications of the surface analyses are shown in Table 2.6, 2.7, 2.8, 2.9 and 2.10.

Table 2.6 Specification of XRD used in this dissertation

Model, Maker	X-ray Source	Rated tube voltage, current	Scan rate	Scan degree
RINT 2000 Ultima, Rigaku	Cu K α	40 kV, 20 mA	1 ° min ⁻¹	20 – 80 °

Table 2.7 Specifications of SEM and TEM used in this dissertation

Technique	Model, Maker	Accelerating Voltage	Resolution
SEM	JSM-6510LA, JEOL	10 kV	1 µm
TEM	Titan 80-300, FEI	300 kV	0.20 nm

Table 2.8 Specification of AES used in this dissertation

Model, Maker	Accelerating Voltage, Probe current	Probe diameter	Etching rate (Ar ⁺ source)
JAMP-9500F, JEOL	10 keV, 15 nA	30 µm	3.2 nm min ⁻¹
PHI-660, Physical Electronic	3 keV, 0.1 µA	1 µm	0.66 nm min ⁻¹

Table 2.9 Specification of XPS used in this dissertation

Model, Maker	X-ray Source	Excitation power	Detection area
JPS-9200, JEOL	Al K α	100 W (10 kV, 10 mA)	ϕ1 mm

Table 2.10 Specification of micro-Raman spectroscopy used in this dissertation

Model, Maker	Laser (frequency, power)	Spectra field	Laser spot size
XploRA, HORIBA	532 nm, 20 – 25mW	150 – 2800 cm ⁻¹	78.5 µm ²

2.6 Summary

Preparation procedures of LPIG electrodes, pH, anion sensing microelectrodes, SECM tip electrode and experimental set-ups were informed. SECM tip

electrode was successfully fabricated. The SECM tip electrode showed a microelectrode behavior in cyclic voltamogram with a sigmoid shape in solution containing a mediator. The theoretical limiting current is close to the obtained limiting current of tip microelectrode. The fabricated SECM tip electrode is possible to apply on investigation of local surface on a substrate electrode.

References

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- [6] A. J. Bard, F.-R. F Fan and M. V. Mirkin, *Electroanalytical Chemistry*, p. 243, Marcel Dekker, Inc., New York, (1994).

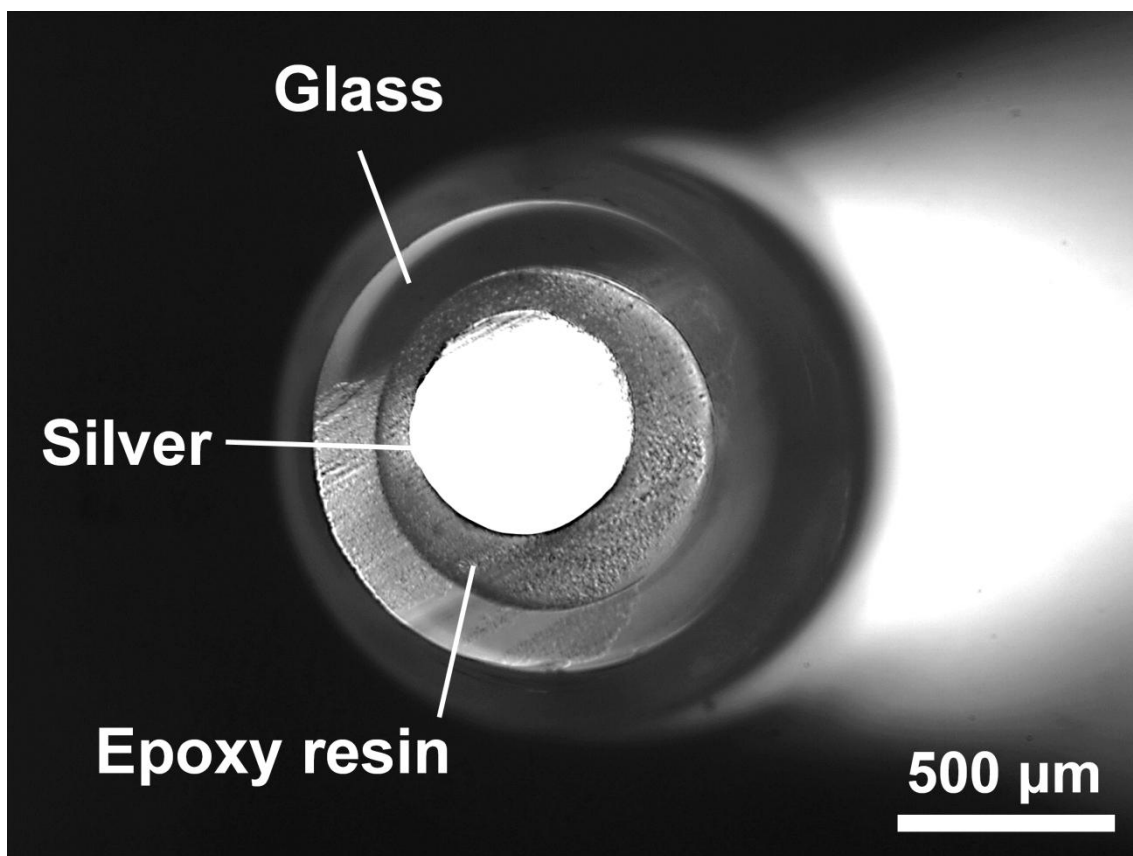


Figure 2.1

Optical microscopic top view image of a silver microelectrode.

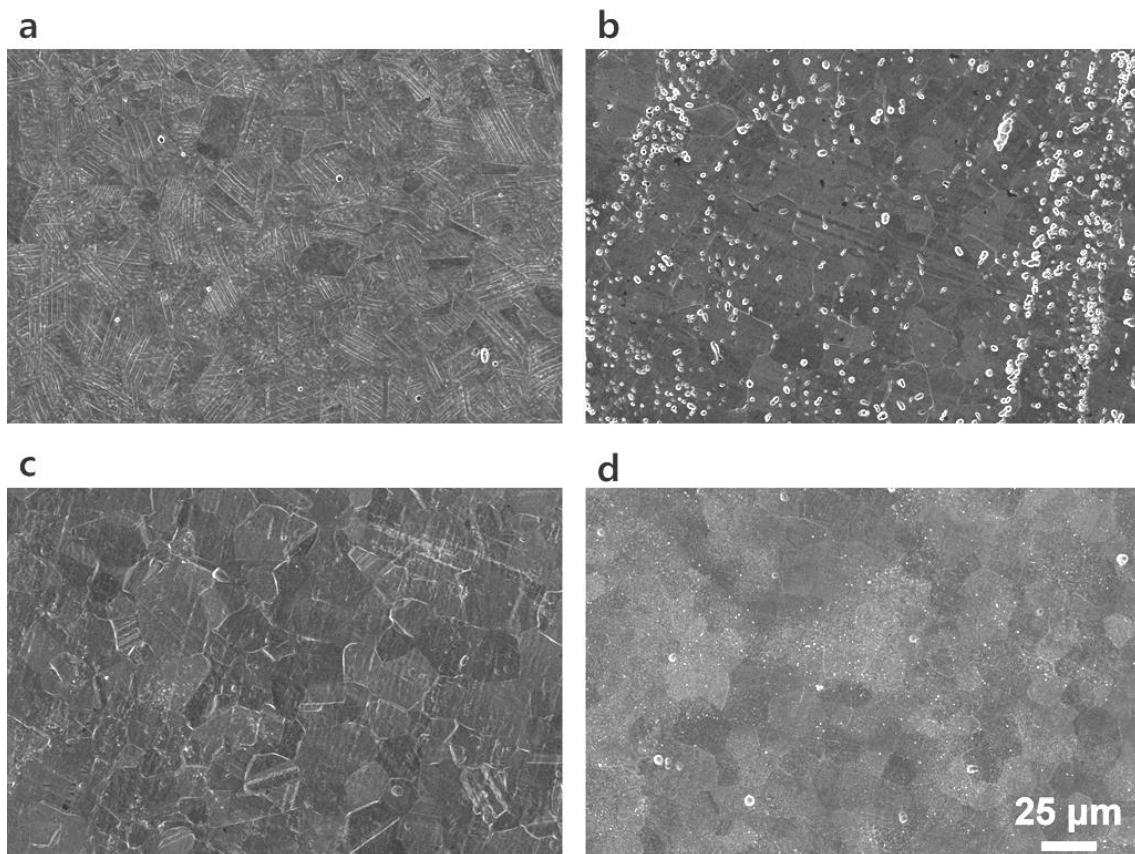


Figure 2.2 SEM images of type (a) 316L, (b) 430, (c) 304 and (d) 443 stainless steels after etching in 10 wt% oxalic acid solution.

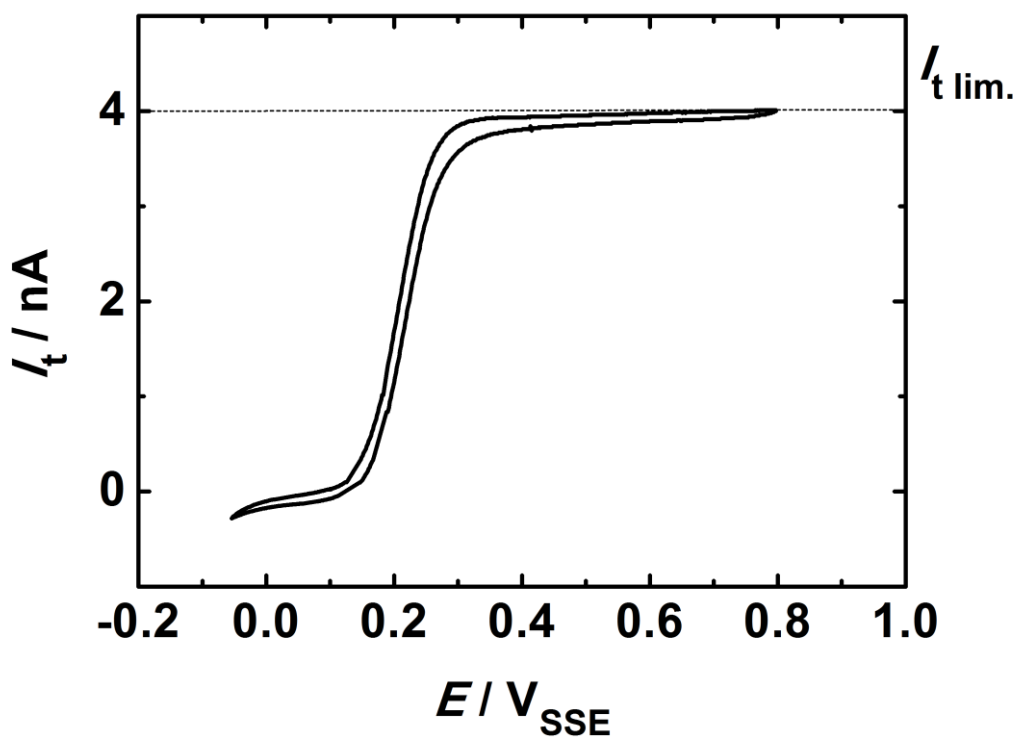


Figure 2.3

Cyclic voltammogram (CV) of Pt tip electrode with a scan rate of 1 mV s^{-1} measured in deaerated pH 8.4 borate solution containing $1.0 \times 10^{-3} \text{ mol dm}^{-3}$ FcMeOH when the platinum tip electrode with a diameter of $30 \mu\text{m}$ is far from the specimen electrode.

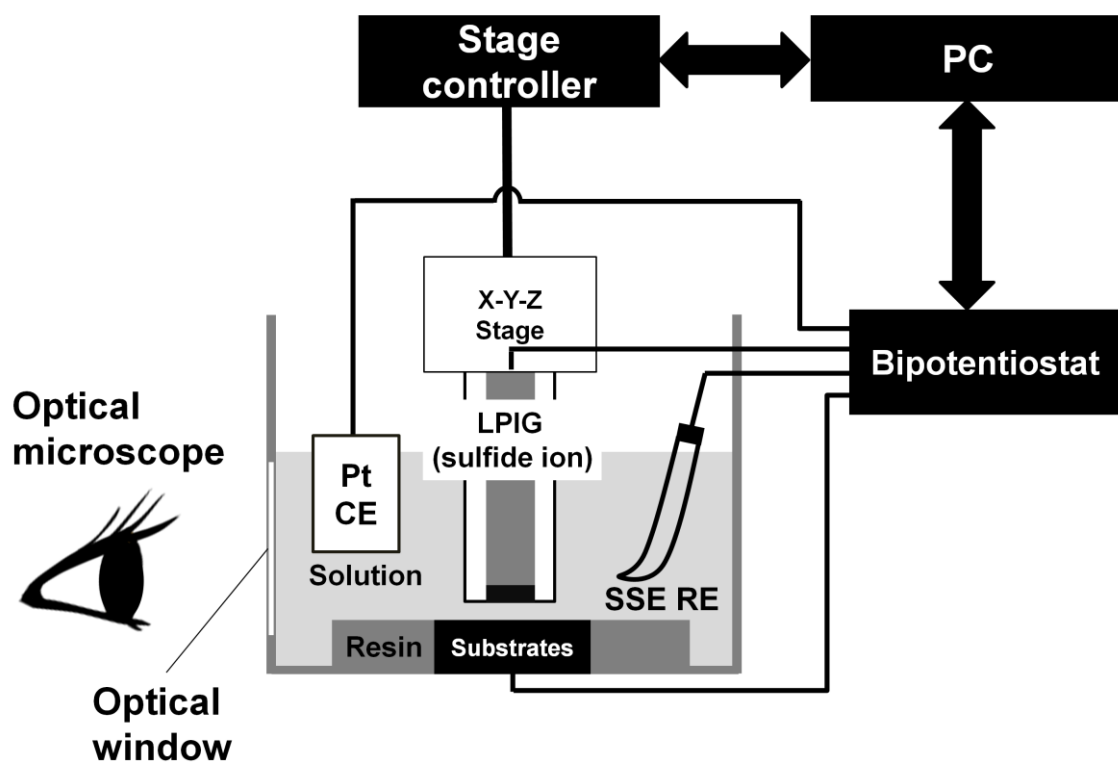


Figure 2.4

Schematic illustration of the experimental set-ups used for generating sulfide ions by potentiostatic polarization.

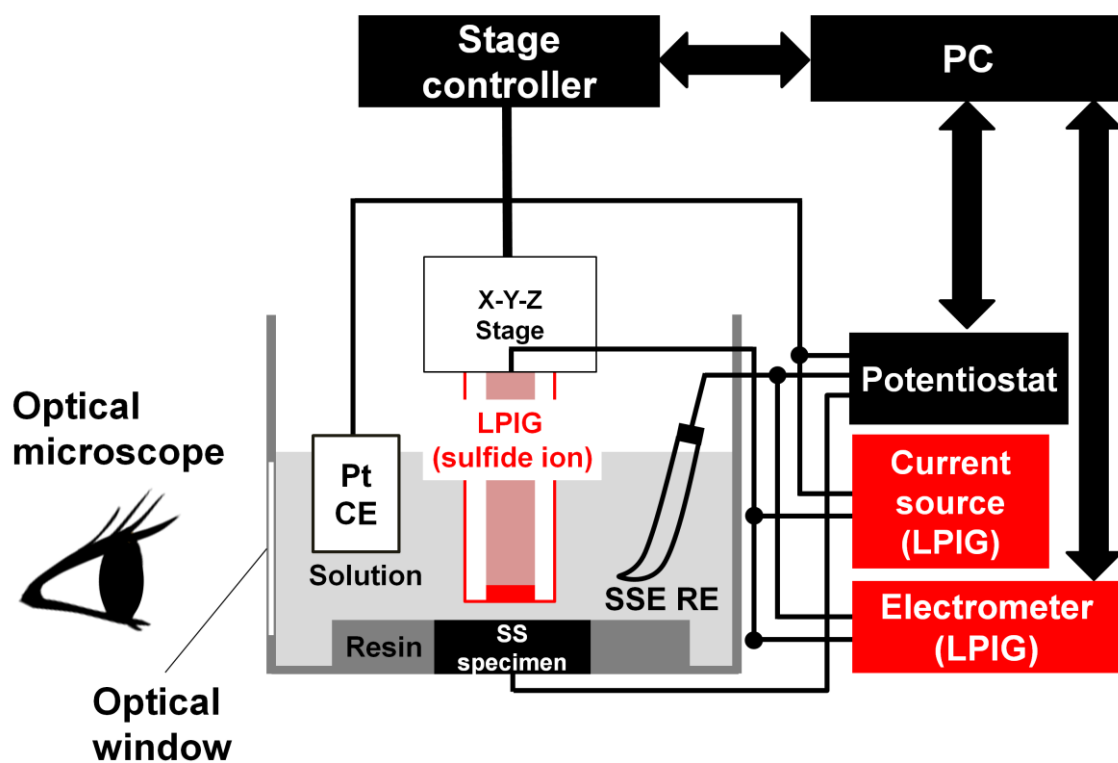


Figure 2.5 Schematic illustration of set-up used for generating sulfide ions by galvanostatic polarization.

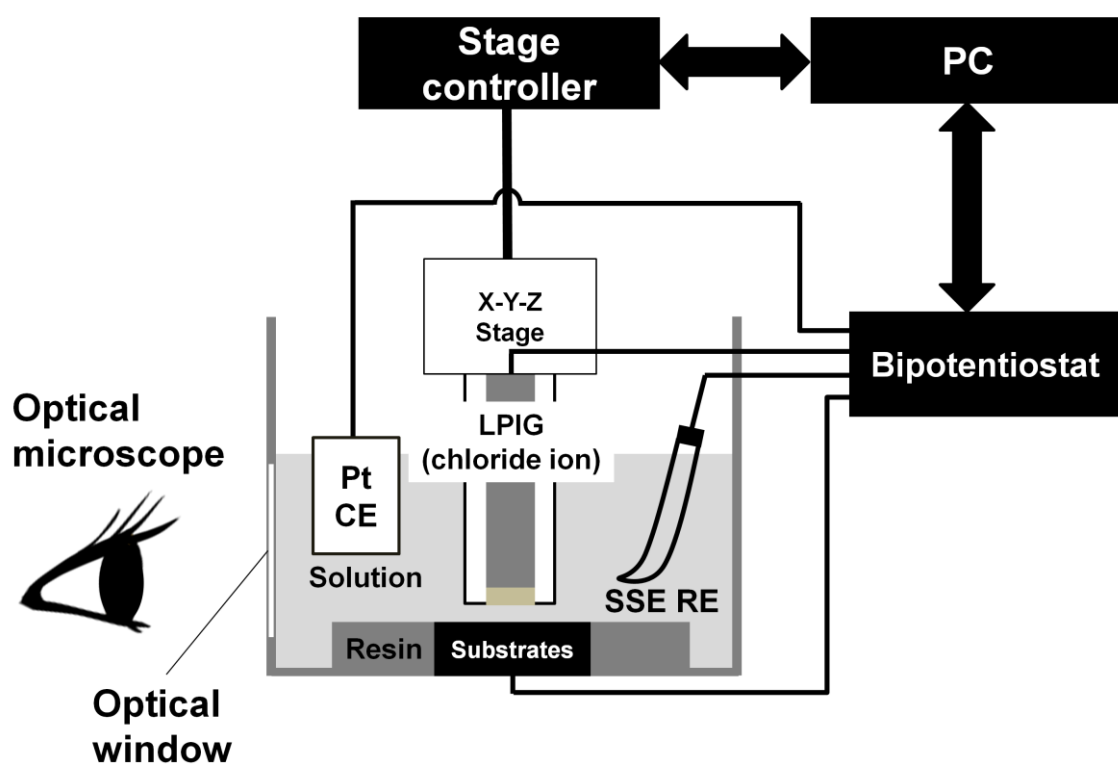


Figure 2.6

Schematic illustration of the experimental set-ups used for generating chloride ions above stainless steel substrate electrodes.

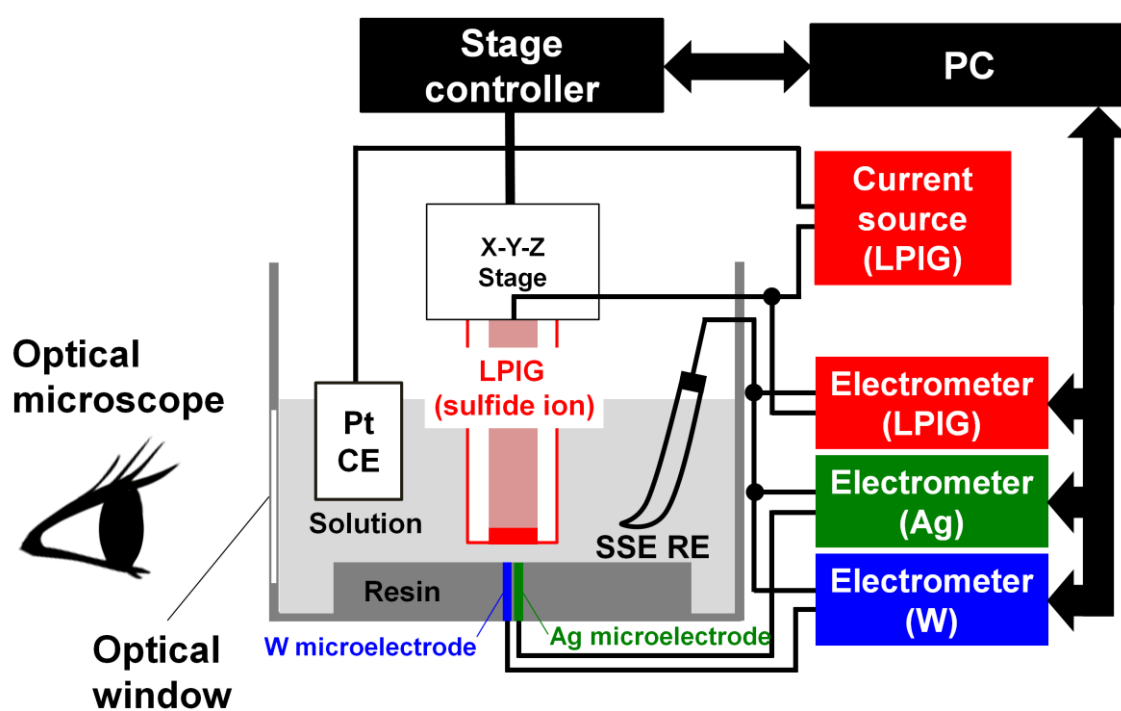


Figure 2.7

Schematic illustration of pH and sulfide ions concentration estimation set-up.

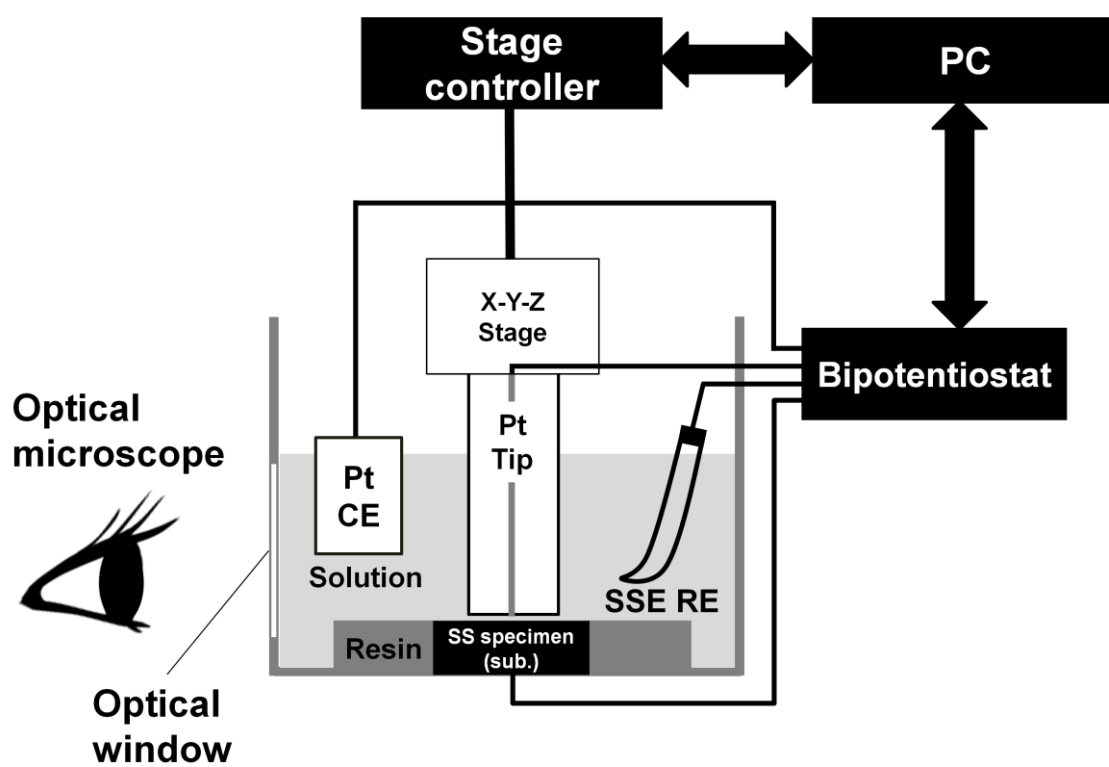


Figure 2.8

Schematic illustration of SECM set-up.

Chapter 3 Anion-generating system

3.1 Introduction

Metals are widely used in many fields and various environments. However, metals show susceptibility to environments, especially containing with sulfide ions, and cause various types of corrosion such as general corrosion, localized corrosion, and stress corrosion cracking. Considerable experience has been acquired concerning sulfide-induced corrosion behavior of metals.[1-5] Many researchers have attempted to create a sulfide ion-containing environment by flowing H_2S gas[6-8] or adding Na_2S [9-11] into aqueous solutions in order not only to control concentration of sulfide ions but also to investigate sulfidation behavior of metals. However, it was difficult to concentrate with an infinitesimal amount of sulfide ions on a local area. Moreover, sulfide ions can produce H_2S , which is an extremely toxic gas and accelerates degradation of the metallic materials by producing protons and sulfide ions in aqueous solutions. It is vital to establish safe experimental systems for handling the risk factors that should be limited to release of a small amount of sulfide ions.

The microelectrode technique is widely used to elucidate the corrosion of various metal surfaces.[12-18] O'Halloran et al. imaged isopotential contour maps of mild steel for investigating activity of localized corrosion sites by using a scanning Ag/AgCl reference electrode system in aqueous chloride solutions.[12] Newmann et al. measured the effect of nitrate on pitting dissolution in sodium chloride solutions by using stainless steel micro-electrodes.[13] Tsuru et al. also imaged potential profile over carbon steel weldment surface with a micro-electrode constructed with a glass capillary tip containing a $\text{Pb}(\text{Hg})/\text{PbSO}_4$ reference electrode in sulfuric acid solution.[14] Krawiec et al. investigated the localized corrosion behavior of a magnesium alloy by means of the micro-capillary cell technique.[15] Zhang et al. studied local anodic dissolution reaction at the crack tip on a pre-cracked steel specimen using the scanning vibrating electrode technique (SVET) and local electrochemical impedance spectroscopy (LEIS).[17] Lister et al. reported imaging of localized S concentrations dissolved from inclusions in stainless steel by using scanning electrochemical microscopy (SECM).[18] Vuillemin et al. injected an aggressive ion-containing solution with a micro-capillary on a stainless steel surface for elucidating depassivation of the surface.[19] The use of a liquid-phase ion gun (LPIG) is a microelectrode technique, type of SECM, and is effective to control the release of infinitesimal anions from a microelectrode.[20-23] Fushimi et al. investigated the local degradation mechanism of a passive film on iron by using a local chloride ion generation system.[20] They also reported that depassivation susceptibility of iron was dependent on applied potential and electric field as well as solution pH.[21] Falkenberg et al. reported the mechanism of single pit initiation and growth on a copper surface by using the combination of an electrochemical quartz crystal microbalance (EQCM) and LPIG.[22] Gabrielli et al. also reported that depassivation

susceptibility of iron was dependent on solution pH.[23]

Despite the fact that an LPIG is suitable for releasing anions above metal surfaces, it was used for a system of chloride ion generation. The use of an LPIG can be an alternative application for sulfide ion generation. In this study, an LPIG was used as a safe system for generation of sulfide ions for the first time. Electrochemistry of an LPIG as a generator of sulfide ions and its application for sulfidation on a silver surface is discussed.

3.2 Experimental

3.2.1 Specimens preparation

A silver wire a diameter of 500 μm was embedded in a glass capillary with an outer diameter of 1 mm using an epoxy resin. The cross section of the silver-glass capillary tip was used as a silver microelectrode after mechanical polishing. A silver plate with a surface area of 0.8 cm^2 was prepared as a substrate electrode.

Electrochemical experiments of using silver microelectrode and/or the silver substrate electrode were carried. However, all the potentials in this chapter were with respect to the reversible hydrogen electrode (RHE) potential. Cyclic voltammetry (CV) of the silver microelectrode was conducted in a potential range between 0.38 and $-0.06 \text{ V}_{\text{RHE}}$ in 0.1 mol dm^{-3} Na_2S solution (pH 13.4) at a scan rate of 20 mV s^{-1} . After a steady state had been obtained in CV, the microelectrode was polarized at 0.4 V_{RHE} in the same solution until the electric charge of 10 mC, $Q_{\text{LPIG.charge}}$, was consumed. On the other hand, potentiodynamic polarization of the silver substrate was performed in a potential range from 0.7 to 1.1 V_{RHE} at a scan rate of 1 mV s^{-1} in pH 8.4 boric-borate buffer solution.

3.2.2 Operation of the LPIG system

Potentiostatic polarization of LPIG.— The silver microelectrode was positioned above the substrate with a distance of 125, 250, 500, 750, 1000 or 10000 μm . A bipotentiostat independently controlled potentials of the microelectrode and the substrate. The LPIG microelectrode potential, E_{LPIG} , was initially kept at 0.4 V_{RHE} for 100 s and then changed to 0.0 V_{RHE} , whereas the silver substrate potential, $E_{\text{Ag.sub.}}$, was potentiostatically controlled at 0.04, 0.14, 0.24, 0.34, 0.54, 0.64 or 1.00 V_{RHE} . The silver substrate was also polarized at the same potential condition without microelectrode polarization as a control experiment. In all electrochemical tests, consistency was confirmed more than 3 times by repetition with different specimens with the same conditions.

Galvanostatic polarization of LPIG.—The LPIG were operated in deaerated pH 8.4 buffer solution (0.15 mol dm^{-3} H_3BO_3 and 0.15 mol dm^{-3} NaB_4O_7) with an

interelectrode distance between the LPIG and the substrate electrode of 125 μm . The potential of the LPIG microelectrode was measured by an electrometer. After the monitoring rest potential of the LPIG, the LPIG was galvanostatically polarized at $-3 \mu\text{A}$ using a battery-driven current source. After immersion for 600 s, the LPIG microelectrode was polarized for 0, 1900, 1950 or 2400 s to generate S species.

3.2.3 Surface characterization

A scanning electron microscope was used to observe the morphology of the silver surface. An X-ray diffraction (XRD) meter was used to examine silver surfaces. XRD patterns were identified with JCPDS files (Ag_2S : No. 14-0072 and Ag: No. 04-0783).

3.2.4 Modeling parameters and conditions

Concentration profiles of anions generated from the LPIG were modeled using a finite element method solver of COMSOL Multiphysics™ 5.0. This module provides a basis for the calculation of the evolution of chemical species transported by diffusion and convection. A transport of diluted species module with a time-dependent reaction was used to solve the diffusion behaviors of anions generated from the LPIG with a two-dimensional geometry. The diffusion of diluted mixtures or solutions is described by Fick's law:

$$J = -D\nabla c \quad [3.1]$$

$$\frac{\partial c}{\partial t} + \nabla J = 0 \quad [3.2]$$

where J is a mass flux, c is the concentration of the species, t is time, and D is the diffusion coefficient. The mesh for the element has a tetrahedral structure in two different sizes, one for the electrode surfaces and one for the bulk solution. The smaller mesh was used for the LPIG microelectrode and the substrate surface of the vicinity of the LPIG, in order to receive precise results concerning the concentration profiles of the electrode surfaces. Figure 3.1 shows the element distribution for the modeling system, with an entire space and an expanded space of the vicinity of the LPIG microelectrode, respectively.

Figures 3.2 show detailed images of the modeling system, which consists of a bulk solution with a pH 8.4 borate buffer solution, the LPIG microelectrode, the substrate, and an electrode on the center of the substrate surface. Some assumptions were made in the model, due to the complicated electrochemical reaction of the LPIG used for simulating the generation model. The assumptions are presented as follows:

- 1) The surface condition of the LPIG microelectrode was planar and the surface asymmetry does not change during operation of the LPIG.

- 2) The buffer effect in the electrolyte is neglected.
- 3) The anions are already present on the surface of the LPIG microelectrode and diffuse into the electrolyte by the flowing cathodic current.

The parameters and geometrical variations for modeling the concentration distribution of anions generated from the LPIG during operation are listed in Tables 3.1 and 3.2, respectively. The modeling parameters were values for diffusion coefficients of anions generated from the LPIG, and the initial concentration of hydroxide ions OH^- in the bulk solution before the LPIG operation. The geometrical variations were classified into the interelectrode factors between the LPIG, the substrate, and the geometry of the LPIG itself. The interelectrode factors were varied as a distance between the LPIG, the substrate surface, and a horizontal distance from the center of the substrate, where the position is under the LPIG. Meanwhile, the geometrical variation for the LPIG microelectrode was an edge angle of the LPIG sheath. Figure 3.3 shows a schematic illustration of the variations for the modeling of various geometries for (a) the interelectrode distance, (b) the distance from the center of the substrate, and (c) the edge angle of the LPIG sheath.

Current transients for experimental results of potentiostatic and galvanostatic polarization were used for modeling the generation of anions during the polarizations. Anion concentration profiles by potentiostatic polarization of the LPIG were modeled for 7 ks. The galvanostatic polarization model for the substrate concentrations of anions were modeled at the interelectrode distance of 125 μm with a current of $-3 \mu\text{A}$ for 2.4 ks.

Table 3.1 Parameters used for modeling the concentration distribution of anions generated from the LPIG microelectrode

Parameter	Value
Diffusion coefficient of $\text{HS}^- / D_{\text{HS}^-}$	$17.3 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$ [24]
Diffusion coefficient of $\text{OH}^- / D_{\text{OH}^-}$	$52.7 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$ [24]
Initial concentration of hydroxide ions in pH 8.4 solution	$1.00 \times 10^{-5.6} \text{ mol dm}^{-3}$

Table 3.2 Geometrical variations for modeling the concentration distribution of anions generated from the LPIG microelectrode

Variation	Detail
Interelectrode distance	from 125 to 10,000 μm
Distance from the center of the substrate	from 0 to 250 μm
Edge angle of the LPIG sheath	from 76° to 90°

3.3 Results

3.3.1 Electrochemical reaction of a silver microelectrode

Figure 3.4a shows a cyclic voltammogram of a silver microelectrode in deaerated $0.1 \text{ mol dm}^{-3} \text{ Na}_2\text{S}$ solution. The CV curve reached in a steady state within a few cycles. The anodic current at potentials higher than ca. $0.2 \text{ V}_{\text{RHE}}$ and the cathodic current at potentials lower than ca. $0.2 \text{ V}_{\text{RHE}}$ seem to bring about sulfidation of silver and reduction of silver sulfide, respectively. The electric charge consumed during CV increases during the anodic current flow, while it decreases to zero during the cathodic current flow (Figure 3.4b), indicating that anodic and cathodic reactions of silver are reversible during the CV in solution. The XRD pattern of the silver electrode polarized at $0.3 \text{ V}_{\text{RHE}}$ for 5.1 C cm^{-2} (Figure 3.5) suggests the formation of Ag_2S . Ag is also detected from the XRD pattern of the silver electrode. Since the solubility of Ag_2S is extremely small ($K_{\text{sp}} = 7.2 \times 10^{-50}$)[25], little Ag_2S was dissolved from the microelectrode in anodic condition.

The results demonstrate that the anodic reaction of silver and the cathodic reaction of silver sulfide correspond to the following backward and forward reactions in an aqueous solution, respectively:



where the reduction of Ag_2S means generation of HS^- into the solution. Standard potential of Eq. 3.3 is as follows:[26]

$$E / \text{V}_{\text{SHE}} = -0.274 - 0.0295 \text{ pH} - 0.0295 \log [\text{HS}^-]. \quad [3.4]$$

From Eq. 3.4, an HS^- concentration $[\text{HS}^-]$ of $10^{-2.3} \text{ mol dm}^{-3}$ can be estimated at $E_{\text{Ag}} = -0.607 \text{ V}_{\text{SHE}} = 1.854 \text{ V}_{\text{RHE}}$ in pH 13.4. In any case, the silver sulfide surface generates HS^- during cathodic polarization. In the following experiments, a silver microelectrode covered with silver sulfide ($\text{Ag}/\text{Ag}_2\text{S}$ microelectrode) was used as an LPIG for generating sulfide ions by forming Ag_2S on the silver microelectrode with the consumption of electric charge for 10 mC.

3.3.2 Estimation of pH and $[\text{HS}^-]$

In order to estimating solution pH and/or $[\text{HS}^-]$ during the LPIG operation, both the tungsten and silver microelectrodes were located as substrates with an interelectrode distance of $125 \text{ }\mu\text{m}$ and connected to different electrometers with the same reference electrode (Figure 2.6). For the calibration of tungsten microelectrode potential to pH, the following

deaerated solutions were used: 0.15 mol dm⁻³ sulfuric acid (pH 0.9), 0.04955 mol dm⁻³ phthalic acid-phthalate buffer (pH 4.0), 0.02489 mol dm⁻³ phosphoric acid-phosphate buffer (pH 6.9), 0.15 mol dm⁻³ boric acid-borate buffer (pH 8.4) and 0.025 mol dm⁻³ sodium hydroxide (pH 10.0). After monitoring the rest potential for 3600 s in solutions of various pH values, the calibrated potential of the tungsten microelectrode was obtained as a function of solution pH.

Figure 3.6 shows the electrode potential of the tungsten microelectrode as a function of solution pH. It is obvious that the potential and pH have a linear relation:

$$E_W / V_{SSE} = 0.0990 - 0.04685\text{pH} . \quad [3.5]$$

The slope is almost in agreement with that reported when a tungsten microelectrode with a diameter of 25 μm was used to estimate various pH values.[11] In this study, the pH value in the interelectrode space during the LPIG operation was estimated by Eq. 3.5. On the other hand, it has been shown that Ag₂S is reduced as follows:[15]



The equilibrium potential of Eq. 3.3 is a function of pH and [HS⁻] as follows:

$$E / V_{SSE} = -0.197 - 0.274 - 0.0295 \text{pH} - 0.0295 \log [\text{HS}^-] . \quad [3.6]$$

The experimental results of estimating pH and [HS⁻] were obtained by monitoring potential of tungsten and silver microelectrodes during potentiostatic and galvanostatic operation of the LPIG.

3.3.3 Electrochemistry of LPIG in alkaline solutions

Figure 3.7a shows transients of current, I_{LPIG} , flowing through an Ag/Ag₂S LPIG microelectrode and electric charge, Q_{LPIG} , consumed on the LPIG microelectrode when the LPIG microelectrode potential, E_{LPIG} , was changed from 0.4 to -0.06 V_{RHE} above 10000 μm distance away from glass substrate in pH 7.3, 8.4, 9.4 or 10.5 solutions. During a polarization at 0.4 V_{RHE} for 100 s, cathodic current does not flow through the LPIG, while cathodic current flows when the LPIG is polarized at -0.06 V_{RHE}. The cathodic current is due to the generation of HS⁻. Cathodic current for HS⁻ generation shows stepwise increase and shows a peak at 200-300 s, but the peak appearance time is not dependent on the solution pH. The stepwise increase of the cathodic currents is thought that the cathodic reaction of Ag₂S is difficult to be a steady-state reaction. It is difficult to reach a fine steady state during the cathodic polarization because of the complexity of HS⁻ generation process, even if the ultra

microelectrode is used. Moreover, it is thought that the closed diffusion layer of generated anions by the glass capillary might be one reason for the stepwise current flowing on LPIG. The diameter of LPIG microelectrode is 1 mm. Since the Ag wire diameter is 200 μm , the glass capillary thickness of the LPIG is 400 μm . This glass capillary thickness would make a non-spherical diffusion layer for anions during their generation. The ions or water molecules is difficult to diffuse from LPIG to solution bulk than spherical diffusion layer. When the Ag wire diameter increases, a thickness of glass capillary should decrease. The Ag wire with a diameter of 500 μm was attempted to generate HS^- . The detailed electrochemical behavior of the LPIG microelectrode with a 500 μm diameter of Ag wire is discussed in later section.

Although the same electric charge of -3 mC is consumed regardless of the solution pH, it can be clearly seen in Figure 3.7b that peak current increases and completion time for cathodic reaction with 3 mC decreases with increase in the solution pH. This indicates that generation of HS^- from the microelectrode is strongly dependent on the concentration of protons or hydroxyl anions. This pH dependency of LPIG current might be related to solution conductivity. The conductivity of a solution depends on the concentration of all ions present, which means that the greater their concentrations, the greater the conductivity. The different diffusion coefficients also contribute to the conductivity. The diffusion coefficient of proton and hydroxide ion is $93.1 \times 10^{-10}\text{ m}^2\text{ s}^{-1}$ and $52.7 \times 10^{-10}\text{ m}^2\text{ s}^{-1}$, respectively.[24] An aqueous solution will have high conductivity in strong acidic or basic solution. In a solution with a larger conductivity, an ohmic drop for electrochemical reaction becomes smaller. It is thought that the cathodic current of Ag_2S increases with increase in the solution pH.

3.3.4 Potentiostatic polarization of LPIG above an insulating surface

3.3.4.1 Geometrical dependencies on generation behavior of anions released from LPIG

Figure 3.8a shows transients of current, I_{LPIG} , flowing through an $\text{Ag}/\text{Ag}_2\text{S}$ microelectrode and electric charge, Q_{LPIG} , consumed on the LPIG microelectrode when the microelectrode potential, E_{LPIG} , was changed from 0.4 to 0.0 V_{RHE} above a glass substrate in pH 8.4 boric-borate buffer solution. No cathodic current flows through the microelectrode during a polarization at 0.4 V_{RHE} for 100 s, but cathodic current flows when the $\text{Ag}/\text{Ag}_2\text{S}$ microelectrode is polarized at 0.0 V_{RHE} . A current spike of ca. $-4\text{ }\mu\text{A}$ at the beginning is due to charging of double layer capacitance at the $\text{Ag}/\text{Ag}_2\text{S}$ microelectrode surface, while the following cathodic current is due to the generation of HS^- . Cathodic current for HS^- generation gradually increases and shows a peak at 500-2000 s depending on the distance between the microelectrode and the substrate. Although the same electric charge of -10 mC is consumed regardless of the distance to the substrate, it can be clearly seen in Figure 3.8b that

peak current increases and peak appearance time decreases with increase in the distance. This indicates that generation of HS^- from the microelectrode is strongly dependent on the geometry of the narrow space between the microelectrode and glass substrate. The narrow space is concentrated by HS^- during the generation. Highly concentrated HS^- might clog the space and lead to decrease in further HS^- generation. Generation and concentration of a certain amount of HS^- existing in the narrow space result in extension of HS^- generation period.

