

Short Communication

Electrochemical Study on Corrosion Resistance of Epoxy-Coated Reinforcing Steel in Bridge Concrete

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Chloride infiltration is one of the major causes for bridge damages in regions where deicing salts are used. In this study, the role of epoxy-coated steel reinforcement in concrete to prevent corrosion is evaluated. Electrochemical impedance spectroscopy (EIS) testing was performed between the embedded steel by applying different potentials at various frequencies to evaluate the chloride ion effect and coating condition. The value of impedance at 1 mHz shows that epoxy-coating has a major influence on impedance values. This behaviour may be due to the combination of coating and corrosion related impedance factors. On comparison, it was found that polarization resistance data and the impedance values measured at the low frequency of 0.001 Hz for epoxy-coated reinforcing specimens were linear. These results indicated that epoxy-coated rebar increased the corrosion protection against chloride infiltration.

Keywords: Epoxy-coated reinforcing steel; Concrete bridge desks; Electrochemical impedance spectroscopy; Chloride ion effect

1. INTRODUCTION

Epoxy-coated reinforcement entered the market of corrosion protection from the early 1970s. West Conshohocken in Pennsylvania was the first place to have a bridge constructed with epoxy-coated reinforcement in 1973 [1].

High usage of deicing salts resulted in the damage of bridges. This led to the need of a research to develop methods that could protect the reinforced steel in concrete from corrosion. The National Bureau of standards conducted experiments to evaluate different organic coatings used for the corrosion protection of reinforcement [2]. The liquid and powder coatings were evaluated based on their resistance to chemical reactivity, prolongation, structural integrity, bond strength along with electrochemical

properties [3]. The best four Epoxy-powder coatings with the properties mentioned were magnified for further research [4].

Deicing salts are used to maintain the integrity of the bridges during winter [5]. However, these salts especially chloride salt infiltrates into the reinforcement of concretes and causes corrosion [6, 7]. Corrosion of the reinforced steel in concrete is one of the vital assessment of concrete bridge decks [8]. Hence, a number of ways have been developed over the years to detect and assess corrosion potential caused due to chloride infiltration [9]. Traditional electrical resistivity testing of concrete provides an indirect measure of the ability of concrete to resist chloride penetration, where increasing resistivity generally correlates to decreasing corrosion potential. This disadvantage is overcome by using an advanced application, electrochemical impedance spectroscopy (EIS) [10]. Measurement of electrical impedance is used by EIS to assess the corrosion potential of steel reinforced in concrete [11, 12]. Current is passed directly to the portion consisting of the surface up to the reinforced steel to measure the amount of damage occurred by chloride infiltration on the entire concrete bridge. Existing research on EIS has been largely focused on development of equivalent circuits for modelling and interpretation of data collected in laboratory experimentation involving testing across a wide range of frequencies. Though the information provided by EIS is specific, the process complexity and long associate testing period makes EIS a difficult application. Specifically, as the use of individual impedance measurements for characterizing bridge deck condition has already been demonstrated, investigations of the sensitivity of EIS measurement for different frequencies corresponding to specific bridge deck properties that influence corrosion of reinforcing steel are warranted. In this research, we were focused on determining the electrochemical assessment of epoxy-coated steel reinforced in concrete bridges after exposure to the environment. The sensitivity of EIS measurement for different frequencies corresponding to specific bridge deck properties that influence corrosion of reinforcing steel were evaluated in this research.

2. MATERIALS AND METHOD

For concrete slab preparation, Portland cement clinker was obtained and used to produce ASTM Type III cement by a cement company. The cementitious materials used in the concrete mixture design consisted of 82 percent Type III Portland cement and 18 percent Class F fly ash by weight. Table 1 provides the chemical composition and its specific gravity.

