

**Original Research Article**

**Electrochemical Studies on the Corrosion Behavior of Mild Steel in NaCl Aqueous  
Solutions with Zinc Ions.**

UNDER PEER REVIEW

**ABSTRACT**

The corrosion behaviors of mild steel in NaCl aqueous solution with different  $Zn^{2+}$  concentrations have been investigated electrochemically. The immersion potentials were influenced by the presence of  $Zn^{2+}$  and were shifted to the positive direction with increasing the  $Zn^{2+}$  concentration in the solutions.  $Zn^{2+}$  suppressed the current density in both cathodic and anodic polarization and the inhibition effects were increased with increasing the  $Zn^{2+}$  concentrations. The electrochemical impedance spectroscopy (EIS) results showed the highest charge transfer resistance in the Zn-rich solution due to the formation of Zn-layer with the steel surface. The Zn-layer thickness was increased and the area of defects in the oxide film on the steel surface was decreased with increasing the  $Zn^{2+}$  concentration. Therefore, it was suggested that the corrosion inhibition ability of mild steel in NaCl aqueous solution was significantly improved with increasing the concentration of  $Zn^{2+}$  in the solution.

*Keywords:* mild steel; corrosion; electrochemical test; polarization; EIS.

## 1. INTRODUCTION

Modern civilization is growing up with advanced constructions. Many engineers and architects prefer steel over wood, glass and other materials for construction purposes due to its durability, unerring strength, pliability and sustainability. Mild steels are one of the good choices for the consumers that abundantly used in many areas. However, mild steels are not corrosion resistant and corrosion of these steels is a global problem that randomly occurring in a wide range of areas such as seawater environment [1-3], acid environment [4, 5] and in concentrated NaCl environment [6]. There are numbers of studies have been carried out regarding mild steel corrosion [7, 8] in natural extract [9], in acid solution [10-13] and in chloride aqueous solutions [14]. Composition of the oxide film that is formed on the steel surface is very much important and plays a significant role in the corrosion inhibition in aqueous solutions. It is recognized that chloride ions are very much aggressive and have a tendency to destroy the oxide film by film thinning, penetration and film rupture mechanisms [14-19]. Usually, metal dissolution is initiated after the destruction of oxide film by the chloride ions [20-23]. Oxide film destruction rate is increased with increasing the chloride ion concentration. Consequently, the metal dissolution rate is also increased [24, 25].

It is quite difficult to prevent the corrosion of steel hundred per cent. However, consumers are always trying to control the corrosion as much as conceivable. Coatings and organic-inorganic inhibitors are often used to diminish the corrosion percentage. There are so many environmental laws have been forced on the use of non-toxic and low-cost materials as corrosion inhibitors. This assortment has encouraged many researchers to discover some inhibitors that will have extensive consideration due to their properties like as environment-friendly, low influence on the human body, low cost, easy to handle and renewability. There are several studies have been carried out that metal cations have a tendency to inhibit the corrosion of steel in aqueous solutions as metal cations are available, low cost and easy to handle. There are some researchers reported that  $Zn^{2+}$  inhibited the corrosion of steel in aqueous solutions by forming a layer with the steel surface [20-23, 26, 27]. Drazic *et al.* [28] explained that the hydrogen evolution reaction rate was suppressed by  $Zn^{2+}$ ,  $Cd^{2+}$ , and  $Mn^{2+}$  in  $H_2SO_4$  solution and thus corrosion of iron was inhibited. Some nuclear power plant uses  $Zn^{2+}$  to control the corrosion of reactor component materials [29]. Several researchers also reported that  $Zn^{2+}$  significantly enhanced the inhibition performance of some traditional corrosion inhibitors [30-35]. Thebault *et al.* [36] stated that  $Zn^{2+}$  is more effective than  $Mg^{2+}$  to inhibit the cathodic reactions on the steel surface in

0.03 M NaCl solution. Tada *et al.* [37] showed that  $Zn^{2+}$  inhibited the cathodic reaction on Zn/Steel couple in 0.01 M NaCl solution. Sakairi *et al.* [38] elucidated that after laser irradiation, the rest potential changes negative to positive direction while the zinc-coated layer is exposed in the 0.01  $kmol\ m^{-3}$  NaCl solution. Hirasaki *et al.* [39] stated that the anodic current was decreased with increasing the  $Zn^{2+}$  concentration in the acid solution.

It has been recognized that  $Zn^{2+}$  appreciably inhibit the corrosion of steels in aqueous chloride solutions. However, the situation of stepwise increasing the zinc ion on the corrosion behavior of mild steel in chloride solution was not focused in the view of electrochemical measures. It is still not fully elucidated the electrochemical behavior and corrosion mechanism of mild steel in NaCl aqueous solution in the presence of  $Zn^{2+}$  with different concentrations. The present research purpose is to clarify the corrosion behavior of mild steel in NaCl aqueous solution with different concentrations of  $Zn^{2+}$  by electrochemical techniques.

## 2. MATERIAL AND METHODS

### 2.1 Testing Samples

Mild steel sheet with 0.7 mm thickness (composition by mass%: C = 0.02; Mn = 0.18; P = 0.015; S < 0.01; and Fe = balance) was used as the sample for this experiment. The sample size was  $7 \times 7$  mm and it was connected to a wire. Each sample was embedded in epoxy resin leaving one side exposed surface. A schematic representation for the preparation of the working electrode for the electrochemical tests is shown in Fig. 1.