3.3.4.2 Geometrical dependencies on the concentration profiles of HS^- and OH^- potentiostatically generated from the LPIG

In this section, the modeling results of a concentration change in HS^- or OH^- are presented during the cathodic potentiostatic polarization of the LPIG above an insulating substrate surface. The simulations of modeling were based on the experimental data of Figure 3.8a with the variations of interelectrode distance between the LPIG microelectrode and an insulating surface, and the distance from the center of the substrate and the edge angle of the LPIG microelectrode sheath.

The effect of the interelectrode distance on the concentration profiles of anions generated from the LPIG.— Figures 3.9 show the concentration profiles of HS^- (Figure 3.9a) and OH^- (Figure 3.9b) above the center of the insulating substrate surface during the operation of the LPIG in a pH 8.4 solution for 7 ks. The concentrations of HS^- and OH^- on the substrate surface increase during the polarization of the LPIG for 7 ks. After a sharp increase in the concentrations of HS^- and OH^- during 0.1 ks, they gradually increase and peak after the polarization of the LPIG for 1 or 2 ks, depending on the interelectrode distance. This result indicates that concentrations of HS^- and OH^- generated from the LPIG are strongly dependent on the narrow interelectrode space volume between the LPIG and an insulating substrate. It can be clearly shown that the concentration of HS^- is three times higher than that of OH^- on the substrate surface, regardless of the interelectrode distance. However, the same amounts of HS^- and OH^- are electrochemically generated from the LPIG (Eq. 3.3). This fact means that HS^- can be more easily concentrated in the interelectrode space than OH^- . Researchers believe that a diffusion coefficient of OH^- $17.3 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$ is three times higher than that of HS^- $52.7 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$, making OH^- diffuse faster into bulk solutions than HS^- does, regardless of the interelectrode distance.[24]

In Figure 3.10, the modeling result of the pH profile on the substrate surface is plotted during the polarization of the LPIG, based on Figure 3.9b. The pH values are always higher than 8.4, which is the bulk solution pH before the polarization of the LPIG, regardless of the interelectrode distance. The value of pH increases with the increase in the interelectrode distance, although the pH profiles show peaks at 1-4 ks, depending on the

interelectrode distance. This fact indicates that the accumulated OH^- generated from the LPIG can change the solution pH, although the amount of OH^- is three times less than HS^- on the substrate surface. A relatively large amount of generated OH^- from 4.85 to $0.099 \times 10^{-3} \text{ mol dm}^{-3}$ can be enough to change the pH of the interelectrode space, where the initial concentration of OH^- was $10^{-5.6} \text{ mol dm}^{-3}$ before operating the LPIG. This increase of pH is due to the simulation condition of the unconcerned buffer effect during operation of the LPIG.

Figures 3.11a and 3.11b show comparisons between the experimental and numerical modeling results of a maximum concentration of HS^- and a maximum value of pH during the potentiostatic polarization of the LPIG above an insulating substrate surface, as a function of an interelectrode distance. Both results for the maximum concentration of HS^- exponentially decrease with an increase in the interelectrode distance, although the concentration of HS^- for experimental value is approximately 50% lower than that of the modeling results. Some research shows that the electrochemical reaction on an $\text{Ag}/\text{Ag}_2\text{S}$ electrode includes a generation of HS^- and OH^- , as well as a formation of a Ag layer, but the morphology change was not considered during the cathodic reaction of the $\text{Ag}/\text{Ag}_2\text{S}$ electrode.[4,5] The morphology change of the Ag layer is thought to affect the kinetics of the cathodic electrochemical reaction. The experimental results for the pH slightly increase to pH 8.7, but the modeling results for the value of pH increase to 11.7 and gradually decrease to 10.8, with the increase in the interelectrode distance. The independent value of pH for the experimental results is possibly related to a buffering effect, even though there is a small increase value of pH from 8.4 to 8.7. However, without considering the buffering effect, the high increase of the pH for modeling occurs due to the generated OH^- from the LPIG.

The effect of the distance from the center of the substrate on the concentration profiles of anions generated from the LPIG.— Figure 3.12 shows the maximum concentration of HS^- during the polarization of the LPIG above an insulating substrate, as a function of a distance from the center of the substrate surface. The maximum concentration was obtained from each interelectrode distance during the polarization of the LPIG for 7 ks. It is clear that the concentration of HS^- has the highest value at the center of the substrate surface, under the LPIG, and gradually decreases with the distance away from the center when the interelectrode distance increases from 125 to 250 μm . However, when the interelectrode distance is greater than 500 μm , the concentration of HS^- is independent of the distance from the center, as well as of the interelectrode distance. This fact indicates that the concentration distribution on the substrate surface is strongly dependent on the diffusion behavior of HS^- .

The effect of the edge angle of the LPIG microelectrode sheath on the concentration profiles of anions generated from the LPIG.— Figure 3.13 shows the HS^- concentration profile with an interelectrode distance of 125 μm when an edge angle of the LPIG microelectrode sheath was changed. The angle is defined by the horizontal line of the LPIG surface and a cross line from 300 μm away from the center of the LPIG. This means

that the thickness of the LPIG glass sheath was sustained as 50 μm with the change in angle. It is clear that the angle that is lower than 90° makes the LPIG shape a truncated cone, and the cylinder shape of the LPIG was formed with a 90° angle. The concentration of HS^- on the substrate surface increases from 10.1 to $14.6 \times 10^{-3} \text{ mol dm}^{-3}$ when the edge angle increases from 76° to 90° . When the edge angle is close to 90° , the glass thickness of the LPIG increases, indicating that the diffusion layer of HS^- in the interelectrode space is reduced by the increased glass capillary of the LPIG sheath. With a truncated cone shape, the LPIG has a relatively larger diffusion layer of HS^- than it does with a 90° edge angle. The local concentration of HS^- in the interelectrode space is affected by the diffusion layer of HS^- , which is related to the geometry of the interelectrode space, as well as to the geometry of the LPIG itself.

3.3.5 Galvanostatic polarization of LPIG above an insulating surface

Figure 3.14 shows changes in electrode potentials of the LPIG microelectrode E_{LPIG} , tungsten microelectrode E_{W} , and silver microelectrode E_{Ag} during the operation of the LPIG microelectrode. Before the operation, the value of E_{LPIG} remains constant. This implies that the LPIG microelectrode is relatively stable and does not release HS^- during that period. However, when the LPIG microelectrode is galvanostatically polarized at $-3 \mu\text{A}$, E_{LPIG} changes to a negative potential. E_{W} and E_{Ag} also shift to negative potentials. It has been shown that Ag_2S is reduced as follows:[15]



The equilibrium potential of Eq. 3.3 is a function of pH and $[\text{HS}^-]$ as follows:

$$E / \text{V}_{\text{SSE}} = -0.197 - 0.274 - 0.0295 \text{ pH} - 0.0295 \log [\text{HS}^-] . \quad [3.6]$$

The reduction of Ag_2S increases pH as well as $[\text{HS}^-]$. The value of pH, converted from Eq. 3.5 by substituting the value of E_{W} , of the solution is sustained at ca. 8.5 before cathodic polarization of the LPIG. However, pH rapidly reaches a constant value of ca. 9.5 after the onset of polarization, and this value is sustained during the polarization. This means that local alkalization in the vicinity of the tungsten microelectrode is in a steady state. It is thought that the mass of OH^- generated from the LPIG microelectrode is balanced between the interelectrode space and bulk solution. During the local alkalization, hydrogen gas did not evolve on the LPIG, whereas E_{LPIG} was sustained at ca. $-0.7 \text{ V}_{\text{SSE}}$. On the other hand, it is possible to estimate the value of $[\text{HS}^-]$ by substituting the values of pH and E_{Ag} into Eq. 3.6. When the LPIG was polarized cathodically, $[\text{HS}^-]$ reached ca. $1.5 \times 10^{-3} \text{ mol dm}^{-3}$ within 100 s and then gradually increased and reached ca. $4.0 \times 10^{-3} \text{ mol dm}^{-3}$ of 2400 s.

When the polarization of the LPIG microelectrode was stopped and the LPIG microelectrode was pulled up to the bulk solution, the values of pH and $[\text{HS}^-]$ immediately decreased, suggesting that the products, OH^- and HS^- , in the interelectrode space are diluted. The concentration of $[\text{HS}^-]$ after the polarization of LPIG are lower than $10^{-6} \text{ mol dm}^{-3}$. However, the sensitivity of W and Ag microelectrode for estimating pH and $[\text{HS}^-]$, respectively, is difficult to discuss in this dissertation. The Ag microelectrode is possible to estimate $[\text{HS}^-]$ from $10^{-3} \text{ mol dm}^{-3}$. From the Eq.3.5, it can be estimated as $E_{\text{W}} = -0.346 \text{ V}_{\text{SSE}}$ in pH 9.5 solution, while $[\text{HS}^-]$ of $10^{-3} \text{ mol dm}^{-3}$ can be estimated by Eq. 3.6 as $E_{\text{Ag}} = -0.636 \text{ V}_{\text{SHE}} = 0.127 \text{ V}_{\text{RHE}}$ in pH 9.5 solution with containing $10^{-3} \text{ mol dm}^{-3} \text{ Na}_2\text{S}$. It was confirmed that E_{W} and E_{Ag} were $E_{\text{W}} = -0.349 \text{ V}_{\text{SSE}}$ and $E_{\text{Ag}} = -0.633 \text{ V}_{\text{SSE}} = 0.126 \text{ V}_{\text{RHE}}$, respectively, in pH 9.5 solution containing with $10^{-3} \text{ mol dm}^{-3} \text{ Na}_2\text{S}$. The space is so small that products from the LPIG accumulated and the buffering effect of the solution did not act effectively to keep the pH in the space. In the following experiments, polarization of the LPIG microelectrode was carried out at an interelectrode distance of 125 μm for 100, 150 or 600 s, corresponding to local $[\text{HS}^-]$ of 1.5, 2.2 and $2.8 \times 10^{-3} \text{ mol dm}^{-3}$, respectively, on the specimen.

3.3.5.1 Geometrical dependencies of the concentration profiles of anions galvanostatically generated from the LPIG microelectrode

In this section, the modeling results of the concentration change in HS^- or OH^- are presented during the cathodic galvanostatic polarization of the LPIG above an insulating substrate. The simulations of modeling progressed with a constant interelectrode distance between the LPIG microelectrode and an insulating surface of 125 μm . The distance from the center of the substrate and the edge angle of the LPIG microelectrode sheath was considered as a variation for the concentration profile of HS^- or OH^- .

Figure 3.15 shows the concentration profiles of HS^- and OH^- during the galvanostatic polarization of the LPIG above an insulating substrate surface in a pH 8.4 solution for 2.4 ks. It is clear that HS^- and OH^- accumulated during the polarization, although the concentration of HS^- is three times higher than that of OH^- on the substrate surface. It is thought that the diffusion coefficient of OH^- is higher than that of HS^- . The concentrations of HS^- and OH^- sharply increase within 0.2 ks and sustain their values of 16.06 and $4.850 \times 10^{-3} \text{ mol dm}^{-3}$, respectively, during 2.4 ks. The galvanic polarization of the LPIG generates HS^- and OH^- , which make constant concentration variations during the polarization, although the initial polarization time during 0.2 ks shows some concentration variations on the substrate surface.

Figures 3.16a and 3.16b show comparisons between the experimental and modeling results of the concentration of HS^- and the value of pH, during the galvanostatic polarization of the LPIG above an insulating substrate surface, as a function of polarization time. The concentration of HS^- and the value of pH are constants after 0.2 ks of the

polarization in both cases of experimental and modeling results, although there is a large difference between experimental and modeling results. Experimental results show a diluted concentration of HS^- that is five times higher as that of the modeling results. Since the increase of pH indicates a decrease in the concentration of protons, the increase of pH means an increase in the concentration of hydroxide ions. Therefore, the experimental and modeling results for the value of pH are approximately 9.5 and 11.5. This fact indicates that the concentration of OH^- for experimental results is 100 times more diluted than that of the modeling results on the substrate surface. It is thought that the concentration difference for both HS^- and OH^- is strongly associated with the efficiency of the galvanic polarization of the LPIG. The modeling for the generation of HS^- and OH^- is based on 100% efficiency of the cathodic reaction of $\text{Ag}/\text{Ag}_2\text{S}$ on the LPIG due to the complicated cathodic reaction of $\text{Ag}/\text{Ag}_2\text{S}$.

The effect of the distance from the center of the substrate on the concentration profiles of anions generated from the LPIG.— Figure 3.17 shows the concentration profile of HS^- during the galvanostatic polarization of the LPIG above an insulating substrate as a function of a horizontal distance from the center of the substrate surface for 2.4 ks. It is clear that the concentration of HS^- has the highest value at the center of the substrate surface of $17.5 \times 10^{-3} \text{ mol dm}^{-3}$, under the LPIG, and gradually decreases to $10.4 \times 10^{-3} \text{ mol dm}^{-3}$ when the distance away from the center is 300 μm . This fact is further evidence that the concentration distribution on the substrate surface is dependent on the diffusion behavior of HS^- .

The effect of the edge angle of the LPIG microelectrode sheath on the concentration profiles of anions generated from the LPIG.— Figure 3.18 shows the HS^- concentration profile with an interelectrode distance at 125 μm when the change in an edge angle of the LPIG microelectrode sheath was from 79° to 90° . The concentration of HS^- on the substrate surface peaks from 13.6 to $17.4 \times 10^{-3} \text{ mol dm}^{-3}$ when the edge angle is narrows from 79° to 90° . It is thought that the diffusion layer of HS^- between the LPIG and the substrate is reduced by an increase in the thickness of the LPIG sheath's glass capillary, along with an increase in the edge angle. The low edge angle of a truncated cone-shaped LPIG expands the diffusion layer of HS^- .

3.3.6 Polarization behaviors of LPIG above a conductive silver surface

3.3.6.1 Anodic polarization of silver substrate

Figure 3.19 shows the dynamic polarization curve of a silver electrode in pH 8.4 boric-borate buffer solution. The corrosion potential is shown at 0.73 V_{RHE} . This is similar to the standard equilibrium potential 0.79 V_{RHE} of the Ag/Ag^+ system, assuming $[\text{Ag}^+] = 10^{-6}$

mol dm⁻³ in the Ag-H₂O system at 25°C.[27]



$$E / V_{\text{SHE}} = 0.799 + 0.05916 \log[\text{Ag}^+] \quad [3.7]$$

The anodic current is attributed to general dissolution of Ag at potentials between 0.73 and 1.6 V_{RHE}. It is difficult to form a silver-hydroxide in pH 8.4 with potential range from 0.73 to 1.6 V_{RHE}. [28] At potentials higher than 1.6 V_{RHE}, however, oxide of Ag forms as follows:[28]



$$E / V_{\text{SHE}} = 1.670 - 0.0886\text{pH} - 0.0295 \log[\text{Ag}^+] \quad [3.9]$$

3.3.6.2 Dependency of distance between LPIG and silver substrate on polarization behaviors of LPIG

Figure 3.20a shows transients of currents I_{LPIG} and $I_{\text{Ag.sub.}}$ of the Ag/Ag₂S LPIG microelectrode and silver substrate, respectively, in a pH 8.4 boric-borate buffer solution when potential of the LPIG microelectrode E_{LPIG} was changed from 0.4 to 0.0 V_{RHE} with potential of the substrate $E_{\text{Ag.sub.}}$ being kept at 1.00 V_{RHE}. As discussed above, the generation of HS⁻ indicates a cathodic current flowing through the microelectrode, although the current spike for charging is observed at the beginning. After 1-2 ks from onset of the HS⁻ generation, peaks are seen in both I_{LPIG} and $I_{\text{Ag.sub.}}$. The value of I_{LPIG} is almost constant, while that of $I_{\text{Ag.sub.}}$ is dependent on the distance between the microelectrode and the substrate. Distance independency of I_{LPIG} disagrees with the case on a glass substrate. Thus, the HS⁻ generation is affected by reaction of HS⁻ with the substrate as well as diffusion in the narrow space.

Figure 3.20b shows the electric charge $Q_{\text{Ag.sub.}}$ consumed at the silver substrate as a function of the electric charge Q_{LPIG} consumed at the Ag/Ag₂S LPIG microelectrode during the generation of HS⁻. The value of $Q_{\text{Ag.sub.}}$ increases linearly with increase in Q_{LPIG} . The slope of the linear relation between $Q_{\text{Ag.sub.}}$ and Q_{LPIG} increases with decrease in the distance between electrodes. The slope at the distance of 125 μm is close to -1, demonstrating that an anodic current equivalent to the cathodic current for HS⁻ generation flows through the silver substrate. It is thought that the anodic reaction on the substrate is dominantly affected by HS⁻ generated from the LPIG microelectrode. From the larger space between electrodes, a large amount of HS⁻ can diffuse out to the bulk solution instead of the silver substrate surface. The shortage of HS⁻ diffusion results in a decrease of the anodic current.

SEM images of the silver substrate surface after the generation of HS⁻ from the LPIG microelectrode (Figure 3.21a) show the formation of a circle-like deposition, which

is composed of a number of needle-like products with lengths of several μm , with a diameter of 1 mm on the surface. The size of the product coincides not with the 1 mm diameter of the LPIG microelectrode itself but with an outer diameter of a microelectrode sheath. The products were confirmed to be Ag_2S from the XRD pattern (Figure 3.21b). The silver substrate surface is locally sulfidized by HS^- ions generated from the microelectrode.

Figure 3.22 shows the electric charge $Q_{\text{Ag.sub.end}}$ consumed at the substrate until completion of HS^- generation as a function of the interelectrode distance. The value of $Q_{\text{Ag.sub.end}}$ decreases with increase in the distance. Since an oxidation current of ca. 1.1×10^{-7} A flows during polarization of the silver substrate at 1.0 V_{RHE} without the presence of HS^- , the value of $Q_{\text{Ag.sub.end}}$ includes an additional electric charge for the oxidation of silver. In order to consider only sulfidation of the silver substrate, the electric charge $Q'_{\text{Ag.sub.end}}$, which is the charge of subtracted from $Q_{\text{Ag.sub.end}}$ by the electric charge consumed for the oxidation, is also plotted in Figure 3.22. Extrapolation of $Q'_{\text{Ag.sub.end}}$ against 0 μm attributes 10.5 mC, which is larger than the electric charge $Q_{\text{LPIG.charge}}$ (=10 mC) for sulfidation of the LPIG microelectrode. The ratio of $Q'_{\text{Ag.sub.end}}$ to $Q_{\text{LPIG.charge}}$ is efficiency of the substrate sulfidation. When the ratio is unity, the substrate is completely sulfidized with all of the HS^- generated from the microelectrode. Figure 3.23 shows the efficiency of sulfidation on silver substrate surface with a function of the interelectrode distance. The sulfidation efficiency is almost unity at distances less than 125 μm . Conversely, shortage of $Q'_{\text{Ag.sub.end}}$ compared with $Q_{\text{LPIG.charge}}$ means loss of substrate sulfidation. This is due to diffusion of HS^- out to the solution bulk. At distances of more than 500 μm , however, sulfidation efficiency seems to be constant. It is thought that not only the area of the silver substrate surface adjacent to the microelectrode but also other areas are sulfidized by HS^- diffused to the solution bulk. On the other hand, a protrusion of silver built up on the microelectrode surface during HS^- generation was observed. At a very close distance, this may lead to the formation of a short circuit between the electrodes, which are inappropriate for sulfidation of the specimen surface using the $\text{Ag}/\text{Ag}_2\text{S}$ LPIG microelectrode in this study.

3.3.6.3 Potential dependence of silver substrate on the polarization behaviors of LPIG

Figures 3.24a and 3.24b show transients of currents I_{LPIG} and $I_{\text{Ag.sub}}$ of the $\text{Ag}/\text{Ag}_2\text{S}$ LPIG microelectrode and silver substrate, respectively, during HS^- generation by changing the LPIG microelectrode potential E_{LPIG} from 0.4 to 0.0 V_{RHE} at a distance of 250 μm when the silver substrate was polarized at various values of $E_{\text{Ag.sub}}$. Regardless of the values of $E_{\text{Ag.sub}}$, the cathodic current for HS^- generation shows almost the same behavior, suggesting that HS^- generation is not affected by the silver substrate potential. However, the current flowing through the silver substrate is strongly associated with the applied potential. As seen in Fig. 3.19, the silver substrate is oxidized and this leads to the flow of an anodic

current at potentials higher than $0.73 \text{ V}_{\text{RHE}}$, while sulfide or water is reduced at lower potentials. Figure 3.24c shows the relation between electric charges $Q_{\text{Ag,sub}}$ and Q_{LPIG} consumed at the LPIG microelectrode and substrate, respectively. The slope corresponds to sulfidation efficiency of the substrate at potentials higher than $0.64 \text{ V}_{\text{RHE}}$. Thus, the efficiency is unity at $1.00 \text{ V}_{\text{RHE}}$. However, negative slopes at potentials lower than $0.54 \text{ V}_{\text{RHE}}$ suggest that a cathodic reaction like reduction of contaminated oxygen is dominant.

Figure 3.25 shows the electric charge $Q_{\text{Ag,sub, end}}$ consumed at the silver substrate until completion of HS^- generation as a function of the substrate potential $E_{\text{Ag,sub}}$. Electric charge $Q'_{\text{Ag,sub, end}}$, which is the charge subtracted from $Q_{\text{Ag,sub, end}}$ by the electric charge Q_{control} corresponding to oxidation reaction of the silver substrate without HS^- generation from the LPIG microelectrode, is also plotted in Figure 3.25. The value of $Q'_{\text{Ag,sub, end}}$ is zero at potentials lower than $0.04 \text{ V}_{\text{RHE}}$. It is apparent that the silver sulfidation is associated with the equilibrium potential of the $\text{Ag}/\text{Ag}_2\text{S}$ system in the presence of HS^- . At potentials higher than $0.14 \text{ V}_{\text{RHE}}$, however, it is independent of $E_{\text{Ag,sub}}$ and almost constant, ca. 8 mC, suggesting that the sulfidation efficiency is ca. 0.8. Sulfidation of the silver substrate using the $\text{Ag}/\text{Ag}_2\text{S}$ microelectrode is possible only at potentials higher than ca. $0.14 \text{ V}_{\text{RHE}}$. This potential independency of the sulfidation depends on mass transport of HS^- generated from the microelectrode rather than electron transfer at the interfaces.

3.4 Potential of LPIG as a sulfide ion generation apparatus

In general experiments to investigate a sulfidation of silver, Ag_2S layer forms on the silver surface in the presence of sulfide ions-containing media such as H_2S , K_2S and Na_2S . [1,4,7,29-31] The sulfidized layer in this study by using $\text{Ag}/\text{Ag}_2\text{S}$ LPIG microelectrode (Figure. 3.5) is Ag_2S . The use of Ag_2S is not new findings. However, it have successfully developed a very safe sulfide ion generator with an amount of HS^- of $5.2 \times 10^{-8} \text{ mol}$. A generation of HS^- is possible to concentrate with an infinitesimal amount of HS^- on a local area for the first time. The average concentration of HS^- is lower than 0.05 ppm in the electrochemical cell of 100 cm^3 in volume until the completion of HS^- generation. This is sufficiently smaller than the ceiling limits of H_2S in air, 20 ppm. [32] It is thought that this experimental system is fairly safe for an HS^- generation apparatus.

The relatively large ($500 \text{ }\mu\text{m}$ in diameter) microelectrode does not show a fine steady state during the HS^- generation. Electrochemical reactions on $\text{Ag}/\text{Ag}_2\text{S}$ LPIG electrode include a generation of HS^- and OH^- as well as a formation of porous Ag layer. From the interface of $\text{Ag}/\text{Ag}_2\text{S}$, HS^- and OH^- should diffuse across the Ag layer to solution. It is difficult to reach a fine steady state in potentiostatic polarization because of the complexity of HS^- generation process, even if the ultra microelectrode is used. Galvanostatic polarization of the $\text{Ag}/\text{Ag}_2\text{S}$ microelectrode also provided to generate HS^- . Galvanostatic polarization of the $\text{Ag}/\text{Ag}_2\text{S}$ microelectrode also enables generation of HS^- . Providing a constant rate of HS^-

generation is beneficial and effective for investigating the charge-transfer controlling process of sulfidation. After the galvanostatic generation, however, hydrogen gas might be generated accompanying a potential shift to a less noble direction and could damage the formed silver sulfide layer.

The modeling results for potentiostatic and galvanostatic polarization of the LPIG of Ag/Ag₂S microelectrode show that the concentration on the substrate electrode surface is highly dependent on geometries of interelectrode distance and the LPIG itself. Variations of the geometries such as the interelectrode distance and the edge angle of the LPIG sheath can cause significant concentration changes in HS⁻ and OH⁻. The modeling steps of the concentration profiles of HS⁻ and OH⁻ are dependent on the geometries, which are associated to fundamental results concerning diffusion behavior of HS⁻ and OH⁻. The information for the dependencies is essential for operating the LPIG. Although some conditions have been neglected for modeling, it was worth challenging for obtaining quantitative information of concentration distribution during operation of the LPIG. In order to obtain a deeper understanding about the concentration profiles of HS⁻ and OH⁻, it is thought that an appropriate Butler-Volmer equation for cathodic reaction of Ag/Ag₂S is necessary. Moreover, the buffer effect is also very important factor for understating generation process of HS⁻ and OH⁻. The establishment of a safe system for generation of sulfide ions will contribute to precise investigation of the sulfidation in various media not only on a silver surface but also on various metal surfaces.

3.5 Summary

Development of a system for safe generation of sulfide ions and sulfidation of a silver surface was attempted for the first time using a microelectrode technique. Cyclic voltammetry and XRD revealed that the electrochemical reactions were reversible as anodic Ag₂S formation on the Ag microelectrode and cathodic HS⁻ generation of the Ag/Ag₂S microelectrode in Na₂S solution. The Ag/Ag₂S microelectrode successfully generated HS⁻ by cathodic polarization in pH 8.4 boric-borate buffer solution. Generation of HS⁻ and OH⁻ were strongly dependent on diffusion of the anions from the microelectrode to the substrate surface and solution bulk. Moreover, concentration on the substrate electrode surface is highly dependent on geometries of interelectrode and LPIG itself. The substrate potential as well as diffusion of HS⁻ influences sulfidation of the silver substrate. Sulfidation by using the Ag/Ag₂S microelectrode is safe and effective to investigate the mechanism and kinetics of sulfidation in various media not only on a silver surface but also on various metal surfaces.

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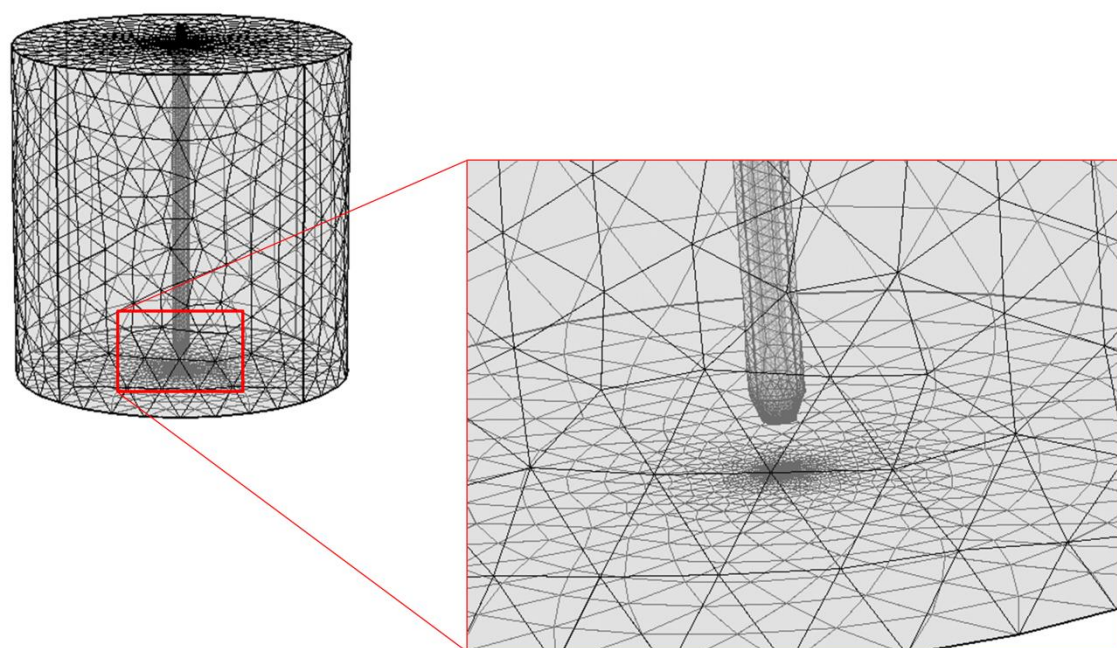


Figure 3.1

Mesh of the tetrahedral element used for the LPIG system modeling with two different sizes for electrodes surfaces and a bulk solution.

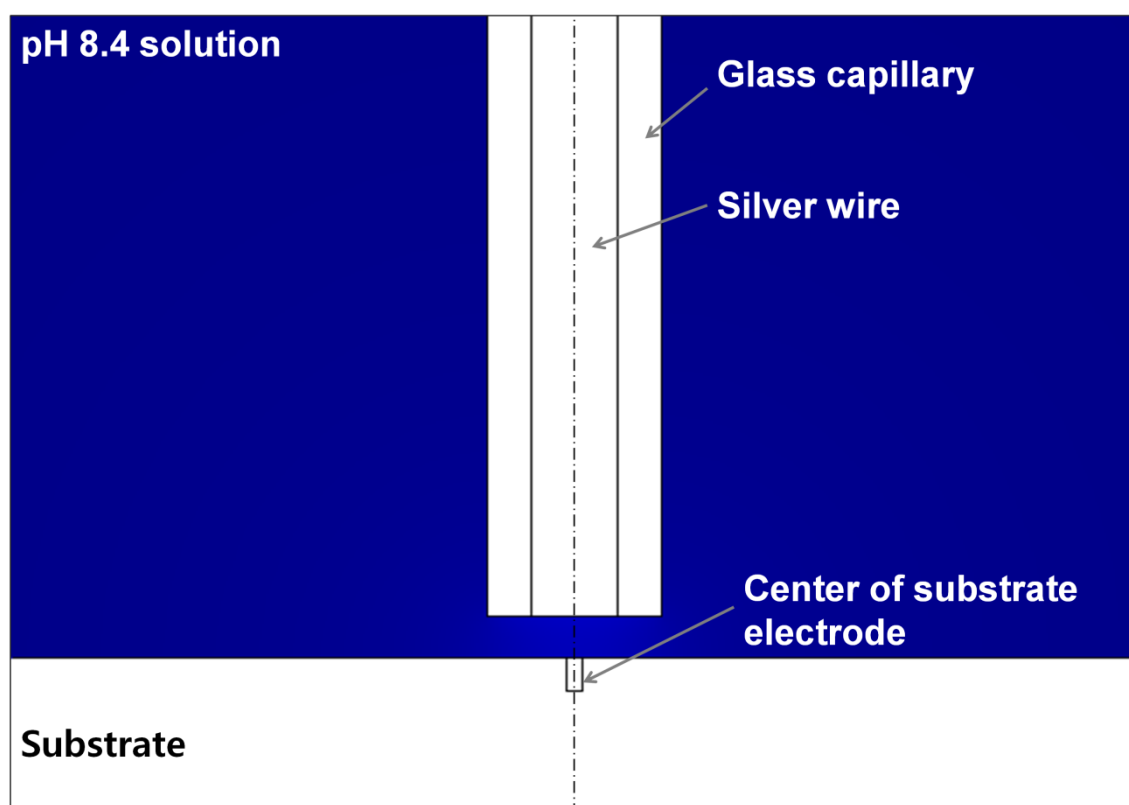


Figure 3.2

Schematic illustration of the LPIG system used for modeling.

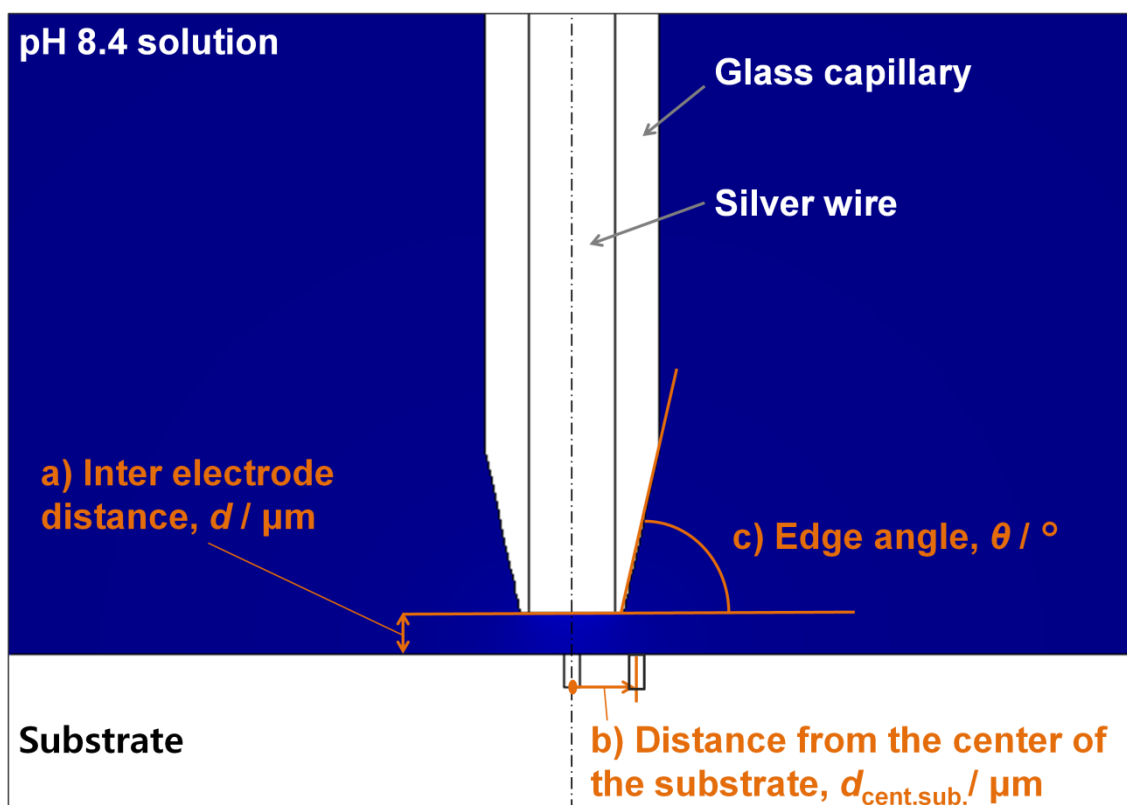


Figure 3.3

Schematic illustration of variations of the modeling of geometries for (a) the interelectrode distance, (b) the distance from the center of the substrate, and (c) the edge angle of the LPIG sheath.

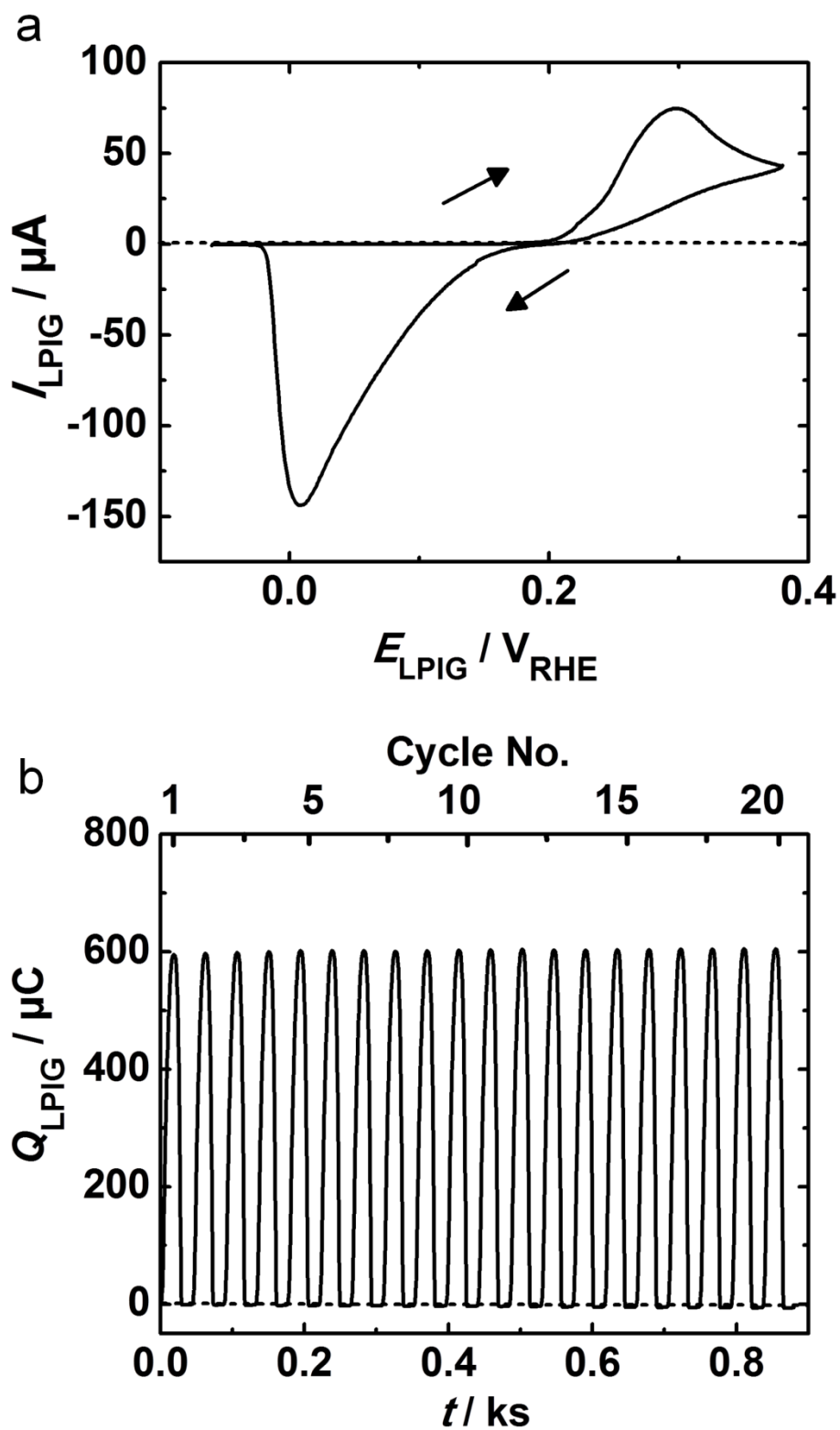


Figure 3.4

(a) Cyclic voltammograms of a silver microelectrode in $0.1 \text{ mol dm}^{-3} \text{ Na}_2\text{S}$ solution. The potential scan rate was 20 mV s^{-1} . (b) Transient of electric charge consumed during CV.

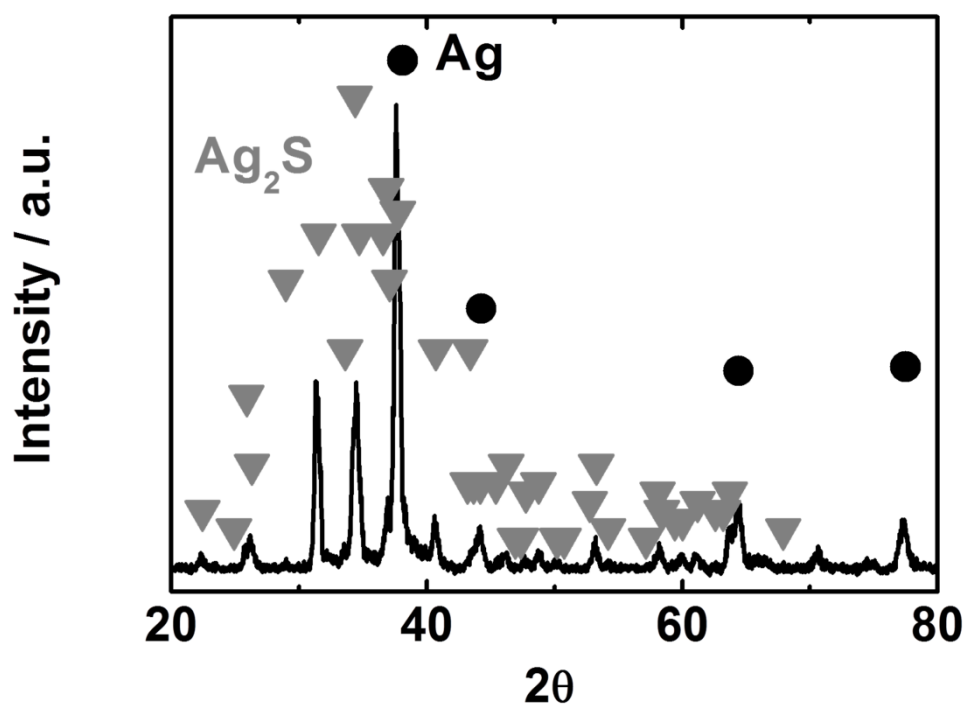


Figure 3.5

XRD pattern of the silver surface polarized at 0.3 V_{RHE} for 5.1 C cm^{-2} in $0.1 \text{ mol dm}^{-3} \text{ Na}_2\text{S}$ solution
 Marks (circle and triangle) were attributed to JCPDS files of Ag_2S : No. 14-0072 and Ag: No. 04-0783, respectively.