Table 1. Chemical analyses of the materials Clinker

Silicon dioxide (SiO_2)	22.3%
Aluminum oxide (Al_2O_3)	4.5%
Ferric oxide (Fe_2O_3)	3.4%
Calcium oxide (CaO)	65.5%
Sodium oxide (Na_2O)	0.4%
Magnesium oxide (MgO)	2.9%
Potassium oxide (K_2O)	0.8%
Equivalent alkali ($\text{Na}_2\text{O}+0.658\text{K}_2\text{O}$)	0.9%
Phosphorous oxide (P_2O_5)	0.2%
Titanium oxide (TiO_2)	0.2%
Sulphur trioxide (SO_3)	<0.01%
Loss on ignition (LOI)	0.01%

12 concrete slabs of $6 \times 20 \times 30$ cm dimensions were made by using a concrete mixture of maximum aggregate size 12 mm and slump size 80 mm. Equal volumes of sand and aggregates were used to allow the mixture to consolidate upon external vibration. To accelerate corrosion activity, the water to cement ratio was increased to 0.60 and the concrete cover over the reinforced steel was adjusted to be 25 ± 2 mm. The slabs were allowed to moist-cure at room temperature for 14 days.

A 100 mm stainless steel rod was placed in the centre of the concrete slab to act as a counter electrode to measure corrosion rate. Necessary connections were then made to the devices by means of joining the stainless steel rod and rebar using wires.

The study comprised of bridge decks built with epoxy-coated reinforcement and bare steel and the preparation of specimens. These samples were exposed to cyclic chloride solution to analyse their corrosion response to measure the service life expectancy of epoxy-coated reinforcement. The concrete samples were crushed to a powder by means of rock-crushing equipment and mortar-pestle till they passed through #20 sieve. ASTM C 1152-90 was followed to measure acid soluble chloride content. EIS was used to monitor the progress and properties of corrosion. A computer-operated Potentiostat and an appropriate software were the major components of the test system.

3. RESULTS AND DISCUSSION

The results of EIS test conducted in a simple solution on a metal sample with good quality coating under controlled laboratory conditions can be easily interpreted. However, interpretation becomes difficult when the electrolyte is a concrete medium and the coating is partially or fully disbanded due to entrapment of moisture between the coating and substrate. These can lead to varying current distribution, interface impedances and physical, chemical reactions. The complexity worsens, once corrosion activity begins, as the corrosion products accumulate and form barriers for ion and electron flow.

EIS test provides potential, impedance and phase angle data for the chosen frequency spectrum [13]. These data can be plotted in different formats to know more about the corrosion state of the system, coating saturation and resistivity of the concrete. A Bode plot is plotted with the modulus of impedance and the phase angle as a function of the frequency of the alternating current [14]. On the other hand, Nyquist plot presents real and imaginary components of the complex impedance response.

In Nyquist plot, large arc shaped response of high real impedance often denote polarization resistance [15]. From figure 1, for bare steel, even though the arc shaped response of high real impedance are present, the plot has insufficient frequency range to describe the curve. Extrapolation of the data will result in estimate errors. Hence, it is not advisable to estimate precise polarization values from the current data. However, these data can be used to determine the time of corrosion initiation.

The Bode and Nyquist plots for typical bare steel specimens at particular times before (Fig. 1a and b) and after (Fig. 1c and d) corrosion initiation is presented in figure 1. A well-developed passive layer is indicated by means of the Nyquist plot (Fig. 1b) slope which implies a high value of polarization resistance. An apparent decrease in impedance mainly at low frequencies can be observed during the occurrence of corrosion, due to the modulus of impedance in Bode plot (Fig. 1a) and the magnitude of real and imaginary component in the Nyquist plot (Fig. 1b).