SiC abrasive paper was used to abrade the exposed surface of the sample from #400 to #4000 grit size. The samples were cleaned in an ultrasonic bath with ethanol and highly purified water before the tests.

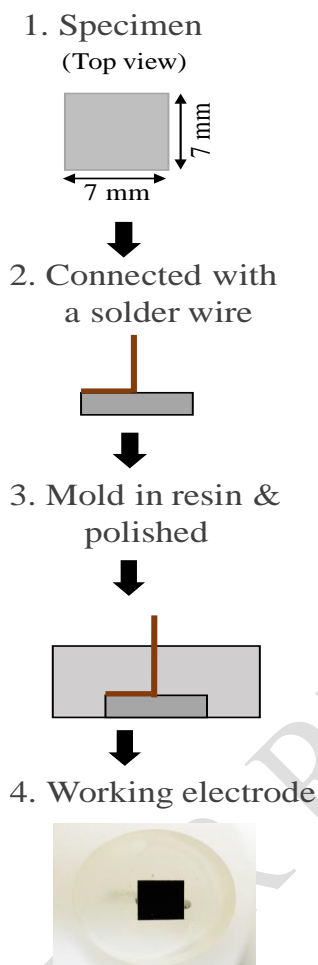


Fig. 1 Schematic representation for the preparation of the working electrode for electrochemical tests.

## **2.2 Experimental solutions**

Three solutions of  $0.1 \text{ mol m}^{-3} \text{ ZnCl}_2$  ( $\text{Zn}_{\text{Sol-L}}$ ),  $0.5 \text{ mol m}^{-3} \text{ ZnCl}_2$  ( $\text{Zn}_{\text{Sol-M}}$ ) and  $1.0 \text{ mol m}^{-3} \text{ ZnCl}_2$  ( $\text{Zn}_{\text{Sol-H}}$ ) were prepared together with  $10 \text{ mol m}^{-3} \text{ NaCl}$  ( $\text{Na}_{\text{Sol}}$ ). The  $\text{Cl}^-$  concentration of all solutions was adjusted to  $10 \text{ mol m}^{-3}$  by NaCl. The  $10 \text{ mol m}^{-3} \text{ NaCl}$  was used as the reference solution. The experimental solutions were prepared by highly purified water (MILLIPORE, Simplicity UV). All the solutions were colorless and transparent before the tests. The pH of the solutions was around neutral. All of the chemicals used in this experiment were special grade from Kanto Chemical Co. Ltd.

## ***2.3 Electrochemical measurements***

Electrochemical measurements were carried out at room temperature in a conventional three-electrode cell system using a computer-controlled potentiostat (IVIUM TECHNOLOGIES, Pocketstat). The exposed surface area of specimens in the solution was  $0.49 \text{ cm}^2$ . Specimens were immersed in

the solutions for 1 h at room temperature before the tests. A Ag/AgCl electrode (SSE) immersed in a saturated KCl solution was used as the reference electrode and a Pt plate was used as the counter electrode. The potentiodynamic polarization measurements were carried out from immersion potential to the cathodic and anodic direction with a scan rate of 60 mV/minute. The cathodic and anodic scans were recorded individually to obtain the specific electrochemical properties of mild steel immersed in the solutions with different concentrations of  $Zn^{2+}$ . The electrochemical impedance spectroscopy (EIS) measurements were carried out at open circuit potential in the frequency range from 10 kHz to 1 mHz and modulation amplitude of 10 mV. Each measurement was performed with three replicates and reproducible data were obtained. The EIS data were analyzed by a software called IVIUM.

### 3. RESULTS AND DISCUSSION

#### 3.1 Immersion Potential

The changes in immersion potentials of the specimens with the  $Zn^{2+}$  concentration in the solutions for 1 h at room temperature are shown in Fig. 2. In all the cases, the potentials are decreased with time. All the measured values of potentials are confined in a range between -0.2 V and -0.41 V, and only slight differences can be noticed. After 3000 s of immersion, all the potentials reach a stable value, and the  $Na_{sol}$  shows the lowest potential as compared to the other solutions. The immersion potentials are shifted to a positive direction with increasing the  $Zn^{2+}$  concentration in the solutions. These results suggest that  $Zn^{2+}$  has a significant influence on the immersion potential of the specimen in the solutions.

