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Title

Inhibition ability of gluconates for fresh water corrosion of mild steel enhanced by metal cations

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Abstract

Inhibition ability of gluconates for fresh water corrosion of mild steel changed with metal cations were investigated by immersion tests and electrochemical impedance spectroscopy (EIS) tests. The results of the tests showed that the inhibition ability of gluconates was enhanced by metal cations that have large "corrosion inhibitory effect of cation, *Y*", in model fresh water. Surface analysis showed that gluconate ligands and metal cations that have large *Y* can bond on mild steel and that they form a protective film on the steel. EIS analysis with an equivalent circuit suggested that metal cations that have large *Y* would reduce the area of defects in the protective film of gluconates.

Introduction

Many studies have been carried out in recent years on corrosion of mild steel, which is used in various industries.[1-6] Fresh water corrosion of mild steel has been investigated by many researchers[7-10] because the corrosion has caused serious problems in industries. Important factors for the fresh water corrosion of mild steel are the corrosive nature of dissolved oxygen and the concentrations of anions (i.e., chloride ions and sulphate ions). Chloride ions play a major role in corrosion because the corrosion protective oxide layer of mild steel is easily destroyed by chloride ions in fresh water.[11-14]

The use of inhibitors is one method that has been reported to decrease the corrosion of steel caused by chloride ions.[15-20] These inhibitors are used to add in corrosive media with chloride ions, and they inhibit the corrosion of mild steels in solutions. In fresh water environments, gluconates have been shown to be effective and non-toxic inhibitors of corrosion of mild steel.[21-25] Touir et al.[23] reported that the main process by which gluconates inhibit corrosion is adsorption of gluconate ligands on the surface of mild steel and formation of a protective film of adsorbed gluconates. Enhancement in the inhibition ability of gluconates for fresh water corrosion of mild steel is required to reduce the use of gluconates for cost-cutting and environmental protection.

The authors have investigated not only the effect of anions but also the effect of metal cations on corrosion to clarify the corrosion mechanism of mild steel in fresh water. Research focused on the effects of metal cations[26] showed that the corrosion rate of mild steel in fresh water decreases with an increase in the novel indicator of metal cations corrosion inhibitory effect of cation, *Y*. Therefore, it can be estimated that the inhibition ability of gluconates for fresh water corrosion would be enhanced by metal cations that have large *Y* in fresh water.

In this study, the difference in the inhibition abilities of sodium, calcium, and zinc gluconates for fresh water corrosion of mild steel was investigated by immersion tests and electrochemical impedance spectroscopy (EIS) tests. The goal of this study is to quantitatively determine the effects of metal cations on the inhibition ability of gluconates for fresh water corrosion of mild steel and to clarify the mechanism of the effect of metal cations on the corrosion inhibition ability of gluconates.

Experimental

Specimens

Mild steel sheets (Size: 7 x 7 x 0.7 mm, composition (at%): C, 0.02; Mn, 0.18; P, 0.015; S, <0.01, and Fe) were used as specimens. In the case of EIS tests, a Pb-free solder wire was connected to each specimen to use as a working electrode. All of the specimens were molded in epoxy resin (Struers Ltd., EpoFix Resin). The exposed surface of the molded specimen was ground with silicon carbide abrasive paper from #240 to #4000 and finally polished by colloidal silica. In the case of immersion tests, the specimens were taken out of the resin after being polished. Before the tests, all of the specimens were cleaned in ethanol and then in highly purified water by an ultrasonic cleaner.

Solutions

Four different solutions, 1 mM NaCl (NaA), 1 mM NaCl with 1 mM sodium gluconate

(NaG), 1 mM NaCl with 0.5 mM calcium gluconate (CaG), and 1 mM NaCl with 0.5 mM zinc gluconate (ZnG), were used as model fresh water. All of the solutions used in the experiments were colorless and transparent before the tests. The chemical formulas of the gluconates are $NaC_6H_{11}O_7$ (sodium gluconate), $C_{12}H_{22}CaO_{14}$ (calcium gluconate), and $C_{12}H_{22}O_{14}Zn$ (zinc gluconate).

Immersion tests

Specimens were immersed in model fresh water for 0.6 Ms (7 d) at 298 K. The mass of each specimen was measured before and after the test. The surface of the specimens was observed by a digital camera (Sony Corporation, NEX-C3) and a scanning electron microscope (SEM, JEOL Ltd., JSL6510-LA). The surface of the immersed specimens was analyzed by an X-ray photoelectron spectroscopy (XPS, JEOL Ltd., JPS-9200) using a monochrome Al Kα X-ray source (1486.6 eV). The analysis area in the experiments was 7.07 mm^2 (3.0 mm in diameter). The pH values were measured by a pH meter (Eutech Instruments Pte. Ltd., CyberScan 6000).

Electrochemical impedance spectroscopy (EIS) tests

EIS tests were carried out by a three-electrode cell using a potentiostat (IVIUM TECHNOLOGIES, Compactstat). Before EIS tests, the specimens were immersed in the solutions for 7 d at 298 K. Open circuit potential (OCP) was measured before the tests, and EIS tests were carried out at OCP. The pre-immersion period was the same as that of the immersion tests. A Pt plate of 18 cm^2 was used as a counter electrode and an Ag/AgCl-saturated KCl electrode was used as a reference electrode. EIS measurements were carried out in the frequency range from 10 kHz to 1 mHz, and a modulation amplitude of 10 mV was used. Reproducible data were obtained in all electrochemical tests.