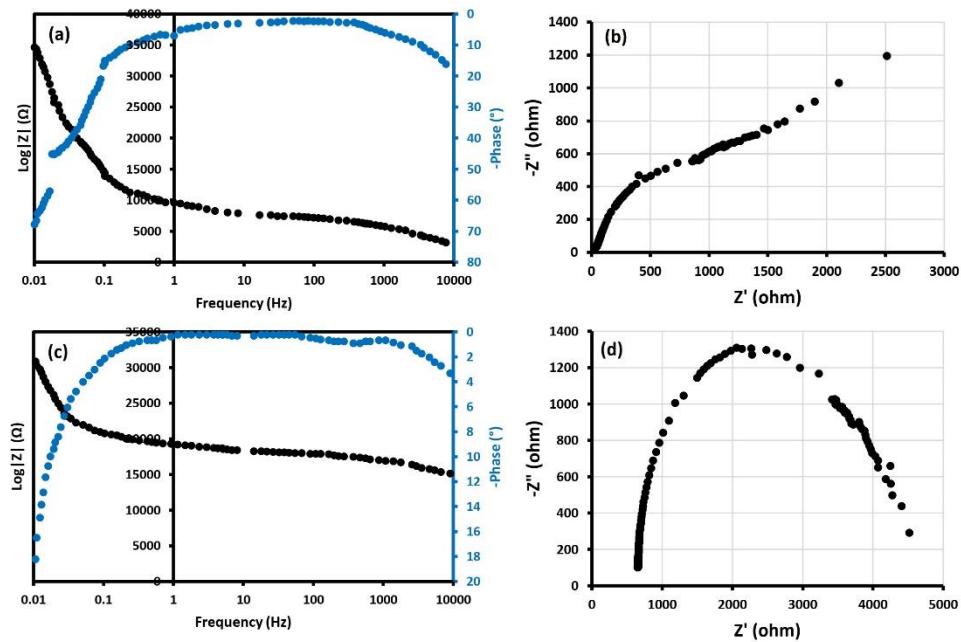


Figure 1. (a) Bode and Phase Angle plots and (b) Nyquist plot of bare steel after 3 months' exposure times, (c) Bode plots and (d) Nyquist plot of bare steel after 12 months' exposure times in 3% sodium chloride

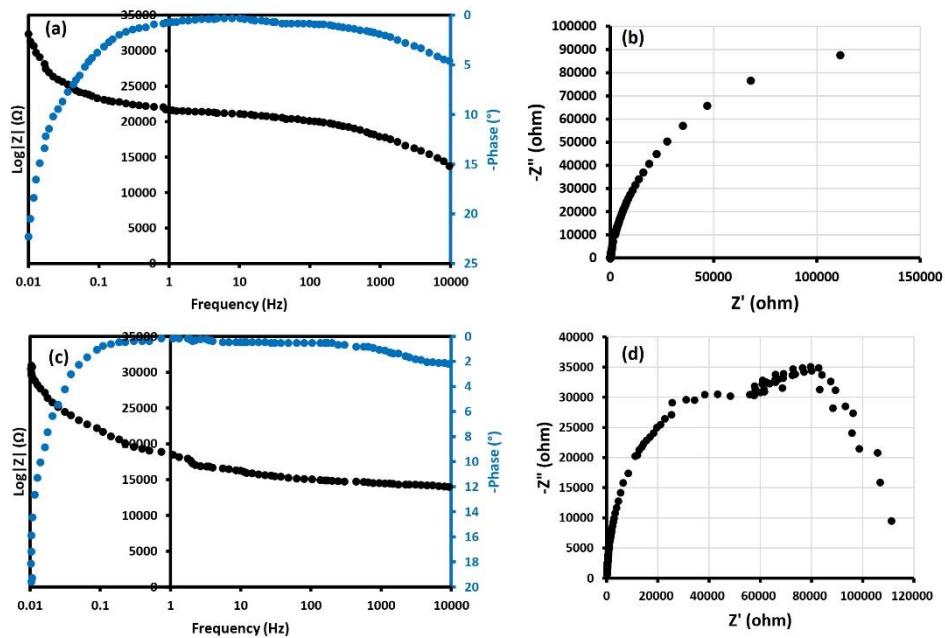


Figure 2. (a) Bode and Phase Angle plots and (b) Nyquist plot of epoxy-coated reinforcing steel after 3 months' exposure times, (c) Bode plots and (d) Nyquist plot of epoxy-coated reinforcing steel after 12 months' exposure times in 3% sodium chloride

The same trends are observed in epoxy coated reinforcement specimens in Figure 2. The Bode and Nyquist plots at particular times before (Fig. 2a and b) and after (Fig. 2c and d) corrosion initiation correlates with the observations by Sagüés and Zayed for partially disbonded coatings in concrete. The impedance in the complex plane prior to corrosion (Fig. 2b) can either denote a system under diffusion

control or a configuration of transmission line, moisture entrapped under the coating. As seen earlier, as corrosion occurs, a drastic decrease in impedance mainly at low frequencies can be observed. There is also a decrease in the magnitude of the phase angle, but becomes complex as more corrosion and coating deterioration activities occur.