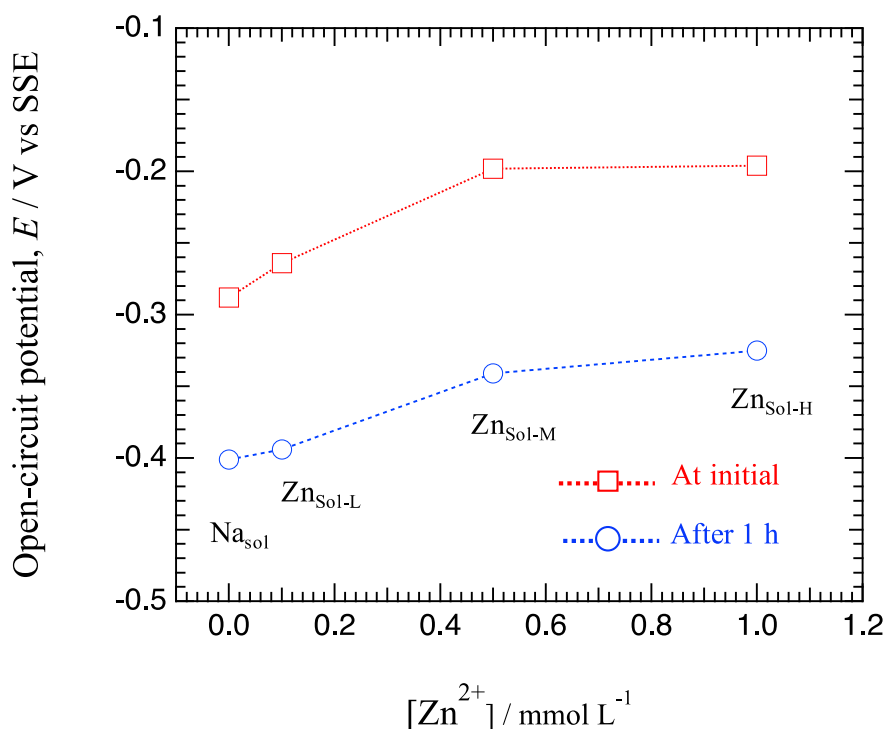


Fig. 2 Changes in open-circuit potential with  $Zn^{2+}$  concentration in the solutions for 1 h at room temperature.

### **3.2 Polarizations measurement**

The cathodic and anodic polarization behaviors were observed in different solutions and are shown in Fig. 3. In the cathodic polarization curves, at around -0.8 V, the lowest current density is observed in the Zn rich solution ( $Zn_{Sol-H}$ ). The highest current density is observed in the  $Na_{Sol}$  as compared to the other solutions. In the anodic polarization curves, at around -0.15 V, the lowest current density is observed in the Zn rich solution ( $Zn_{Sol-H}$ ) as compared to the other solutions. The highest current density is also observed in the  $Na_{Sol}$  as compared to the other solutions. The polarization behavior demonstrates that the presence of  $Zn^{2+}$  suppresses the current density in both cathodic and anodic polarization, and the inhibition effect is increased with increasing the  $Zn^{2+}$  concentration in the solutions.

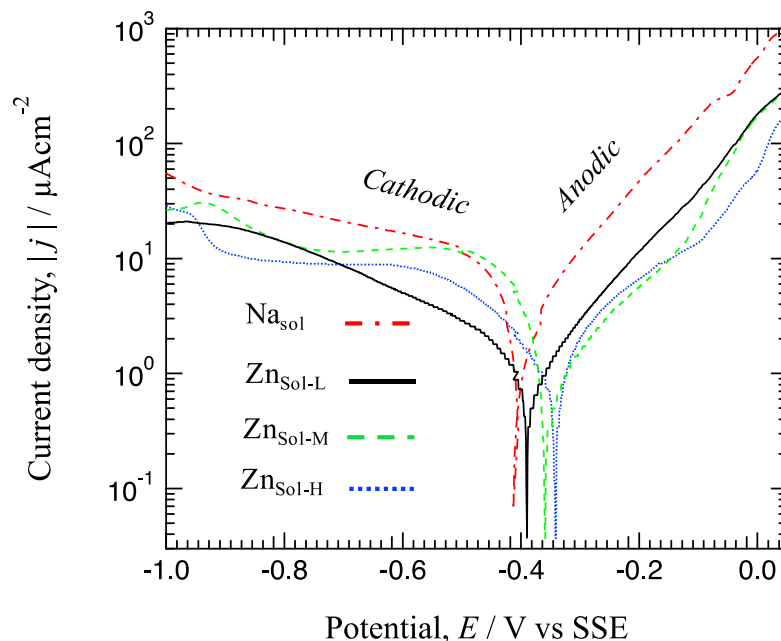


Fig. 3 Potentiodynamic cathodic and anodic polarization curves after immersion in the solutions for 1 h at room temperature.

### 3.3 EIS measurements

EIS measurements were carried out at room temperature. Before the measurement, samples were immersed in the solution for 1 h. Figs. 4 a), b) and c) show the Bode diagram of impedance, phase shift plot, and Nyquist plot respectively. The fitted lines are also shown in Figs. 4 a), b) and c) which were calculated by an equivalent circuit shown in Fig. 5. The equivalent circuit pretends an electrode with a protective film having a defect [35, 40]. The equivalent circuit consists (Fig. 5) of bulk solution resistance ( $R_{sol}$ ), solution resistance of the defects in the protective film ( $R_d$ ), charge transfer resistance of metal dissolution at the metal/solution interface inside the defect ( $R_{ct}$ ), constant phase element of the double layer at the metal/solution interface of the defect ( $Q_{dl}$ ) and the constant phase element of the protective film ( $Q_f$ ). The fitted lines match well to the experimental plots (Figs. 4 a), b) and c)), and all the experimental spectra can be well described by the mentioned equivalent circuit. The protective Zn-layer formed on the immersed specimens may have some defects that led to the formation of pits [35]. The magnitude of impedance signifies the corrosion resistance of steel [20-23, 26, 27]. From Fig. 4 a), it is found that the Zn-rich solution ( $Zn_{sol-H}$ ) shows the highest and the  $Na_{sol}$  shows the lowest impedance among the used solutions.