Results and Discussion

Immersion tests

Appearances of immersed specimens

The appearances of bottled specimens after immersion for 7 d in the test solutions are shown in Fig. 1 (a). There was a large amount of yellow corrosion products in the NaA solution, and intense corrosion would have occurred on the specimens in that solution without gluconates. On the other hand, no corrosion products were observed in other solutions containing gluconates, and the NaG and CaG solutions changed from colorless to yellow. The color changes mean that the mild steel was dissolved into solutions as Fe^{3+}. The color of the ZnG solution was hardly changed after immersion. Therefore, it can be considered that ZnG

is the most effective solution for inhibiting the corrosion of mild steel in this study. The surfaces images of specimens after immersion for 7 d in the solutions are shown in Fig. 1 (b). Yellow corrosion products were observed on the specimen immersed in NaA solution. The corrosion products were very fragile and were easily detached from the surface by water flow. A part of the surface of the specimen immersed in NaA solution had a metallic gloss, suggesting that the surface of the specimen was divided into the anodic region and the cathodic region during immersion tests. The surfaces of the specimens immersed in solutions containing gluconates had no corrosion products and had a metallic gloss. The surfaces of specimens immersed in NaG and CaG solutions had various colors. This optical phenomenon can be explained by the formation of transparent films on the mild steel, and the transparent films probably caused interference. There was almost no change in the surface of the specimen immersed in ZnG solution, and the solution containing zinc ions and gluconates would therefore have a high level of corrosion inhibition ability.

Surface SEM images

SEM observations of the specimen surfaces after immersion were carried out to clarify the difference in detailed corrosion morphology of the mild steel immersed in different solutions. Fig. 2 shows SEM images of specimen surfaces (a) before immersion and after immersion for 7 d in (b) NaA, (c) NaG, (d) CaG, and (e) ZnG solutions. The corrosion products on the specimens were completely removed before SEM observation by ultrasonic cleaning. The specimen before immersion has a smooth surface (Fig. 2 (a)). The surface of the mild steel immersed in NaA solution at the anodic site shown in Fig. 1 (b) was observed by SEM and it exhibits clear grain boundaries (Fig. 2 (b)). These clear grain boundaries mean that intense uniform corrosion occurred on the mild steel in NaA solution.[26] Pits on the specimen are observed after immersion in NaG solution (Fig. 2 (c)). Large pits and a smooth surface are observed after immersion in CaG solution (Fig. 2 (d)); however, the number of pits was less than 5 on the surface of specimen immersed in CaG solution. It has been reported that a few large pits on mild steel is one of the features of steel that has a good corrosion protective film,[27-29] suggesting that the corrosion protective ability of the film formed in CaG solution was better than that of the film formed in NaG solution. A small number of pits and a smooth surface are observed on the specimen after immersion in ZnG solution (Fig. 2 (e)). The results of SEM observation also suggest that zinc ions and gluconates had good corrosion inhibition ability for mild steel in the model fresh water.

Surface analysis

Surface observations in this study showed that gluconates and metal cations in the

solution influence on the corrosion behavior of mild steel, and it is thought that gluconate ligands and metal cations form a protective film on the mild steel. XPS surface analyses of the specimens immersed in solutions containing gluconates were carried out to determine the formation of a protective film. Fig. 3 shows XPS wide spectra of the specimens after immersion for 7 d in solutions containing gluconates (NaG, CaG, and ZnG). C, O, and Fe peaks can be seen in all of the spectra in this figure. There is no peak related to Na 1s of the specimens after immersion in all solutions, suggesting that Na^+ in the solution cannot form any compound on the mild steel. On the other hand, clear peaks of metal cations such as Ca^{2+} and Zn^{2+} are observed for the specimens after immersion in CaG and ZnG solutions. From narrow spectra of Ca2p in the CaG spectrum and of Zn2p3/2 in the ZnG spectrum, the peaks of Ca 2p1/2 (351.2 eV),[30] Ca 2p3/2 (347.7 eV), [30] and Zn 2p3/2 (1021.8 eV)[31] indicate the formation of $CaCO_3$ and $Zn(OH)_2$ on the mild steel after immersion in the solutions. After the XPS analysis, the chemical composition of the compounds of metal cations formed on the mild steel was defined. The definition enabled calculation of the corrosion inhibitory effect, *Y*, of each metal cation using equation (1):[26]

$$Y = X \times \Delta V \quad (1)$$

where *X* is the hardness of metal cations and ΔV is the molar volume ratio. The hardness of cations, *X*, is expressed as follows:[32, 33]

$$X = [X^0_M + (\sum I_n)^{1/2}]^2 / 10 \quad (2)$$

where X^0_M is the electronegativity of metal atoms and I_n is the total ionized potential from neutral metal atoms to a given oxidized state, n. The value of *X* indicates the tendency of bonding between metal cations in solution and hard bases (i.e., OH^-) on the oxide film of mild steel and in the gluconate ions.[32, 33] The molar volume ratio, ΔV, is expressed as follows:[26]

$$\Delta V = [V_{Fe2O3} / |V_{cat} - V_{Fe2O3}|] / 10 \quad (3)$$

where V_{cat} is the molar volume of the precipitated metal cations and V_{Fe2O3} is the molar volume of γ-Fe_2O_3. ΔV indicates the tendency of protective ability against corrosion of the metal cation layer formed on the mild steel.[26] *Y*, *X*, and ΔV of the metal cations which were calculated by equations (1) - (3) are listed in Table 1. The molar volume [cm^3/mol] was calculated from the density of the compound of metal cations [g/cm^3] and molar mass of the compound [g/mol].[34, 35]

Figure 4 shows XPS narrow spectra of C 1s on specimens after immersion for 7 d in model fresh water. The C 1s spectra could be deconvoluted into three peaks (285.0 eV, 287.0 eV, and 288.5 eV), indicating three chemical forms of C present on the mild steel surface.