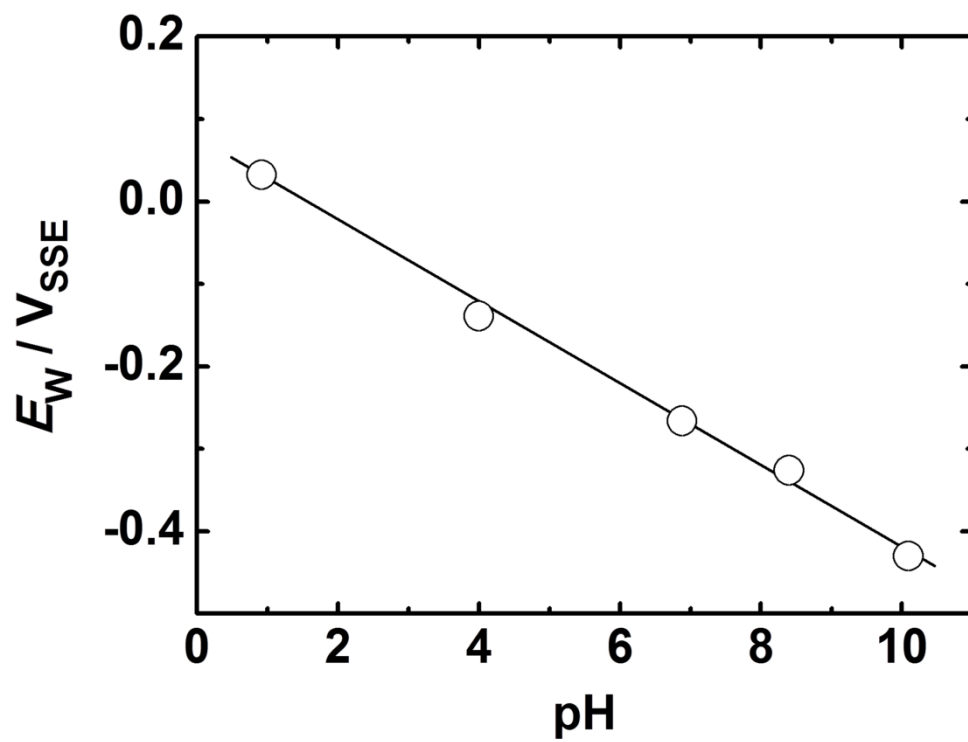


Figure 3.6

Electrode potential of the tungsten microelectrode of the substrate as a function of solution pH.

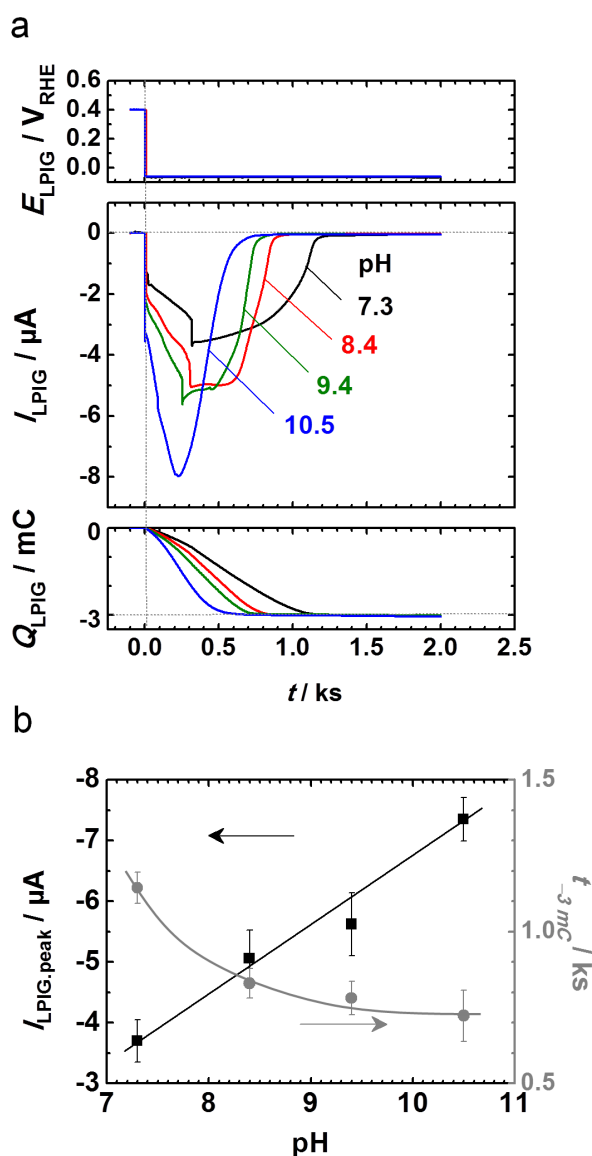


Figure 3.7

(a) Transients of current I_{LPIG} and electric charge Q_{LPIG} when the potential E_{LPIG} of an Ag/Ag₂S microelectrode was kept at 0.4 V_{RHE} for 100 s and changed to -0.06 V_{RHE} in pH 7.3, 8.4 boric-borate buffer solution, 9.4 or 10.4 NaOH solution. The 200 μm diameter of silver wire (Nilaco, AG-401265) was used for fabricating Ag/Ag₂S LPIG microelectrode. The LPIG microelectrode was polarized at 0.3 V_{RHE} 0.1 mol dm⁻³ Na₂S solution until the electric charge of 3 mC, $Q_{\text{LPIG,charge}}$, was consumed. (b) Completion time for consuming -3 mC of cathodic reaction for Ag/Ag₂S microelectrode as a function of solution pH.

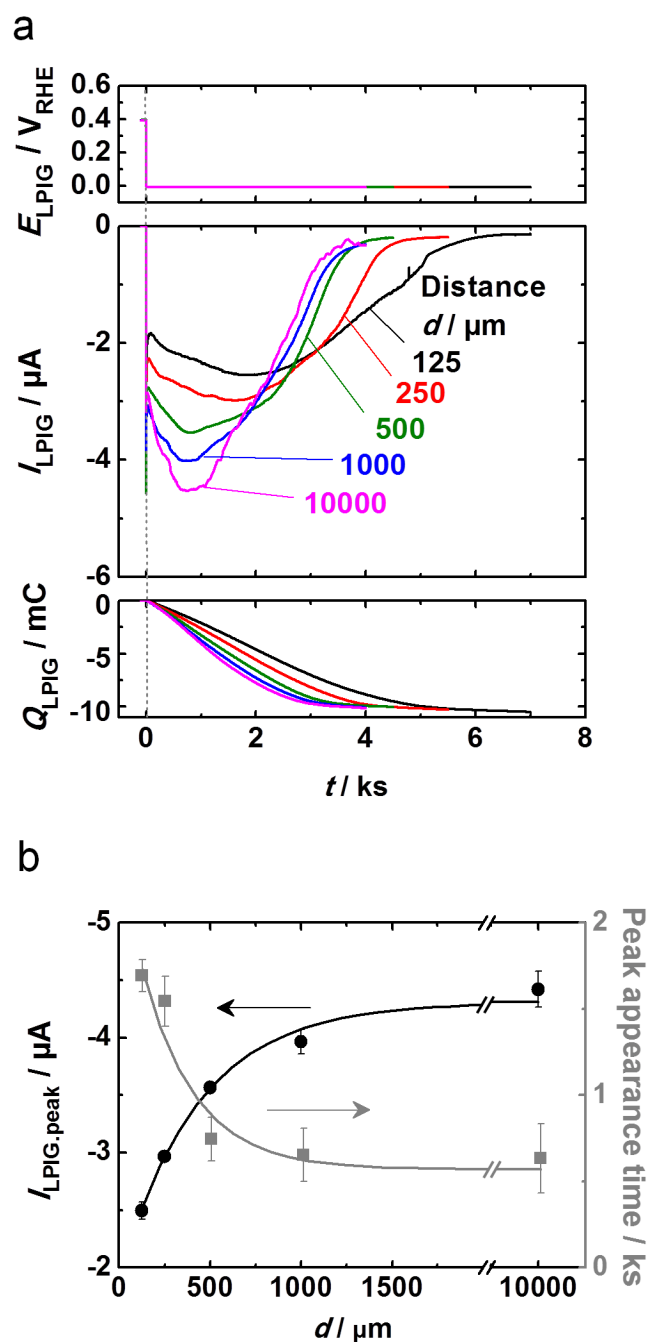


Figure 3.8

(a) Transients of current I_{LPIG} and electric charge Q_{LPIG} when the potential E_{LPIG} of an Ag/Ag₂S microelectrode was kept at 0.4 V_{RHE} for 100 s and changed to 0.0 V_{RHE} in pH 8.4 boric-borate buffer solution. The microelectrode, charged Ag₂S of 10 mC, was positioned above a glass plate with a distance of 125, 250, 500, 1000, or 10000 μm . (b) Peak current and peak appearance time as a function of distance between the microelectrode and glass substrate.

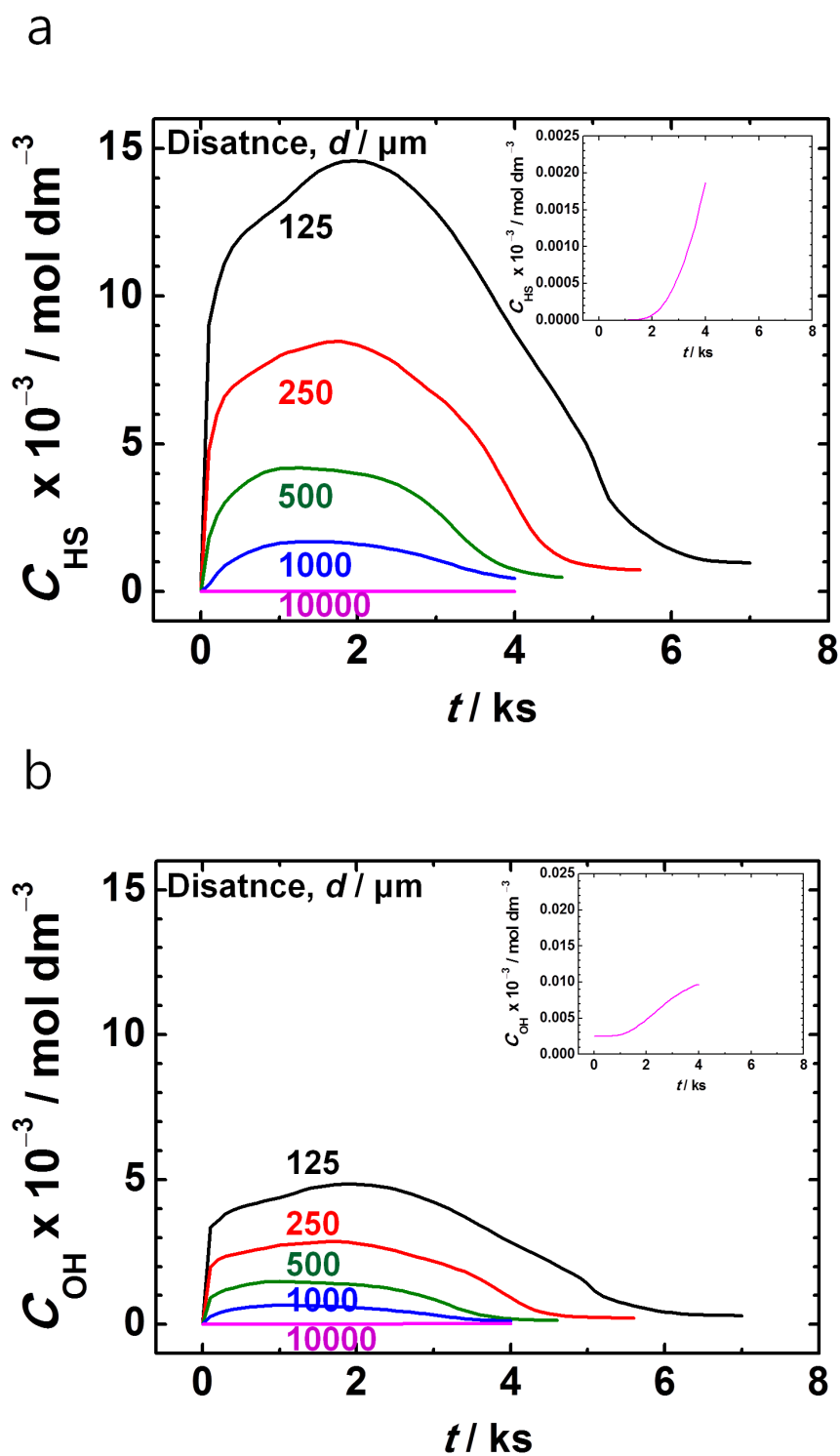


Figure 3.9

Concentration profiles of (a) HS^- and (b) OH^- during the potentiostatic polarization of the LPIG above an insulating substrate surface in a pH 8.4 solution for 7 ks.

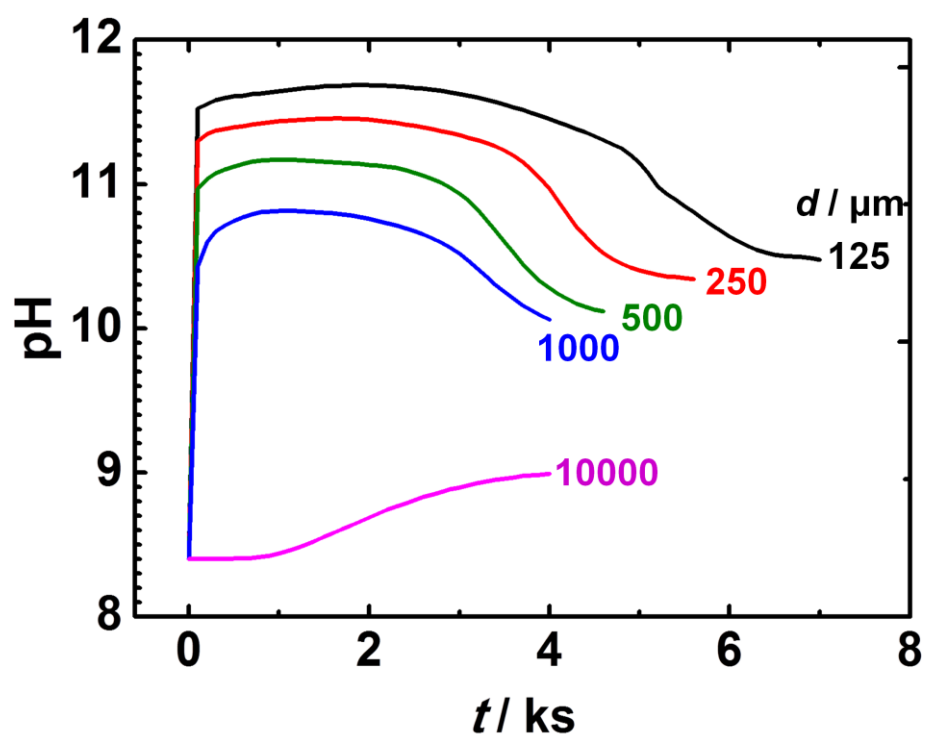


Figure 3.10

pH profile on the substrate surface during the potentiostatic polarization of the LPIG for 7 ks based on the results from Figure 3.7 b.

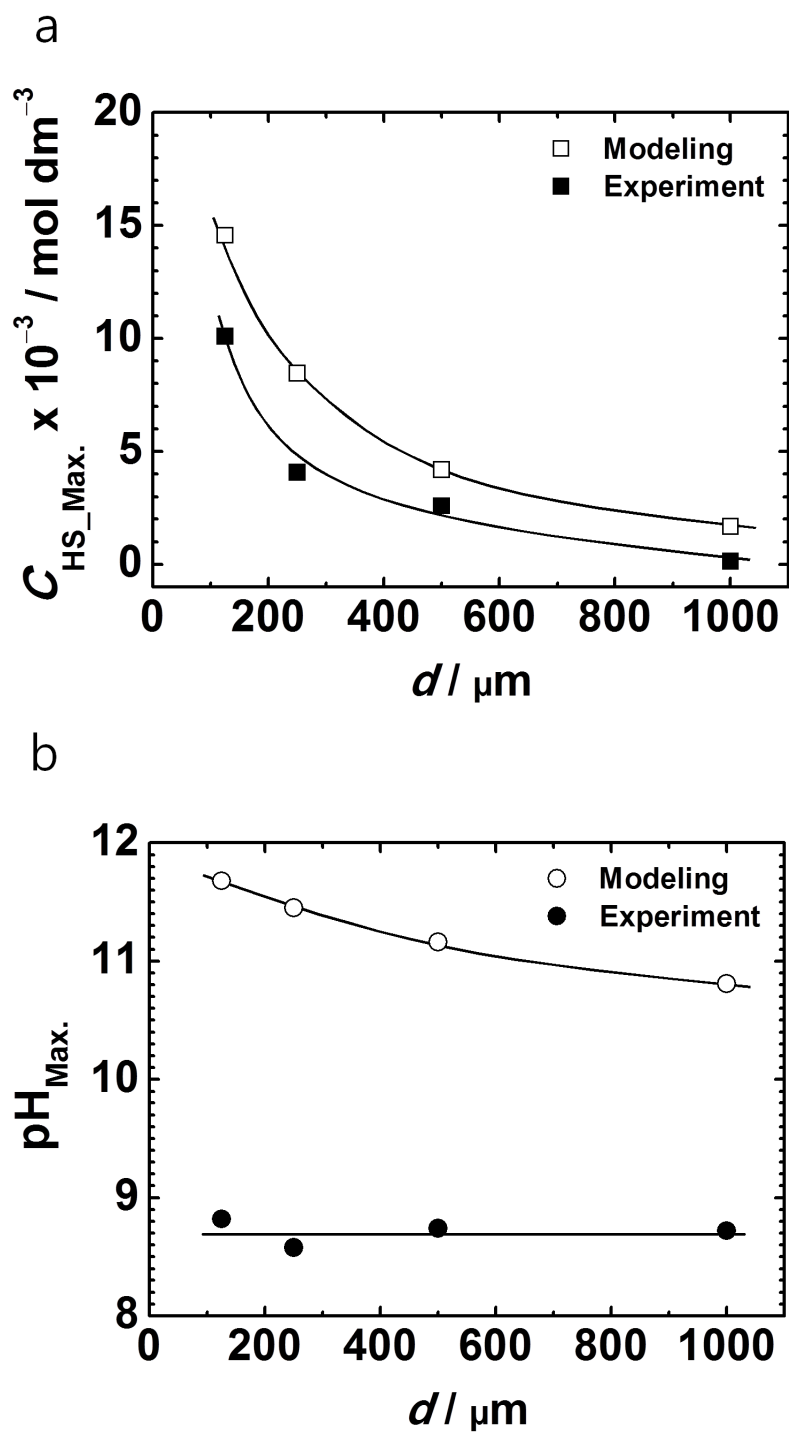


Figure 3.11

Comparison between the experimental and modeling results of (a) the maximum concentration of HS^- and (b) the maximum value of pH during the potentiostatic polarization of the LPIG above an insulating substrate surface as a function of an interelectrode distance.

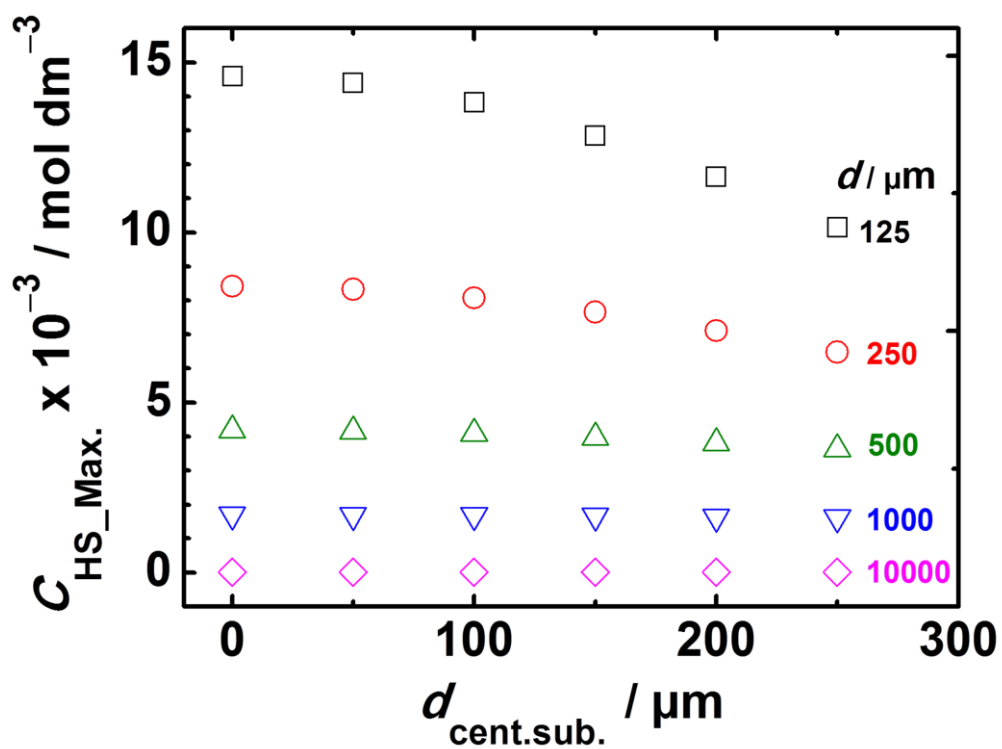


Figure 3.12

Maximum concentration of HS^- during the potentiostatic polarization of the LPIG above an insulating substrate for 7 ks, as a function of the distance from the center of the substrate surface.

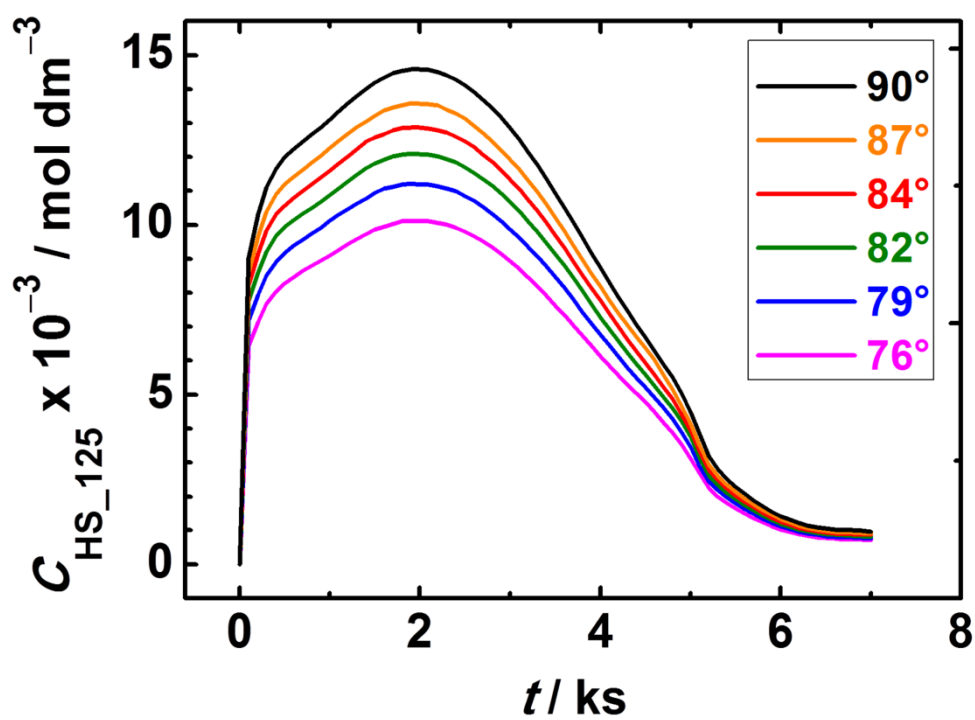


Figure 3.13

HS^- concentration profile with an interelectrode distance at $125 \mu\text{m}$, when an edge angle of the LPIG microelectrode sheath was changed.

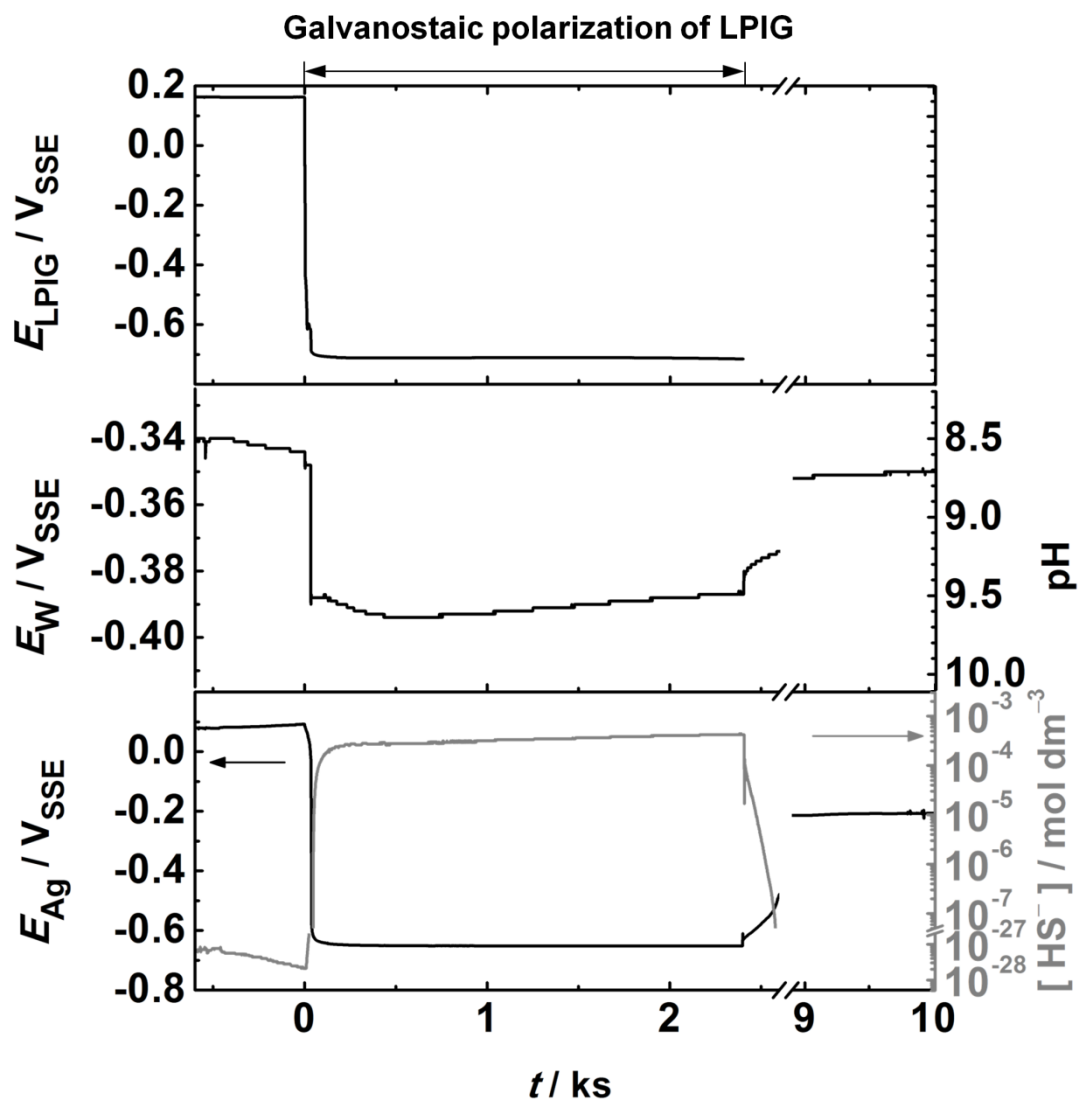


Figure 3.14

Changes in electrode potentials of the LPIG microelectrode E_{LPIG} , tungsten microelectrode E_{W} , and silver microelectrode E_{Ag} before and after the LPIG microelectrode was galvanostatically polarized at $-3 \mu\text{A}$. The value of pH and $[\text{HS}^-]$ were estimated using Eqs. 3.4 and 3.3.

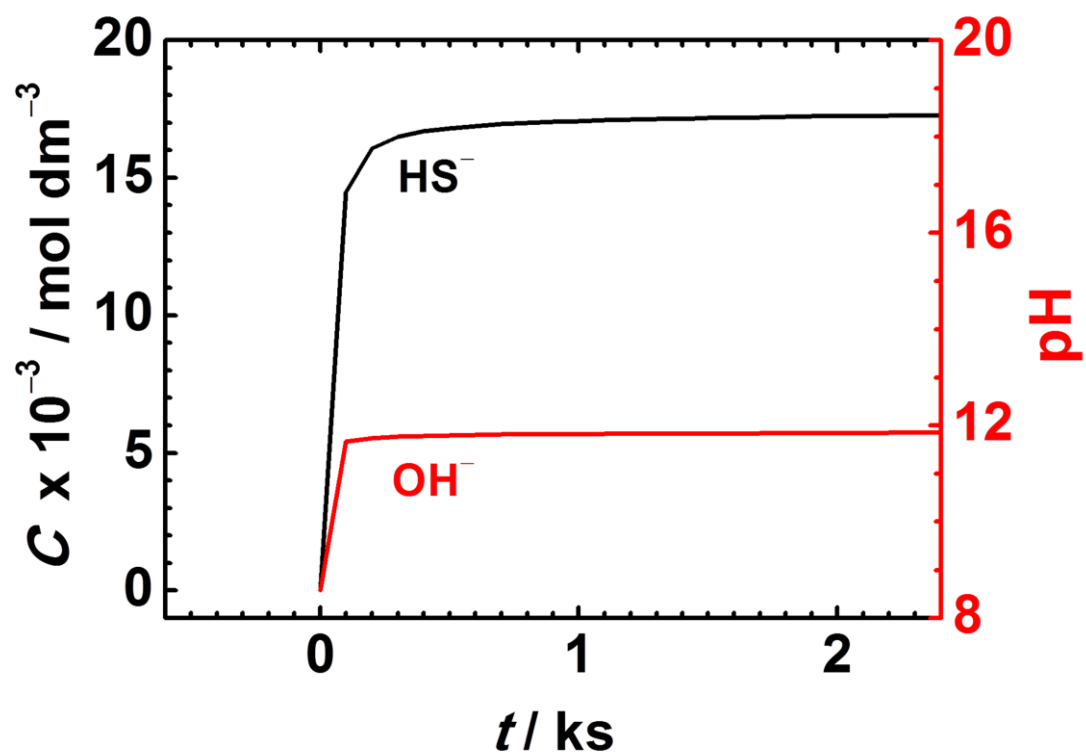


Figure 3.15

Concentration profiles of HS^- and OH^- during the galvanostatic polarization of the LPIG above an insulating substrate surface in a pH 8.4 solution for 2.4 ks.

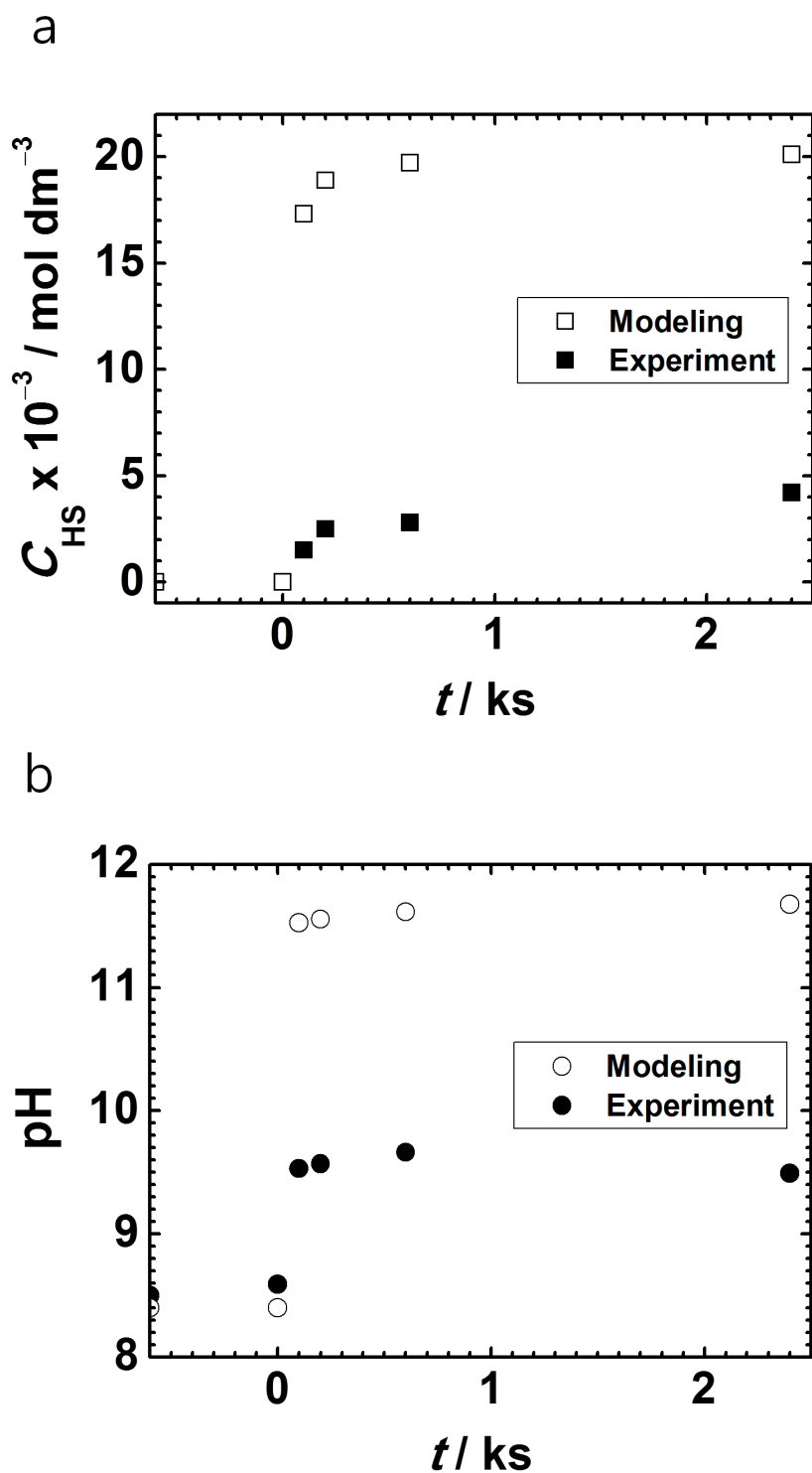


Figure 3.16

Comparison between the experimental and modeling results of (a) the concentration of HS^- and (b) the value of pH during the galvanostatic polarization of the LPIG above an insulating substrate surface, as a function of polarization time.

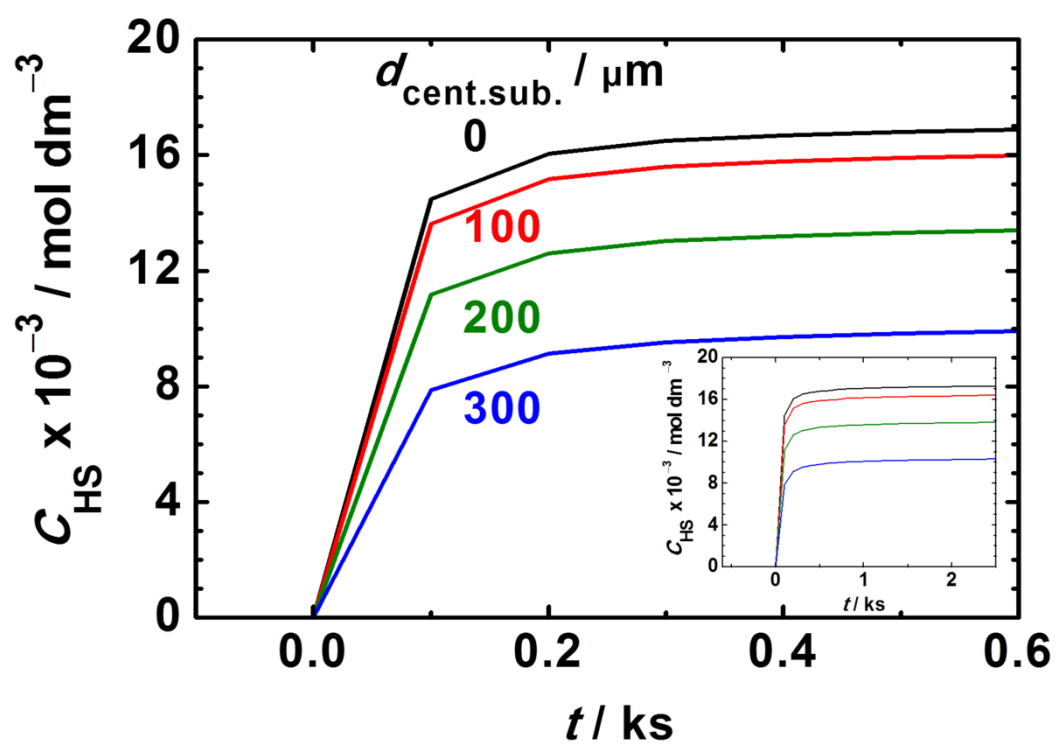


Figure 3.17

Change of $[\text{HS}^-]$ during the galvanostatic polarization of LPIG above an insulating substrate, as a function of a horizontal distance from the center of substrate surface for 2.4 ks.

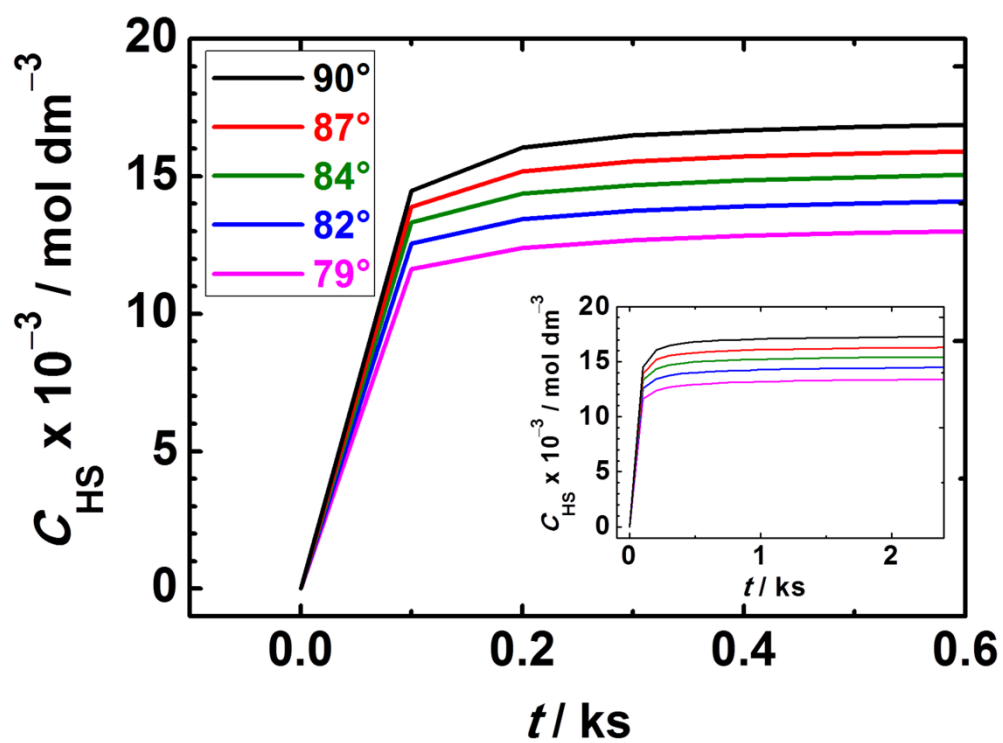


Figure 3.18

HS^- concentration profile with an interelectrode distance at $125 \mu\text{m}$, when an edge angle of the LPIG microelectrode sheath was changed from 79° to 90° .

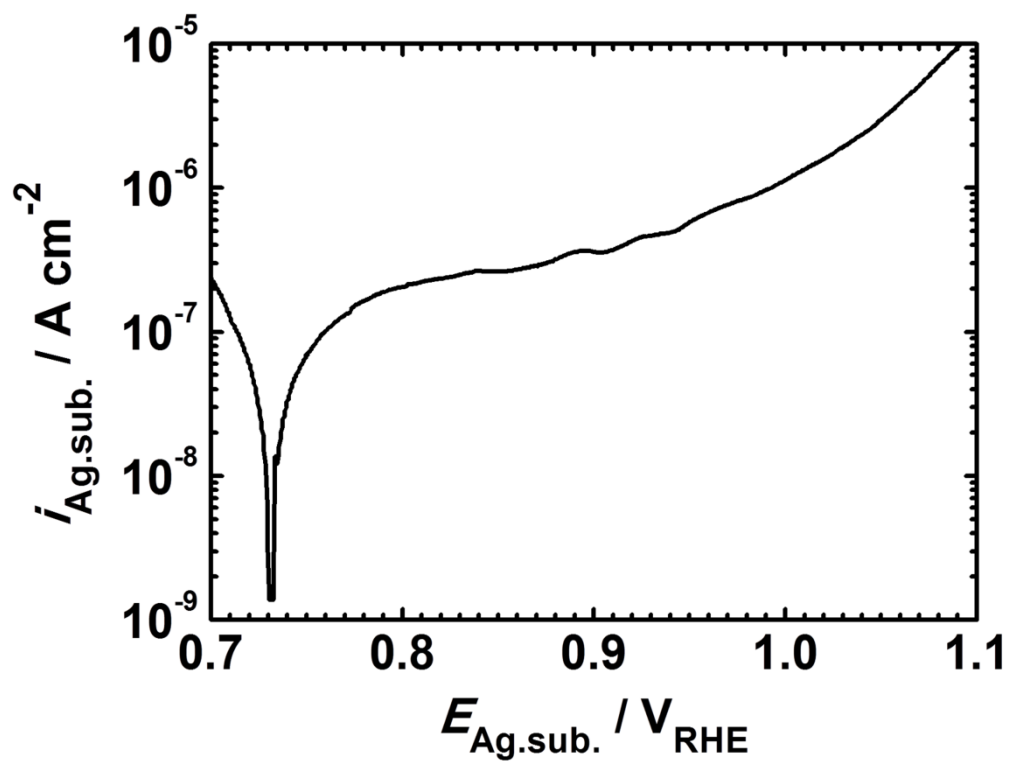


Figure 3.19

Dynamic polarization curve of the silver substrate at a scanning rate of 1 mV s^{-1} in pH 8.4 boric-borate buffer solution.