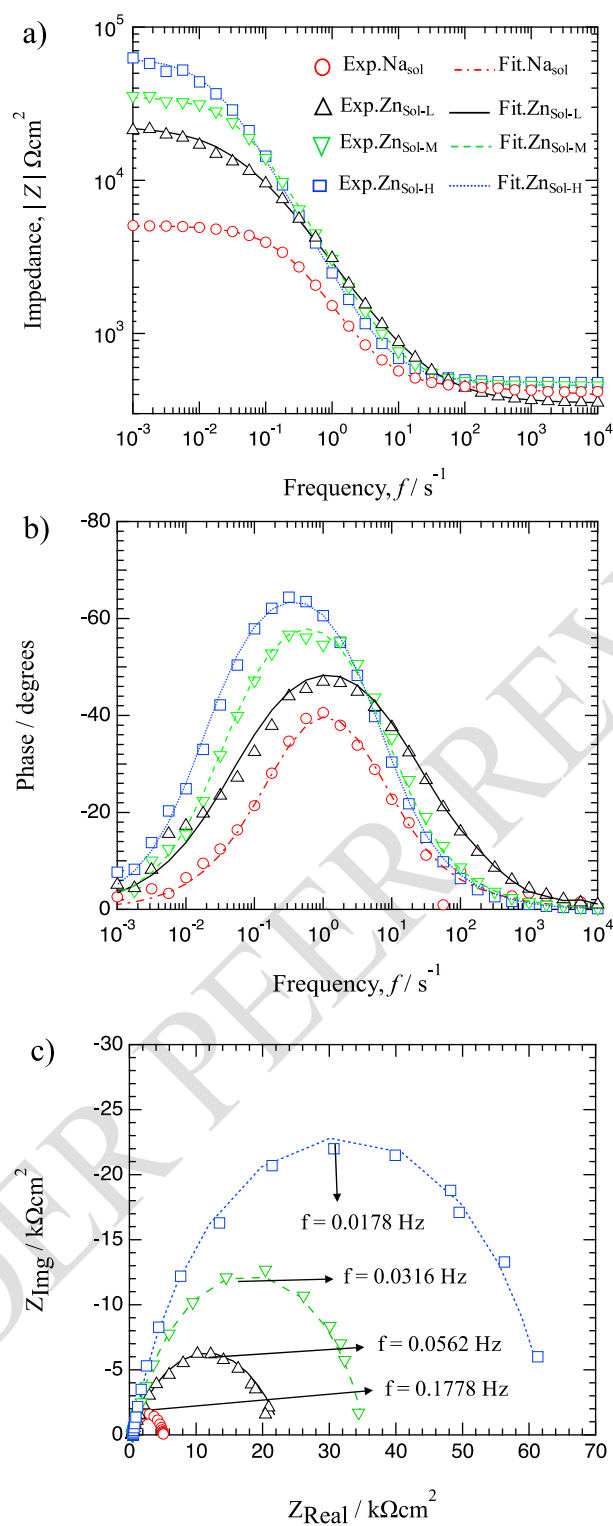


Fig. 4 Bode diagram of a) impedance, b) phase shift plot and c) Nyquist plot of specimen immersed in the solutions for 1 h at room temperature.

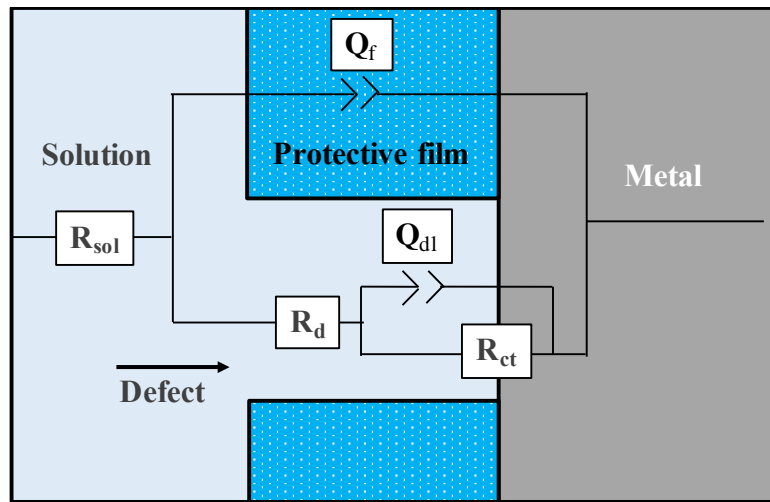


Fig. 5 Equivalent circuit of mild steel electrode with a protective film having defect to fit the EIS data.

The largest phase shift is detected in Zn-rich solution as compared to the other solutions (Fig. 4 b)). From the Nyquist plot (Fig. 4 c)), semicircle plots are observed in all the solutions. However, the radius of the semicircle is increased with increasing the  $Zn^{2+}$  concentration.