The largest peak at 285.0 eV can be attributed to C–C and C=C bonds. The peak at 287.0 eV is attributed to the carbon atom of the C–O bond.[36] The peak at 288.5 eV is not clarified, and sodium gluconate powder was therefore analyzed to identify the peak at 288.5 eV in Fig. 4. Fig. 5 shows XPS narrow spectrum of C 1s for sodium gluconate powder. A peak at 288.5 eV also appeared. The results indicate that the peak at 288.5 eV is derived from gluconate ligands, suggesting that gluconate ligands can adsorb on mild steel after immersion in all solutions containing gluconates and can form a protective film.

The surface compositions of the specimens after immersion in solutions containing gluconates for 7 d are shown in Table 2. The compositions were calculated from the peak heights of the main orbitals (Fe2p3/2, C1s, O1s, Na1s, Ca2p3/2, and Zn2p3/2). The atomic percentage of Fe follows the sequence NaG > CaG > ZnG, and a large atomic percentage of Fe suggests that there would be many pits (metal exposed sites) on the surface of the immersed specimen. On the other hand, the percentage of C follows the sequence ZnG > CaG > NaG, and a large atomic percentage of C indicates that almost all of the surface of the specimen is covered by gluconate ligands. These estimations correspond well to the area of pits on the immersed specimens observed in Fig. 2.

Mass change measurements

Mass changes were determined for quantitative evaluation of the corrosion rate of mild steel in solutions. The mass change rate calculated from mass loss after immersion for 7 d in solutions as a function of *Y* is shown in Fig. 6. The mass change rate of mild steel immersed in NaA solution without gluconates is also shown in Fig. 6 as control data. The mass change rates of mild steel immersed in solutions containing gluconates are lower than that in NaA solution, indicating that gluconates in the solutions can inhibit the corrosion of mild steel. It is also shown that the mass change rate of the mild steel decreased with an increase in *Y* of metal cations in solutions. The correlation coefficient and a linear line calculated by linear regression are also shown in Fig. 6. The correlation coefficient is -0.99, indicating that there is strong relationship between the mass change rate of mild steel and *Y* value of metal cations in solutions. The results indicated that the corrosion inhibition ability of gluconates for mild steel would increase with an increase in the *Y* value of metal cations in model fresh water.

pH measurements

The pH measurements of the test solutions before and after immersion for 7 d are shown in Table 3, where pH_{int} is pH of the solutions before immersion and pH_{corr} is pH of the solutions after immersion. The pH_{int} values of the solutions are almost the same (around pH 5.8). The pH_{corr} value of each solution increased in comparison to the pH_{int} value, and pH_{corr} values of

the solutions containing gluconates decreased with increase in *Y* of metal cations. Mahdavian et al.[25] reported that the increase of solution pH after corrosion might be related to the release of OH^- formed at cathodic sites and Fe^{2+} formed at anodic sites on mild steel. The Fe^{2+} would finally be oxidized to Fe^{3+} in the solutions. Several researchers reported that the solution pH decreases with the hydrolysis of Fe^{2+} and Fe^{3+},[37, 38] however, the pH always increased with corrosion in this study (Table 3). For this reason, the highest pH_{corr} of the NaA solution also suggests that the most intense corrosion occurred on mild steel in the NaA solution among the solutions used in this study.

EIS tests

EIS measurements were carried out to clarify the corrosion resistance of mild steel in solutions and estimating the surface structure of mild steel in the solution containing inhibitors. The OCP values before EIS tests in the solutions were -620 mV for NaA, -443 mV for NaG, -302 mV for CaG and -119 mV for ZnG (vs Ag/AgCl-saturated KCl electrode), and the OCP values in the solutions containing gluconates increased with an increase in *Y* of metal cations. Figure 7 shows (a) impedance and (b) phase shift plots of a Bode diagram of EIS of the mild steel after immersion for 7 d in the solutions. The magnitude of impedance at low frequencies in Bode plots indicates the corrosion resistance of the specimen in solutions. In other words, the magnitude indicates the inhibition ability of the protective film of gluconates and metal cations on mild steel. The magnitudes shown in Fig. 7 (a) indicate that the corrosion inhibition ability of the film formed in ZnG solution is higher than that of the film formed in other solutions. The fitted lines shown in Fig. 7 (a) and (b) were calculated by an equivalent circuit (Fig. 7 (c)) that simulates an electrode with a protective film having defects.[39] In Fig. 7 (c), R_{sol} is resistance of bulk solution, R_d is resistance of the defects in the protective film, R_{ct} is charge transfer resistance of the metal/solution interface inside the defects, Q_{dl} is the constant phase element of the double layer at the interface, and Q_f is the constant phase element of the protective film. The fitted lines correspond well to the experimental plots (Fig. 7 (a) and (b)). Furthermore, pits were observed on the specimens immersed in solutions containing gluconates as shown in Fig. 2, suggesting that the protective film of gluconates formed on the immersed specimens had some defects that led to the formation of pits. On the other hand, the fitted lines of NaA solution correspond well to the experimental plots, although NaA solution did not contain gluconates. It can be estimated

that the corrosion products formed on the specimen immersion for 7 d in NaA solution as shown in Fig. 1 (b) played the role as a protective film on mild steel. For these reasons, the equivalent circuit was suitable for an electrode in this study.