In figure 2, the semi-circle at high frequency indicated that a conductive path has been formed. The circle has small diameter due to low coating pore resistance. The large incomplete semicircles at low frequencies denotes the charge transfer reaction. The diffusion controlled corrosion process in the metal substrate was indicated by the diffusion tail following the second semi-circle. The phase angle diagram has a phase angle shift at the low frequency attributing to the diffusion process.

The potential values for active corrosion for both bare and epoxy coated steel appears to be more negative than -350 mV. Active corrosion can only be assumed when there is a corresponding decrease in impedance. It was observed that the epoxy coated bars had a strong effect on impedance when the value was measured at 1 mHz. It may be due to combination of coating and corrosion related impedance factors. However, the low frequency impedance reduction compliments the variations in open-circuit potential. They indicate when corrosion occurs in the specimen. The same is true for partially or fully disbanded coating.

Overall, non-corroding epoxy coated reinforced specimens had an impedance modulus on the order of 10^6 ohms at 1 mHz. A few specimens had high impedance as 10^8 ohms with corresponding potential values, positive than -200 mV. Whereas actively corroding epoxy coated reinforced specimen had impedance modulus less than 10^4 ohms.

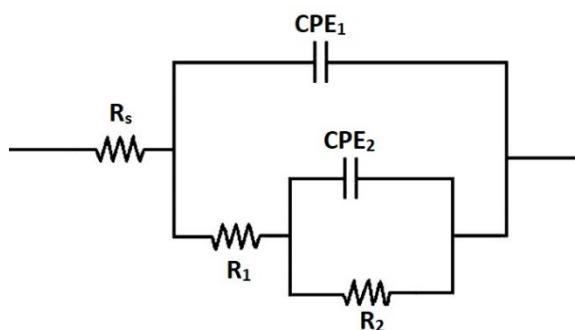


Figure 3. Schematic diagram of proposed equivalent circuit.

The electrochemical impedance data gained from this corrosion system can be analyzed and taken by the equivalent circuit model demonstrated in Figure 3 [16, 17]. The corrosion resistance of solution, the resistance of the protective film on the reinforcing steel surface and the charge transfer resistance of the corrosion process are signified by R_s , R_1 and R_2 respectively. CPE1 is the constant phase angle element that includes the film capacitance and deviation parameter n_1 , while the constant phase angle element CPE2 includes the double-layer capacitance and deviation parameter n_2 . The fitted data of the parameters in the equivalent circuit model for bare and epoxy-coated reinforcing steel are listed in Table 2 and Table 3, respectively.

Table 2. Electrochemical parameters from the fitting using the equivalent circuit in Figure 3 for bare reinforcing steel under different immersion times

Exposure times (months)	R_s ($\Omega \text{ cm}^2$)	CPE ₁ ($\mu\text{F cm}^{-2}$)	R_1 ($\Omega \text{ cm}^2$)	CPE ₂ ($\mu\text{F cm}^{-2}$)	R_2 ($\Omega \text{ cm}^2$)
3	5.96	53.24	998	189.4	582
12	40.25	39.14	2240	68.2	1356

Table 3. Electrochemical parameters from the fitting using the equivalent circuit in Figure 3 for epoxy-coated reinforcing steel under different immersion times

Exposure times (months)	R_s ($\Omega \text{ cm}^2$)	CPE ₁ ($\mu\text{F cm}^{-2}$)	R_1 ($\text{k}\Omega \text{ cm}^2$)	CPE ₂ ($\mu\text{F cm}^{-2}$)	R_2 ($\text{k}\Omega \text{ cm}^2$)
3	9.86	47.52	112.24	243.6	73.41
12	8.42	44.38	58.92	82.9	34.27