The electrochemical impedance parameters are shown in Table 1.

**Table 1. Calculated electrochemical impedance parameters of mild steel after immersion in the solutions for 1 h at room temperature.**

Solutions	$R_d$ ( $k\Omega cm^2$ )	$R_{ct}$ ( $k\Omega cm^2$ )	$Q_{dl}$ ( $\mu s^n \Omega^{-1} cm^{-2}$ )	$n_{dl}$	$Q_f$ ( $\mu s^n \Omega^{-1} cm^{-2}$ )	$n_f$	$R_c$ ( $k\Omega cm^2$ )	$\eta$ (%)
Na <sub>sol</sub>	0.10	4.95	3.34	0.71	3.50	0.69	5.05	-
Zn <sub>Sol-L</sub>	0.12	21.00	1.19	0.71	1.02	0.72	21.12	76
Zn <sub>Sol-M</sub>	0.13	37.50	0.98	0.74	0.99	0.72	37.63	87
Zn <sub>Sol-H</sub>	0.15	62.50	0.85	0.75	0.78	0.73	62.65	92

The corrosion resistance ( $R_c$ ) and the inhibition efficiency ( $\eta$ ) were calculated by the Eqs. (1) and (2):

$$R_c = R_d + R_{ct} \quad (1)$$

$$\text{Inhibition efficiency } (\eta\%) = \frac{R_{c\_sol} - R_{c\_ref}}{R_{c\_sol}} \times 100 \quad (2)$$

Where  $R_{c\_sol}$  and  $R_{c\_ref}$  are the values of corrosion resistance in the  $Zn^{2+}$  containing solutions and in the reference solution (Na<sub>sol</sub>). From Table 1, it is found that the  $\eta$  and  $R_c$  change as follows,  $Zn_{Sol-H} >$

$Zn_{Sol-M} > Zn_{Sol-L} > Na_{Sol}$ . These results indicate that the charge transfer may be prevented by the Zn-layer that was formed on the steel surface and the thickness of the Zn-layer has been calculated based on the EIS data presented in Table 1 by the Eq. (3) [41]:

$$Q_f = \frac{\epsilon_{Zn} \times \epsilon_0 \times A_S}{d_{Zn}} \quad (3)$$

Here,  $Q_f$  is the constant phase element of the protective film ( $\mu Fcm^{-2}$ ),  $\epsilon_{Zn}$  is the dielectric constant of ZnO ( $\epsilon_{Zn} = 25.59$ ) between the frequency range 1 mHz and 10 kHz at 300 K [41],  $\epsilon_0$  is the dielectric permittivity of vacuum ( $8.854 \times 10^{-8} \mu Fcm^{-1}$ ),  $A_S$  is the area of the surface ( $cm^2$ ) and  $d_{Zn}$  is the thickness of the Zn-layer (cm).

The calculated values of Zn-layer thickness with the  $Zn^{2+}$  concentration in the solutions are shown in Fig. 6. In the case of  $Na_{sol}$ , the Na-layer may not be formed on the surface. From the surface analysis, it was explained that Na or Na-related compound cannot form a layer on the metal surface [21, 35, 42]. Therefore, it is deliberated that the layer thickness is zero in  $Na_{sol}$ . In the case of  $Zn_{Sol-L}$ , the thickness of the Zn-layer is about 22 nm and the thickness is increased with increasing the  $Zn^{2+}$  concentration (Fig. 6). The Zn-layer may have not shielded the whole surface of the steel sample. The layer may have some defects.  $Q_{dl}$  represents the area of defects in the protective film on the steel surface [21, 35, 42, 43]. Otani et al. [35] reported that the decrease in  $Q_{dl}$  indicates that  $Zn^{2+}$  can decrease the area of defects in the protective film by forming a layer on mild steel in model freshwater. The defect area has been calculated by comparing with the double layer capacitance of Fe ( $20 \mu Fcm^{-2}$ ) [44-46].

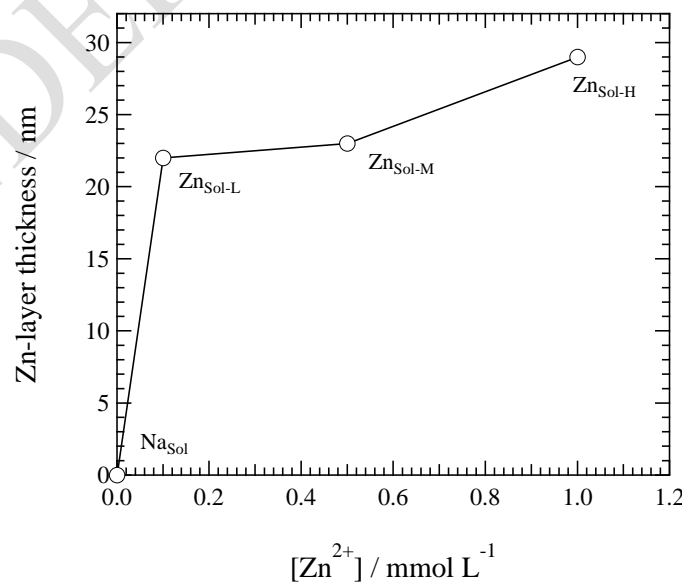


Fig. 6 Thickness of the Zn-layer on the steel surface with  $Zn^{2+}$  concentrations.