The fitted parameters of the equivalent circuit are shown in Table 4. The corrosion resistance, R_c, and the inhibition efficiency, η, were calculated by the following equations:

$$R_c = R_d + R_{ct} \quad (4)$$

$$\eta\% = (R_{c_inh} - R_c) / R_{c_inh} \times 100 \quad (5)$$

where R_{c_inh} and R_c are the values of corrosion resistance in the presence and absence of gluconates in 1 mM NaCl, respectively. All of the parameters shown in Table 4 are average values that were calculated from three measurements obtained in the same condition. The values in Table 4 indicate that η and R_c of the specimens after immersion for 7 d in solutions containing gluconates follow the sequence ZnG> CaG> NaG. The values of R_{ct} drastically increased with an increase in *Y* of metal cations in solutions. This indicates that metal cations that have large *Y* would bond at the defect sites, and the bonded compounds of large *Y* metal cations may prevent charge transfer at the sites. This effect of metal cations is thought to be the main reason for the inhibition ability of gluconates for fresh water corrosion of mild steel was improved by metal cations. The values of the constant phase element magnitude of the double layer at the interface, Q_{dl}, in CaG and ZnG solutions are smaller than those in NaA and NaG solutions. Mahdavian et al.[25] reported that the values of constant phase element magnitude of the double layer at the interface of the defects in a protective film of gluconates depends on the total area of defects in the film. For this reason, the decrease in Q_{dl} indicates that Ca^{2+} and Zn^{2+} can decrease the defect in the protective film on mild steel in model fresh water.

R_c as a function of *Y* is shown in Fig. 8, and R_c obtained in NaA solution without gluconates is shown as control data. The results show that the R_c increases with an increase in *Y*. The correlation coefficient and a linear line calculated by linear regression are also shown in Fig. 8. The correlation coefficient was 0.97, and this value indicates that the corrosion resistance of mild steel in solutions containing gluconates has a strong relationship with *Y*. These EIS results also suggest that metal cations that have large *Y* would enhance the inhibition ability of gluconates for fresh water corrosion of mild steel.

Model of the enhancement of corrosion inhibition ability of gluconates by metal cations

A possible model of enhancement of corrosion inhibition ability of gluconates by metal cations based on the results of this study will be described below. Fig. 9 shows schematic

images of the process by which a gluconate inhibits corrosion of mild steel in model fresh water containing gluconates with Na^+ ((a) and (b)) and containing gluconates with Zn^{2+} ((c) and (d)). Based on the XPS analysis in this study and previous studies,[23, 40] a protective film of gluconates would be formed on mild steel in model fresh water, and the film would have defects in solution. Thus, oxide layer of mild steel will be exposed at the defect sites. The structures of oxide layers on steels in neutral solutions have been reported by many researchers,[41-44] and a multi-layer structure composed of Fe_3O_4 (inner layer) and γ-Fe_2O_3 (outer layer) were proposed.[43, 44] Based on the film structure, the exposed oxide layer of mild steel at the defect sites in the film would be γ-Fe_2O_3. The corrosion mechanism of mild steel in fresh water containing gluconates and Na^+ will be explained. In the initial stage of the immersion, protective films of gluconates with defects would form on the mild steel. However, the chloride ions (Cl^-) would destroy the oxide films at the defect sites in the protective film of gluconates (Fig. 9 (a)), and then localized corrosion would progress at the defect sites by the anodic reaction and the cathodic reaction (Fig. 9 (b)), and finally, the localized corrosion would lead to the formation of pits on the immersed specimen as shown in Fig. 2 (c). The inhibition mechanism of gluconates with Zn^{2+} for fresh water corrosion of mild steel will be explained. The values of Y, X, and ΔV of Zn^{2+} are larger than those of other metal cations shown in Table 1. Several studies[26, 32, 33] have shown that metal cations that have large X can easily bond with OH^- on the oxide films of mild steel and in the gluconates adsorbed on the oxide film. For this reason, Zn^{2+}would bond to the oxide film at the defect sites and to the protective films of gluconates (Fig. 9 (c)). Then, Zn^{2+} would form the metal cation layer on the oxide film at defect sites and on the protective film of gluconates (Fig. 9 (d)). It has been also shown that metal cations that have large ΔV would form the defectless and highly protective layer on mild steel,[26] therefore, the metal cation layer of Zn^{2+} would have good protective ability against Cl^- attack in the solution. For these reasons, Zn^{2+} with large Y would contribute to the enhancement of the inhibition ability of gluconates for mild steel in fresh water.

Conclusions

The inhibition ability of gluconates for fresh water corrosion of mild steel changed with metal cations was investigated by immersion tests with XPS analysis and EIS tests.

1) Metal cations that have large Y, which depends on the hardness of metal cations and the molar volume ratio of the iron oxide and precipitated cations, would enhance the corrosion inhibition ability of gluconates.

2) Metal cations that have large *Y* may decrease defect sites in the protective film of gluconates on mild steel.