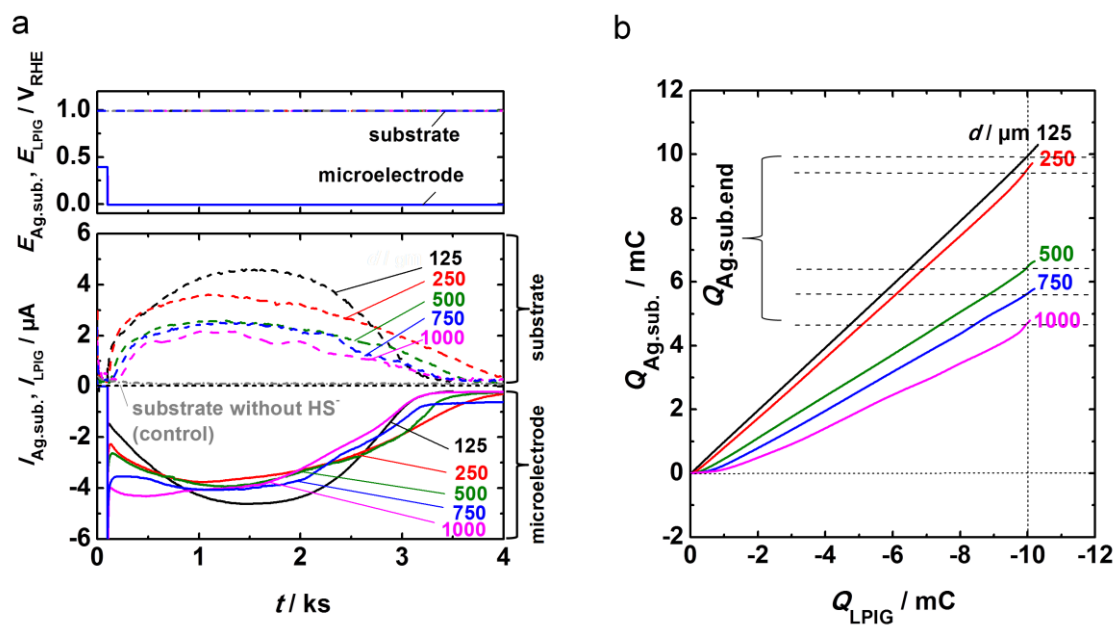
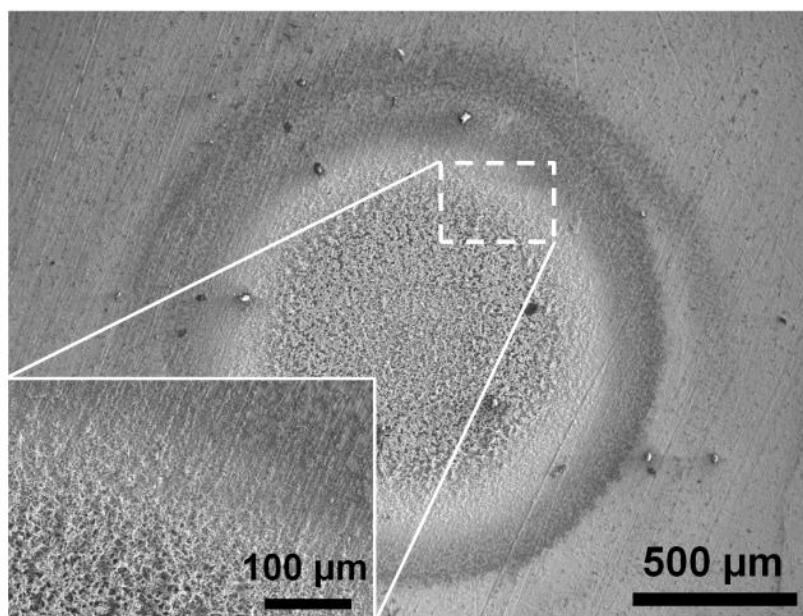


Figure 3.20

(a) Transients of currents I_{LPIG} and $I_{\text{Ag.sub.}}$ flowing through the Ag/Ag₂S microelectrode and silver substrate electrode, respectively, when potential E_{LPIG} of the microelectrode was changed from 0.4 to 0.0 V_{RHE} while the silver substrate electrode was polarized at $E_{\text{Ag.sub.}} = 1.0$ V_{RHE} in pH 8.4 boric-borate buffer solution. The microelectrode, charged Ag₂S of 10 mC, was positioned above the substrate with a distance of 125, 250, 500, 750, or 1000 μm . (b) Relation between electric charges $Q_{\text{Ag.sub.}}$ and Q_{LPIG} consumed at the silver substrate and Ag/Ag₂S microelectrode, respectively.

a



b

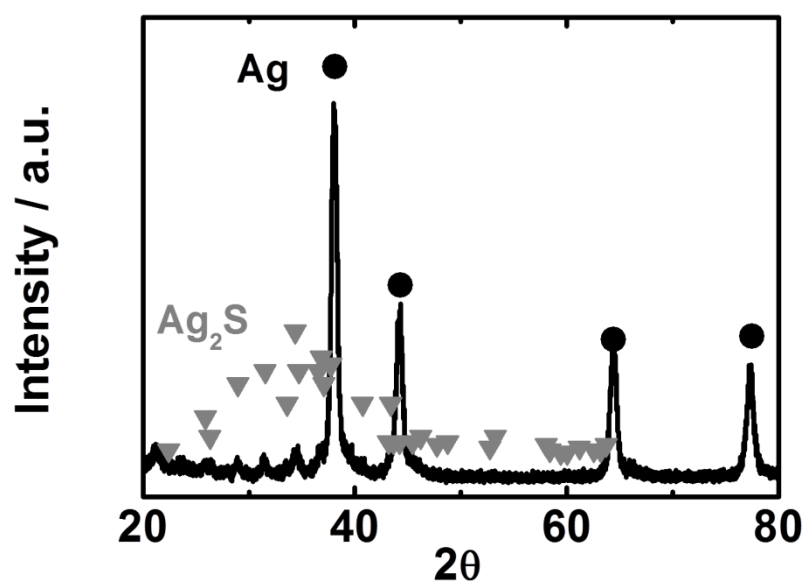


Figure 3.21

(a) SEM images and (b) XRD pattern of the silver substrate surface after HS^- generation at the potential $0.0 \text{ V}_{\text{RHE}}$ with a distance of $125 \mu\text{m}$.

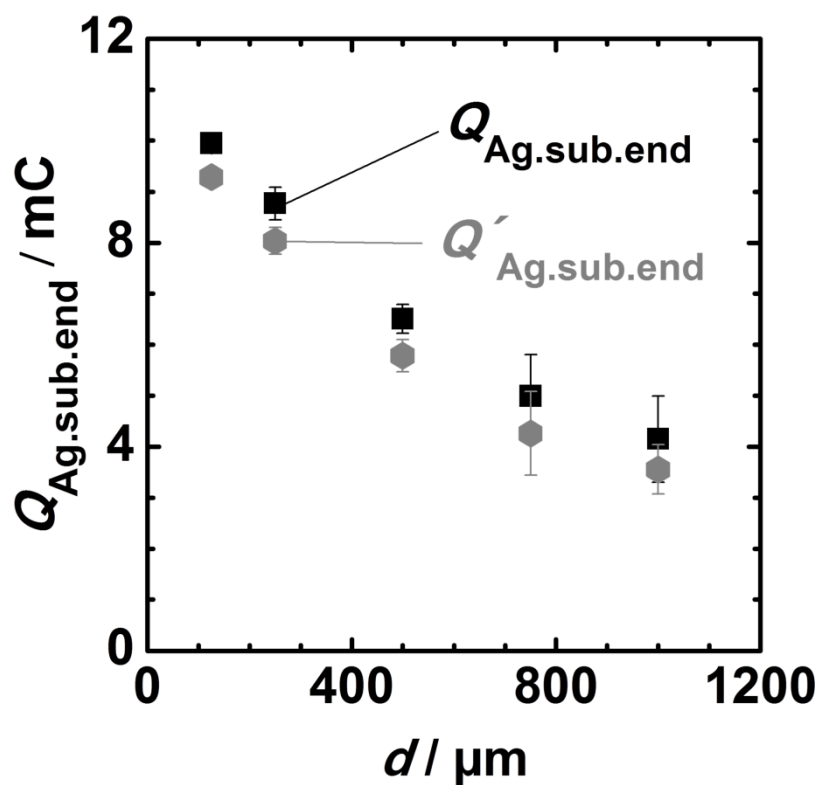


Figure 3.22

Electric charge $Q_{\text{Ag.sub.end}}$ consumed at the silver substrate until the HS^- generation of 10 mC is completed as a function of the distance d . The charge $Q'_{\text{Ag.sub.end}}$ was $Q_{\text{Ag.sub.end}}$ subtracted by that consumed for substrate oxidation in a separate experiment without the microelectrode.

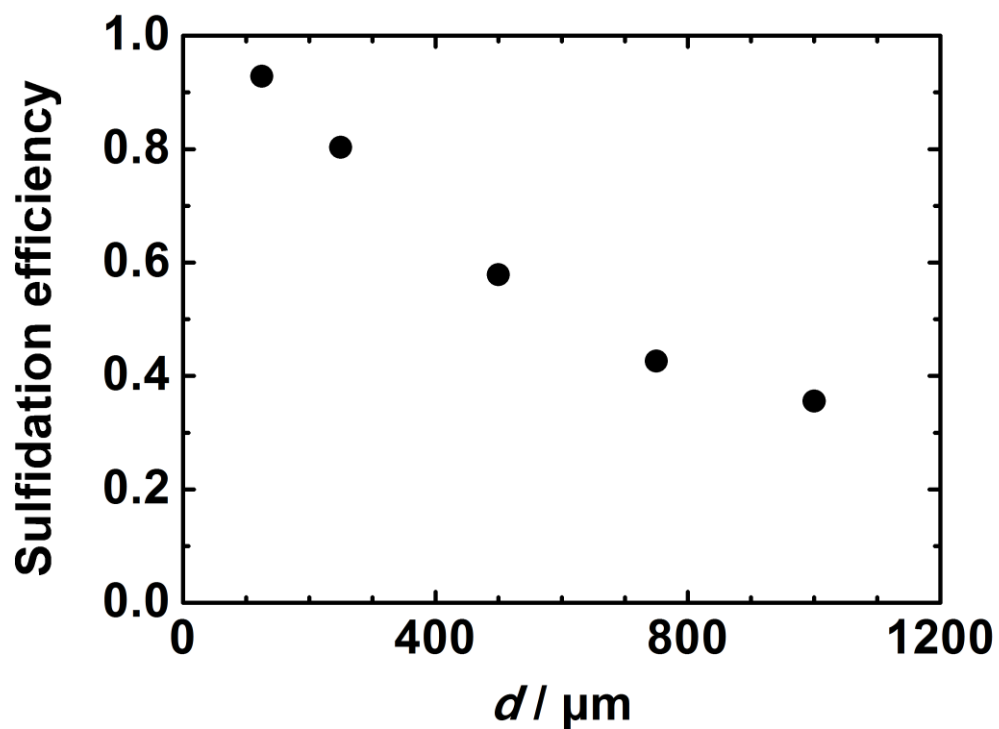


Figure 3.23

Efficiency of sulfidation on silver substrate surface with a function of the interelectrode distance between LPIG and silver substrate electrode, and the efficiency was obtained from the ratio of $Q'_{\text{Ag.sub.end}}$ to $Q_{\text{LPIG.charge}}$ (10 mC).

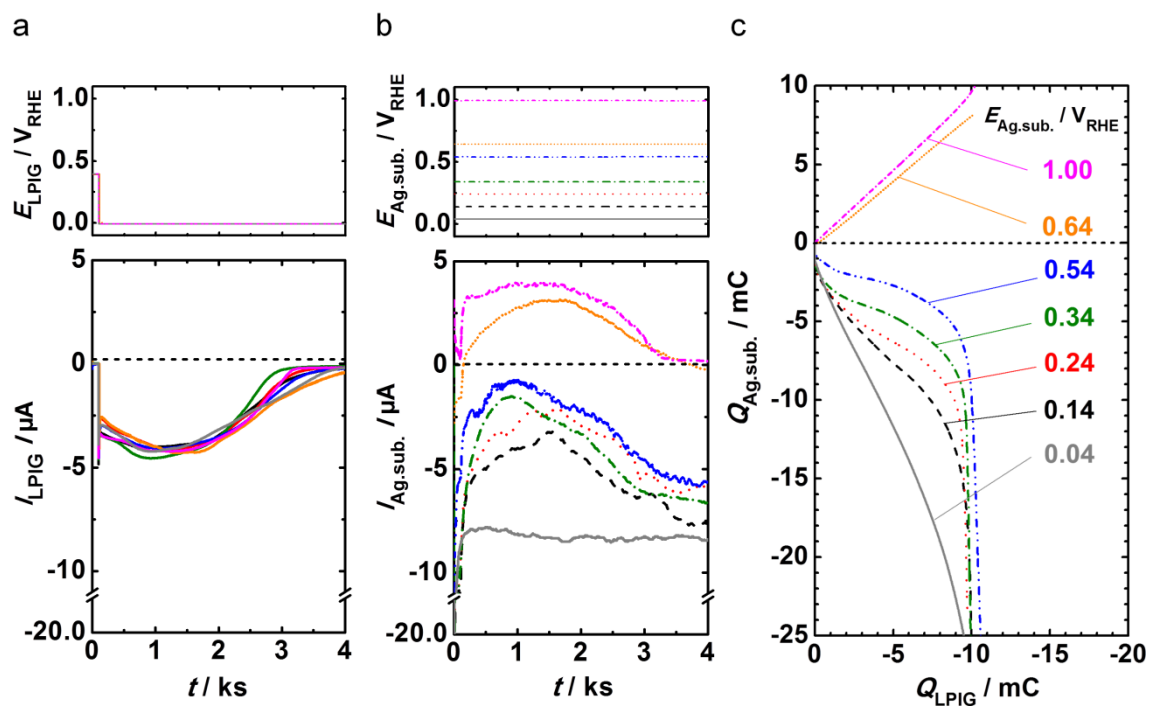


Figure 3.24

(a, b) Transients of currents I_{LPIG} and $I_{\text{Ag.sub.}}$, and (c) relation between electric charges $Q_{\text{Ag.sub.}}$ and Q_{LPIG} when potential E_{LPIG} was changed from 0.4 to 0.0 V_{RHE} with the substrate polarized at $E_{\text{Ag.sub.}} = 0.04, 0.14, 0.24, 0.34, 0.54, 0.64$, or 1.00 V_{RHE} . The interelectrode distance was kept at 250 μm .

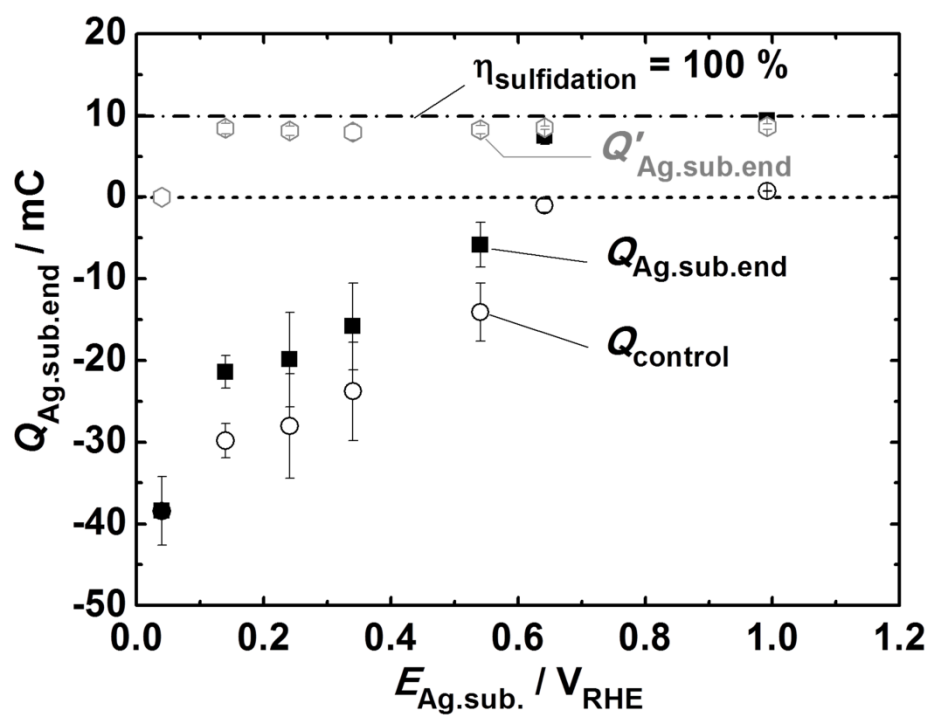


Figure 3.25

Electric charge $Q_{\text{Ag.sub.end}}$ consumed at the silver substrate until HS^- generation of 10 mC is completed as a function of the substrate potential $E_{\text{Ag.sub.}}$. The charge $Q'_{\text{Ag.sub.end}}$ was subtracted from $Q_{\text{Ag.sub.end}}$ by that of $Q_{\text{Ag.sub.control}}$ consumed for oxidation.

Chapter 4 Effect of hydrogen sulfide ions on passive behavior of type 316L stainless steel

4.1 Introduction

Corrosion resistance of stainless steel is thought to be dependent on degradation of the passive film, which is important to understand a precursor process involved in localized corrosion such as pitting corrosion and to estimate the long-term performance of the material. Inclusions of sulfides such as manganese sulfide, MnS, are known to provide pitting corrosion sites of stainless steel.[1-3] As for the roles of MnS in pitting corrosion, it has been generally agreed that electrochemical and/or chemical reactions of MnS release S species such as SO_4^{2-} , HSO_3^- , $\text{S}_2\text{O}_3^{2-}$, S and S^{2-} . The released S species change the composition of the local solution contiguous to the inclusion and lead to a decrease of pH near the micro-area. The decrease in pH and the presence of aggressive S species result in transition of the passive surface to a transpassive state, causing exposure of the substrate to the solution, which is the initiation of pitting corrosion.[1-5] Eklund suggested that the dissolution of MnS gives rise to acidification of the solution by producing sulfate ions:[1]



Solution acidification is also caused by production of thiosulfate ions:[2]



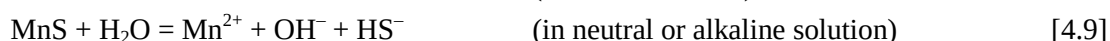
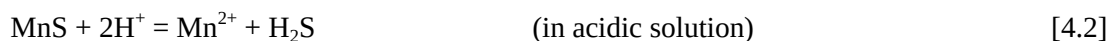
In both cases, elemental sulfur is finally formed. Meanwhile, Wraglén proposed that elemental sulfur formed by MnS dissolution leads to further acidification as follows:[5]



Many possible explanations for the detrimental effects of various S species causing initiation and/or propagation of pitting corrosion on stainless steels have been presented. Most previous studies have focused on the overall processes, including

destabilization of the passive film, removal of the film, and initiation and/or propagation of pits. Since degradation of the passive film is the initial process of pitting corrosion, it is important to contemplate the change in passivity or passive film until depassivation.

When stainless steel is exposed to an aqueous solution, a small amount of MnS on the stainless steel surface dissolves because its solubility in water is 4.7 ppm at 291 K.[6]



Furthermore, the dissociations of H_2S and HS^- in aqueous solutions are as follows:



The values of pK_a for Eqs. 10 and 11 are 7.05 and 19.0, respectively, at 298 K.[7] The dissociation of HS^- is negligibly small and H_2S generates mainly protons during its dissociation. Thus, the primary dissolution reaction of MnS momentarily increases pH of the local solution near the MnS. However, little attention has been given to the effect of HS^- on the passivity of stainless steel.

The use of a liquid-phase ion gun (LPIG) is a microelectrode technique, a type of scanning electrochemical microscopy (SECM), which is effective for controlling the release of infinitesimal anions to a local space in the solution.[8] Recently, it has developed an LPIG to release a ppm-order amount of HS^- by cathodic polarization of a silver microelectrode covered with a silver sulfide (Ag_2S) layer.[9] The total amount of HS^- during the operation of the LPIG is in a safe order. It is possible to control the concentration of HS^- in the vicinity of the LPIG by its polarization. Application of the LPIG to other metal surfaces is expected to elucidate the mechanism and/or kinetics of depassivation of the stainless steel surface in a solution containing HS^- . This study is the first study in which the LPIG was applied to type 316L stainless steel as a generator of HS^- . The effect of HS^- on degradation of the passive film is discussed.

4.2 Experimental

4.2.1 Specimen preparation

Stainless steel.— Type 316L stainless steel specimen was used in this chapter. The rod type specimen was embedded in epoxy resin with a surface area of 0.07 cm^2 and mechanically ground with SiC papers down to 4000 grit and then rinsed with distilled water.

Liquid-phase Ion Gun (LPIG).— The procedure for fabrication the LPIG microelectrode is basically the same as that reported in Chapter 3. A silver microelectrode was prepared from a silver wire with a purity of 99.9% and a diameter of 500 μm by embedding in a 1 mm diameter glass capillary with epoxy resin. The microelectrode was polarized at $-0.7 V_{\text{SSE}}$ in deaerated $0.1 \text{ mol dm}^{-3} \text{ Na}_2\text{S}$ solution until the electric charge of 10 mC was consumed.

Scanning Electrochemical Microscope (SECM).— A platinum microelectrode with a diameter of 30 μm was used as a tip electrode of an SECM. The probe electrode preparation is described in Chapter 2.3. The substrate electrode of type 316L stainless steel was used. All electrodes were mechanically ground with SiC papers down to 4000 grit and then rinsed with distilled water.

4.2.2 Operation of the LPIG system

The LPIG were operated in deaerated pH 8.4 buffer solution ($0.15 \text{ mol dm}^{-3} \text{ H}_3\text{BO}_3$ and $0.15 \text{ mol dm}^{-3} \text{ NaB}_4\text{O}_7$) with an interelectrode distance between the LPIG and the substrate electrode of 125 μm . The potential of the LPIG microelectrode was measured by an electrometer. After the monitoring rest potential of the LPIG, the LPIG was galvanostatically polarized at $-3 \mu\text{A}$ using a battery-driven current source. After immersion for 600 s, the LPIG microelectrode was polarized for 0, 1900, 1950 or 2400 s to generate S species. After the polarization of LPIG, the LPIG microelectrode was pulled up to the bulk solution with a stage moving period within 2 s. The detailed procedure for operating the LPIG was schematically described in Figure 4.1.

4.2.3 Impedance measurement

After the polarization of LPIG for 0, 100, 150 or 600 s, potentiostatic polarization of the specimen electrode at 0.4 or 0.9 V_{SSE} for 100 s and following electrochemical impedance measurement. The electrochemical impedance spectroscopy (EIS) were continuously conducted using a potentiostat (SP-150, Biologic) with average values of more than 50 times of an each data. In the impedance and EIS measurements, the electrode potential was perturbed by $\pm 10 \text{ mV}$ in a constant frequency at 15 Hz for 7500 s and in a frequency range from 10^4 to 10^{-1} Hz , respectively.

4.2.4 Mott-Schottky measurement

After the polarization of LPIG for 0, 100, 150 or 600 s, potentiostatic polarization of the specimen electrode at 0.4 V_{SSE} for 100 s and following Mott-Schottky (M-

S) analysis were conducted. The M-S analysis was promptly conducted at a frequency of 15 Hz and at a potential of 0.4 or 0.9 V_{SSE} and stepwise-shifted potentials to -0.4 or $0.4 V_{SSE}$, respectively, with average values of more than 50 times of an each data. At this frequency, the capacitive property of the electrode surface was dominated the impedance response in an EIS measurement as discussed later. A software package (EC-lab, Biologic) was used to fit curves of the impedance data.

4.2.5 SECM measurement

The tip electrode of the SECM was positioned above the 316L specimen substrate electrode with an interelectrode distance of 20 μm using a stepping motor X-Y-Z stage and an optical microscope. After the LPIG operation for 600 s in the vicinity of the specimen surface, the specimen was polarized at 0.4 V_{SSE} for 100 s in deaerated pH 8.4 buffer solution and the specimen surface was monitored by SECM in a solution containing $1.0 \times 10^{-3} \text{ mol dm}^{-3}$ hydroxymethylferrocene, FcMeOH. The tip electrode and the 316L specimen substrate electrode were connected to a bipotentiostat and polarized independently at $E_t = 0.6 V_{SSE}$ and $E_s = -0.2 V_{SSE}$, respectively, for a tip generation/substrate collection (TG/SC) mode. Simultaneously, the tip electrode was scanned in an area of 3000 μm^2 square with stepwise of $dx = 30 \mu\text{m}$ and $dy = 30 \mu\text{m}$, respectively, and intermissions of 0.5 s and 5 s, respectively.

4.2.6 Surface analysis

The surface of the stainless steel specimen was analyzed by an Auger electron spectroscope. Ar^+ sputtering at an etching rate of 3.2 nm min^{-1} equivalent to silica was used for obtaining a depth profile of the local specimen surface with an electron beam diameter of 30 μm . Moreover, the composition of the stainless steel surface was analyzed by an X-ray photoelectron spectroscopy with Al $K\alpha$ radiation. The detection area of photoelectrons was in a diameter of 1 mm with a repeat ion of the acquisition of each spectrum to 300 times due to the small photoelectron intensity obtained from the small detection area. Photoelectron spectra were analyzed by using Spec Surf software (JEOL). The C 1s peak from contaminant carbon at 285.1 eV was used as a reference for charge correction. [10] In all electrochemical experiments and surface analyses, consistencies were confirmed more than 3 times by repetition with different specimens under the same conditions. The surface of type 316L stainless steel was characterized by using a Raman spectrometer equipped with an optical microscope (BX41, OLYMPUS) and a cooled CCD detector (Synapse, HORIBA Jobin Yvon). The stainless steel surface was excited by a laser with a diameter of 10 μm , delivering a power of 0.20 - 0.25 mW at a frequency of 532 nm.

4.3 Results

4.3.1 Anodic polarization of type 316L stainless steel

Figure 4.2 shows a dynamic polarization curve of the type 316L stainless steel electrode in deaerated pH 8.4 buffer solution. An active-passive transition is not observed and the anodic current reaches a passivity-maintaining current at potentials lower than ca. 0.5 V_{SSE}, implying that the specimen surface is spontaneously passivated before the polarization. At a potential higher than 0.5 V_{SSE}, the anodic current increases and a peak is observed at 0.7 V_{SSE}, which is attributed to the oxidation of metal cations and/or alloying elements in the passive film or stainless steel substrate.[11-14] At a potential higher than 0.8 V_{SSE}, the anodic current decreases and reaches a secondary passivation.

4.3.2 Changes in electrode potentials of E_{LPIG} and E_{316L} of the LPIG and stainless steel

The LPIG microelectrode in the vicinity of the stainless steel substrate was galvanostatically polarized at $-3 \mu A$ in pH 8.4 buffer solution. Figure 4.3 shows the changes in electrode potentials E_{LPIG} and E_{316L} of the LPIG and the stainless steel, respectively. In all cases, before the LPIG operation, E_{LPIG} does not shift, whereas E_{316L} shifts to a positive potential. This means that the LPIG is relatively stable without releasing HS⁻. The stainless steel surface is in a passive state and the passivity seems to be gradually improved. When the LPIG microelectrode is cathodically polarized, i.e., in the galvanostatic polarization of the LPIG, however, E_{LPIG} immediately shifts to $-0.7 V_{SSE}$, indicating that Ag₂S is reduced and generates OH⁻ and HS⁻. [15]



The equilibrium potential of Eq. 4.12 is a function of pH and [HS⁻] as follows:[16]

$$E / V_{SHE} = -0.274 - 0.0295 \text{ pH} - 0.0295 \log [HS^-] . \quad [4.13]$$

The rest potential E_{316L} of stainless steel is gradually shifted to a negative potential with increase in [HS⁻]. It seems that the products from the LPIG accelerate the anodic reaction of the stainless steel surface.

4.3.3 Effect of HS⁻ on semiconductive properties of passive film formed on type 316L stainless steel

Figure 4.4 is a double logarithmic plot of current density of the stainless steel specimen and time during the potentiostatic polarization when the polarization was started after the LPIG operation for 0, 100, 150 or 600 s. As discussed in Chapter 3.3.4, these operation periods correspond to $[\text{HS}^-]$ of 0.0, 1.5, 2.2 and $2.8 \times 10^{-3} \text{ mol dm}^{-3}$, respectively, on the surface of stainless steel substrate within the narrow space between the local specimen and the LPIG. It is clear that the current density decreases exponentially with time. The slope in the absence of HS^- is ca. -1 , indicating that a high field mechanism is adopted for the formation of a passive film on the surface.[17] However, the slope becomes less steep in the presence of HS^- and the effect increases with increase in $[\text{HS}^-]$. In the presence of OH^- and HS^- generated from the LPIG, potentiostatic polarization of the specimen electrode at $0.4 V_{\text{SSE}}$ allowed a relatively large anodic current to flow. The current density flowing at 100 s also increases with increase in $[\text{HS}^-]$, indicating that a more conductive passive film is formed on the specimen surface in the solution with HS^- than that formed without HS^- .

Following polarization of the stainless steel specimen electrode at $0.4 V_{\text{SSE}}$ for 100 s with or without HS^- , impedance measurement was carried out at the same potential at 15 Hz. At this frequency, the capacitive property of the electrode surface was dominated the impedance response in an EIS measurement as discussed later. Figure 4.5 shows the change in impedance $|Z|$ during potentiostatic polarization at $0.4 V_{\text{SSE}}$. It is obvious that the value of $|Z|$ gradually increases with polarization time, indicating that the stability of the passive surface improves during the polarization. The value of $|Z|$ is also dependent on $[\text{HS}^-]$ and becomes smaller in a solution containing with larger $[\text{HS}^-]$. Even after stopping the LPIG operation, the slope of $|Z|$ with time does not change regardless of $[\text{HS}^-]$, and $|Z|$ without HS^- is higher than that with HS^- . This implies that the passive film formed in solution with HS^- is less stable than that formed without HS^- . Although the polarization affects stabilization of the film, dilution of HS^- in the solution is not so effective to stabilize the passive film after the film has been meta-stabilized by the presence of HS^- . The passive film is in a relatively unstable state.

After the impedance measurement at the constant frequency, EIS was immediately carried out in a frequency range from 10^4 to 10^{-1} Hz at the same potential at $0.4 V_{\text{SSE}}$. The specimen in this study has a relatively small area, and the spectroscopy was needed to repeat several times at lower frequencies. However, consumed electric charge of 10 mC for Ag_2S layer on Ag microelectrode is difficult to sustain its cathodic polarization at $-3 \mu\text{A}$ for more than 3000 s, it was difficult to operate the spectroscopy measurement at the the lower frequency range than 0.1 Hz. A small discrepancy was observed at frequencies lower than 1 Hz, though Kramers–Kronig transformation[18-19] diagram was satisfied at most frequencies. Figure 4.6 shows Bode plots of the stainless steel specimen. Although there are some scatterings in the data, the plot is fitted with a so-called Randles-type $R_{\text{ct}}C_{\text{c}}-R_{\text{el}}$ equivalent electronic circuit, where R_{ct} and R_{el} are solution resistance and charge transfer resistance, respectively, and C_{c} is capacitance. Since the capacitance of a passive film/electrolyte interface consists of capacitance of the space charge layer C_{SC} and capacitance of the Helmholtz layer C_{H} in series,

$$\frac{1}{C_c} = \frac{1}{C_{SC}} + \frac{1}{C_H}. \quad [4.14]$$

Assuming that the value of C_H is 0.1 mF cm^{-2} for austenitic stainless steels in alkaline solutions,[20,21] the C_{SC} value was close to the measured value of C_c . Hence, C_c is considered to be C_{SC} in this paper. The values of R_{el} , R_{ct} and C_c as a function of $[\text{HS}^-]$ are shown in Table 4.1. The values of R_{el} are almost constant because $[\text{HS}^-]$ is less than $10^{-6} \text{ mol dm}^{-3}$ at maximum and is too low to change the solution conductivity. With increase in $[\text{HS}^-]$ during the passivation, however, C_c does not significantly change but R_{ct} decreases, clearly corresponding to the increase in passivation–maintaining current and the decrease in $|Z|$ shown in Figures. 4.4 and 4.5, respectively. It is thought that an electronically damaged passive film was formed by the presence of HS^- .

Table 4.1 Values of solution resistance R_{el} , charge transfer resistance R_{ct} and capacitance C_c from curve fitting with an equivalent electric circuit of $R_{el} + (R_{ct}C_c)$ plots when EIS of type 316L stainless steel was performed in a solution containing HS^-

$[\text{HS}^-] / 10^{-3} \text{ mol dm}^{-3}$	$R_{el} / \Omega \text{ cm}^2$	$R_{ct} / \text{k}\Omega \text{ cm}^2$	$C_c / \mu\text{F cm}^{-2}$
0	527 ± 2.03	781 ± 20.6	15.3 ± 0.11
1.5	538 ± 1.15	741 ± 47.8	16.1 ± 0.68
2.2	527 ± 0.87	707 ± 29.7	16.5 ± 0.25
2.8	534 ± 1.52	295 ± 6.08	17.6 ± 0.23

Figure 4.7 shows an M-S plot of the stainless steel specimen after passivation in the solution with or without HS^- . The capacitance was measured at 15 Hz as was the capacitance shown in Figure 4.5. This frequency is seen to be in the region dominated by a capacitive response in Figure 4.6. Though the negative slope is observed at potentials higher than $0.3 \text{ V}_{\text{SSE}}$, due to the continuous growth of the film, the positive slope in M-S plot means that the specimen has an n-type semi-conductive property. Regardless of the $[\text{HS}^-]$ in the solution, a linear relation is observed at potentials from -0.15 to $-0.05 \text{ V}_{\text{SSE}}$. The Mott-Schottky equation of an n-type semiconductor is defined as follows:

$$\frac{1}{C_{SC}^2} = \frac{2}{\epsilon\epsilon_0 e N_D} \left(E - E_{fb} - \frac{kT}{e} \right), \quad [4.15]$$

where ϵ is the dielectric constant, ϵ_0 is the vacuum permittivity constant, e is the elementary charge, N_D is the donor density, E_{fb} is the flat-band potential, k is the Boltzmann constant and T is the absolute temperature. The values of E_{fb} and N_D are shown in Table 4.2. E_{fb} is independent of $[\text{HS}^-]$, meaning that the structure and/or chemical composition of the passive

film on stainless steel is not affected by the presence of HS^- in the solution during passivation. Meanwhile, the value of N_D increases with increase in $[\text{HS}^-]$. Since semi-conductivity is associated with the band structure of a space charge layer formed in a passive film and the surface state at the electrolyte/film interface, N_D is correlated with the concentrations of oxygen vacancies and interstitial metal ions in the film.[22] The increase in N_D implies that the presence of HS^- during the passivation induces more donor levels in the passive film. However, the increased concentration of dopants is not large enough to affect the structure and chemical composition of the film.

Table 4.2 Values of flat-band potential E_{fb} and donor density N_D from M-S plots measured in a solution containing HS^-

$[\text{HS}^-] / 10^{-3} \text{ mol dm}^{-3}$	E_{fb} / V_{SSE}	$N_D / 10^{20} \text{ cm}^{-3}$
0	-0.229 ± 0.004	4.19 ± 0.39
1.5	-0.232 ± 0.002	4.84 ± 0.59
2.2	-0.234 ± 0.007	5.21 ± 0.34
2.8	-0.233 ± 0.002	5.99 ± 0.11

Figure 4.8 shows an SECM tip current image of the stainless steel specimen surface, which was polarized at $0.4 V_{SSE}$ for 100 s in a solution containing $2.8 \times 10^{-3} \text{ mol dm}^{-3}$ of HS^- using the LPIG microelectrode. The Ag_2S layer on the LPIG microelectrode with a diameter of 500 μm was located at almost the center of a 3 mm diameter stainless steel specimen at a distance of 125 μm . TG/SC mode SECM was carried out with polarization of the tip and substrate electrodes at $0.6 V_{SSE}$ and $-0.2 V_{SSE}$, respectively, in deaerated pH 8.4 buffer solution containing $1.0 \times 10^{-3} \text{ mol dm}^{-3}$ FcMeOH as a redox mediator. The anodic current flowing through the tip electrode corresponds to oxidation of FcMeOH, which is associated with surface reactivity of the substrate. Since a passive film on a stainless steel substrate has an n-type semiconductive property, the reactivity is strongly related to donor density or thickness of the passive film. Several studies have shown that a higher tunneling current will flow in the case of a thinner and/or a more defective oxide film than in the case of a thicker and/or a less defective oxide film.[23-25] In the image, the passive film on the stainless steel can be distinguished from the insulating epoxy resin by a bright circle surrounded by four dark corners of the edge. The striped pattern and dispersed black spots in the image are considered to be the result of a tip movement artifact and residual abrasive particles, respectively. Moreover, the brightest circle is at the center of the specimen surface. The diameter of the circle is ca. 500 μm , which coincides with the diameter of the Ag_2S layer on the LPIG microelectrode. This indicates that a relatively reactive part on/in the passive film is induced by the LPIG operation. The products generated from the LPIG might cause the formation of a more defective film and/or a thinner film partially in the vicinity of the

LPIG microelectrode tip compared with the area away from the LPIG microelectrode tip. Furthermore, a slightly dark arc is seen on the outside of the brightest circle of the stainless steel specimen. The diameter of the arc is almost the same as the diameter of the glass sheath of the LPIG microelectrode. This region seems to be slightly less reactive than the stainless steel surface distant from the LPIG microelectrode location.

4.3.4 Surface analysis of passive film formed on 316L stainless steel

Figure 4.9 shows AES differential spectra of type 316L stainless surface obtained after polarization at $0.4 V_{SSE}$ for 100 s in a solution with or without the LPIG operation, in which the estimated $[HS^-]$ was $2.8 \times 10^{-3} \text{ mol dm}^{-3}$. The peaks at 152, 221, 272, 505, 529, 562, 598, 651, 703 and 848 eV are assigned to S-LVV, Mo-MNN, C-KLL, O-KLL, Cr-KLL, Fe-LMM, Fe- $L_{2,3}M_{2,3}$, Fe- $L_{2,3}M_{4,5}$, Fe- $L_{2,3}M_{4,5}$ and Ni-LMM of AES signals, respectively.[26-31] It is clear that elemental sulfur is present on the stainless steel surface containing HS^- but not on the other surface formed without containing HS^- . It is thought that the atomic S is incorporated into passive layer when it was formed in solution with HS^- .

Figure 4.10 shows an AES depth profile of the stainless steel specimen after polarization at $0.4 V_{SSE}$ for 100 s in a solution with or without the LPIG operation, in which the estimated $[HS^-]$ was $2.8 \times 10^{-3} \text{ mol dm}^{-3}$. It was clear that the specimen surfaces were covered with oxide of the passive film. Assuming that the passive film-substrate interface is located at the transition with a half of the atomic concentration of oxygen, the passive film formed in a solution with HS^- shows the same thickness as that of the passive film formed in a solution without HS^- . It was also observed that a very small amount of elemental S is contained in the outmost passive film of the sample formed in the solution with HS^- . The atomic concentrations of Fe (Figure 4.11a) and Cr (Figure 4.11b) are ca. 10 at% larger in the passive film formed in a solution with HS^- than in the passive film formed in a solution without HS^- , while the atomic concentrations of Ni (Figure 4.11c) and O (Figure 4.11d) in the film with HS^- are ca. 10 at.% smaller than those in the passive film without HS^- , though the difference is relatively small. Metallic Ni seems to be depleted in the film but to have accumulated in the film/substrate interface. These results coincide with results of previous studies.[32-35]

Figure 4.12 shows photoelectron spectra of (a) Fe $2p_{3/2}$, (b) Cr $2p_{3/2}$, (c) O $1s$ and (d) S $2p_{3/2}$ obtained from type 316L stainless steel surface after polarization at $0.4 V_{SSE}$ for 100 s in pH 8.4 buffer solution with or without the LPIG operation, in which the estimated $[HS^-]$ was $2.8 \times 10^{-3} \text{ mol dm}^{-3}$. Although several oxidation states for iron, chromium and sulfur have reported, the oxidation state of Fe^{2+} , Fe^{3+} or Cr^{3+} for iron or chromium oxides and SO_4^{2-} , SO_3^{2-} or S^{2-} for sulfur species were identified in/on the passive film. After background subtraction, spectra were deconvoluted into several curves for the oxidation states of iron, chromium, oxygen and sulfur, using reference XPS peak energies listed in Table 4.3. The peak intensity ratio of Fe^{3+}/Fe^{2+} , $(Fe^{3+}+Fe^{2+})/Fe^0$, Cr^{3+}/Cr^0 and OH^-/O^{2-} depended on the presence

of HS^- (Table 4.4). $\text{Fe}^{3+}/\text{Fe}^{2+}$, $(\text{Fe}^{3+}+\text{Fe}^{2+})/\text{Fe}^0$ and $\text{Cr}^{3+}/\text{Cr}^0$ show 40%, 10% and 5%, respectively, higher values in the passive film formed with HS^- than those in the passive film formed without HS^- , indicating that the ionic valence of passive film was changed the presence of HS^- . The peak binding energy of Fe^{3+} , Fe^{2+} , Cr^{3+} , OH^- and O^{2-} shifts to low binding energy ca. 0.4, 0.4, 0.2, 0.2 and 0.2 eV, respectively, in the passive film formed with presence of HS^- , while the peak binding energies of sulfur species do not shift. The higher binding energy shift of Fe cations is thought to be related to be ca. six times higher portion of Fe oxides in the passive film than chromium oxides in the passive film (Figure 4.11). These shifts indicate that the change in charge of those ions and each core electron of the ions is submitted to a variation as discussed later. Meanwhile, a peak of S^{2-} is observed due to the cathodic polarization of LPIG, although there are peaks of SO_3^{2-} and SO_4^{2-} .

Table 4.3 Reference XPS peaks of Fe, Cr, O and S species used in this dissertation

Elements	Binding energy / eV	Oxidation state	Reference
Fe 2p _{3/2}	706.8	Fe^0	36
	710.5	Fe^{2+}	36
	709.5	Fe^{3+}	37
Cr 2p _{3/2}	573.6	Cr^0	38
	576.3	Cr^{3+}	38
O 1s	529.9	OH^-	39
	531.4	O^{2-}	39
S 2p _{3/2}	161.2	S^{2-}	40
	166.6	SO_3^{2-}	40
	168.3	SO_4^{2-}	40

Table 4.4 XPS peak intensity ratio of cations and anions in the passive film formed without or with presence of HS^-

	Peak intensity ratio				
	$\text{Fe}^{3+}/\text{Fe}^{2+}$	$(\text{Fe}^{3+}+\text{Fe}^{2+})/\text{Fe}^0$	$\text{Cr}^{3+}/\text{Cr}^0$	$\text{OH}^-/\text{O}^{2-}$	$(\text{SO}_4^{2-} + \text{SO}_3^{2-})/\text{S}^{2-}$
without HS^-	0.94	5.28	4.28	0.77	—
with HS^-	1.41	5.76	4.46	0.96	0.69

4.3.5 Effect of HS^- on a secondary passivity of type 316L stainless steel

Figure 4.13 shows a double logarithmic plot of current density of the stainless steel specimen and time during the potentiostatic polarization at $0.9 V_{\text{SSE}}$ after the LPIG operation for 0, 100, 150 or 600 s. The operation periods correspond to $[\text{HS}^-]$ of 0.0, 1.5, 2.2 and $2.8 \times 10^{-3} \text{ mol dm}^{-3}$, respectively, on the surface of stainless steel substrate within the interelectrode space between the local specimen and the LPIG. It is clear that the current density decreases exponentially with polarization time, and the slope in the absence of HS^- is ca. -1 , indicating that a high field mechanism is adopted for the formation of a passive film on the surface.[17] However, the slope becomes less steep in the presence of HS^- and increases with increase in $[\text{HS}^-]$. Potentiostatic polarization of the specimen electrode at $0.9 V_{\text{SSE}}$ allowed a relatively large anodic current flowing. The current density flowing at 100 s also increases with increase in $[\text{HS}^-]$, indicating that a more electrically conductive passive film is formed on the specimen surface in the solution with HS^- than that formed without HS^- .