The calculated values of the defect area with the  $\text{Zn}^{2+}$  concentration in the solutions is shown in Fig. 7. The area of defects of the film is decreased with increasing the  $\text{Zn}^{2+}$  concentration. It is assumed that metal dissolution occurs at the defects. Therefore, metal dissolution or corrosion rate is reduced with decreasing the area of the defects. In addition, the resistance at the defect ( $R_d$ ) is increased (Table 1) with increasing the  $\text{Zn}^{2+}$  concentration in the solutions, which also indicate that the area of defects may be decreased with increasing the  $\text{Zn}^{2+}$  concentration. At the high concentration ( $\text{Zn}_{\text{Sol-H}}$ ), Zn may have scattered uniformly on the surface and formed a layer that covered the area of the surface more than the area of the surface covered by the other solutions ( $\text{Zn}_{\text{Sol-L}}$  and  $\text{Zn}_{\text{Sol-M}}$ ). The uniformed and comparatively thicker layer of  $\text{Zn}^{2+}$  decreased the defect area that shielded the surface from the aggressive chloride ions hence metal dissolution reactions are inhibited. Consequently, the highest charge transfer resistance was obtained in the Zn-rich solution ( $\text{Zn}_{\text{Sol-H}}$ ) as compared to the others.

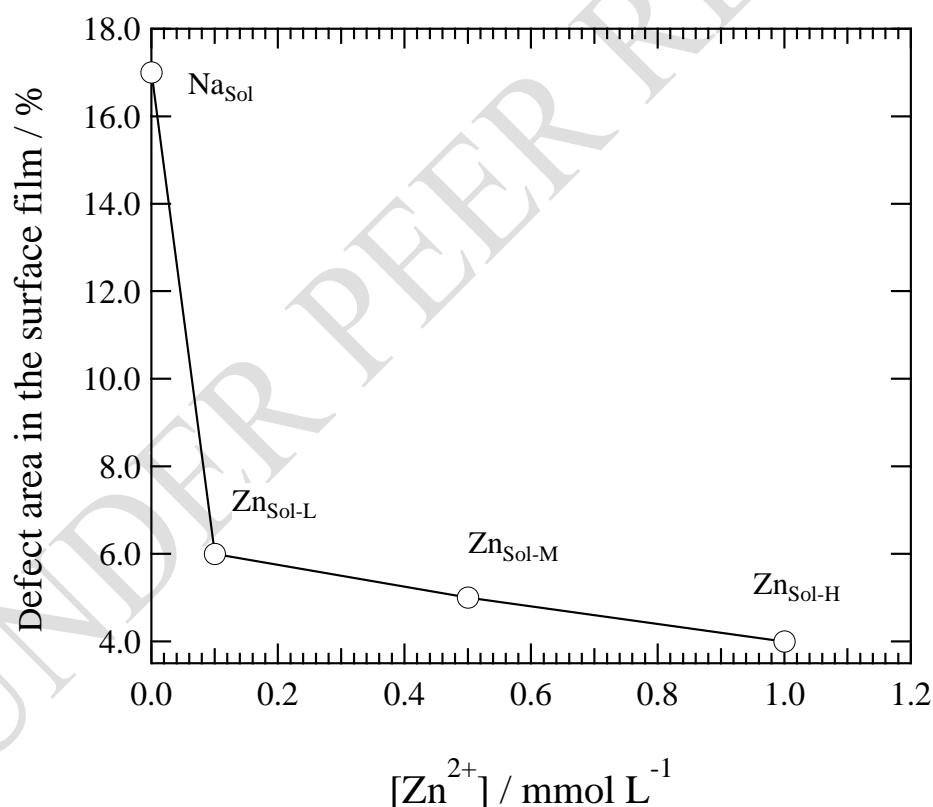


Fig. 7 Defect area of the surface film with  $\text{Zn}^{2+}$  concentrations.

### 3.4 $R_{ct}$ and corrosion inhibition efficiency

There is a close relationship between the charge transfer resistance ( $R_{ct}$ ) and the corrosion rate of steel in solutions.