3) Gluconate ligands would adsorb on the oxide film of mild steel, and metal cations that have large *Y* would bond to the oxide film and to the protective film of gluconates.

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Tables

Table 1 Corrosion inhibitory effect of cation, *Y*, hardness of metal cation, *X*, and molar volume ratio, ΔV of used metal cations in this study.

Metal cation	Na^{+}	Ca^{2+}	Zn^{2+}
Corrosion inhibitory effect of cation, Y[26]	0.26	2.59	6.65
Hardness of metal cation, X[32, 33]	1.01	2.59	4.64
Molar volume ratio, ΔV[26]	0.26	1.00	1.43

Table 2 Surface composition obtained by XPS of specimens after immersion in model fresh water containing gluconates for 7 d.

Element (at%)	Fe	C	O	Na	Ca	Zn
NaG	9.2	25.6	65.1	-	-	-
CaG	4.7	45.7	45.4	-	4.2	-
ZnG	2.7	66.3	26.5	-	-	4.5

Table 3 The pH of the solution used in immersion tests, before immersion of specimens (pH_{int}), and after immersion of specimens (pH_{corr}).

Solutions	pH_{int}	pH_{corr}
NaA	5.9	7.7
NaG	5.6	7.3
CaG	5.8	6.9
ZnG	5.8	6.4

Table 4 Calculated values of electrochemical impedance parameters of mild steel after immersion in model fresh water for 7 d.

Solutions	R_{ct} ($k\Omega cm^2$)	Q_{dl} ($\mu s^n \Omega^{-1} cm^{-2}$)	n_{dl}	R_d ($k\Omega cm^2$)	Q_f ($\mu s^n \Omega^{-1} cm^{-2}$)	n_f	R_c ($k\Omega cm^2$)	η (%)
NaA	8	6×10^3	0.65	10	71	0.62	18	-
NaG	8	13×10^3	0.92	17	161	0.68	25	26
CaG	90	8	0.80	9	11	0.76	99	81
ZnG	618	11	0.94	21	28	0.76	639	97

Figures

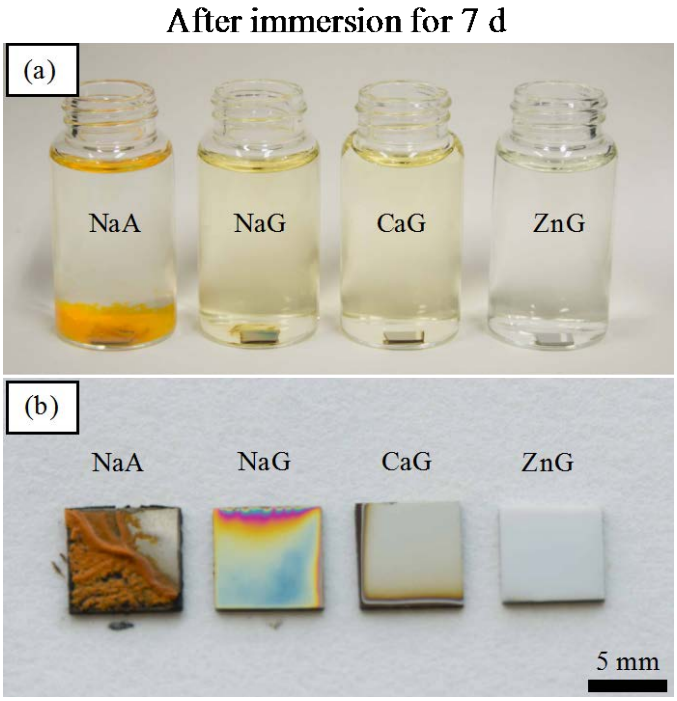

Fig. 1 (a) Appearance of bottled specimens after immersion for 7 d in model fresh water, and (b) surface images of specimens after immersion for 7 d in the solutions.