Following polarization of the stainless steel specimen electrode at $0.9 V_{\text{SSE}}$ for 100 s with or without HS^- , impedance measurement was carried out at the same potential at 15 Hz. At this frequency, the capacitive property of the electrode surface was dominated the impedance response in an EIS measurement as discussed later. Figure 4.14 shows the change in impedance $|Z|$ during potentiostatic polarization at $0.9 V_{\text{SSE}}$. In the case when the stainless steel surface is polarized without presence of HS^- , $|Z|$ gradually increases with polarization time. In the case when the stainless steel surface is polarized with presence of HS^- , the increase in $|Z|$ becomes steep, and the value of $|Z|$ becomes large in a higher $[\text{HS}^-]$. After stopping the LPIG operation, the value of $|Z|$ gradually decreases regardless of $[\text{HS}^-]$, but $|Z|$ without HS^- is still lower than that with HS^- . This implies that the passive film formed in solution with HS^- at $0.9 V_{\text{SSE}}$ is stable than that formed without HS^- . The passive film formed with HS^- is more resistive than that formed without HS^- .

After the impedance measurement at the constant frequency, EIS was immediately carried out in a frequency range from 10^4 to 10^{-1} Hz at the same potential at $0.9 V_{\text{SSE}}$. Figure 4.15 shows Bode plots of the stainless steel specimen. The plot is also fitted with Randles-type $R_{\text{ct}}C_{\text{c}}-R_{\text{el}}$ equivalent electronic circuit. The values of R_{el} , R_{ct} and C_{c} as a function of $[\text{HS}^-]$ are shown in Table 4.5. The values of R_{el} are almost constant because $[\text{HS}^-]$ is less than $10^{-6} \text{ mol dm}^{-3}$ at maximum and is too low to change the solution conductivity. With increase in $[\text{HS}^-]$ during the passivation, C_{c} does not significantly change but R_{ct} slightly increases, corresponding to the increase in anodic current density and $|Z|$ shown in Figures. 4.13 and 4.14, respectively. It is thought that a electrically resistive passive film was formed by the presence of HS^- .

Table 4.5 Values of solution resistance R_{el} , charge transfer resistance R_{ct} and capacitance C_c from curve fitting with an equivalent electric circuit of $R_{el} + (R_{ct}C_c)$ plots when EIS of type 316L stainless steel was performed in a solution containing HS^-

$[HS^-] / 10^{-3} \text{ mol dm}^{-3}$	$R_{el} / \Omega \text{ cm}^2$	$R_{ct} / \text{k}\Omega \text{ cm}^2$	$C_c / \mu\text{F cm}^{-2}$
0	308 ± 1.15	456 ± 47.1	34.4 ± 0.74
1.5	306 ± 0.45	496 ± 44.4	34.3 ± 0.30
2.2	308 ± 0.62	533 ± 8.34	33.6 ± 0.26
2.8	305 ± 0.31	555 ± 5.05	32.6 ± 0.34

Figure 4.16 shows an M-S plot of the stainless steel specimen after passivation in the solution with or without HS^- . The negative slope in M-S plot means that the specimen has an p-type semi-conductive property. Regardless of the $[HS^-]$ in the solution, a linear relation is observed at potentials from 0.70 to 0.82 V_{SSE} . The Mott-Schottky equation of an p-type semiconductor is defined as follows:

$$\frac{1}{C_{SC}^2} = \frac{2}{\epsilon_0 e N_A} \left(E_{fb} - E - \frac{kT}{e} \right), \quad [4.16]$$

where N_A is the acceptor density. The values of E_{fb} and N_A are shown in Table 4.6. E_{fb} is independent of $[HS^-]$, and the value of N_A does significantly not change regardless of $[HS^-]$. This indicates that the structure and/or chemical composition of the passive film on stainless steel is not affected by the presence of HS^- in the solution during passivation, although there seems a gray-color layer was deposited on the stainless steel surface after the polarization. The detailed deposited layer will be discussed in later section. Meanwhile, N_A is correlated with the concentrations of metal ions vacancy and oxygen ions interstitial in the film.[22] The constant value in N_A implies that the presence of HS^- during the passivation is difficult to change acceptor levels in the passive film.

Table 4.6 Values of flat-band potential E_{fb} and acceptor density N_A from M-S plots measured in a solution containing HS^-

$[HS^-] / 10^{-3} \text{ mol dm}^{-3}$	E_{fb} / V_{SSE}	$N_A / 10^{20} \text{ cm}^{-3}$
0	1.02 ± 0.04	4.30 ± 0.31
2.8	1.02 ± 0.02	4.27 ± 0.19

4.3.6 Surface analysis of secondary passive film formed on 316L stainless steel

Figure 4.17 shows optical microscopic image of stainless steel substrate surface after polarized at $0.9 V_{SSE}$ in a solution with the LPIG operation containing $2.8 \times 10^{-3} \text{ mol dm}^{-3}$ of HS^- . The image was obtained from the optical microscope coupled with Raman spectroscopy. There seems to be a formation of circle-like coating with a diameter of ca. 1 mm on the surface. The size of the product coincides with an outer diameter of a LPIG microelectrode sheath, although the formed product is difficult to distinguish. Figure 4.18 shows Raman spectra of the stainless steel surface after passivation at $0.9 V_{SSE}$ in a solution with or without the LPIG operation containing HS^- . Although strong peaks are found at 138, 208, 408 and 465 cm^{-1} , being attributed to iron-sulfide for 138, 208 and 465 and molybdenum disulfide for 408 cm^{-1} , other peaks for iron sulfide are not observed at 282 and 298 cm^{-1} . Table 4.7 presents the reference of sulfides. A spectrum of the stainless steel surface polarized at the same potential but without HS^- shows no peaks within the range from ca. 250 to 300 cm^{-1} . It is think that the characterization of the formed sulfide layer on stainless steel surface is not clear from this characterization.

Table 4.7 Identification of Raman peaks of some metal-sulfides

Raman shift peak / cm^{-1}	Sulfide	Reference
138	Iron sulfide (Fe_{1+x}S)	41
208	Iron sulfide (FeS)	42
260	Iron sulfide (FeS)	42
282	Iron sulfide (FeS)	42
298	Iron sulfide (FeS)	42
408	Molybdenum disulfide (MoS_2)	43
465	Iron sulfide (FeS)	42

4.4 Discussion

The effect of HS^- on the passivity of type 316L stainless steel was investigated by using an LPIG microelectrode. Electrochemical and surface analyses revealed that the presence of HS^- makes a passive film defective and conductive by increasing oxygen vacancies and metal cations.

It has been widely proposed that the presence of aggressive anions changes the passivity and leads to localized corrosion on stainless steels.[44-48] Three main depassivation models have been proposed in the presence of aggressive anions.[49] The adsorption model[50,51] is associated with the absorption of aggressive anions on the passive film. The adsorbed anions transfer metal cations to the electrolyte by forming a complex of metal cations on the film. As a result, the passive film is thinned and/or

removed. According to the penetration model,[52,53] the depassivation of metal is due to the transfer of aggressive anions through the passive film to the metal surface. The adsorbed and/or contaminated anions introduce higher ionic conductive paths through the film and lead to a rapid release and removal of metal cations. The passive film breakdown model[53,55] is related to mechanical breakdown of the film. The adsorption of aggressive anions on the passive film reduces surface tension, resulting in a mechanical break. All of the proposals are based on the prior adsorption of aggressive anions on a passive film followed by the depassivation process of the film. The adsorption of an anion is associated with polarizability when it is adsorbed on metal cations.[56] The higher polarizability the anion has, the stronger is the adsorption of the anion on cations of the passive film. Polarizability of sulfides such as S^{2-} 2200 mm² mol⁻¹ or HS^- 1330 mm² mol⁻¹, respectively, is approximately two-times higher than that of halides and OH^- 770 mm² mol⁻¹. [56] Therefore, the adsorption of HS^- might be prior to that of OH^- on a stainless steel surface in a solution containing HS^- .

When the stainless steel surface was polarized at 0.4 V_{SSE} in a solution containing HS^- , adsorbed HS^- was preferentially incorporated into the formed passive film. It was confirmed from AES and M-S analysis that elemental S existed on the outermost passive film. If the outermost S species is present as HS^- or S^{2-} , oxygen anion transfer from the electrolyte to the outermost lattice of the film should be inhibited. In order to maintain a charge balance in the film against the existence of HS^- or S^{2-} , metal cations and/or oxygen vacancies need to be produced at substrate/film and/or passive film/electrolyte interfaces, resulting in the concentrations of metal cations and oxygen vacancies becoming larger in the film. This is also supported by results in Figures 4.11 and 4.12 showing that the HS^- adsorption results in an increase of donor density in the film. In the passive film formed in the presence of HS^- , peak binding energy of iron and chromium cations as well as oxygen anions shifted to low the energy direction. It is clearly known that shift of a binding energy of XPS spectrum is related to a change in a binding energy of a core electron of an atom or an ion.[57] Since the core binding energy depended on electrostatic interaction between a core electron and a nucleus and can be changed by the electrostatic shielding (screening effect) of the nuclear charge, the electronic charge can change the shielding by removal or addition of electrons. A lose of valence electron charge increases the binding energy as a result of decreasing the shielding, while an addition of the electron charge lowers the binding energy due to increasing a shielding.[57] When the HS^- is adsorbed on metal cations in the passive film, relatively high polarizable electron charge cloud of HS^- than OH^- is more ready to overlap that of a metal cation and interrupts covalent bonding of metal cation-O or -OH. The metal cations and oxygen anions experience an addition of valence charge, and then a core electron bonding to metal cation or oxygen anion nucleus decreases by the electrostatic shielding of the nuclear charge. The observed binding energy shift in the photoelectron spectra can be attributed to a charge shielding on Fe^{3+} , Fe^{2+} , Cr^{3+} , OH^- and O^{2-} . When passive film is formed with HS^- , the cation or oxygen vacancy

concentration is increased. It is thought that the increase in cation interstitial or vacancy of oxygen affects metal-O or -OH bond in the passive film by the adsorption of HS^- . The higher amount of cations can easily adsorb HS^- on cation sites in passive film, and this process could be an additional effect to the shift of the binding energy of a core electron in metal cations or oxygen anions in the passive film. Although HS^- are possible to covalently bind oxygen anions in passive film by substitution or adsorption, the atomic concentration of S is 50-times smaller than that of O at the outermost layer of passive film. Therefore, the covalent bond of HS^- with metal cations in the passive film is not dominant.

Though it is thermodynamically forming S^0 from HS^- in pH 9.5 the polarization at potentials higher than $-0.594 \text{ V}_{\text{SSE}}$ which enables to induce the oxidation of HS^- to SO_4^{2-} . [58] Increase in local concentration of HS^- in the vicinity of the stainless steel specimen surface might lead to change an electrochemical potential of the surface. A relatively small impedance of the stainless steel surface formed in the solution with HS^- was due to the existence of HS^- in solution during the passive film formation. However, increase in impedance was also observed during the anodic polarization continuously even after the stop of HS^- enrichment by the LPIG operation. Thus, it is suggested that no oxidation of HS^- occurs on the stainless steel surface, though further study on ionic state of S species during a polarization of specimen surface is needed for further understanding about oxidation states of sulfide ions and local acidification of a local solution.

Meanwhile, the concentration of Ni decreased in the film when the oxide film was formed in the solution containing with HS^- . Olefjord et al. reported that Ni does not participate in passive film formation. [32] Castle et al. suggested that metallic Ni is enriched at the substrate/passive film interface during passivation because it is relatively noble compared with other metallic elements in stainless steel. [34] It is thought that the presence of other enriched metallic elements in a film forming in the solution containing with HS^- makes it difficult for metallic Ni to be concentrated at the interface. In any case, the passivity of the stainless steel surface is strongly affected by the adsorption of HS^- .

When the stainless steel surface was polarized at $0.9 \text{ V}_{\text{SSE}}$ in a solution containing HS^- , it seemed like adsorbed HS^- formed sulfide layer on passive film. Although there were some satellite peaks of Raman spectrum for iron- or molybdenum sulfide, the presence of sulfide layer did not confirmed by Raman spectroscopy technique. The formed sulfide layer with a light-gray color was seen on stainless steel surface as shown in Figure 4.17. It was founded that sulfide layer disappeared, even if the 532 nm laser power was decreased 1% less than 0.2 mW. Other surface analyses such as AES and SEM were also attempted to characterize the formed sulfide layer on stainless steel. However, the formed layer disappeared during vacuum extraction in a chamber of those facilities. It is thought that the thin layer has a porous layer, when it was formed during aqueous solution. It is difficult to sustain its porous layer not only in a vacuum but also in a non-vacuum during an excitation by laser. Even though the thin sulfide layer on stainless steel surface was difficult to characterize its chemical composition, the value of impedance was change during the

operation of LPIG (Figure 4.14). The steep change in impedance during cathodic polarization of LPIG indicates the passive film formed in solution with HS^- at $0.9 V_{\text{SSE}}$ is electrically resistive than that formed without HS^- . EIS results also supported that electrically resistive layer was formed in the presence of HS^- . However, semiconductive property of the formed layer was not changed as shown in Mott-Schottky results (Figure 4.16).

A deteriorating effect of HS^- on the passivity of stainless steel has been reported.[45] However, this study is the first study to examine the role of HS^- in the initiation of localized corrosion of type 316L stainless steel using an LPIG. HS^- adsorption is one of the important conditions causing instability of a passive film, which would be a trigger of localized corrosion of the steel. Figure 4.19 shows optical microscopic image after potentiostatic polarization at $0.4 V_{\text{SSE}}$ for 600 s in a 1.0 mol dm^{-3} NaCl solution when a defective part of stainless steel surface had been formed by using the LPIG. It was confirmed the formation of pits in the defective part on the surface. It is thought that pitting was preferentially and locally initiated and/or propagated from the defective part of the passive film when the surface was exposed to the Cl^- -containing solution. Meanwhile, when passivation potential is high at $0.9 V_{\text{SSE}}$, the adsorbed HS^- on metal cations in passive film forms sulfide layer on stainless steel surface. It was thought that adsorbed HS^- on metal cations in passive film forms sulfide layer due to the higher passivation potential, although the detailed sulfide layer formation as a function of potential was difficult to investigated because formed sulfide layer was not sustained on surface of stainless steel during surface analyses. The *in-situ* characterization can elucidate a mechanism of formation of sulfide layer, which is associated with adsorption HS^- on stainless steel surface.

4.5 Summary

The effect of hydrogen sulfide ions, HS^- , on passivity of type 316L stainless steel was investigated in pH 8.4 buffer solution using the LPIG technique. Galvanostatic polarization of the Ag/Ag₂S LPIG microelectrode generated locally both HS^- and OH^- on the stainless steel surface. The passivity of the stainless steel became relatively unstable due to the formation of a more defective n-type semiconductive passive film at $0.4 V_{\text{SSE}}$ with HS^- than that formed without HS^- . AES revealed an increase of metal cations and oxygen vacancies in the passive film formed in a solution containing HS^- . The adsorption of HS^- during passivation of the stainless steel surface could lead to the formation of a defective passive film. Change in the stability of a passive film due to the presence of HS^- might be a trigger for the initial depassivation of stainless steel. Adsorbed HS^- on metal cations in passive film can be possible to form an electrically resistive p-type sulfide layer on stainless steel surface with a high passivation potential at $0.9 V_{\text{SSE}}$.

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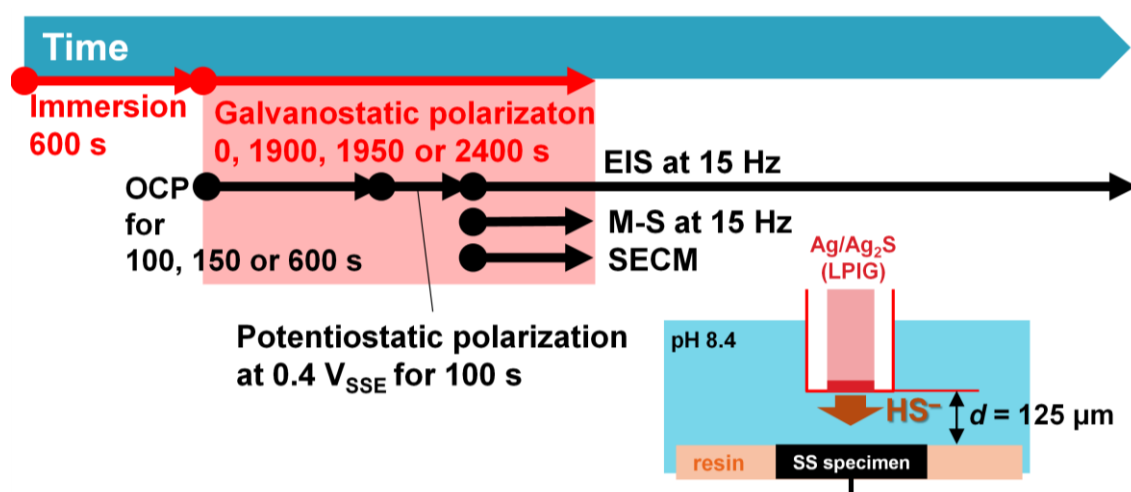


Figure 4.1 Schematic image of the LPIG and type 316L stainless steel substrate operation procedures.

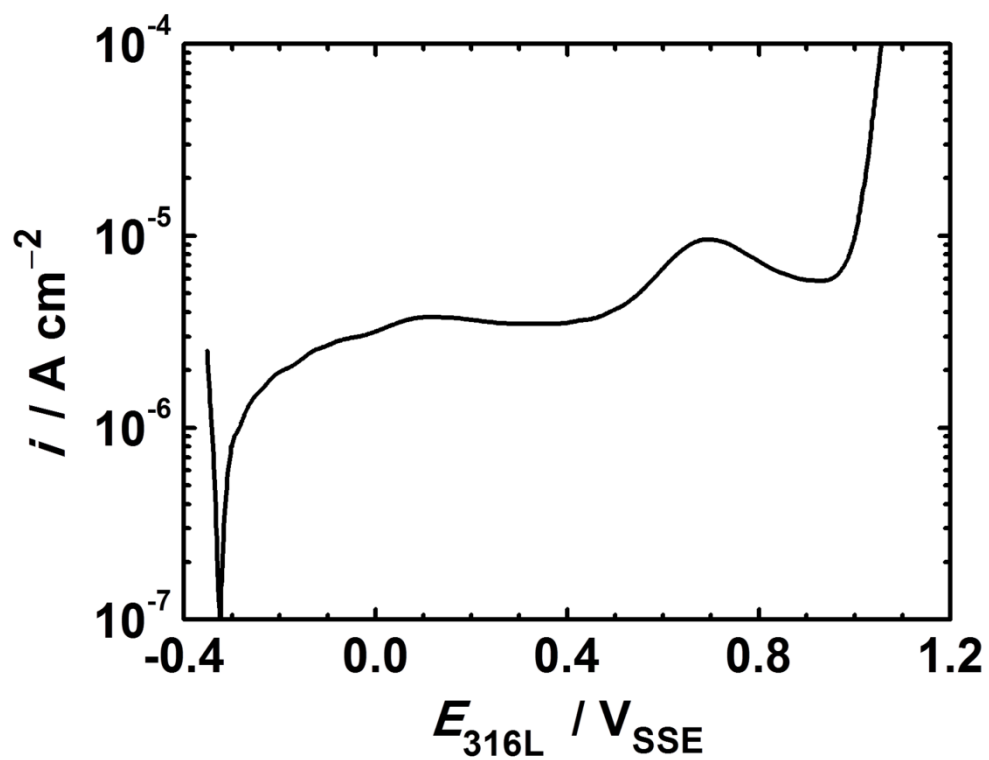


Figure 4.2 Potentiodynamic polarization curve of type 316L stainless steel at a scan rate of 1 mV s^{-1} in a deaerated pH 8.4 boric-borate buffer solution.

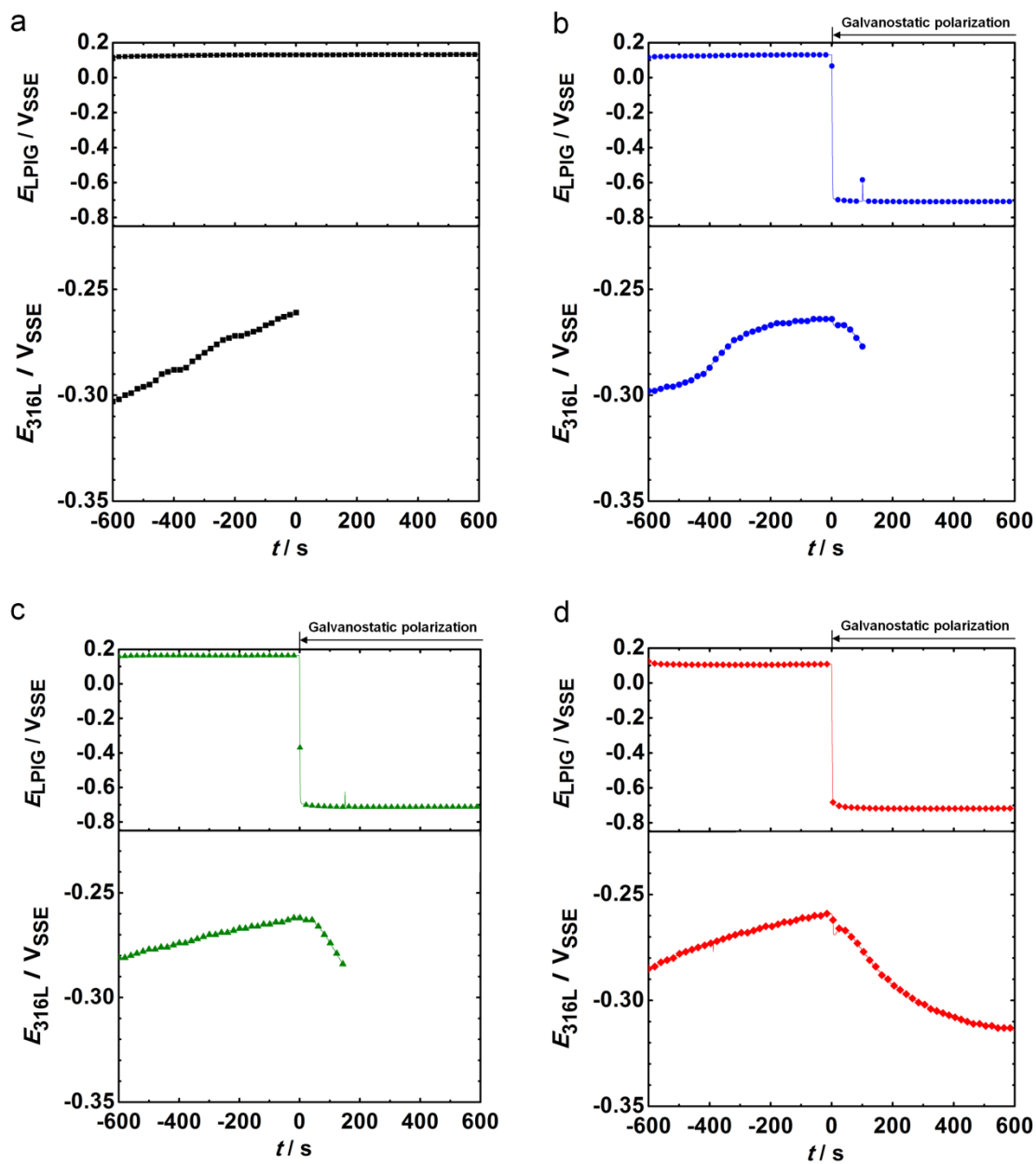


Figure 4.3 Changes in electrode potentials E_{LPIG} and $E_{316\text{L}}$ of the LPIG microelectrode and stainless steel substrate electrode, respectively, before and after the LPIG operation to accumulate HS^- in the interelectrode space at (a) 0.0, (b) 1.5, (c) 2.2 or (d) $2.8 \times 10^{-3} \text{ mol dm}^{-3}$.

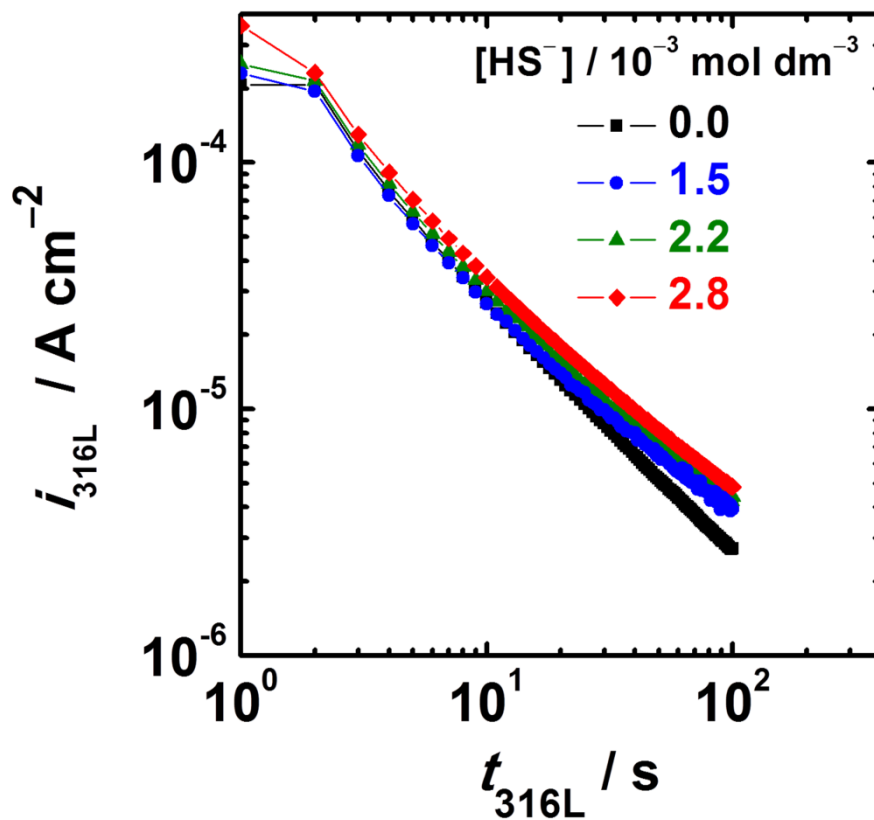


Figure 4.4 Double logarithmic plot of current density of the stainless steel specimen and time during potentiostatic polarization at $0.4 \text{ V}_{\text{SSE}}$ when polarization was started after the LPIG operation for 0, 100, 150 or 600 s, corresponding to the accumulation of 0.0, 1.5, 2.2 or $2.8 \times 10^{-3} \text{ mol dm}^{-3}$ of HS^- .

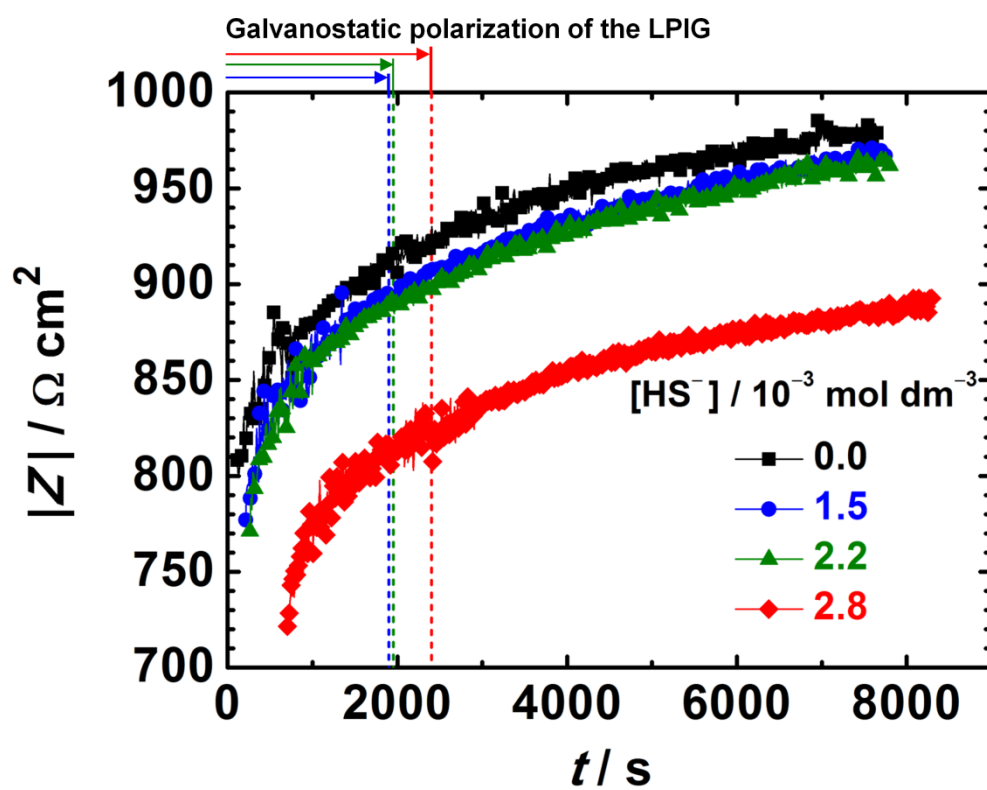


Figure 4.5 Change in impedance $|Z|$ measured at a frequency of 15 Hz during potentiostatic polarization of stainless steel at $0.4 \text{ V}_{\text{SSE}}$ with $[\text{HS}^-]$ of 0.0, 1.5, 2.2 or $2.8 \times 10^{-3} \text{ mol dm}^{-3}$.

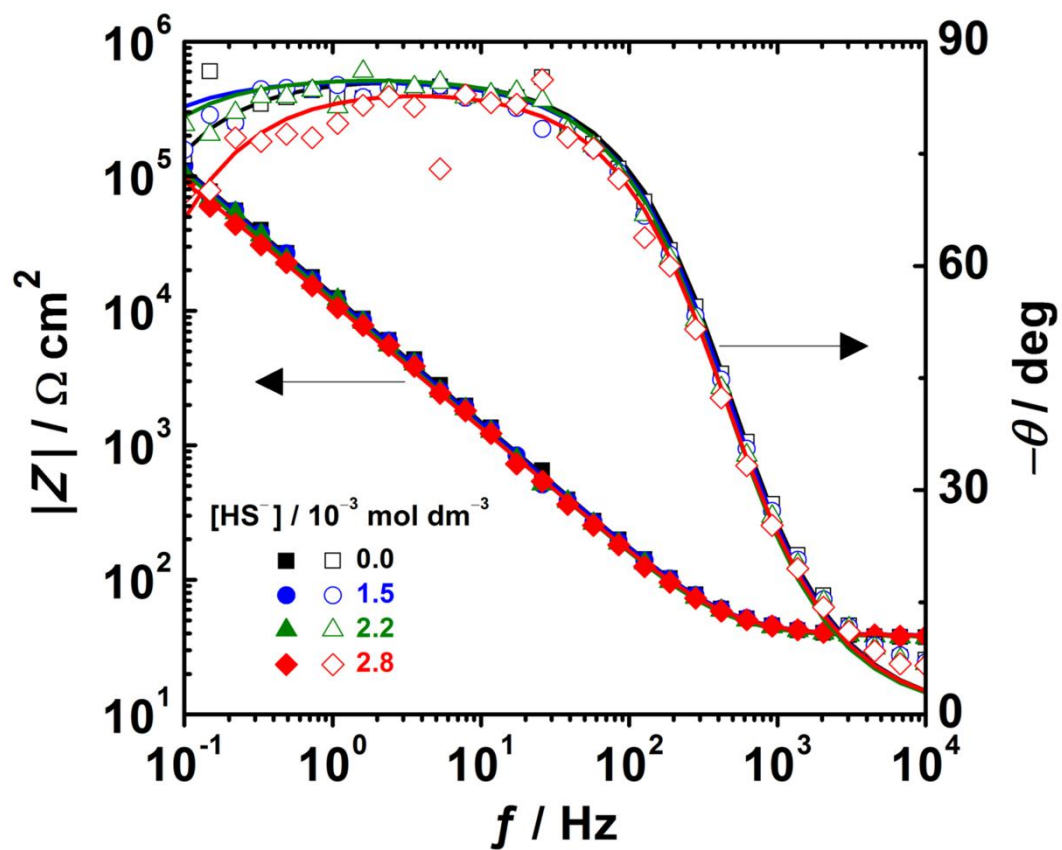


Figure 4.6 Bode plots of a stainless steel specimen polarized at 0.4 V_{SSE} after impedance measurement (Figure 4.5).

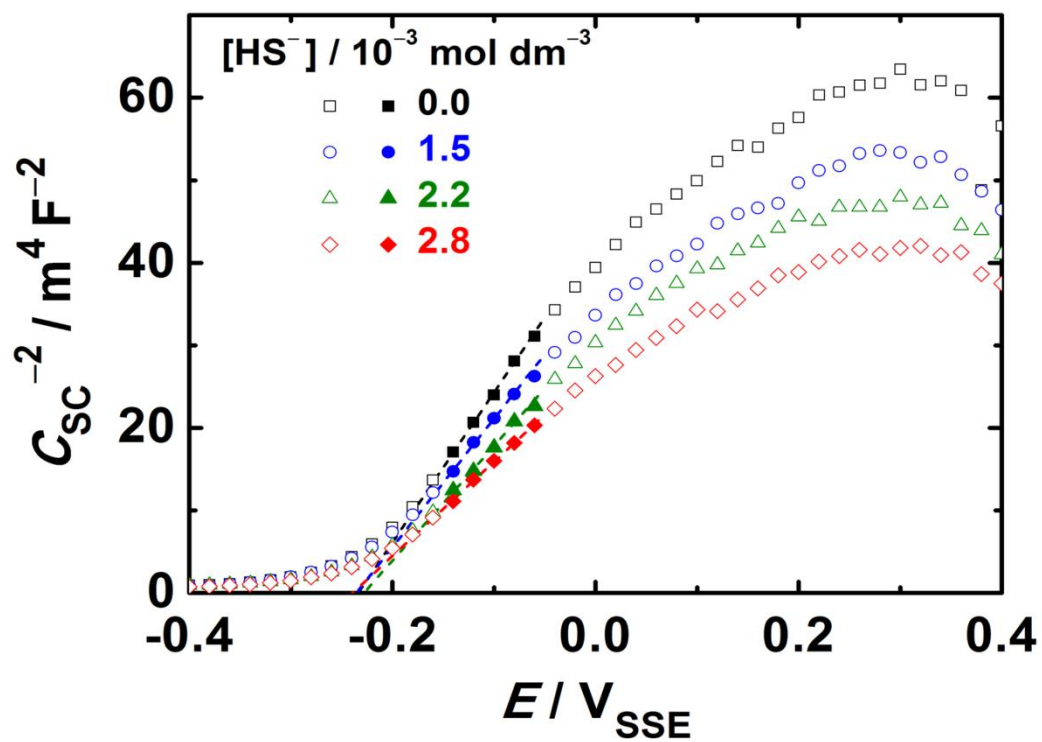


Figure 4.7 Mott-Schottky (M-S) plot of the stainless steel specimen after passivation at $0.4 V_{SSE}$ in a solution containing 0.0, 1.5, 2.2 or $2.8 \times 10^{-3} \text{ mol dm}^{-3}$ of HS^- .

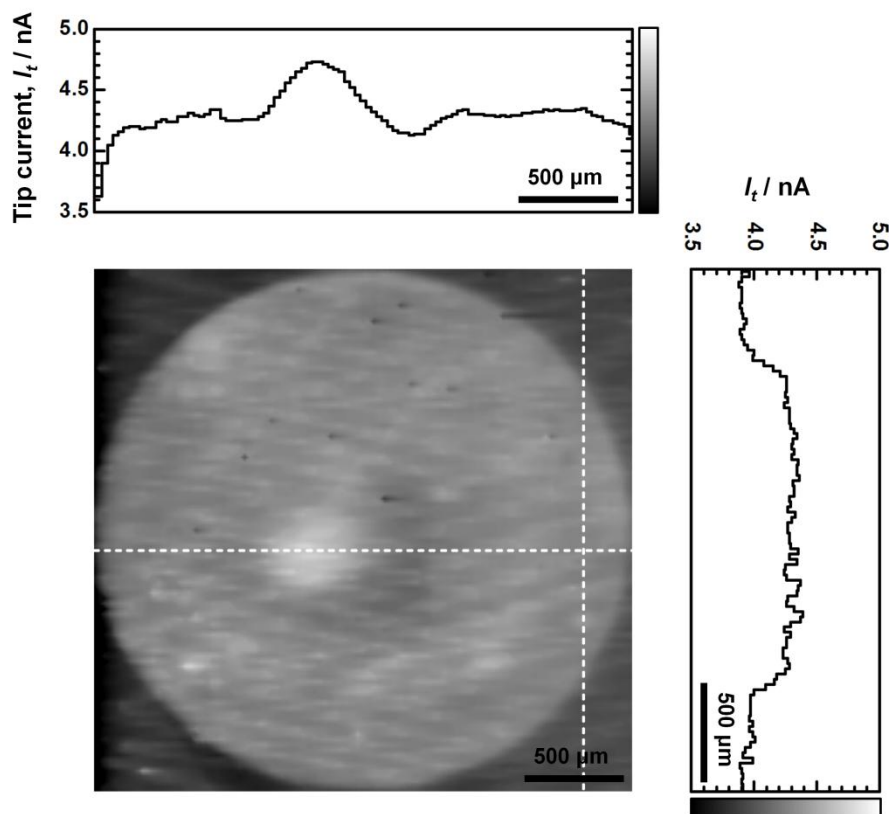


Figure 4.8 SECM tip current image of the stainless steel specimen surface, which was polarized at $0.4 V_{SSE}$ for 100 s in a solution containing $2.8 \times 10^{-3} \text{ mol dm}^{-3} \text{ HS}^-$ using $\text{Ag}/\text{Ag}_2\text{S}$ of 500 μm in diameter in the LPIG. Microelectrode tip and substrate specimen electrode of the SECM were polarized at $0.6 V_{SSE}$ and $-0.2 V_{SSE}$, respectively, in deaerated pH 8.4 buffer solution containing $1 \times 10^{-3} \text{ mol dm}^{-3} \text{ FcMeOH}$ with an interelectrode distance of 20 μm .

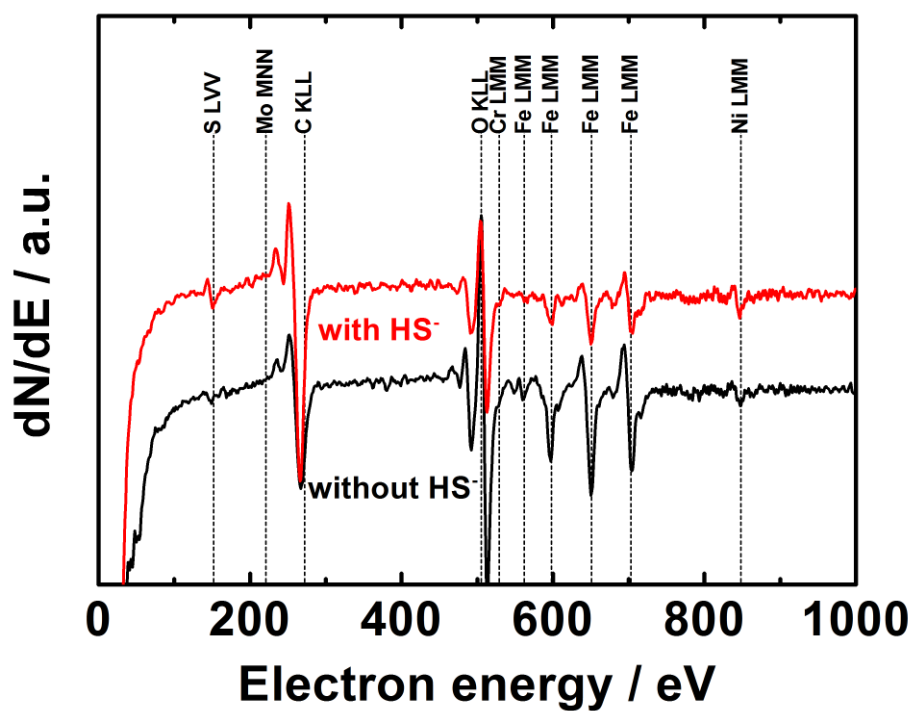


Figure 4.9 AES differential energy spectra of type 316L stainless steel surface polarized at 0.4 V_{SSE} with or without the LPIG operation containing $2.8 \times 10^{-3} \text{ mol dm}^{-3}$ of HS⁻.