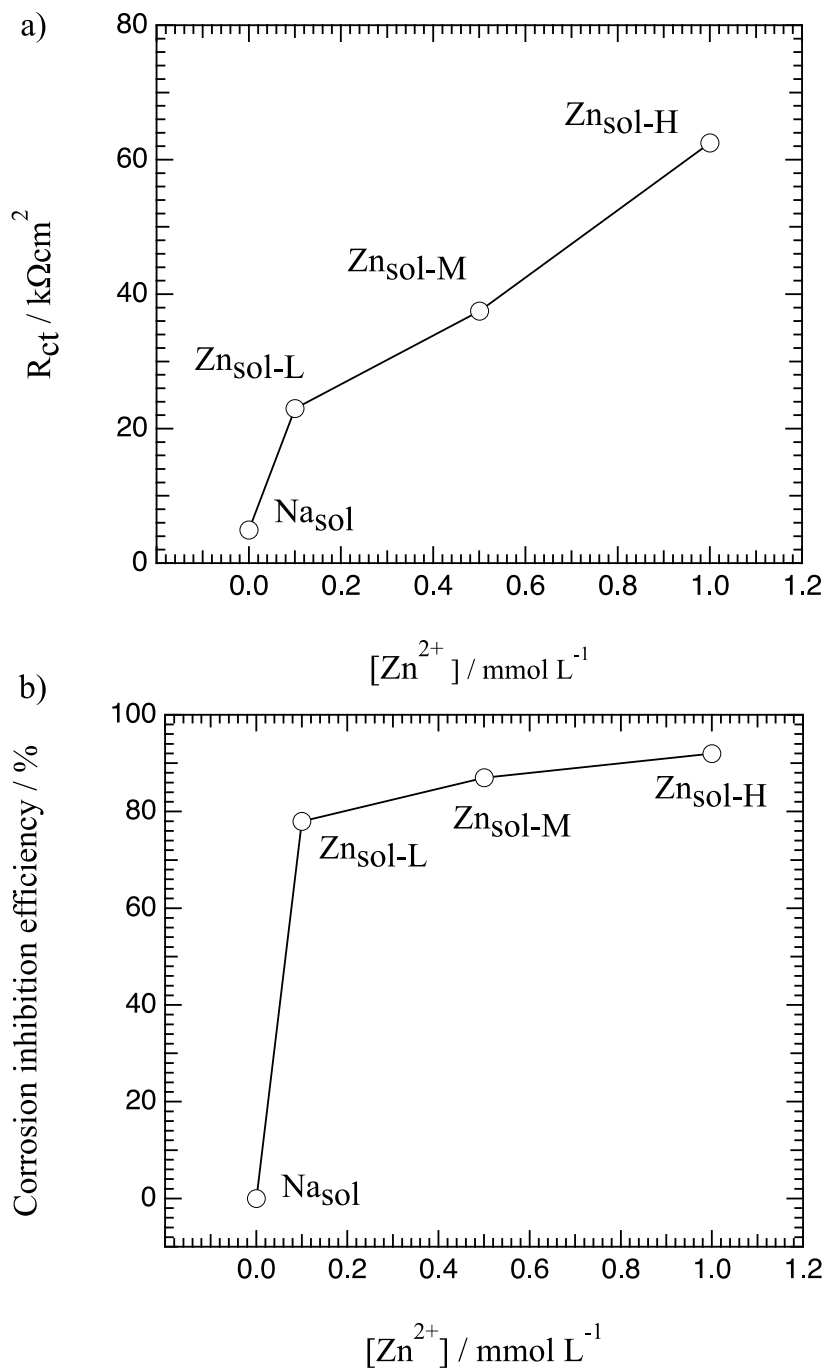


Fig. 8 a) Changes in  $R_{ct}$  and b) Corrosion inhibition efficiency as a function of  $Zn^{2+}$  concentration in the solutions.

The  $R_{ct}$  was calculated, and it was plotted against the  $Zn^{2+}$  concentration in the solutions. Fig. 8 a) shows the  $R_{ct}$  as a function of  $Zn^{2+}$  concentration.  $R_{ct}$  is increased with increasing the concentration of  $Zn^{2+}$  in the solutions. As it is well known that corrosion resistance is increased with increasing the  $R_{ct}$ . These results suggest that the corrosion resistance ability of steel is increased with increasing the concentration of  $Zn^{2+}$  in the solutions. To find out the relation between the corrosion inhibition ability and the  $Zn^{2+}$  concentration, corrosion inhibition efficiencies were calculated. Fig. 8 b) shows the corrosion inhibition efficiencies of  $Zn^{2+}$  as a function of concentration in which mean values of EIS data were used. The corrosion inhibition efficiency of  $Na^+$  was considered zero. The inhibition efficiency is increased with increasing the concentration of  $Zn^{2+}$ .

### **3.5 Corrosion inhibition mechanism**

Based on the experimental results, a corrosion inhibition mechanism could be suggested.  $Zn^{2+}$  forms a layer on the oxide film and decreases the defect area of the surface film. The Zn-layer protects the  $Cl^-$  attack and inhibits the corrosion reactions on the steel surface. In the case of low concentration of  $Zn^{2+}$  ( $Zn_{Sol-L}$ ), though the Zn-layer is formed, (the thickness of the layer is about 22 nm) the layer may not cover the whole surface. For this reason,  $Cl^-$  attack at the defect sites and destroy the surface films and accelerate the metal dissolution (Fig. 9 a)). In the case of medium concentration of  $Zn^{2+}$  ( $Zn_{Sol-M}$ ), Zn-layer thickness is increased and covered the surface more than that in low concentration (Fig. 9 b)). In the case of high concentration ( $Zn_{Sol-H}$ ), the Zn-layer is uniformed and comparatively thicker (thickness of the layer is about 29 nm) than other solutions ( $Zn_{Sol-L}$  and  $Zn_{Sol-M}$ ) (Fig. 9 c)). The defect area is decreased by the Zn-layer due to smoothly scattering of  $Zn^{2+}$  on the surface and the coverage of the Zn-layer on the surface more than that in  $Zn_{Sol-L}$  and  $Zn_{Sol-M}$  (Fig. 9 c)). Zn-layer with the steel surface protects the chloride ions to destroy the oxide film as well as protects the steel to oxidize. Consequently, the corrosion inhibition efficiency was increased in the Zn-rich solution ( $Zn_{Sol-H}$ ) as compared to the other solutions.