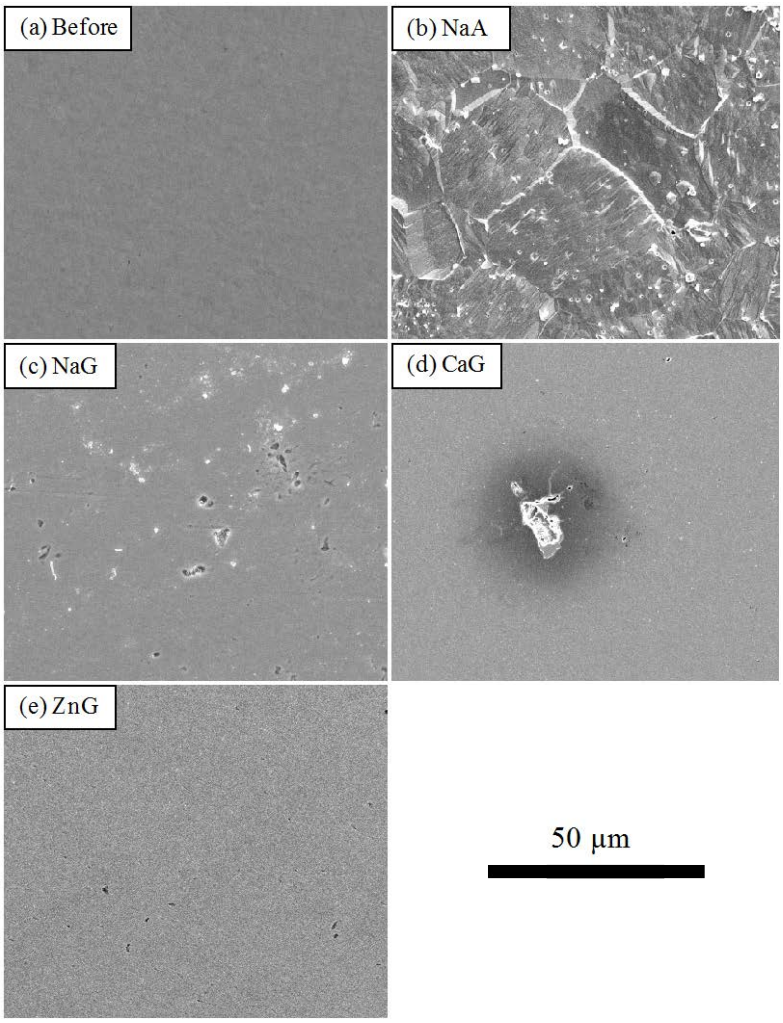

Fig. 2 SEM images of the specimen surface (a) before immersion and after immersion for 7 d in (b) NaA, (c) NaG, (d) CaG, and (d) ZnG solutions.

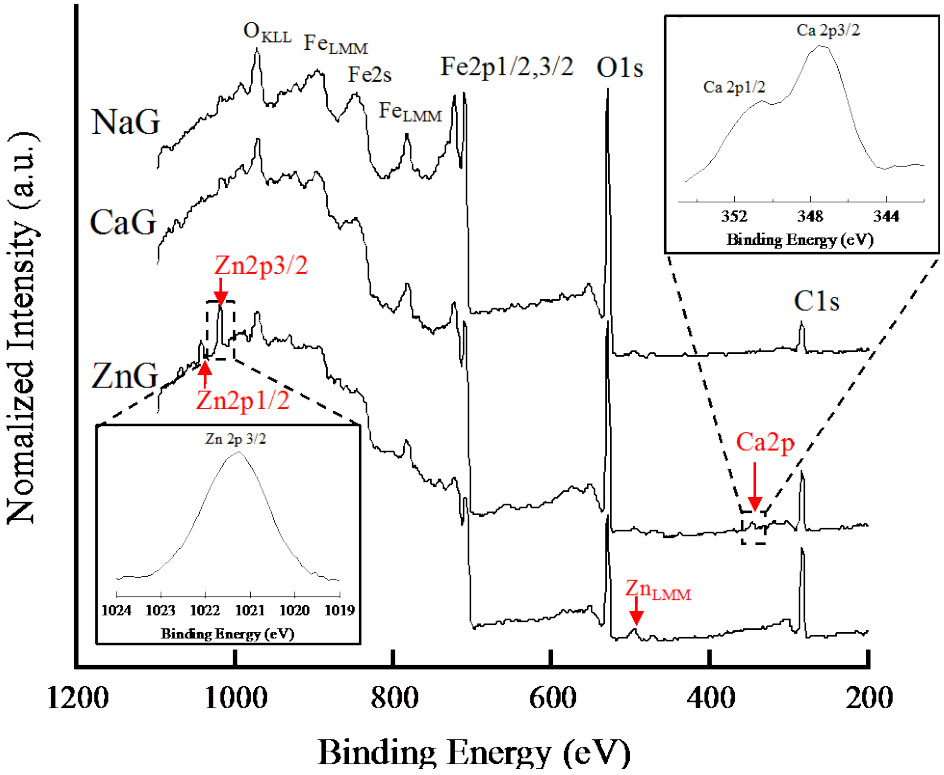

Fig. 3 XPS wide and narrow spectra of metal cations on specimens after immersion for 7 d in model fresh water containing gluconates.

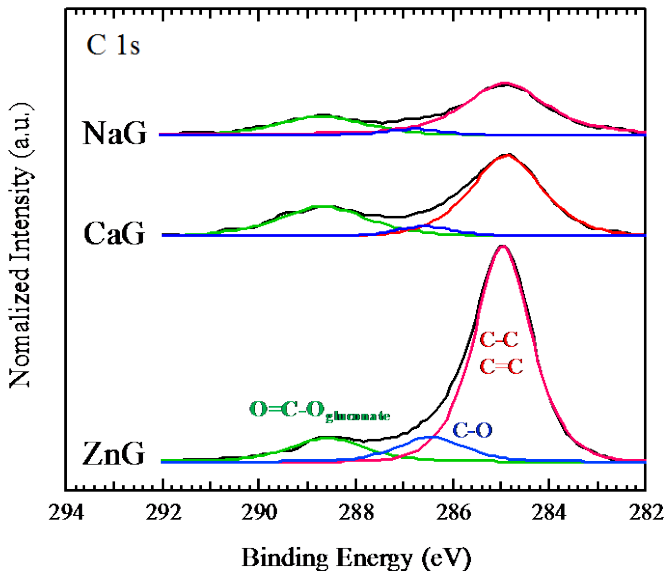

Fig. 4 XPS narrow spectra of C 1s on specimens after immersion for 7 d in model fresh water containing gluconates.