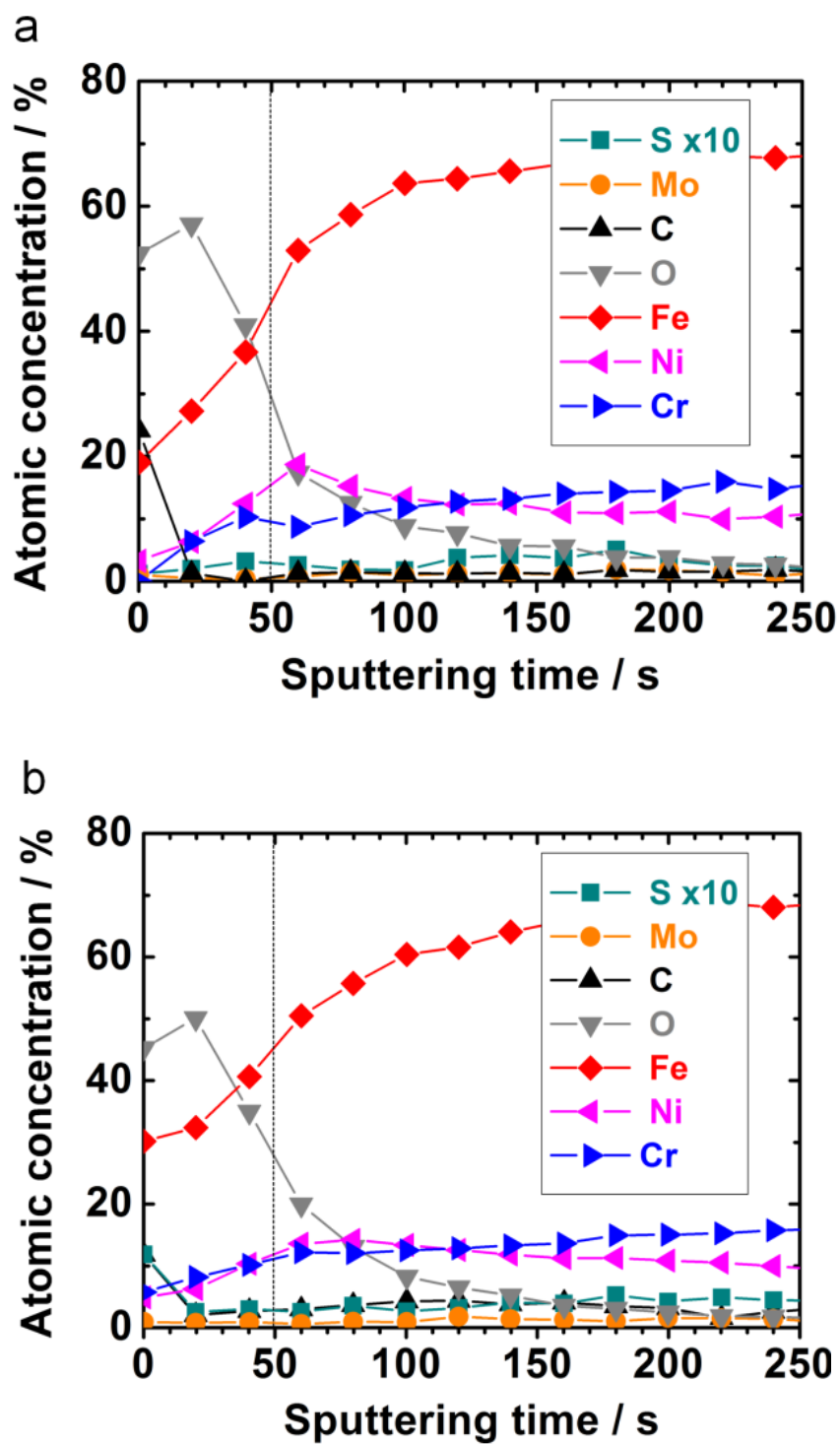


Figure 4.10 AES depth profiles of the stainless steel specimen after polarization at 0.4 V_{SSE} for 100 s in a solution (a) without or (b) with the LPIG operation containing $2.8 \times 10^{-3} \text{ mol dm}^{-3}$ of HS⁻.

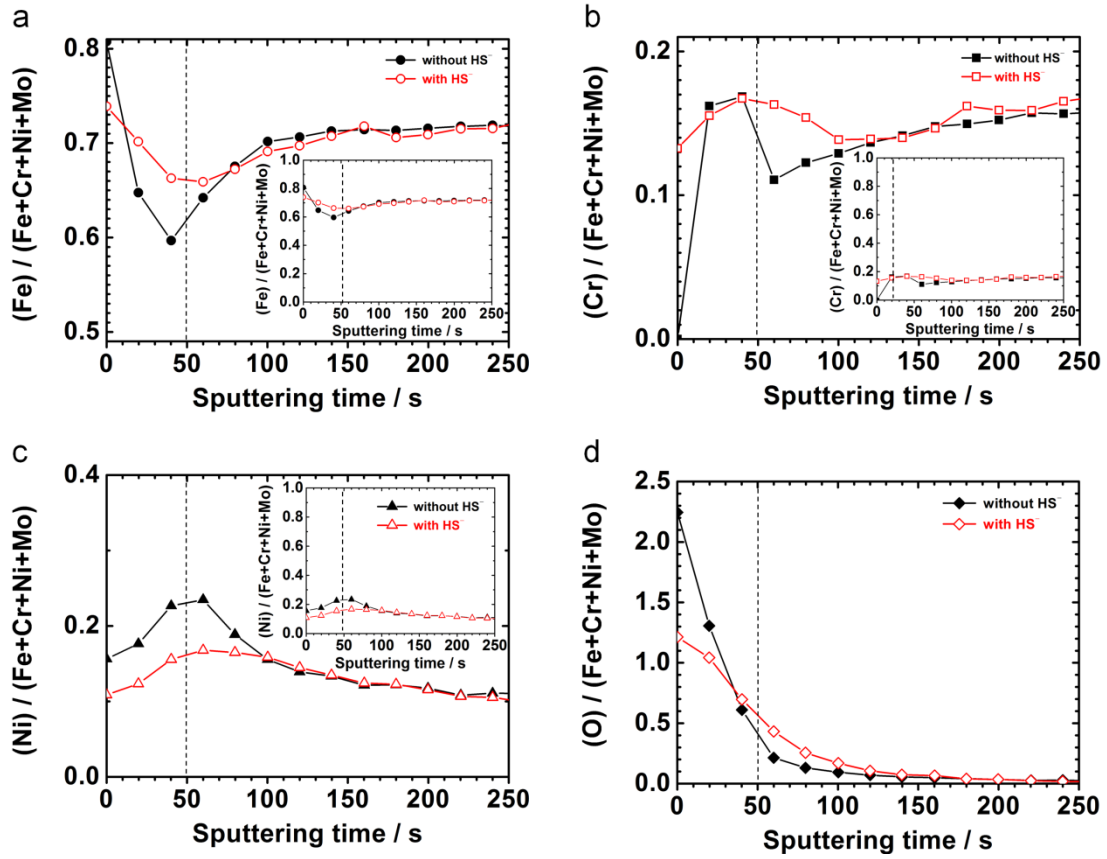


Figure 4.11 Atomic ratios of (a) Fe, (b) Cr, (c) Ni and (d) O to major metal cations calculated from Figure 4.9.

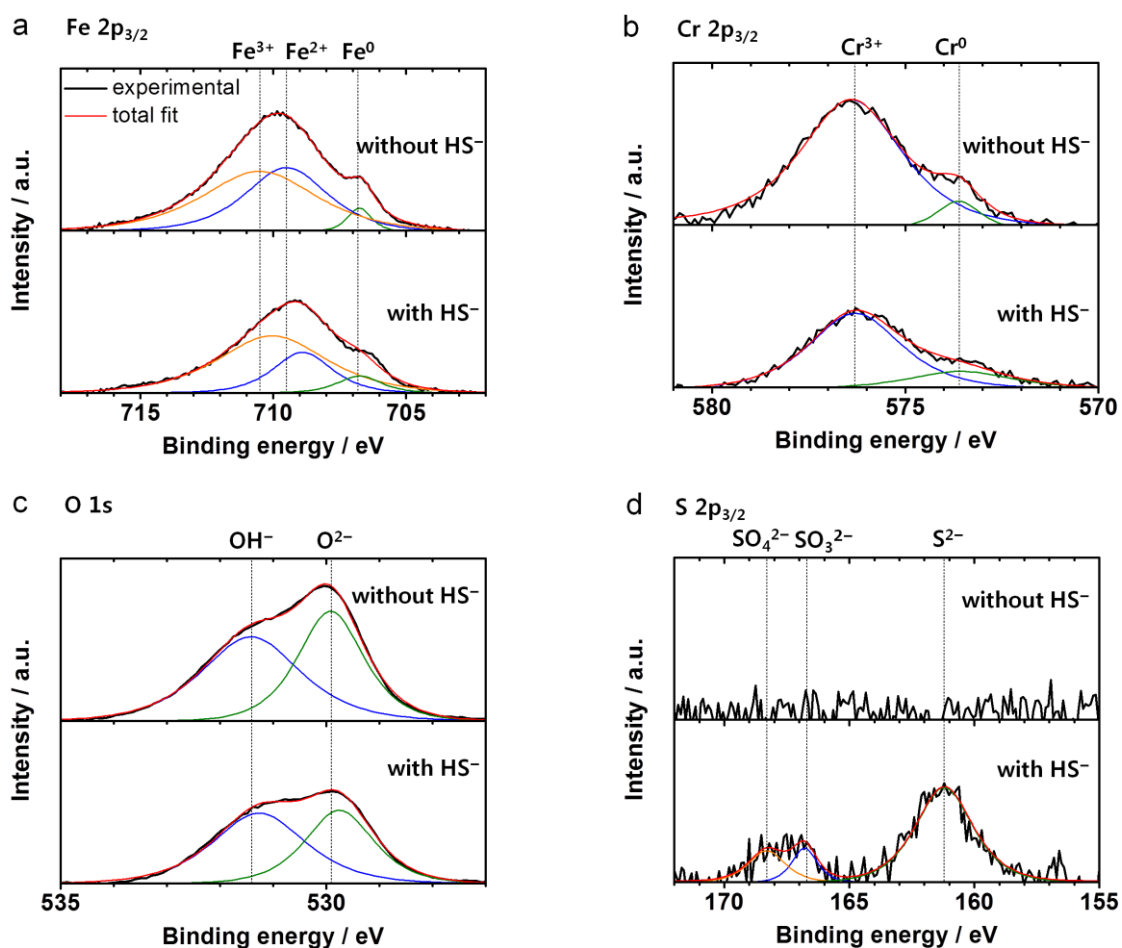


Figure 4.12 (a) Fe 2p_{3/2}, (b) Cr 2p_{3/2}, (c) O 1s and (d) S 2p_{3/2} of photoelectron spectra of 316L stainless steel specimen after polarization at 0.4 V_{SSE} for 100 s in a solution without or with the LPIG operation containing 2.8 × 10⁻³ mol dm⁻³ of HS⁻.

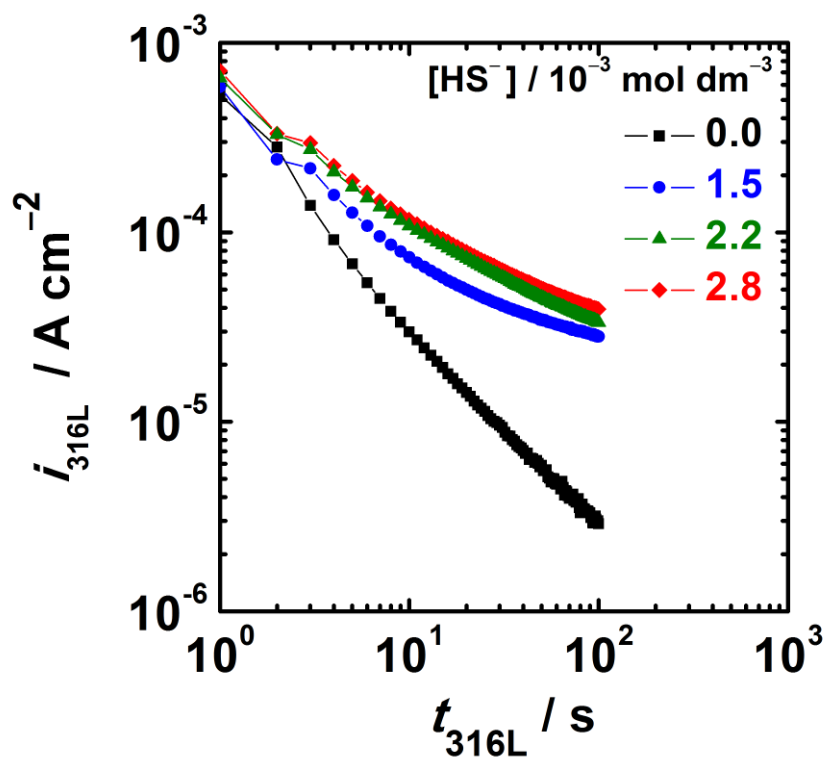


Figure 4.13 Double logarithmic plot of current density of the stainless steel specimen and time during potentiostatic polarization at $0.9 \text{ V}_{\text{SSE}}$ when polarization was started after the LPIG operation for 0, 100, 150 or 600 s, corresponding to the accumulation of 0.0, 1.5, 2.2 or $2.8 \times 10^{-3} \text{ mol dm}^{-3}$ of HS^- .

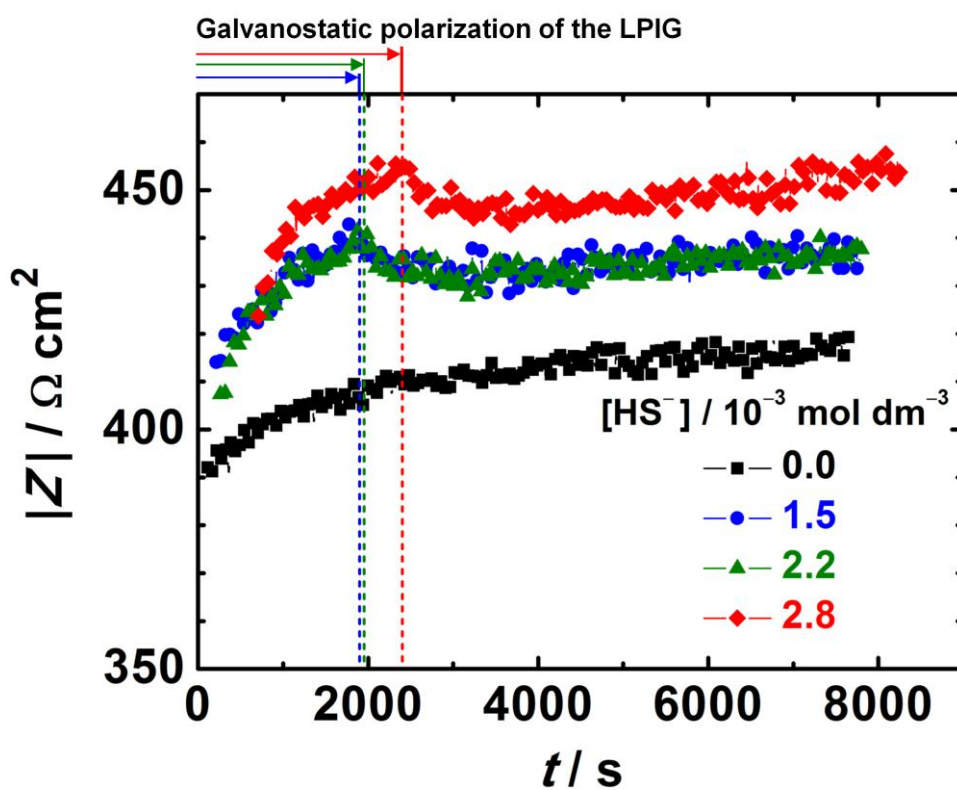


Figure 4.14 Change in impedance $|Z|$ measured at a frequency of 15 Hz during potentiostatic polarization of stainless steel at 0.9 V_{SSE} with $[\text{HS}^-]$ of 0.0, 1.5, 2.2 or $2.8 \times 10^{-3} \text{ mol dm}^{-3}$.

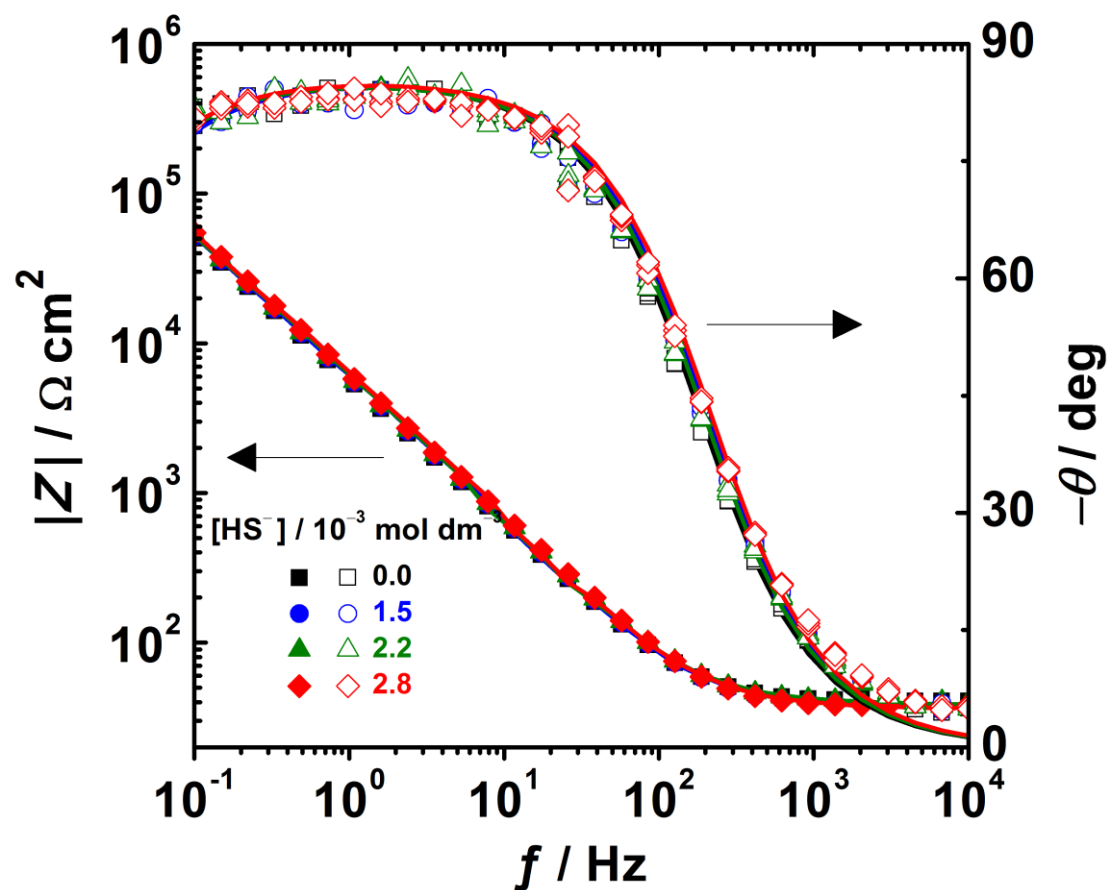


Figure 4.15 Bode plots of a stainless steel specimen polarized at 0.9 V_{SSE} after impedance measurement (Figure 4.14).

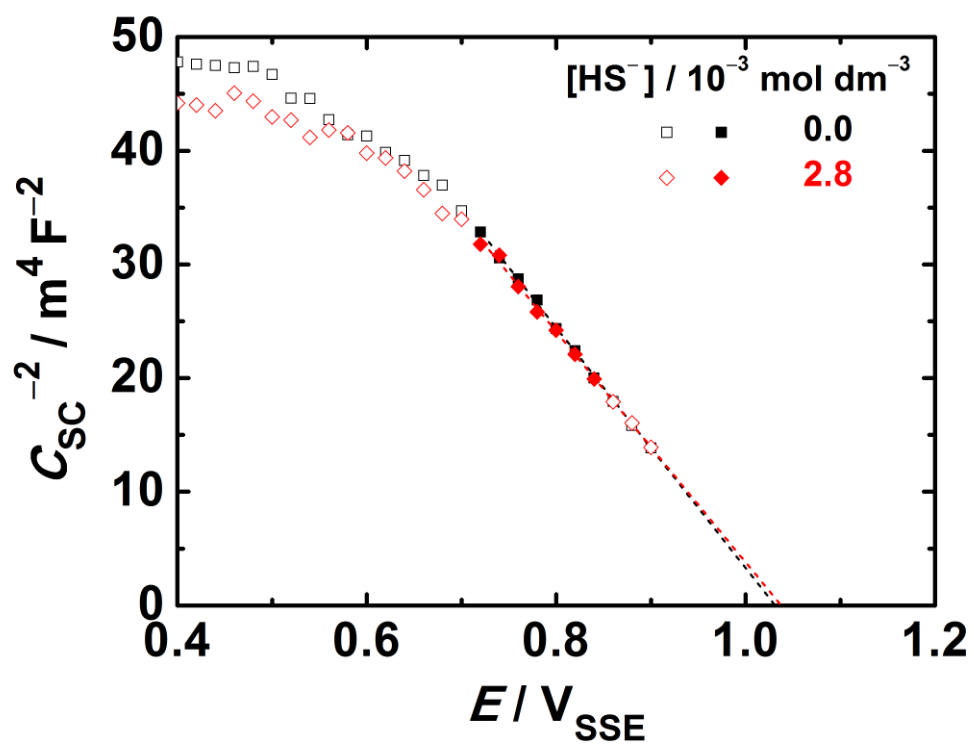


Figure 4.16 Mott-Schottky (M-S) plot of the stainless steel specimen after passivation at 0.9 V_{SSE} in a solution without or with the LPIG operation containing $2.8 \times 10^{-3} \text{ mol dm}^{-3}$ of HS^- .



Figure 4.17 Optical microscopic image of the stainless steel surface after passivation at $0.9 V_{SSE}$ in a solution containing $2.8 \times 10^{-3} \text{ mol dm}^{-3}$ of HS^- by operation of LPIG.

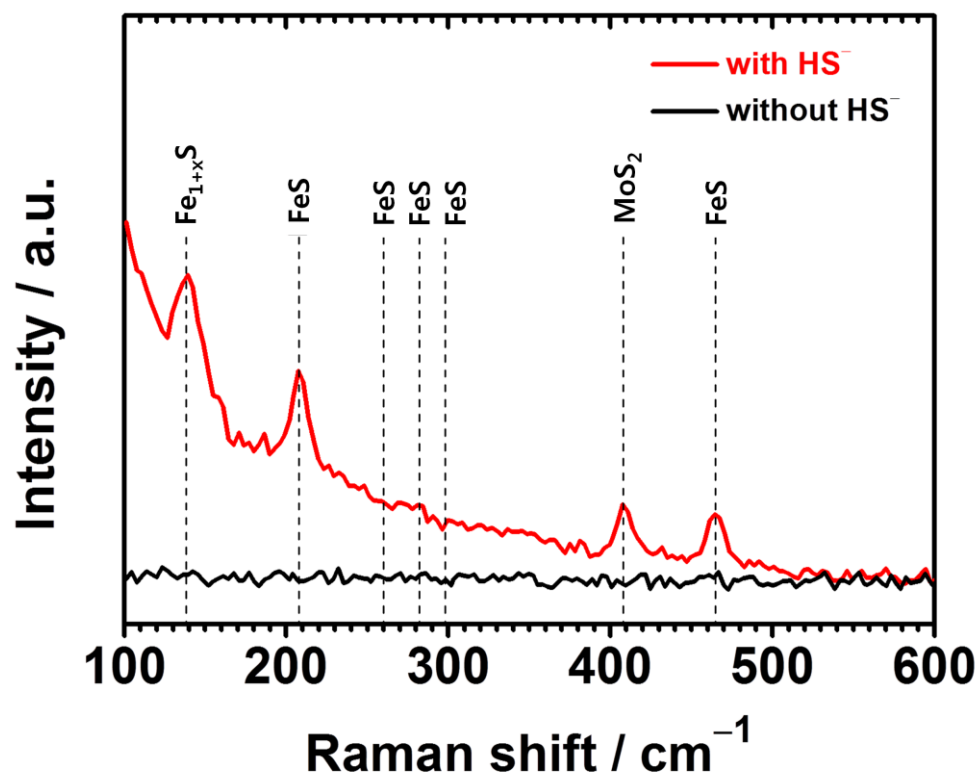


Figure 4.18 Raman spectra of the stainless steel surface after passivation at 0.9 V_{SSE} in a solution without or with the LPIG operation containing $2.8 \times 10^{-3} \text{ mol dm}^{-3}$ of HS^- . The analysis position was determined by using OM coupled with micro-Raman sepectroscopy (Figure 4.17).

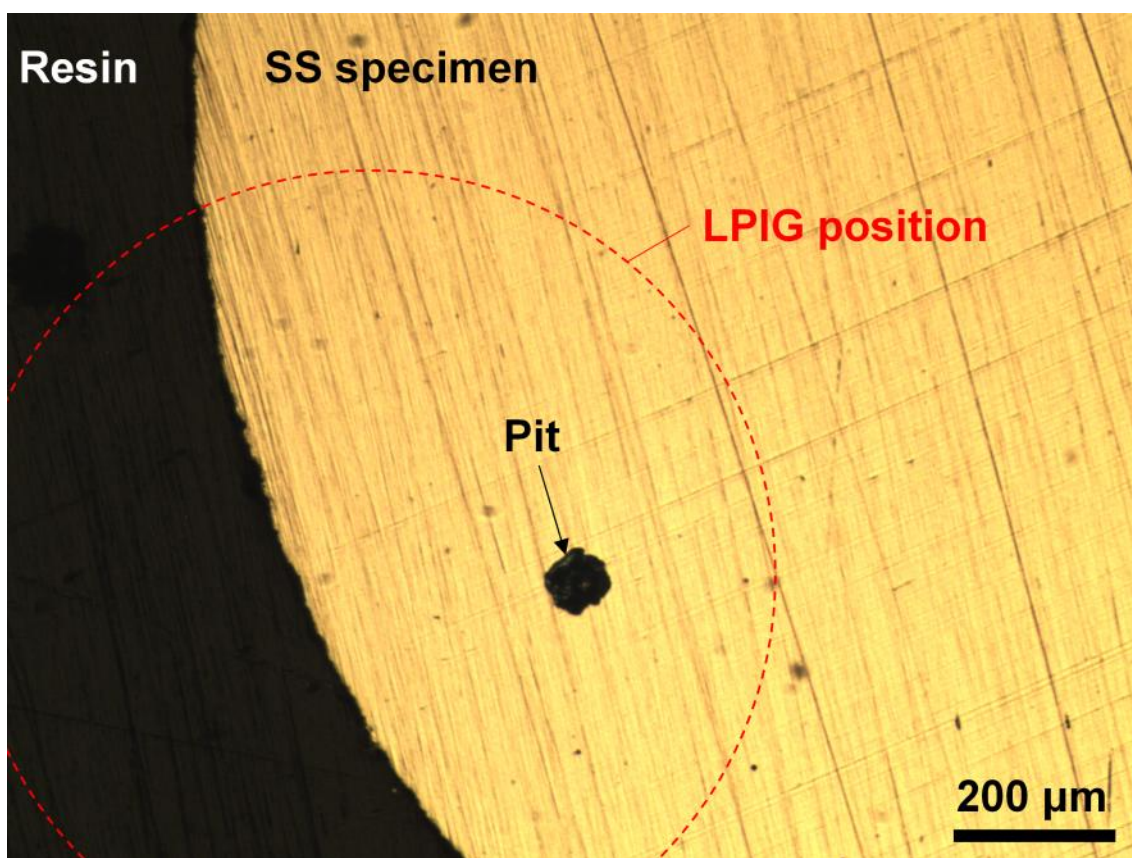


Figure 4.19 Optital Microscopic image of the stainless steel specimen polarized at $0.4 V_{SSE}$ for 600 s in a 1.0 mol dm^{-3} NaCl solution after passivated at $0.4 V_{SSE}$ for 100 s in a solution with the LPIG operation containing $2.8 \times 10^{-3} \text{ mol dm}^{-3}$ of HS^- .

Chapter 5 Evaluation of localized corrosion resistance of Stainless steels

5.1 Introduction

Stainless steel is a corrosion-resistive Fe-based material with a minimum of 11 wt% Cr content. Corrosion resistance of stainless steel is attributed to the presence of Cr and/or Fe-oxide in a passive film formed on the surface with a thickness of several nanometers. Prevention of the degradation of stainless steel by a passive film is dependent on the chemical composition of the stainless steel substrate. However, stainless steels are susceptible to localized corrosion, especially pitting, in a corrosive environment that contains Cl^- . The pitting resistance equivalent (PRE) number, which is calculated as $\text{wt\% Cr} + (3.3 \text{ wt\% Mo} + 0.5 \text{ wt\% W}) + 16 \text{ wt\% N}$, indicates the localized corrosion resistance of stainless steel.[1] The larger the PRE number of stainless steel is, the greater is the resistance of the stainless steel to localized corrosion. The PRE number is related to the contribution of elements to the resistance of a passive film on stainless steel. Alloying Cr forms noncrystalline Cr_2O_3 on stainless steel by a direct reaction of Cr with H_2O and improves the resistance to localized corrosion.[2] Alloying Mo enhances the protectiveness of a passive film to Cl^- by increasing oxygen affinity of the stainless steel.[3] Alloying W inhibits localized corrosion by dissolved WO_4^{2-} from the passive film to an aqueous electrolyte or by forming insoluble WO_3 , which enhances the stability of the passive film.[4] Alloying N decreases local pH by decreasing acidity in a pit due to NH_4^+ formation and promotes repassivation.[5] Although the PRE number is useful for comparing the degrees of localized corrosion resistance of various stainless steels, it is just an index and is not sufficient to provide kinetic information during localized corrosion of stainless steel. Kinetic information of localized corrosion of stainless steel might be related to the initiation and/or a propagation of localized corrosion. In order to investigate the initiation of localized corrosion of various stainless steels, it is necessary to evaluate and compare kinetic parameters of localized corrosion prior to the initiation of pitting.

A scanning electrochemical microscope (SECM),[6] which can be used to estimate electrochemical reactivity at local sites of the electrode surface, is useful for studying the precursor process of localized corrosion. A liquid-phase ion gun (LPIG), which is a type of SECM, is useful to release infinitesimal anions from a silver microelectrode, which is covered by a silver chloride layer, by cathodic polarization.[7] Fushimi et al. investigated the local breakdown mechanism of a passive film on iron by using the LPIG technique.[7] They also reported that the breakdown of a passive film on iron depended on the substrate potential, electrical field applied to the film and pH of the solution.[8] Falkenberg et al. studied single pit initiation and its growth mechanism on a copper surface by the combination of an electrochemical quartz crystal microbalance and an LPIG.[9] Gabrielli et al. investigated the

pH dependence of the breakdown of a passive film on a pure iron surface by using an LPIG.[10] Although there have been many studies on the localized corrosion behavior of stainless steels in a solution containing Cl^- , [11-13] little attention has been given to quantitative evaluation of the initiating localized corrosion on stainless steel. The use of the LPIG technique is an alternative and/or advanced application to provide kinetic information on localized corrosion of stainless steel in an environment containing Cl^- . This study was conducted to estimate the amount of Cl^- that is necessary to initiate localized corrosion on commercially available type 430, 304 and 443 stainless steels.

5.2 Experimental

5.2.1 Specimens

A silver microelectrode for a LPIG was fabricated by embedding a silver wire with purity of 99.9% and a diameter of 500 μm in a glass capillary with an outer diameter of 1 mm using epoxy resin. The cross section of the silver-glass capillary tip was used as a silver microelectrode after mechanical polishing with SiC papers down to 4000 grit and rinsing with distilled water. Type 304, 430 and 443 stainless steels were used as specimens. The chemical compositions and PRE numbers of the stainless steels are shown in Table 5.1. Stainless steel with a surface area of 1 cm^2 was mounted in epoxy resin, ground mechanically with SiC paper down to 1500 grit, rinsed with distilled water, and used as a substrate electrode of LPIG.

Table 5.1 Pitting resistance equivalent number ($\text{PRE} = \text{wt\% Cr} + (3.3 \text{ wt\% Mo} + 0.5 \text{ wt\% W}) + 16 \text{ wt\% N}$) of stainless steels used.

Type	PRE
430	16.6
304	18.5
443	21.2

5.2.2 Electrochemical experiments

Electrochemical experiments of the LPIG and/or the stainless steels were carried out in an electrochemical cell of 100 cm^3 in volume with a platinum counter electrode and an Ag/AgCl/sat. KCl reference electrode (SSE). Cyclic voltammetry (CV) of the LPIG was carried out in a potential range between -0.35 and $0.45 \text{ V}_{\text{SSE}}$ in 0.1 mol dm^{-3} NaCl at a scan rate of 20 mV s^{-1} . After a steady state had been obtained in CV, the microelectrode was polarized at $0.3 \text{ V}_{\text{SSE}}$ in the same solution until the electric charge Q_{LPIG} of 10 mC was consumed. Meanwhile, potentiodynamic polarization of the stainless steels was performed in

a potential range from $-0.05 V_{E_{\text{corr}}}$ to a passive state at a scan rate of 1 mV s^{-1} in 0.15 mol dm^{-3} of H_2SO_4 (pH 0.9) and Na_2SO_4 (pH 5.9) with or without containing 1.0 mol dm^{-3} NaCl solution. When the current density reached $10^{-4} \text{ A cm}^{-2}$, the scanning direction of potential was reversed and the polarization was carried at the same rate down to the point where the curve intersected the anodic scanned curve. In this polarization, a transpassivation was defined as the state, at which the current density reached $10^{-4} \text{ A cm}^{-2}$. [14-16]

5.2.3 LPIG set-up

The LPIG microelectrode was positioned above the substrate with a distance of $75 \text{ }\mu\text{m}$. A bipotentiostat independently controlled potentials of the microelectrode and the substrate as follows. The LPIG microelectrode potential, E_{LPIG} , was initially kept at $0.3 V_{\text{SSE}}$ for 100 s and then changed to $-0.2 V_{\text{SSE}}$, whereas the stainless steel substrate potential, E_{SS} , was potentiostatically controlled at $0.4 V_{\text{SSE}}$ throughout. In all electrochemical tests with LPIG, reproducibility was confirmed more than 3 times by repetition with different specimens with the same condition.

5.2.4 pH and $[\text{Cl}^-]$ sensing microelectrodes

In order to estimate solution pH and/or $[\text{Cl}^-]$ during the LPIG operation, both the tungsten and silver microelectrodes were located as substrates connected to different electrometers with the same reference electrode as I introduced in chapter 2 of (Figure 2.6). The calibration method of tungsten microelectrode potential to pH is basically identical with that explained in chapter 3. The relation between the tungsten microelectrode potential to pH is as follows:

$$E_{\text{W}} / V_{\text{SSE}} = 0.0990 - 0.04685\text{pH} . \quad [3.5]$$

Meanwhile, equilibrium reaction of the silver microelectrode with respect to Cl^- is as follows:[17]



Standard potential of Eq. 5.1 at room temperature is as follows:[17]

$$E / V_{\text{SSE}} = -0.05916 \log[\text{Cl}^-] . \quad [5.2]$$

In order to identify the sensitivity of $[\text{Cl}^-]$ for the microelectrodes, electrode potential of tungsten and silver microelectrode was monitored in 0.15 mol dm^{-3} of H_2SO_4 (pH 0.9) containing 10^{-4} , 10^{-3} , 10^{-2} , 10^{-1} or 10^0 mol dm^{-3} $[\text{Cl}^-]$. After monitoring the rest potential for

3600 s in solutions with various $[\text{Cl}^-]$, the calibrated potential of the tungsten and silver microelectrode were obtained as a function of $[\text{Cl}^-]$. Figure 5.1 shows electrode potential of the tungsten and the silver microelectrode as a function of $[\text{Cl}^-]$. It is obvious that the electrode potential of tungsten is almost constant and the calculated pH value by Eq. 3.5 within value ranges between 1.0 to 0.9. It is thought that the electrode potential of tungsten microelectrode is not significantly affected by $[\text{Cl}^-]$ in the solution. The electrode potential of silver microelectrode is shifted to the negative potential direction and has a linear relation with $[\text{Cl}^-]$, when the $[\text{Cl}^-]$ is higher than $10^{-2} \text{ mol dm}^{-3}$:

$$E / V_{\text{SSE}} = -0.134 - 0.067 \log[\text{Cl}^-]. \quad [5.3]$$

The slope is almost in agreement with Eq. 5.2, while the potential of silver microelectrode is shifted compared to that of theoretical equilibrium potential. It is thought that a silver chloride layer formed in the bare silver microelectrode surface is not electrochemically stable than ideal silver chloride layer formed on silver surface. Hence, the electrode potential of silver microelectrode does not change in solution containing less than $10^{-2} \text{ mol dm}^{-3}$ of Cl^- . This indicates that it is difficult to keep electrochemical equilibrium silver chloride layer on silver microelectrode surface with smaller than $10^{-2} \text{ mol dm}^{-3}$ of Cl^- . The silver microelectrode for sensing $[\text{Cl}^-]$ is applicable in a solution with more than $10^{-2} \text{ mol dm}^{-3}$ of Cl^- .

5.2.5 Surface analyses

The surfaces of the stainless steel specimens polarized at $0.4 V_{\text{SSE}}$ for 100 s in H_2SO_4 and Na_2SO_4 solution were analyzed by an Auger electron spectroscope (AES). Ar^+ sputtering at an etching rate of 0.66 nm min^{-1} equivalent to silica was used for obtaining a depth profile of the local specimen surface. Transmission electron microscopy with energy dispersive spectrometry (TEM-EDS) was used for characterizing the chemical composition profiles of the local surface of type 443 stainless steel after polarization at $0.4 V_{\text{SSE}}$ for 100 s in H_2SO_4 solution.

5.2.6 Modeling parameters and conditions

Concentration profiles of chloride anions generated from the LPIG were modeled using a finite element method solver of COMSOL Multiphysics™ 5.0 as mentioned in chapter 3. The calculation method and assumptions are identical to that used in chapter 3, while some parameters are different. The parameters for modeling the concentration distribution of Cl^- are listed in Table 5.2 and 5.3. Current transients obtained in the LPIG experiment with the stainless steel were also used in FEM calculation. The modeling parameters were values for diffusion coefficients of anion generated from the LPIG and the initial concentrations of proton ions of bulk solution before the LPIG operation. The

geometrical variation was used as the substrate surface and a horizontal distance from the center of substrate where the position is under the LPIG. Current transients for experimental results of potentiostatic polarizations were used for modeling generation of anion during the polarizations. Change in anion concentration by potentiostatic polarization of the LPIG was modeled for each time for rapid increase of current flowing to stainless steel substrate electrodes.

Table 5.2 Parameters used for modeling the concentration distribution of Cl^- .

Parameter	Value
Diffusion coefficient of $\text{Cl}^- / D_{\text{Cl}^-}$	$20.3 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$ [18]
Diffusion coefficient of $\text{H}^+ / D_{\text{H}^+}$	$93.1 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$ [18]
Initial concentration of proton ions in H_2SO_4 solution	$1.00 \times 10^{-0.9} \text{ mol dm}^{-3}$
Initial concentration of proton ions in Na_2SO_4 solution	$1.00 \times 10^{-5.9} \text{ mol dm}^{-3}$

Table 5.3 Variations used for modeling the concentration distribution of Cl^- .

Variation	Detail
Distance from the center of substrate	from 0 to 500 μm

5.3 Results

5.3.1 Electrochemical reaction of a silver microelectrode

Figure 5.2a shows a cyclic voltammogram of a silver microelectrode in deaerated $0.1 \text{ mol dm}^{-3} \text{ NaCl}$ solution. The CV reached in a steady state within a few cycles. The anodic current at potentials higher than ca. $0.1 V_{\text{SSE}}$ and the cathodic current at potentials lower than ca. $0.1 V_{\text{SSE}}$ seem to be formation of silver chloride and reduction of silver chloride, respectively. In CV, the electric charge consumed increases during the anodic current flow, while it decreases to zero during the cathodic current flow (Figure 5.2b), indicating that anodic and cathodic reactions of the electrode are reversible during this potential range in this solution. Since the solubility of AgCl is small ($K_{\text{sp}} = 1.56 \times 10^{-10}$) [19], the amount of AgCl dissolved from the microelectrode is negligibly small. The results indicate that the anodic reaction of silver and the cathodic reaction of silver chloride correspond to the following backward and forward reactions in an aqueous solution, respectively:



In Eq. 5.1, the reduction of AgCl means a generation of Cl^- from the microelectrode into the solution. Standard potential of Eq. 5.1 at room temperature is as follows:[17]

$$E / V_{\text{SSE}} = -0.05916 \log[\text{Cl}^-]. \quad [5.2]$$

From Eq. 5.2, a concentration $[\text{Cl}^-]$ of $10^{-1.1} \text{ mol dm}^{-3}$ can be estimated at $E_0 = 0.076 V_{\text{SSE}}$. Therefore, the silver chloride surface generates Cl^- during cathodic polarization at potentials lower than $0.07 V_{\text{SSE}}$. In the following experiments, a silver microelectrode covered with silver chloride (Ag/AgCl microelectrode) was used as an LPIG for generating the source of Cl^- . In most cases, AgCl formed on the silver microelectrode with the consumption of electric charge for 10 mC.

5.3.2 Anodic polarization of stainless steels

Figure 5.3a shows potentiodynamic polarization curves of type 430, 304 and 443 stainless steels in $0.15 \text{ mol dm}^{-3} \text{ H}_2\text{SO}_4$ solution. Corrosion potential of type 430 stainless steel is lower than corrosion potentials of type 304 and 443 stainless steels, while the corrosion potentials of type 304 and 443 are similar. Active-passive transition appeared for all stainless steels. A peak current at the transition-potential seems to be a critical parameter for primary passivation. The lower corrosion potential and larger critical current of type 430 stainless steel are related to the chemical composition since type 430 stainless steel contains smaller alloying elements of Cr and/or Ni than those of type 304 or 443 stainless steel. Alloying Cr plays a role in expansion of the passive region of stainless steel and results in a decrease of Fe dissolution from stainless steel,[20] while the relatively noble alloying element Ni rather than alloying Fe and Cr also suppresses the general dissolution of Fe by accumulation at the metal substrate-passive film interface.[21] Meanwhile, type 430, 304 and 443 stainless steels show similar passive currents, $4\text{--}10 \mu\text{A cm}^{-2}$, and the passive current is lowest at ca. $0.4 V_{\text{SSE}}$. No localized corrosion was observed in this solution even after polarization up to $1.0 V_{\text{SSE}}$. Figure 5.3b shows potentiodynamic polarization curves of type 430, 304 and 443 stainless steels in $0.15 \text{ mol dm}^{-3} \text{ Na}_2\text{SO}_4$ solution. Corrosion potentials of type 430 and 443 stainless steels are lower than that of type 304 stainless steel, due to the alloying element Ni, which makes the corrosion potential of stainless steel positive.[21] No active-passive transition was observed for any of the three type of stainless steels and the anodic current reached a passivity-maintaining current smaller than $4 \mu\text{A cm}^{-2}$ at potentials lower than ca. $0.7 V_{\text{SSE}}$, implying that the specimen surface had been spontaneously passivated before the polarization, probably just after the specimen preparation. The passivity-maintaining current is in the order of type $304 \approx 443 < 430$ stainless steels, indicating that the passive film formed on type 430 stainless steel is more conductive than those formed on type 304 and 443 stainless steels. At potentials higher than $0.69 V_{\text{SSE}}$, the anodic current increases and shows a peak at $0.90 V_{\text{SSE}}$ for type 304 and 443 stainless steels and a peak at $1.09 V_{\text{SSE}}$ for type 430 stainless steel. It is attributed to the oxidation of alloying Fe, Cr or Ni in the passive film and/or stainless steel substrate.[22] At higher potentials, the anodic current decreases and reaches a secondary passivation. In this solution, no localized

corrosion occurs and reaches a secondary passivation. In this solution, no localized corrosion also occurred.