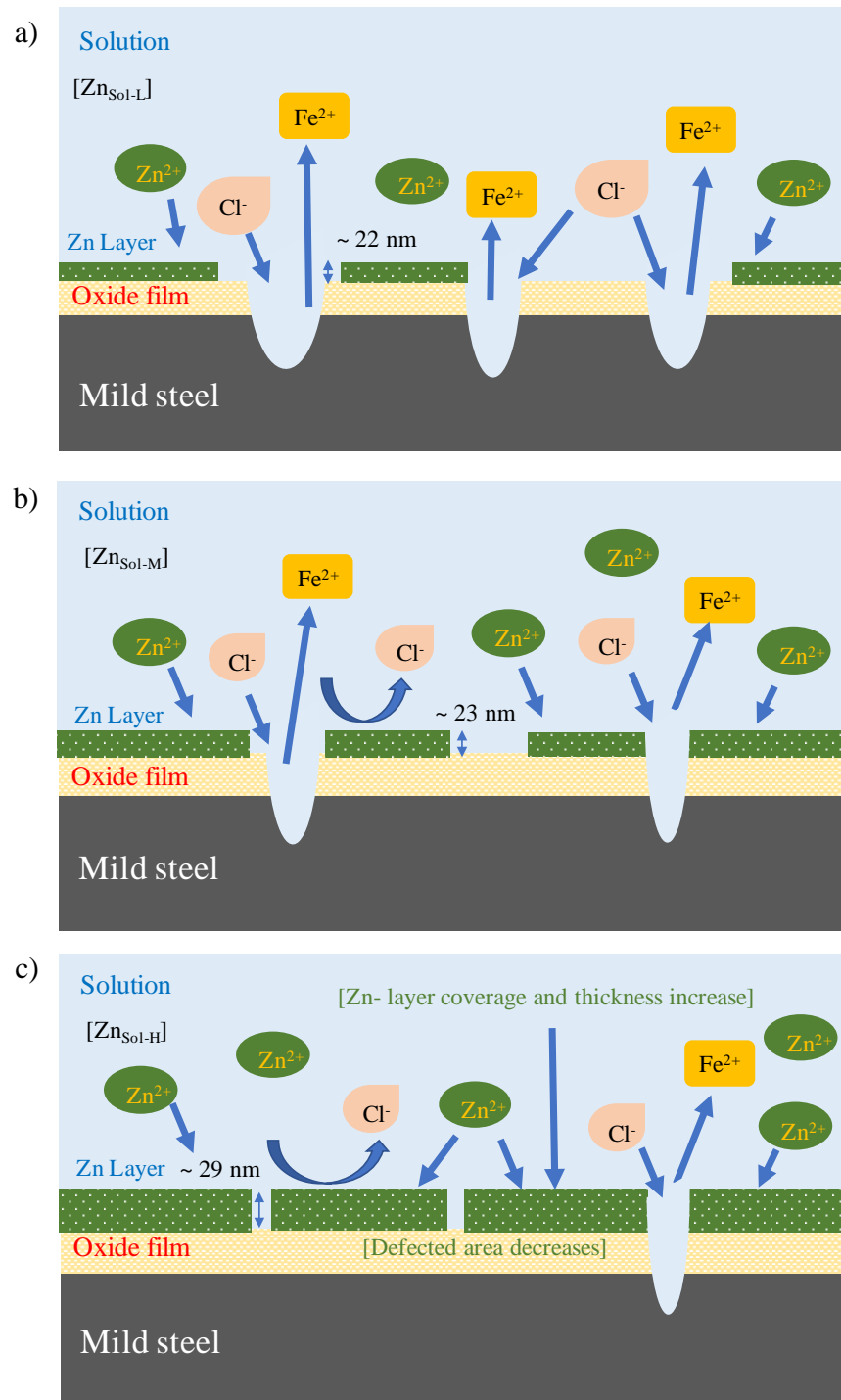


Fig. 9 Corrosion inhibition mechanism by Zn<sup>2+</sup> at a) low concentration (Zn<sub>Sol-L</sub>), b) medium concentration (Zn<sub>Sol-M</sub>), and c) high concentration (Zn<sub>Sol-H</sub>).

#### 4. CONCLUSION

The corrosion behavior of mild steel in NaCl aqueous solution with different concentration of Zn<sup>2+</sup> has been investigated by electrochemical tests and the following conclusions can be drawn:

- Zn-rich solution ( $Zn_{Sol-H}$ ) showed the highest immersion potential as compared to the other solutions.
- Both cathodic and anodic currents were suppressed in the presence of  $Zn^{2+}$  in the solutions.
- Charge transfer resistance (corrosion resistance) was increased with increasing the concentration of  $Zn^{2+}$  in the solutions.
- $Zn^{2+}$  formed a layer with the steel surface and the thickness of the Zn-layer was increased with increasing zinc ion concentration.
- Zn-rich solution ( $Zn_{Sol-H}$ ) showed the highest corrosion inhibition efficiency.

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