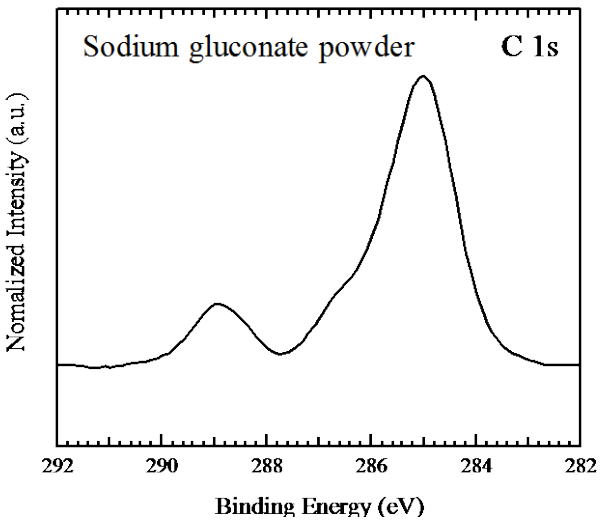

Fig. 5 XPS narrow spectrum of C 1s on sodium gluconate powder.

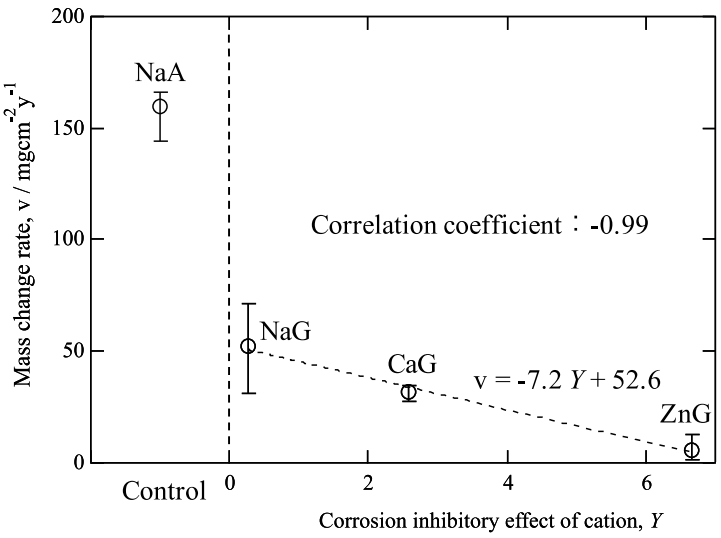

Fig. 6 Mass change rate as a function of *Y*. The mass change rate of NaA is a control data.

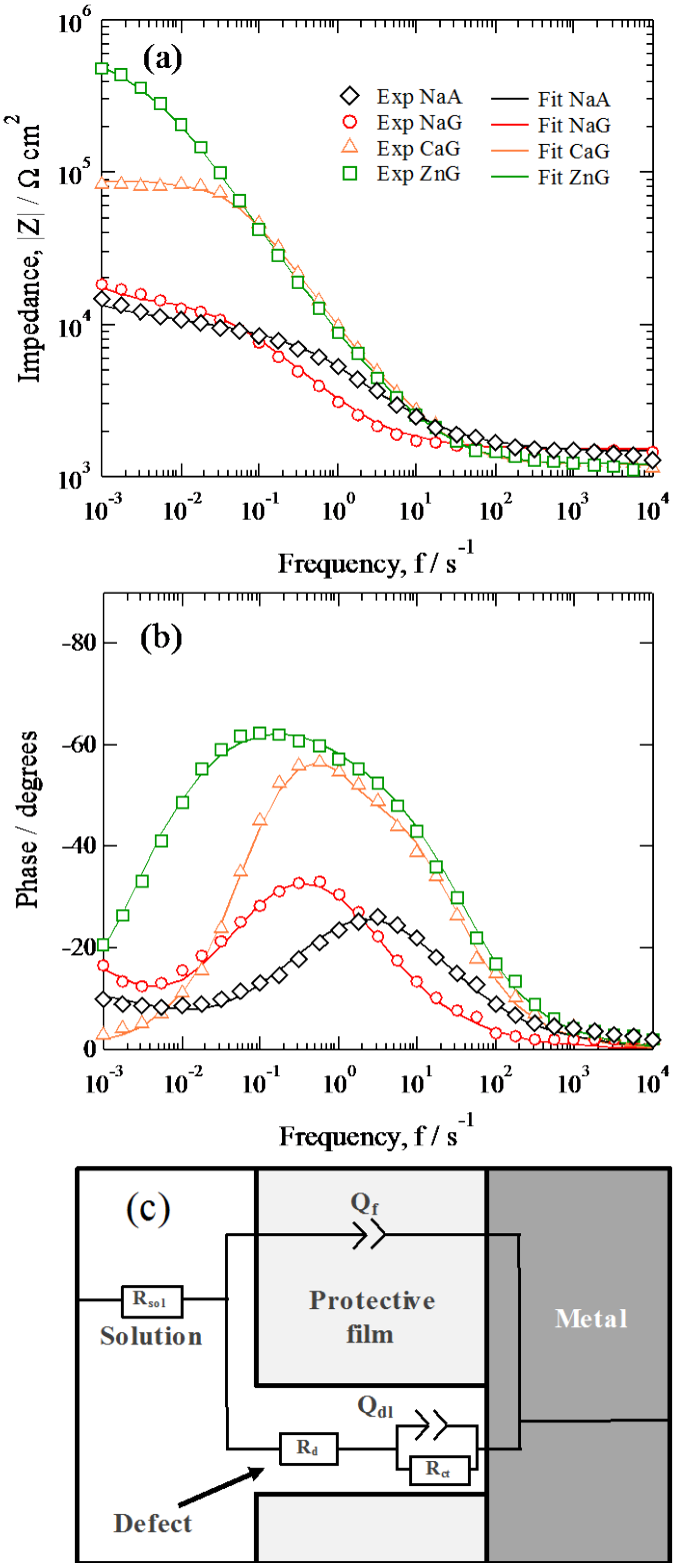

Fig. 7 Bode diagram of (a) Impedance and (b) phase shift after immersion for 7 d in the solutions and fitted lines calculated by an equivalent circuit. (c) Equivalent circuit with a schematic diagram of a mild steel electrode with a protective film having a defect.