5.3.3 Current transients of LPIG and stainless steels during operation of LPIG

Figures 5.4a and 5.4b show transients of the LPIG current I_{LPIG} and stainless steel substrate current I_{ss} in H_2SO_4 and Na_2SO_4 solutions, respectively, when LPIG potential E_{LPIG} was changed from 0.3 to $-0.2 \text{ V}_{\text{SSE}}$ at 100 s while stainless steel specimen potential E_{ss} was kept at $0.4 \text{ V}_{\text{SSE}}$. In both solutions, before the E_{LPIG} change, no anodic current and only a small anodic current flow in the LPIG and specimen electrodes, respectively, indicating that the LPIG is in a standby to generate Cl^- and the specimen surface is in a passive state. In H_2SO_4 solution, the current of specimens at 100 s is in the order of type 304 < 443 < 430 stainless steels. The larger current of type 443 might be related to its passivity and/or localized corrosion resistance as discussed later. In Na_2SO_4 solution, on the other hand, the current at 100 s becomes in the order of type 443 < 304 < 430 stainless steels, which is as same as that of the passivity-maintaining current observed in potentiodynamic polarization curves. After the cathodic change of E_{LPIG} at 100 s, however, a cathodic current flows in the LPIG electrode regardless of solution pH, due to the generation of Cl^- . A larger anodic current also starts to flow in some stainless steel specimens. A slightly larger current starts to flow in type 430 and 304 stainless steels at 1.55 and 10.6 s, respectively, after the cathodic change of E_{LPIG} in H_2SO_4 solution and at 0.72 and 15.4 s, respectively, after the E_{LPIG} change in Na_2SO_4 solution, although type 304 stainless steel in Na_2SO_4 solution shows a metastable current fluctuation. Increases in anodic current depending on the type of steel and solution pH should be correlated with some anodic processes on stainless steel and the LPIG operation. Although non-faradaic processes including change in electric conductivity and/or capacitance in the inter-electrode space due to concentrated Cl^- and/or reorganization of the surface and double layer might be related to the increase in anodic current, it would be negligible because of the small time constant. Meanwhile, strong dependency of the slightly increased current on the type of steel means that faradaic processes on the stainless steel surface including degradation of the film should occur additionally with the original passivation process of the surface. In the case of application of an LPIG to passivated pure iron [7,8], dissolution of Fe(III) species from the passive film was observed during the initiation of film breakdown by concentrated Cl^- from the LPIG. Fe(III) species diffused to the LPIG were reduced and the so-called feedback phenomenon, that is repetition of the redox reaction of Fe(III) and Fe(II) between the microelectrode and degrading surface, was observed. If film degradation is initiated on the stainless steel surface due to concentration of Cl^- , some alloying elements in the stainless steel might dissolve. However, the increased anodic current I_{ss} through type 430 stainless steel in H_2SO_4 solution is ca. $2 \mu\text{A}$, which is significantly smaller than the increased cathodic current of LPIG, ca. 0.2 mA . Therefore, there was almost no feedback of the redox reaction of Fe(III) and Fe(II) species on stainless steel in this study. Following the slight increase in

current of type 430 and 304 stainless steels by the LPIG operation, on the other hand, the anodic currents rapidly increase at 0.2 and 32 s, respectively, after the E_{LPIG} change in H_2SO_4 solution and at 12 and 37 s, respectively, after the E_{LPIG} change in Na_2SO_4 solution. Type 443 stainless steel also suddenly allows an increase in anodic current flow at 39 s after the E_{LPIG} change in Na_2SO_4 solution, while there is no increase during and after the LPIG operation in H_2SO_4 solution. These large anodic currents of the specimen electrode mean the initiation and/or propagation of localized corrosion of stainless steel. Type 443 stainless steel in H_2SO_4 solution does not suffer from localized corrosion by operation of the LPIG charged with $Q_{\text{LPIG}} = 10 \text{ mC}$. In any case, the time t_d until a rapid increase in I_{SS} starts after the cathodic change of E_{LPIG} is considered to be an induction period for the initiation of localized corrosion due to the LPIG operation. Additionally, the cathodic electric charge Q_d consumed by the LPIG electrode for t_d is considered to be the amount of Cl^- needed for corrosion initiation. Table 3 shows the parameters obtained from the LPIG operation. The relations between those parameters and localized corrosion resistance of stainless steel are discussed later.

Table 5.4 **Parameters obtained from LPIG technique in H_2SO_4 and Na_2SO_4 solutions; time for rapid increase of anodic currents after LPIG operation, t_d , the consumed electric charge at that the time t_d , $|Q_d|$**

Type	t_d / s		$ Q_d / \text{mC}$	
	H_2SO_4	Na_2SO_4	H_2SO_4	Na_2SO_4
430	7.0 ± 0.41	13 ± 1.1	1.9 ± 0.88	2.5 ± 0.49
304	34 ± 5.1	38 ± 6.1	9.2 ± 0.91	4.8 ± 0.91
443	Passivated	40 ± 8.3	Passivated	7.0 ± 0.50

5.3.4 Estimation of pH and $[\text{Cl}^-]$ during the operation of LPIG

Experimental estimation by using tungsten and silver microelectrode.—

Figure 5.5 shows changes in electrode potentials of the LPIG microelectrode E_{LPIG} , tungsten microelectrode E_{W} , and silver microelectrode E_{Ag} when the LPIG microelectrode potential, E_{LPIG} , was changed from 0.3 to $-0.2 \text{ V}_{\text{SSE}}$ above $75 \mu\text{m}$ distance away from substrate in $0.15 \text{ mol dm}^{-3} \text{ H}_2\text{SO}_4$ solution. During a polarization at $0.3 \text{ V}_{\text{SSE}}$ for 100 s, cathodic current does not flow, indicating no Cl^- generation from the LPIG. However, when the LPIG microelectrode is polarized at $-0.2 \text{ V}_{\text{SSE}}$, cathodic current of I_{LPIG} flows. It has been shown that AgCl is reduced and Cl^- generates. The current transient of I_{LPIG} is similar to that of I_{LPIG} above type 304 and 443 stainless steel shown in Figure 5.4a. E_{W} and E_{Ag} also shift to negative potentials. The reduction of AgCl increases pH as well as $[\text{Cl}^-]$. The value of pH, converted from Eq. 3.5 by substituting the value of E_{W} , of the solution is increases from ca sustained at

ca. -1.0 to 3.5 after the onset of cathodic polarization. This means that the amount of protons decreases in the vicinity of the tungsten microelectrode. However, it is obvious that H^+ is not generated from the LPIG microelectrode based on Eq. 5.1. It is thought that adsorption of proton on inner Helmholtz layer (IHL) on tungsten surface and hydration of tungsten by water molecule or proton are interrupted by a compulsory supply of Cl^- (generation of Cl^- from LPIG) which adsorbs on IHL. The relative change in amount of proton in Helmholtz layer could not be as a steady-state during the cathodic polarization of the LPIG. This process of local Cl^- supply during the cathodic polarization of LPIG is the reason why E_w shifts, while E_w does not shift in a solution containing $[Cl^-]$. Meanwhile, it is possible to estimate the value of $[Cl^-]$ by Eq. 5.3. When the LPIG was polarized cathodically, $[Cl^-]$ gradually increases and peaks ca. 0.4 mol dm^{-3} within 40 s and then slightly decreases and reached ca. 0.3 mol dm^{-3} for 160 s. When the polarization of the LPIG microelectrode was finished at 155 s for generating 10 mC of Cl^- , the values of $[Cl^-]$ slightly decreased within 5 s, suggesting that the Cl^- in the interelectrode space is still concentrated and slowly diffused to bulk solution. Although it is difficult to discuss the $[Cl^-]$ lower than $10^{-2} \text{ mol dm}^{-3}$, the Ag microelectrode is possible to estimate $[Cl^-]$ from $10^{-2} \text{ mol dm}^{-3}$. From the Eq.5.3, it can be estimated the $[Cl^-]$, shown in Table 5.5, for each time parameter of stainless steel for initiating localized corrosion, t_d , obtained from Figure 5.4. Sufficient $[Cl^-]$ for initiating localized corrosion is different with a type of stainless steel, while type 443 stainless steel is sustained its passivity in $[Cl^-] < \text{ca. } 0.4 \text{ mol dm}^{-3}$ for 60 s polarization at 0.4 V_{SSE} in 0.15 mol dm^{-3} H_2SO_4 (pH 0.9) solution.

Table 5.5 $[Cl^-]$ converted E_{Ag} by Eq. 5.3 obtained from LPIG operation in H_2SO_4 for the time parameter, t_d .

Type	$[Cl^-]$ at $t_d / \text{mol dm}^{-3}$
430	0.022
304	0.394
443	Passivated

Numerical modeling for estimating pH and $[Cl^-]$.— The LPIG prepared with $Q_{LPIG} = 10 \text{ mC}$ allows generation of $1.0 \times 10^{-7} \text{ mol } Cl^-$. When the LPIG is located above the specimen surface with an interelectrode distance of $75 \text{ } \mu\text{m}$, a volume of ca. $1.0 \times 10^{-7} \text{ dm}^3$ is estimated as an interelectrode solution between the LPIG and the specimen. Assuming that there is no Cl^- diffusion to the bulk solution during the LPIG operation, Cl^- with a mean concentration of 1.0 mol dm^{-3} can accumulate in the local solution.

Numerical modeling may be effective to estimate $[Cl^-]$ for localized corrosion by the LPIG operation. $[Cl^-]$ was calculated numerically from the current transient of the

LPIG microelectrode with an interelectrode distance of 75 μm during the LPIG operation in H_2SO_4 and Na_2SO_4 solution by using the diffusion model. $[\text{Cl}^-]$ at the specimen surface increases within 1 s after the commencement of cathodic polarization of the LPIG (Figure 5.6). It is clear that the increasing rate is independent of specimen type but is strongly dependent on solution pH. The maximum $[\text{Cl}^-]$ of 3.0 and 3.6 mol dm^{-3} are obtained at 31 s in H_2SO_4 solution and 60 s in Na_2SO_4 solution, respectively, though localized corrosion occurs in the stainless steel before the complete consumption of chloride in Na_2SO_4 . The rapid consumption of chloride in H_2SO_4 is probably due to large conductivity of the solution as well as acidity. The conductivity of H_2SO_4 solution was 11.4 S m^{-1} , which was three-times larger than that of Na_2SO_4 solution (3.79 S m^{-1}). In a solution with a larger conductivity, an ohmic drop for electrochemical reaction becomes smaller. However, $[\text{Cl}^-]$ at the surface decreases after the cathodic current peak of the LPIG because of Cl^- diffusion to the solution bulk as well as Cl^- exhaustion at the LPIG. In the case of type 443 stainless steel in H_2SO_4 solution, no localized corrosion was initiated, indicating that the accumulation of Cl^- at the surface was not sufficient for this specimen to initiate localized corrosion. It is apparent that type 443 has a high resistance to local breakdown of the passive surface. In any case, a critical $[\text{Cl}^-]$ inducing local breakdown of the passive surface is almost independent of solution pH but is dependent on steel type. It is also thought that type 304 is more resistive than type 430 because the critical concentration is about two-times higher.

Figure 5.7 shows maximum $[\text{Cl}^-]$ during the cathodic polarization of the LPIG above stainless steel substrate as a function of a distance from the center of the substrate surface in H_2SO_4 and Na_2SO_4 solutions. It is clear that $[\text{Cl}^-]$ has the highest value at center of the substrate surface, under the LPIG, and gradually decreases from the maximum concentration to ca. 0 mol dm^{-3} with the distance away from the center to 500 μm , an outer diameter of a microelectrode sheath, with regardless of solution pH. However, when the interelectrode distance is farther than 500 μm , the concentration of HS^- is independent of the distance from the center as well as the interelectrode distance. The value of maximum $[\text{Cl}^-]$ is ca. 30% higher in H_2SO_4 than in Na_2SO_4 . This is also related to the higher cathodic current flowed on LPIG in H_2SO_4 than in Na_2SO_4 . This indicates that concentration distribution on the substrate surface is strongly dependent on a cathodic current for generating $[\text{Cl}^-]$. Meanwhile, the value of calculated $[\text{Cl}^-]$ on the stainless steel surface is approximately seven times higher in all Cl^- generation period than that estimated by silver microelectrode shown in Figure 5.5. From the interface of Ag/AgCl , Cl^- should diffuse across the Ag layer to solution. It is difficult to reach a fine steady state in potentiostatic polarization because of the complexity of Cl^- generation process. Numerical modeling is progressed through an assumption; Ag/AgCl surface is present as only AgCl itself and does not form Ag layer during the same cathodic reaction of entire surface of AgCl . The Cl^- directly diffuses from the entire surface of AgCl to the solution with respect to the current flowed to the AgCl . The ignored factors for a diffusion of Cl^- from AgCl layer to Ag and identical generation rate on the entire surface of AgCl layer could be the reason for the large difference of $[\text{Cl}^-]$ on stainless steel

substrate surfaces.

Table 5.6 [Cl⁻] obtained from numerical modeling during the LPIG operation in H₂SO₄ and Na₂SO₄ solutions at the time for rapid increase of anodic currents after LPIG operation, t_d .

Type	[Cl ⁻] at t_d / mol dm ⁻³	
	H ₂ SO ₄	Na ₂ SO ₄
430	1.01	1.32
304	2.74	2.32
443	Passivated	2.37

5.3.5 Pitting and repassivation potential of stainless steels

The LPIG prepared with an electric charge of 10 mC allows generation of 1.0×10^{-7} mol Cl⁻ ions. When the LPIG is located above the substrate surface with an interelectrode distance of 125 μ m, the volume of an inter-electrode space is 9.82×10^{-8} dm³. Assuming that there is no Cl⁻ diffusion to bulk solution during the LPIG operation, Cl⁻ ions can be accumulated with the mean concentration of 1.0 mol dm⁻³ in the inter-electrode space. Here, stainless steels were polarized in Cl ions-containing solution with an equivalent concentration, 1.0 mol dm⁻³, to LPIG operation.

Figures 5.8a and 5.8b show cyclic potentiodynamic polarization curves of the type 430, 304 and 443 stainless steels in H₂SO₄ and Na₂SO₄ solutions, respectively, both containing 1.0 mol dm⁻³ NaCl. Specimens in H₂SO₄ show active and passive states and then pitting or trans-passive state, while specimens in Na₂SO₄ show passive states and then pitting or trans-passive state, depending on potential. In the case of H₂SO₄, in whole potential region, type 430 stainless steel allows flowing of current larger than type 304 and 443 stainless steels. This steel flows a passivity maintaining current of 2.5×10^{-4} A cm⁻² at $-0.2 V_{SSE}$ while both type 304 and 443 stainless steels flow the current density of 10^{-5} A cm⁻² in potential regions from -0.1 to $0.1 V_{SSE}$ and from -0.15 to $0.05 V_{SSE}$, respectively. In the case of Na₂SO₄, type 430 stainless steel experiences a larger current density than those of type 304 and 443 stainless steel. Type 430 stainless steel flows the passivity maintaining current density of 3 μ A cm⁻² at potentials higher than $-0.1 V_{SSE}$, while type 304 and 443 stainless steels flow the passivity maintaining current density of 2 μ A cm⁻² in potential regions from -0.05 to $0.3 V_{SSE}$ and from -0.1 to $0.4 V_{SSE}$, respectively. Here, pitting potential E_p is obtained as an intersectional potential of the tangent line at the potential of passivity maintaining current density of 10^{-4} A cm⁻² and the other tangent line from the lowest passive current density, while repassivation potential E_r is defined as a cross sectional potential of reverse scan and

the anodic polarization curve. The E_p is a minimum potential to progress trans-passive reaction such as a stable pit. The E_r is a maximum potential, at which passive film is sustained its passivity without initiation of a pit (meta-stable pit). In the potential range between E_p and E_r , meta-stable pit can be initiated, whereas the meta-stable pit cannot propagate to stable pit. Table 5.7 presents the parameters obtained from Figure 5.8. In general, the E_p and E_r of stainless steels increase with increase in PRE value. It is indicated that localized corrosion resistance of stainless steel is well manifested as PRE value. However, the E_r of type 443 stainless steel in H_2SO_4 is lower than that of type 304 stainless steel and does not dependent on PRE. This means that the type 443 stainless steel is less resistive or more sensitive localized corrosion in H_2SO_4 than in Na_2SO_4 but it is resistive to stable pit initiation than that to type 304 stainless steel in solution pH 0.9. Furthermore, the E_p and E_r are dependent on solution pH, being higher Na_2SO_4 than that in H_2SO_4 . It is reasonable because the solution acidity strongly affects the oxidation of alloying elements.

Table 5.7 **Pitting potential, E_p , and repassivation potential, E_r , obtained from cyclic potentiodynamic polarization curves of type 304, 430 and 443 stainless steels in $0.15 \text{ mol dm}^{-3} H_2SO_4$ and Na_2SO_4 solution containing $1.0 \text{ mol dm}^{-3} NaCl$.**

Type	pitting potential, E_p / V_{SSE}		repassivation potential, E_r / V_{SSE}	
	H_2SO_4	Na_2SO_4	H_2SO_4	Na_2SO_4
430	-0.13 ± 0.06	-0.29 ± 0.04	-0.29 ± 0.04	0.05 ± 0.05
304	0.23 ± 0.01	-0.05 ± 0.01	-0.05 ± 0.01	0.31 ± 0.01
443	0.27 ± 0.02	-0.17 ± 0.03	-0.17 ± 0.03	0.40 ± 0.01

5.3.6 Evaluation of parameters of localized corrosion resistance on stainless steels

The time t_d and electric charge $|Q_d|$ to initiate a pit were measured during the LPIG operation to stainless steels in 5.3.3, while the potentials of E_p and E_r were observed from cyclic potentiodynamic polarization of the steel in chloride ions-containing solution in 5.3.5. Figure 5.9 shows these parameters obtained in solutions of H_2SO_4 and Na_2SO_4 as a function of PRE value. In H_2SO_4 solution, t_d and $|Q_d|$ of type 443 stainless steel cannot be plotted because no pitting occurred. The t_d , $|Q_d|$ and E_p increase with increase in PRE regardless of solution pH, indicating that localized corrosion on the stainless steels corresponds to alloying element portions. However, the value of t_d for type 304 and 443 stainless steels are similar in Na_2SO_4 , while the value of $|Q_d|$ is higher for type 443 stainless steel than type 304 stainless steel. It is clear that type 443 stainless steel is needed to consume

more Cl^- to initiate a pitting than type 304 stainless steel, indicating that this steel is the most resistive against pitting initiation. Meanwhile, the $|Q_d|$ values of type 304 and 443 stainless steels obtained in the solution of H_2SO_4 are significantly larger than those obtained in Na_2SO_4 solutions, means that a large amount of Cl^- is needed to initiate localized corrosion in acid.

5.3.7 Surface analysis of passive film on stainless steels

Figures 5.10 show AES depth profiles of specimen surfaces of type 430, 304 and 443 stainless steels polarized at $0.4 V_{\text{SSE}}$ in H_2SO_4 and Na_2SO_4 solution. It is clear from the presence of O with high atomic concentrations that stainless steel surfaces were covered with oxide films. Assuming that the interface between the oxide film and substrate is located at the transition with a half of the atomic concentration of O, oxide films of stainless steels formed in H_2SO_4 and Na_2SO_4 solutions have similar thicknesses of ca. 3 nm. This is in good agreement with the previously reported thicknesses of 2 to 4 nm for passive films on stainless steels.[22-28] The atomic concentration of Fe in the oxide film formed in H_2SO_4 solution is ca. 20 at%, which is lower than that in the oxide film formed in Na_2SO_4 solution as shown in Figure 5.11. Conversely, the atomic concentration of Cr is ca. 20 at% and is larger in the film formed in H_2SO_4 than in the film formed in Na_2SO_4 regardless of the type of stainless steel. These results also coincide with results of previous studies [23,28-31] showing that the passive films formed in acid have higher proportions of chromium oxide than do those formed in neutral or alkaline solution. Figure 5.12a shows a TEM image of a cross-sectional surface of type 443 stainless steel after potentiostatic polarization at $0.4 V_{\text{SSE}}$ for 100 s in H_2SO_4 solution. The dark and grey areas correspond to the substrate and oxide film, respectively. Although the oxide film is slightly blurred, it is continuously covered with the substrate with a thickness of 2.9 nm. EDS line analysis was carried out along the red line around the surface in the image (Figure 5.12b). It was revealed that the oxide film-substrate interface is located 2 nm from the outermost surface, at which the atomic concentration of O becomes half of that at the bulk substrate. These thicknesses are in good agreement with that obtained from the AES depth profile. TEM-EDS line analysis also showed that Cr is depleted but that ca. 20 at% of Fe is present in the outermost layer of the film. The higher portion of Fe than Cr in the oxide film formed on type 443 stainless steel coincides with that obtained from the AES depth profile, though TEM-EDS showed higher portions of Fe and Cr than those obtained from AES both by ca. 5 at%. Moreover, there is a concentrated elemental Cu at the oxide film-substrate interface.

5.4 Discussion

LPIG tests and dynamic polarization for type 430, 304 and 443 stainless steels were carried out in H_2SO_4 and Na_2SO_4 solutions. Some parameters obtained from these electrochemical measurements correspond to the PRE number of stainless steel. Furthermore,

the LPIG electrode current flowing until the initiation of localized corrosion gives the critical $[\text{Cl}^-]_d$ needed for breakdown of the passive film formed on stainless steel. It was confirmed that the LPIG test is effective for evaluating localized corrosion resistance of stainless steel.

Localized corrosion is directly related to degradation of the passive film on stainless steel. The thickness of the passive film generally increases with increase in applied potential and increase in solution pH.[30] In the case of type 304 stainless steel, the thickness of the passive film formed at $0.45 \text{ V}_{\text{SSE}}$ was reported to range from 1.5 nm at pH 0.0 to 3.0 nm at pH 6.5.[31]. However, the thickness measured from the AES depth profile was ca. 3 nm regardless of solution pH. Moreover, it has been shown that a passive film of stainless steel formed in an acidic solution consists mainly of chromium and iron oxides.[26-29,31] An increase in solution pH decreases the dissolution rate of Fe [28-32] and increases the portion of iron oxide in the oxide film. An increase of iron oxide was also confirmed in the profile; that is, the fraction of Fe in the film formed in Na_2SO_4 solution was larger than that formed in H_2SO_4 solution. Since the oxide film has a larger portion of chromium oxide, the film becomes more resistive to localized corrosion.[1-5] The higher Cr concentration and lower Fe concentration in the oxide film formed in H_2SO_4 solution than the concentrations in oxide films formed in Na_2SO_4 solution support the typical features of a passive film on stainless steel. Therefore, it is thought that the small portion of chromium oxide and/or large portion of iron oxide in the oxide film formed in Na_2SO_4 solution would make the film susceptible to localized corrosion compared with the film formed in H_2SO_4 solution.

Although localized corrosion resistance of stainless steels is discussed with PRE number in this study, a contribution of Cr concentration to the number is predominant. It is well known that an addition of Cr into stainless steel shifts the pitting potential of the steel to a positive potential [33,34] and is effective to increase a localized corrosion resistance of the steel.[33-38] This is due to increase in the ratio of chromium oxides in passive film formed on the steel [36-38] as confirmed in Fig. 5.10. Therefore, it is thought that the small portion of chromium oxide and/or large portion of iron oxide in the film formed in Na_2SO_4 solution would make the film susceptible to localized corrosion compared to the film formed in H_2SO_4 solution. However, a minor alloying effect, which is not contained in PRE number, on the localized corrosion resistance of stainless steel should be considered.[37-46] Alloying Ni is known as an austenitic stabilizing element of stainless steel without participating in the formation of a passive film. Alloying nickel is known as an austenitic stabilizer element of stainless steel without participating in a formation of passive film.[38] Metallic Ni can be enriched at a passive film-substrate interface during passive film formation. Ni is relatively noble compared with other metallic elements in stainless steel such as Fe and Cr. [39-41] Kim et al. reported that enriched Ni enhanced passivation of stainless steel in an acidic chloride solution by increasing the dissolution of further alloying elements.[42] Enrichment of Ni at the interface between the oxide film and substrate was also confirmed in the AES depth profile in type 304 stainless steel and is thought that type 304 stainless steel showed higher E_r than that of type 443 stainless steel. It was reported that alloying Cu enhances general

corrosion resistance of stainless steel by suppressing dissolution of the main alloying elements Fe and/or Cr and by forming metallic Cu on the outermost surface in an acidic solution. [44-46] Moreover, the addition of Cu in stainless steel enhanced localized corrosion resistance by forming an insoluble salt such as CuCl that plays a role of protection of the oxide film in an acidic solution.[45] The presence of Cu at the passive film-substrate interface suppresses localized corrosion propagation even after removal of the passive film and exposure of the bare substrate. TEM-EDS clearly showed the existence of elemental Cu at the oxide film-substrate interface of type 443 stainless steel. This might be a reason why a meta-stable state could not be observed on this steel because the amounts of alloying Ni and Cu in this steel are large. Localized corrosion resistance of stainless steels has frequently been discussed by using pitting potential E_p . [2,3,11,13] Measurement of E_p might be an effective way to evaluate localized corrosion resistance.[45-48] However, this value shows an energy state of passivity at so-called “Achilles heel” which is a specific features such as inclusions of substrate and is discussed not only thermodynamically but also statistically. Although E_p corresponded to the PRE number in this study, it is difficult to discuss the kinetics of localized corrosion with this value for stainless steel. On the other hand, the LPIG test provides kinetic parameters. It is thought that t_d and $|Q_d|$ reflect an induction process of passive film breakdown or localized corrosion progressing on the stainless steel surface. The value of t_d is equivalent to incubation time, and $|Q_d|$ corresponds to the amount of Cl^- needed for initiating localized corrosion. The critical Cl^- concentration $[\text{Cl}^-]_d$ is dependent on the type of stainless steel but is almost independent of solution pH. $[\text{Cl}^-]_d$ is related to the initiation of localized corrosion. Iron- and chromium-chlorides are more soluble into an aqueous solution than oxides. Concentration of Cl^- in the local solution between the LPIG and steel surface leads to replacement of oxides with chlorides in the film. It is thought that localized corrosion resistance of the steel corresponds to the order of enrichment with chromium oxide rather than iron oxide, though the thicknesses of oxide films on stainless steels are almost the same.

5.5 Summary

Localized corrosion resistance of type 430, 304 and 443 stainless steels in 0.15 mol dm^{-3} of H_2SO_4 and Na_2SO_4 solutions was evaluated by using the LPIG technique, in which a silver microelectrode covered with a silver chloride layer with an electric charge of 10 mC was used. Localized corrosion was initiated on type 430 and 304 steels in H_2SO_4 solution and on all types of steel in Na_2SO_4 solution by locally generated Cl^- from the LPIG microelectrode. The induction period t_d , cathodic electric charge Q_d and estimated concentration of Cl^- $[\text{Cl}^-]_d$ needed for the initiation corresponded to the PRE number as well as pitting potential of the steel. It was clear that the most corrosion-resistive steel in this study was type 443 stainless steel. AES and TEM-EDS of this stainless steel revealed enrichment of elemental copper at the interface between the oxide film and substrate and of chromium oxide rather than iron oxide in the oxide film.

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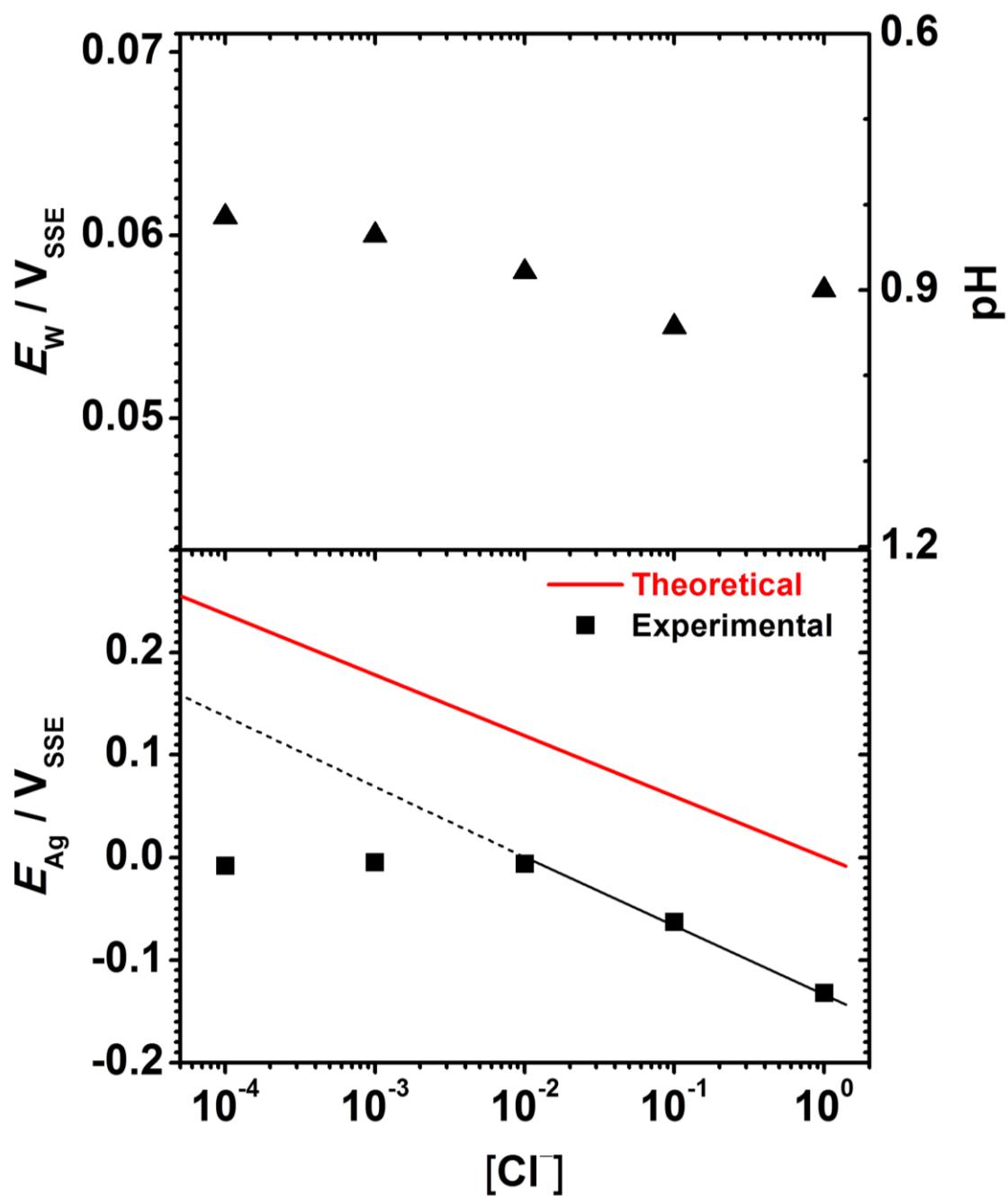
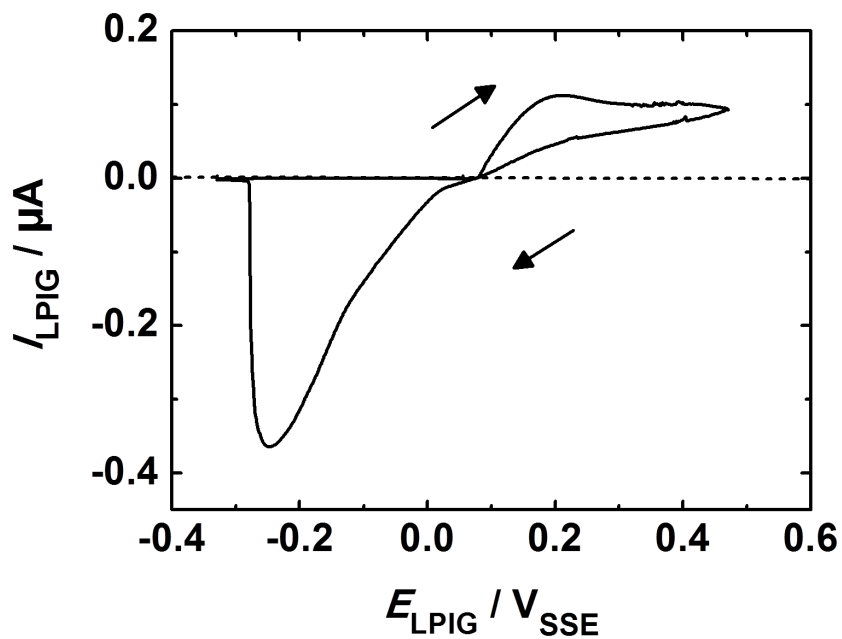


Figure 5.1 Electrode potential of the tungsten and silver microelectrode as a function of $[Cl^-]$ in 0.15 mol dm $^{-3}$ of H_2SO_4 (pH 0.9) containing 10^{-4} , 10^{-3} , 10^{-2} , 10^{-1} or 10^0 mol dm $^{-3}$ $[Cl^-]$

a



b

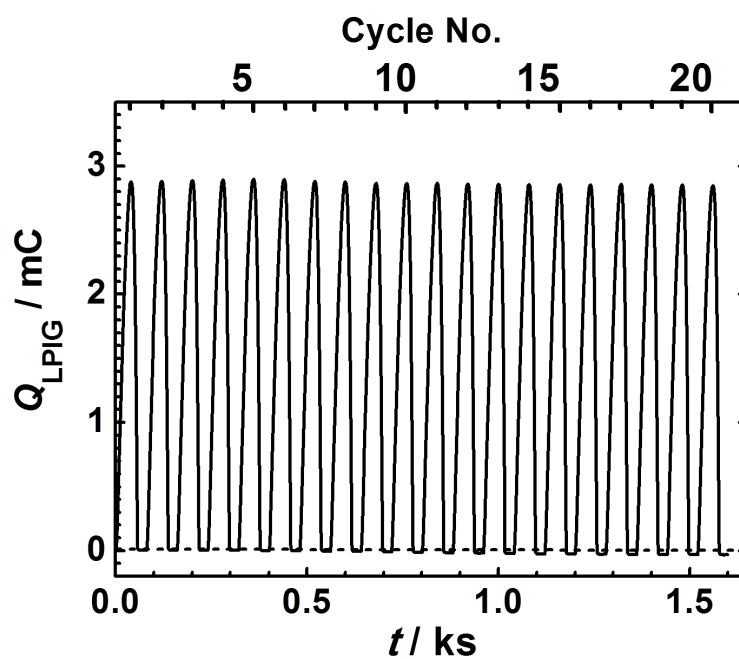


Figure 5.2 (a) Cyclic voltammograms of silver microelectrode in 0.1 mol dm^{-3} NaCl solution. The potential scan rate was 20 mV s^{-1} . (b) Transient of electric charge consumed during CV.

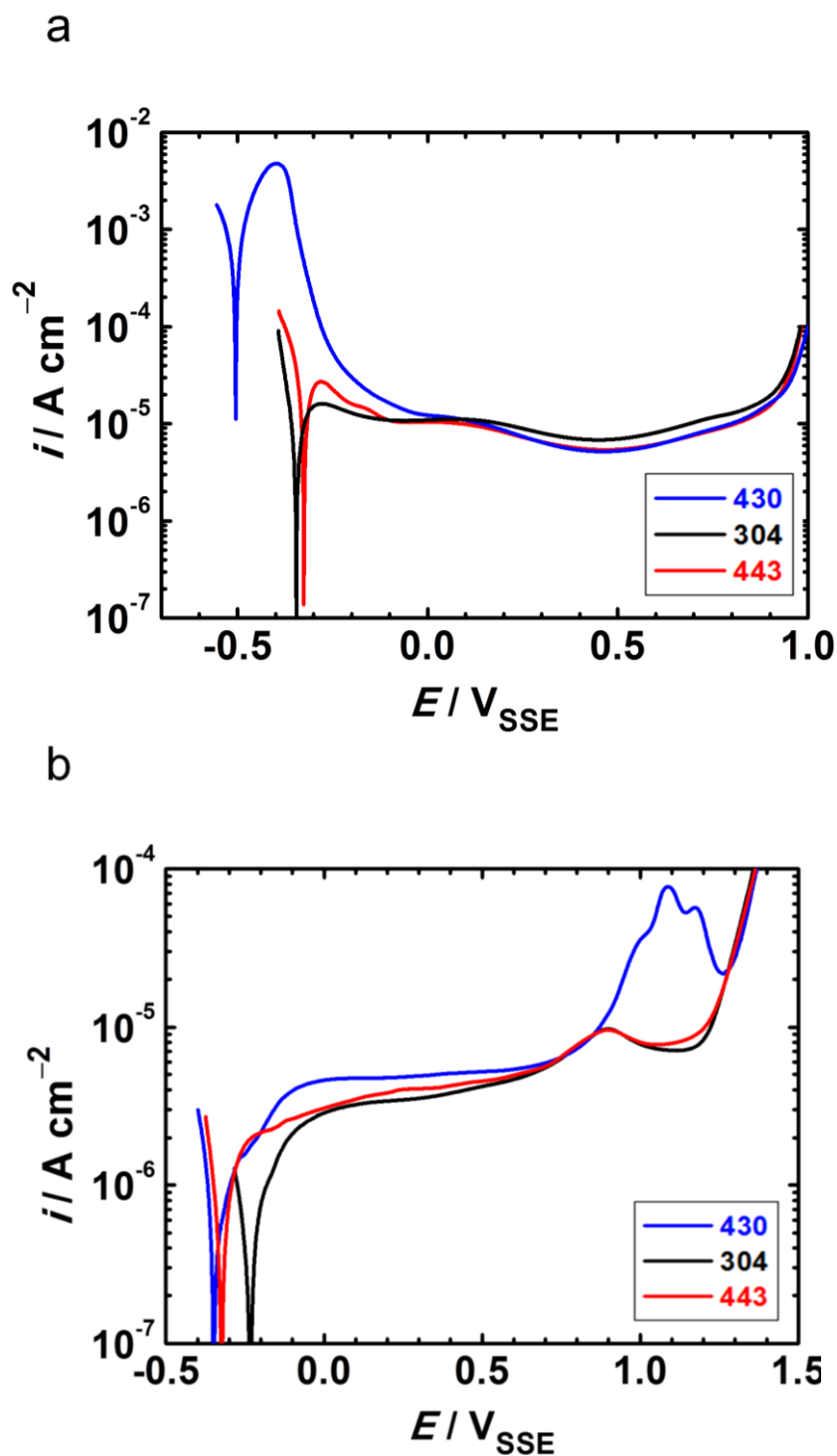


Figure 5.3 Potentiodynamic polarization curves of type 430, 304 and 443 stainless steels in (a) 0.15 mol dm⁻³ of H₂SO₄ solution (pH 0.9) and (b) Na₂SO₄ solution (pH 5.9). Potential scan rate was 1 mV s⁻¹.

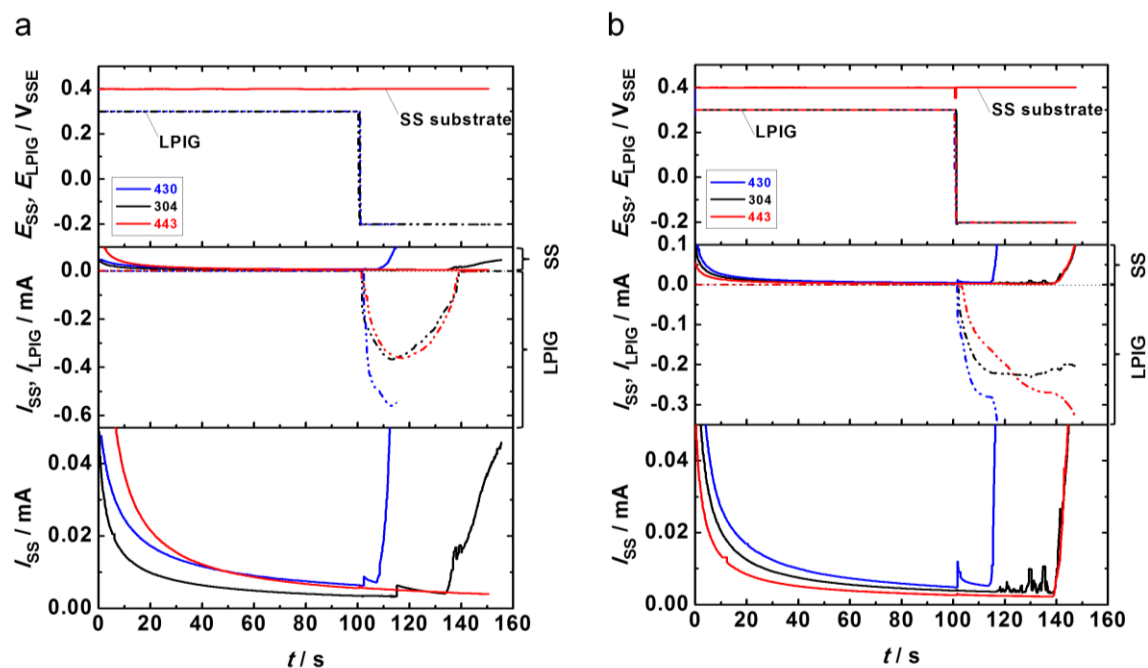


Figure 5.4 Transients of currents I_{LPIG} and I_{SS} of the LPIG microelectrode and stainless steel substrates, respectively, in (a) 0.15 mol dm^{-3} of H_2SO_4 solution and (b) Na_2SO_4 solution when the electrode potential of the LPIG, E_{LPIG} , was changed from 0.3 to $-0.2 \text{ V}_{\text{SSE}}$ with potential of the stainless steel substrate, E_{SS} , being kept at $0.4 \text{ V}_{\text{SSE}}$.

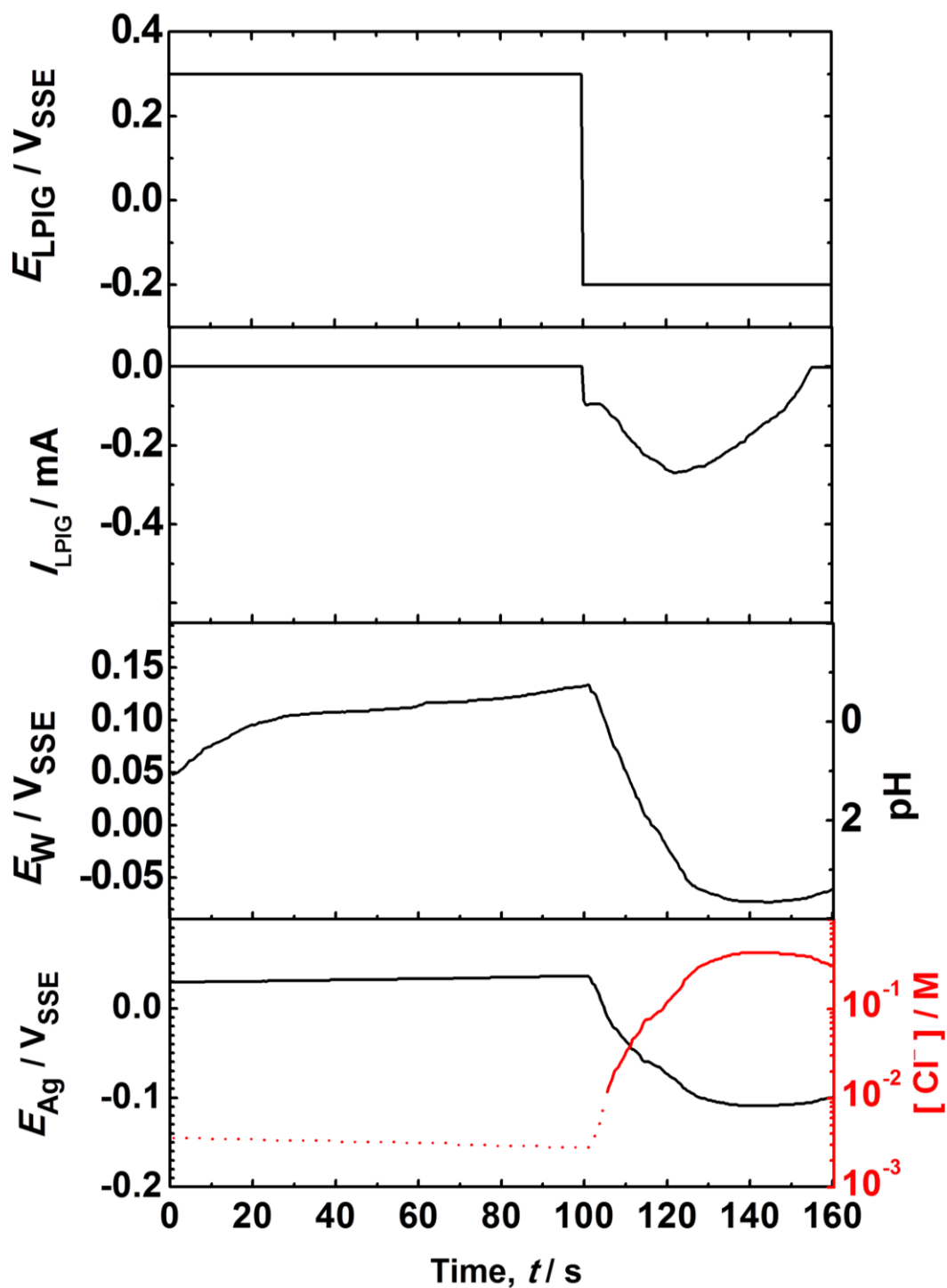
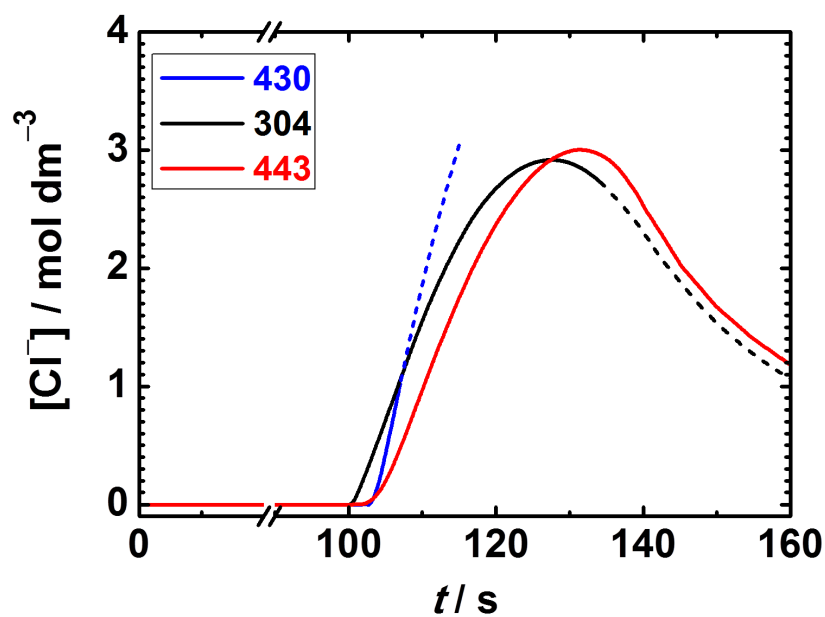


Figure 5.5 Changes in electrode potentials of the LPIG microelectrode E_{LPIG} , tungsten microelectrode E_{W} , and silver microelectrode E_{Ag} when the potential of LPIG microelectrode was kept at 0.3 V_{SSE} for 100 s and changed to -0.2 V_{SSE} in 0.15 mol dm⁻³ of H₂SO₄ (pH 0.9). The value of pH and [Cl⁻] were estimated using Eqs. 3.5 and 5.3.

a



b

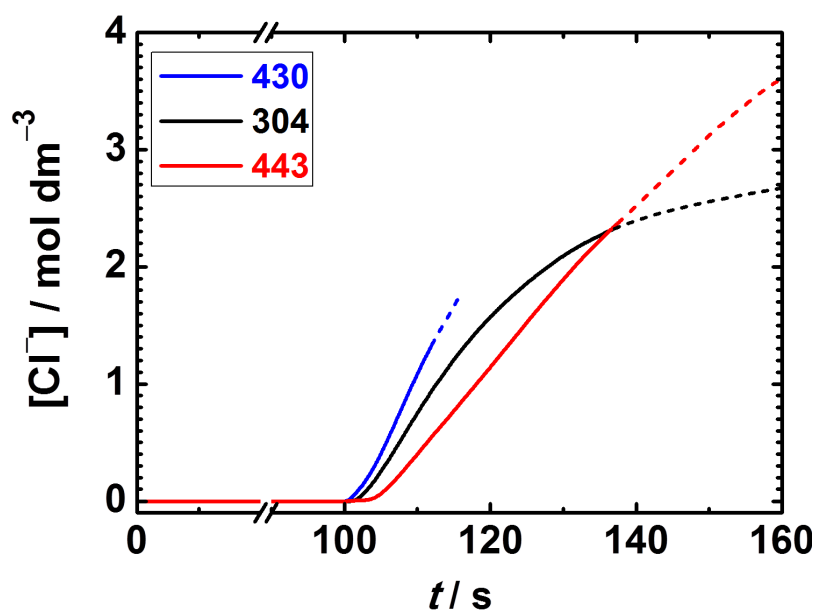


Figure 5.6 Change in $[\text{Cl}^-]$ at the specimen surface numerically calculated from LPIG current in (a) 0.15 mol dm^{-3} of H_2SO_4 solution and (b) Na_2SO_4 solution. $[\text{Cl}^-]$ after commencement of a rapid increase in I_{SS} , is plotted by a dashed line.

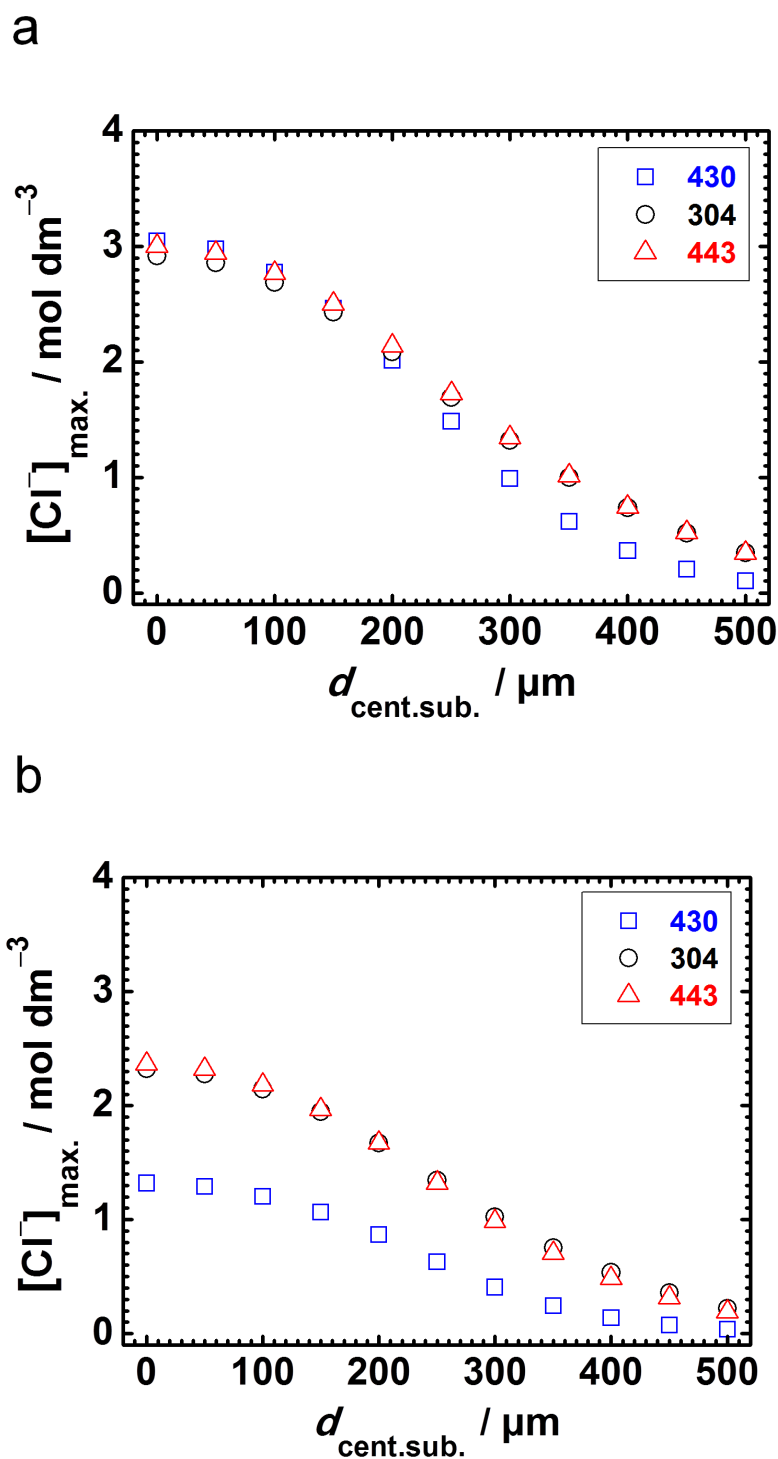


Figure 5.7 Change in maximum $[\text{Cl}^-]$ on stainless steel substrates surfaces as a function of a horizontal distance from the center of substrate surface in (a) 0.15 mol dm^{-3} of H_2SO_4 and (b) Na_2SO_4 solutions when the potential of LPIG microelectrode was changed at $-0.2 \text{ V}_{\text{SSE}}$ in 0.15 mol dm^{-3} of H_2SO_4 (pH 0.9) for 60 s.

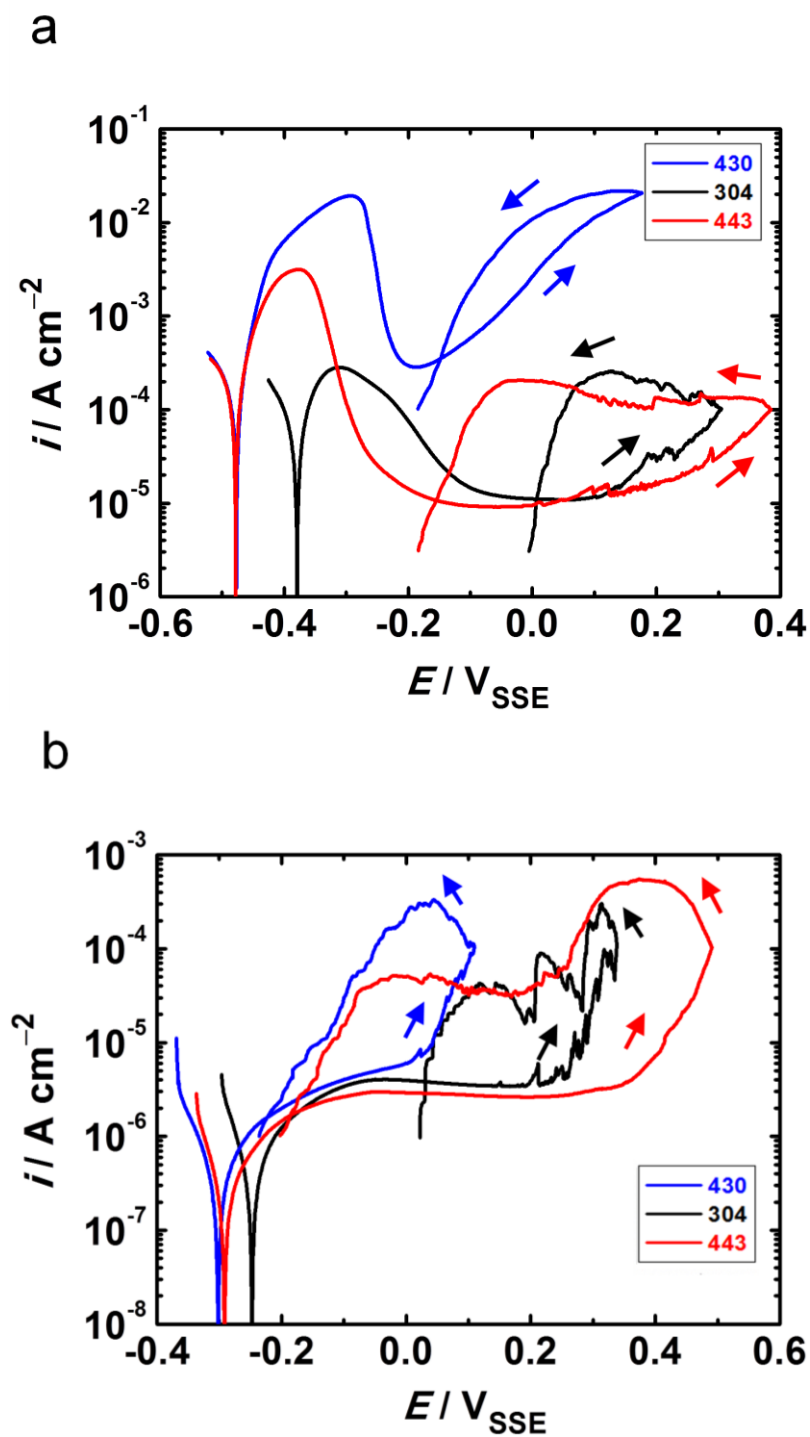


Figure 5.8 Cyclic potentiodynamic polarization curves of type 430, 304 and 443 stainless steels in 0.15 mol dm^{-3} of (a) H_2SO_4 solution and (b) Na_2SO_4 solution both containing 1.0 mol dm^{-3} of NaCl .

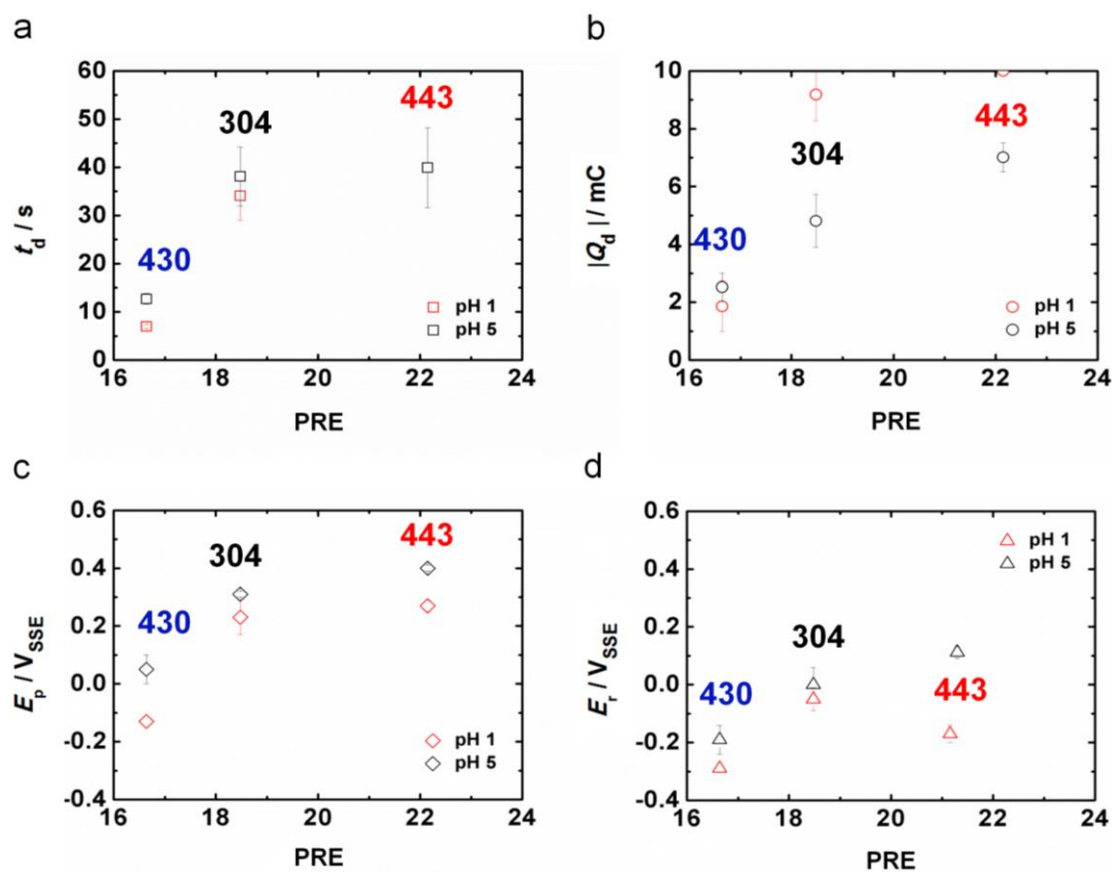


Figure 5.9 Parameters (a) t_d , (b) Q_d , (c) E_p , and (d) E_r obtained in H_2SO_4 and Na_2SO_4 solutions as a function of PRE number.

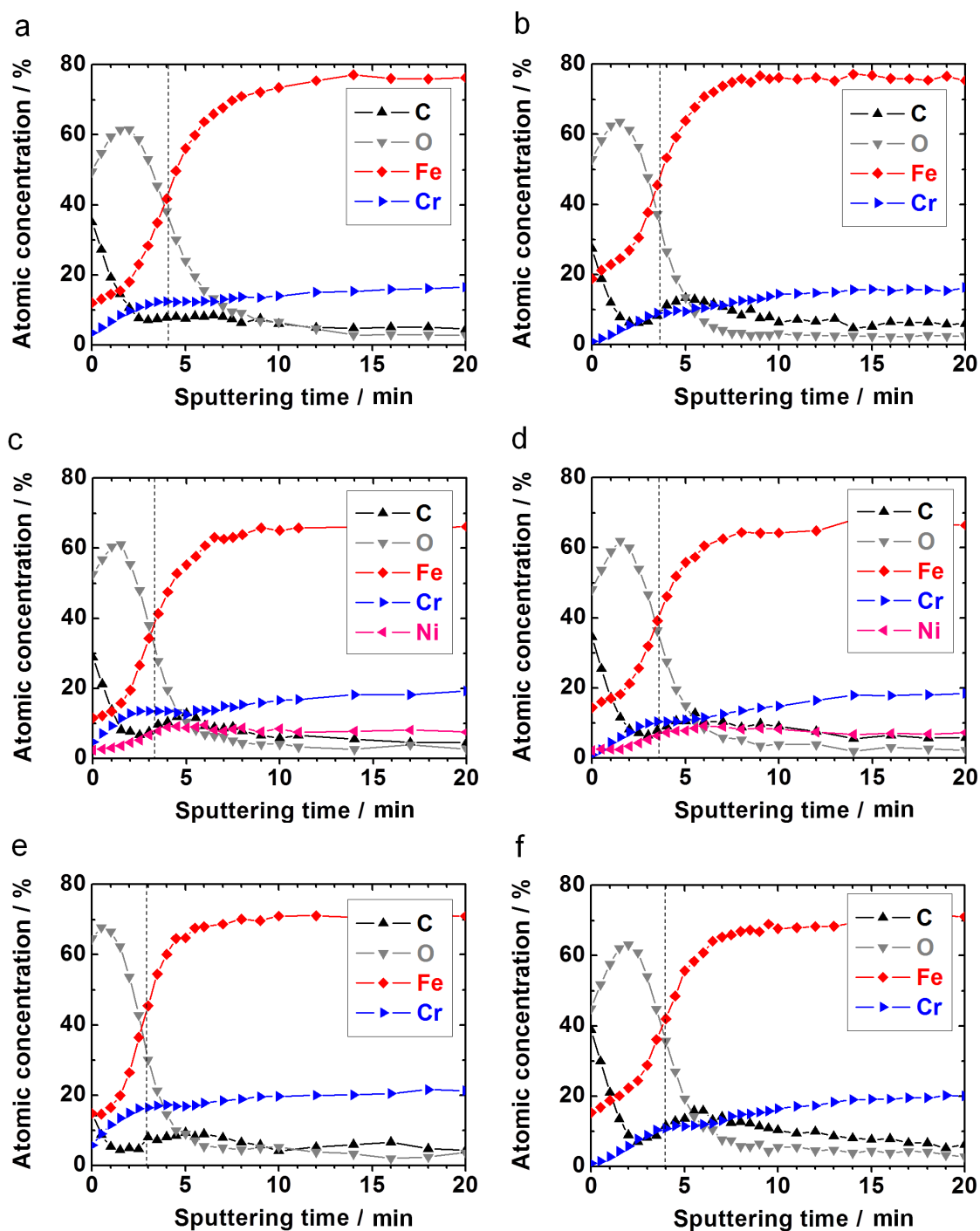
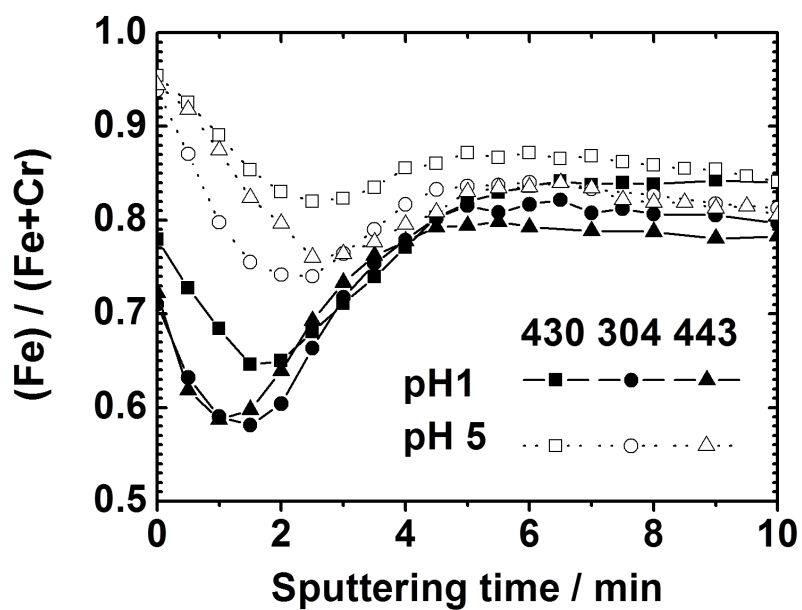


Figure 5.10 AES depth profiles of type (a,b) 430, (c,d) 304 and (e,f) 443 stainless steels polarized at $0.4 V_{SSE}$ for 100 s in (a,c,e) H_2SO_4 solution and (b,d,f) Na_2SO_4 solution.

a



b

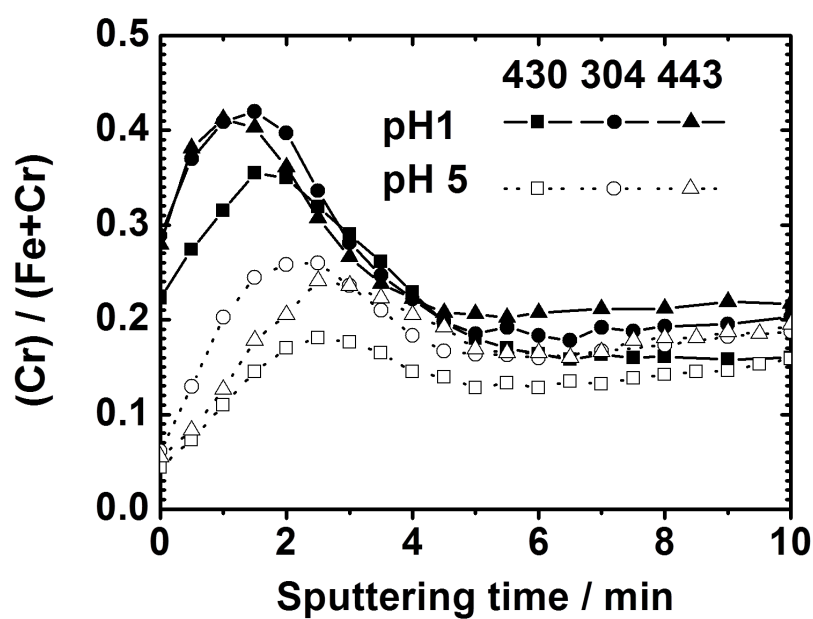
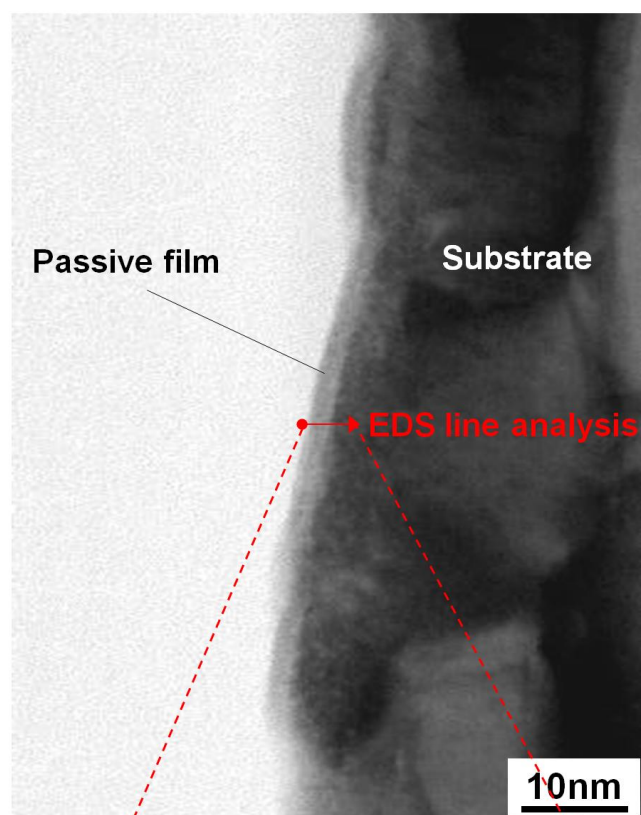


Figure 5.11 Profiles of (a) Fe/(Fe+Cr) and (b) Cr/(Fe+Cr) ratio obtained in Fig. 5.11.

a



b

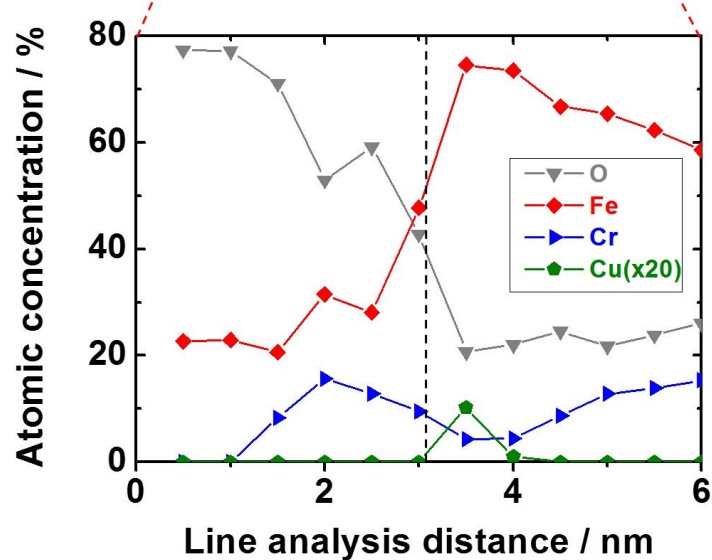


Figure 5.12 (a) TEM image and (b) chemical composition profile of the surface of type 443 stainless steel after potentiostatic polarization at 0.4 V_{SSE} for 100 s in H_2SO_4 solution.

Chapter 6 Conclusion

Stainless steels suffer from localized corrosion in aqueous solution containing chloride ions. Localized corrosion of stainless steel is strongly dependent on concentration of aggressive chloride ions and degradation behavior of passive film on stainless steel. Aggressive ion seems to attack and to break down the film. The presence of MnS inclusions in the steel results in enhancement of the localized corrosion. It is considered that the passive film near MnS inclusion is degraded due to some S species released from the inclusion and initiates the localized corrosion. The localized corrosion process of stainless steel is ordered as a sequence of i) stability-change in passive film, ii) initiation, i.e., removing of the passive film, and iii) propagation of localized corrosion. Therefore, the initial stability-change in passive film followed by removing degraded passive film is regarded as the most important process in the localized corrosion. Though the propagation process is being treated quantitatively as a function of concentration of chloride ions and pH in the corroded morphology, the role of hydrogen sulfide ions, one of the primal S species, for the stability-change in passive film has not been clear. The reason why the role is still unclear is a difficulty in proving the event initiating the localized corrosion. Since corrosion is an electrochemical phenomenon, electrochemical technique must be effective to investigate the localized corrosion. However, it is difficult to find out the site where the localized corrosion initiates and to record how the corrosion initiates at the one site. It is also difficult to carry out the investigation with a safe method. Some aggressive anions of S species such as H_2S are extremely toxic. Quantitative investigation of localized corrosion with environment including H_2S has been limited as well as the qualitative investigation. The development of a state-of-the-art experimental technique and application to investigate the role of aggressive anions for localized corrosion are expected.

In this dissertation, two anion generation systems (liquid-phase ion guns, LPIGs) were developed and applied to study degradation of passivity of stainless steels. The system successfully generated sulfide ions or chloride ions in aqueous solution with a maximum concentration of $10^{-2} \text{ mol dm}^{-3}$ in the vicinity of the specimen surface. Using LPIG, change in stability of passive film, initiation and/or propagation of localized corrosion, and local corrosion resistance of stainless steel were investigated not only qualitatively but also quantitatively.

In the Chapter 1, brief knowledge concerning stainless steel, passivity and passivity breakdown were reviewed. The purpose of this dissertation was also introduced.

Chapter 2 presented experimental setups and general procedure used in this dissertation.

In Chapter 3, LPIG for generating sulfide ions was developed using a microelectrode technique and applied to local sulfidation of a silver surface in pH 8.4 boric acid-borate buffer solution. Sulfidation of silver and reduction of silver sulfide are reversible on the LPIG microelectrode in Na_2S solution, corresponding to anodic Ag_2S formation and cathodic HS^- generation, respectively. It was confirmed that cathodic polarization of the LPIG

microelectrode covered with Ag_2S successfully generated HS^- in pH 8.4 buffer solution. Generation of HS^- from the LPIG was accompanied with equivalent generation of OH^- . Both anions-generation was strongly affected by the sulfidation reaction of substrate surface and the diffusion to solution bulk. Substrate sulfidation was also highly dependent on geometries of interelectrode narrow space and LPIG itself as well as the substrate potential. This local sulfidation technique with LPIG treated only small amount of S species of 5.2×10^{-8} mol. It was expected that this technique is a safe method using sulfide ions and is effective to investigate the mechanism and kinetics of sulfidation in various metal surfaces.

In Chapter 4, LPIG for generating sulfide ions was applied to investigate a degradation type 316L stainless steel surface in pH 8.4 boric acid-borate buffer solution. Galvanostatic polarization of the LPIG microelectrode generated both HS^- and OH^- above the stainless steel surface. Maximum concentration of HS^- and pH were determined by potentiometry with silver and tungsten microelectrodes as $4 \times 10^{-3} \text{ mol dm}^{-3}$ and 9.5, respectively, and simulated numerically. Generation of these anions by LPIG in the vicinity of the stainless steel results in an increase of anodic polarization current flowing through the stainless steel. Electrochemical impedance spectroscopy, Mott-Schottky analysis and scanning electrochemical microscopy revealed that a relatively defective passive film was formed in solution containing HS^- than that formed in solution containing no HS^- . AES and XPS revealed that the passive film formation accompanied the contamination of sulfide ions from solution containing HS^- . It was suggested that the HS^- adsorbed with high polarizability on the film surface were incorporated in the film and makes the film conductive as donor levels. Change in the stability of the passive film was expected to be a trigger for the initial depassivation of stainless steel in chloride-containing solution.

In the Chapter 5, the LPIG for generating chloride ions was applied to evaluate localized corrosion resistance of type 430, 304 and 443 stainless steels in sulfuric acid and sodium sulfate solutions. Rapid increase in anodic current flowing through stainless steel was observed during potentiostatic polarization of the LPIG microelectrode, corresponding to the initiation and propagation of localized corrosion on stainless steel due to an enrichment of chloride ions generated from LPIG. The period and electric charge for the initiation of localized corrosion were dependent on pitting resistance equivalent number (PRE) indicating that these parameters obtained from the operation of LPIG became new parameters of kinetic information for evaluating localized corrosion resistance of not only stainless steels but also other passive materials. Type 443 stainless steel showed a longer period and a larger charge during cathodic polarization of LPIG than other type 430 and 304 stainless steels, suggesting that type 443 was more resistant against localized corrosion than type 430 and 304 stainless steels. AES and TEM-EDS revealed the presence of Cu at the passive film/substrate interface played an important role of superior localized corrosion resistance of type 443 stainless steel than that of type 430 and 304 stainless steels.

The Chapter 6 conclusion in this dissertation.

It is concluded that the LPIG is a useful technique to generate aggressive anions locally in solution and to investigate a degradation behavior of corrosion resistant. The knowledge obtained through this dissertation provides not only the development and characteristics of LPIG but also new aspects for understanding localized corrosion of stainless steel. The use of LPIG technique was successfully clarified the initial process of degradation of passive film as its stability-change induced by hydrogen sulfide ions and the initiation and/or propagation of localized corrosion by chloride ions. The LPIG generating chloride ions can also be used to evaluate the localized corrosion resistance of stainless steels.

The findings about roles of sulfide ions and chloride ions in degradation of passive film through this dissertation will contribute to a fundamental understanding of localized corrosion of stainless steels and a developing additional model for an initiation of localized corrosion. Application of LPIG to stainless steel is expected to investigate not only other S species such as thiosulfate, sulfate and sulfite which are possible to release from MnS but also other aggressive anions such as bromide, iodide and fluoride ions in stability-change of passive film. It is also expected to investigate the degradation of passive film on stainless steel exposed to environment coexisting aggressive anions, which might be related to competitive adsorption on the passive film or a synergistic effect on the surface. Moreover, chloride ions generation system is applicable to evaluate localized corrosion resistance of other stainless steels as well as other metals and alloys. The obtained information could be applied to investigate localized corrosion behavior of other engineering materials as well as other stainless steels. It is also applicable to improve an estimation of the lifetime of materials, enabling appropriate guidance for designing alloys or anti-corrosion strategies for nuclear power plants, nuclear fuel reprocessing plants, desalination facilities and oil and gas industrial facilities.

Appendix

Symbols used in this thesis

A	[-]	austenite phase in stainless steel
a	[μm]	radius of tip electrode of SECM
C	[$\times 10^3 \text{ mol dm}^{-3}$]	concentration of generated species from LPIG during polarization
c	[mol dm^{-3}]	concentration of diffusing species
C_c	[F cm^{-2}]	capacitance obtained by impedance measurement
C_{Fc}	[mole]	concentration of mediator FcMeOH
C_H	[F cm^{-2}]	Helmholtz layer capacitance
C_{HS}	[$\times 10^3 \text{ mol dm}^{-3}$]	concentration of hydrogen sulfide (HS^-) during polarization of LPIG
$C_{\text{HS}_{125}}$	[$\times 10^3 \text{ mol dm}^{-3}$]	concentration of hydrogen sulfide (HS^-) during polarization of LPIG at the interelectrode distance of 125 μm
$C_{\text{HS}_{\text{Crit}}}$	[$\times 10^3 \text{ mol dm}^{-3}$]	critical concentration of hydrogen sulfide (HS^-) during polarization of LPIG at interelectrode distance
C_{OH}	[$\times 10^3 \text{ mol dm}^{-3}$]	concentration of hydrogen oxide (OH^-) during polarization of LPIG
C_{SC}	[F cm^{-2}]	capacitance of space charge layer
D	[$\text{m}^2 \text{ s}^{-1}$]	diffusion coefficient of diffusing species
d	[μm]	interelectrode distance between LPIG and substrate surface
$d_{\text{cent.sub.}}$	[μm]	horizontal distance from the center of substrate where the position is under the LPIG
dx	[μm]	x-axis scan interval distance for SECM
dy	[μm]	y-axis scan interval distance for SECM
E	[V]	electrode potential
e	[C]	elementary charge, $e = 1.602176 \times 10^{-19} \text{ C}$
E_0	[V]	equilibrium potential of electrochemical system
E_{316L}	[V]	electrode potential of type 316L stainless steel
E_{Ag}	[V]	electrode potential of silver microelectrode
$E_{\text{Ag.sub.}}$	[V]	electrode potential of silver substrate
$E_{\text{a-p}}$	[V]	active-to-passive transition potential
E_{corr}	[V]	corrosion potential
E_{fb}	[V]	flat-band potential
E_{LPIG}	[V]	electrode potential of LPIG
E_p	[V]	pitting potential
E_{pp}	[V]	primary passive potential
E_r	[V]	repassivation potential
E_{SS}	[V]	electrode potential of stainless steel
E_t	[V]	Pt tip microelectrode
E_{tp}	[V]	trans passive potential
E_W	[V]	electrode potential of tungsten microelectrode
F	[-]	ferrite phase in stainless steel
f	[Hz]	frequency
F	[C mol^{-1}]	Faraday constant, $F = 96485 \text{ C mol}^{-1}$
$I_{\text{Ag.sub.}}$	[A]	current flowing through silver substrate electrode
I_c	[mA]	slope of t_d and $ Q_d $
I_{LPIG}	[A]	current flowing through LPIG
$I_{\text{LPIG,peak}}$	[A]	peak current appearance time during potentiostatic polarization of LPIG
I_{SS}	[A]	current flowing through stainless steel substrate electrode during polarization of LPIG
I_t	[A]	tip microelectrode of SECM
$I_{t \text{ lim.}}$	[A]	limiting current of tip microelectrode of SECM

$I_{t,lim.th.}$	[A]	theoretical limiting current of tip microelectrode of SECM
i	[A cm ⁻²]	current density
i_{316L}	[A]	current flowing through 316L stainless steel after polarization of LPIG above 316L stainless steel
J	[mol m ² s ⁻¹]	diffusion flux
K_{sp}	[-]	solubility product constant
k	[J K ⁻¹]	Boltzmann constant, $k = 1.38065 \times 10^{-23}$ J K ⁻¹
M	[-]	martensite phase in stainless steel
M	[-]	magnification in photomicrographs
n	[-]	number of electrons participating in electrochemical reaction
N_c'	[mol s ⁻¹]	I_c / F , $F = 96485$ C mol ⁻¹
N_D	[cm ⁻³]	donor density
$N_{d,Cl}$	[mol]	the average amount of chloride ions for initiating localized corrosion on stainless steels
N_g	[-]	number of grains per square inch
N_l	[-]	number of grain-boundary intercepts
n_g	[-]	ASTM G grain size number
n_p	[-]	primary quantum number
$pH_{crit.}$	[-]	critical pH during the polarization of LPIG
pK_a	[-]	acid dissociation constant at logarithmic scale
PRE	[-]	pitting corrosion resistance equivalent number
$Q_{Ag,sub.}$	[mC]	charge consumed for silver substrate electrode
$Q_{Ag,sub.end}$	[mC]	consumed at silver substrate until completion of HS ⁻ generation as a function of the interelectrode distance
$Q'_{Ag,sub.end}$	[mC]	charge of subtracted from $Q_{Ag,sub.end}$ by the electric charge consumed for the oxidation
$Q_{control}$	[mC]	charge corresponding to oxidation reaction of the silver substrate without HS ⁻ generation from the LPIG microelectrode
Q_d	[mC]	consumed electric charge at t_d
Q_{LPIG}	[mC]	charge consumed during polarizations of LPIG
$Q_{LPIG.charge}$	[mC]	charge consumed for forming AgCl or Ag ₂ S layer on LPIG microelectrode
R_{ct}	[Ω cm ²]	charge transfer resistance
R_{el}	[Ω cm ²]	solution resistance
S	[-]	grain size constant for line intercept method
T	[K]	absolute temperature
t	[s]	time
$t_{-3 mC}$	[s]	time for consuming 3 mC by cathodic reaction of Ag ₂ S
t_{316L}	[s]	polarization time for 316L stainless steel after polarization of LPIG above 316L stainless steel
t_d	[s]	time at a rapid increase of current of stainless steel substrate after the cathodic polarization of LPIG
V_{Ecorr}	[V]	electrode potential from corrosion potential of stainless steel electrode
$V_{O^{..}}$	[-]	oxygen vacancy in passive film
Z	[Ω cm ²]	impedance
2θ	[°]	diffraction angle of XRD measurement
θ	[°]	edge angle of LPIG sheath
ϵ	[-]	dielectric constant, $\epsilon = 40$
ϵ_0	[J ⁻¹ C ² m ⁻¹]	vacuum permittivity constant, $\epsilon_0 = 8.85419 \times 10^{-12}$ J ⁻¹ C ² m ⁻¹
ϕ	[mm]	diameter of detection area for XPS analysis

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