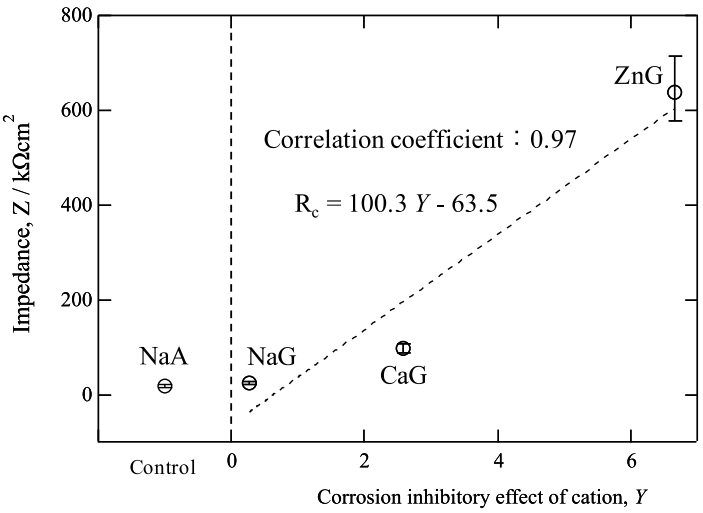

Fig. 8 Corrosion resistance, R_c, as a function of Y. The R_c of NaA is a control data.

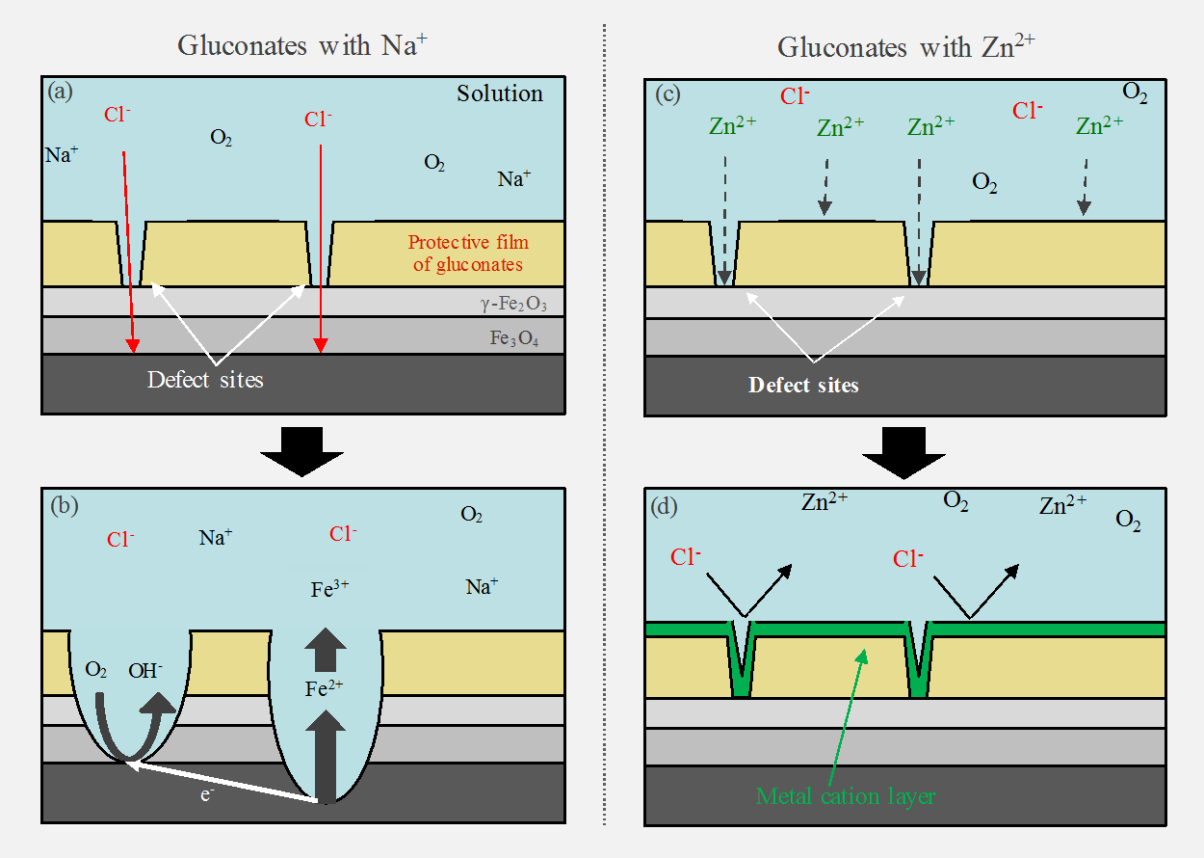

Fig. 9 Schematic images of the process by which a gluconate inhibits corrosion of mild steel in model fresh water containing gluconates with Na^+ ((a) and (b)) and containing gluconates with Zn^{2+} ((c) and (d)).