Table 2 and Table 3 represent the fitting parameters based on the equivalent circuit shown in Fig. 3. It can be found that the passive film resistance R_1 increased as the immersion times increases, which reflects that the protective properties of the passive film become strong. Comparing CPE₁ and CPE₂, it was found that CPE₁ are lower than CPE₂ [18]. This represents that the formed passive film is thin and the double layer at the interfaces has a high capacitive behavior. For epoxy-coated reinforcing steel under immersion times of 12 months, the passive film resistance decreases which can be attributed to the creation of damage on the surface of epoxy-coated reinforcing steel.

Figure 4 indicates current density of the bare and epoxy-coated reinforcing steel in 3% sodium chloride. Epoxy coated bars are passive in nature, as they are seen with a current density of about $0.01 \mu\text{A/cm}^2$. This value is negligible with respect to life expectancy. At the same time, bare steel bars has a current density of $3 \mu\text{A/cm}^2$ indicating high corrosion activity taking place in the system [19]. The time required for a concrete slab with bare steel bars to crack was 12 months when subjected to 3% sodium chloride exposure. The epoxy coated steel concrete bars remained intact.

The passive current density must be low enough to prepare a lower potential and to protect the steel from chloride initiated attack by keeping steel potential below the critical value. In this research, epoxy coated steel concrete bars revealed lower values of corrosion current density during one year in comparison with the results of other studies [20-23] which introduces a new approach to improve the corrosion resistance of structures.

On comparison, it was found that polarization resistance data and the impedance values measured at the low frequency of 0.001 Hz for epoxy-coated reinforcing specimens are linear in nature, as seen in figure 5. The only exception is one value with the polarization resistance being relatively higher than the impedance, 10^8 ohm cm^2 and 10^4 ohms , respectively.

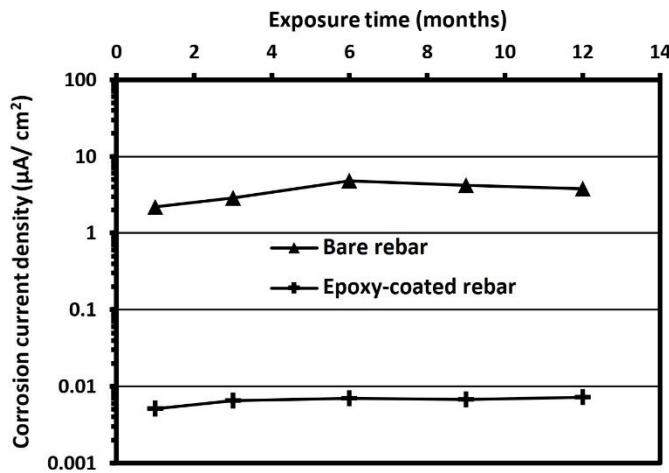


Figure 4. Current density of the bare and epoxy-coated reinforcing steel at different exposure times in 3% sodium chloride

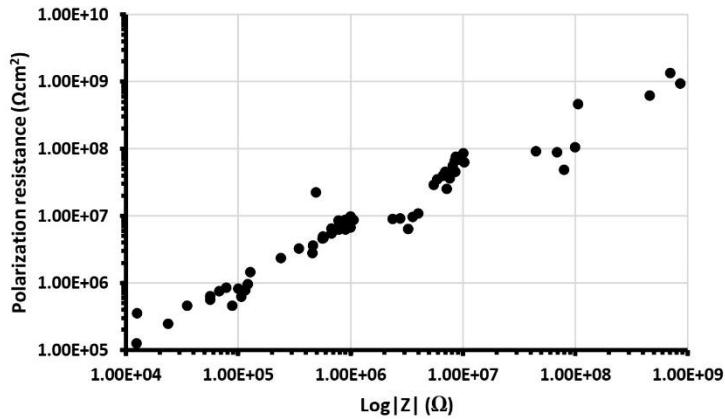


Figure 5. Polarization resistance vs. impedance of epoxy-coated reinforcing samples at 1 mHz in 3% sodium chloride

On the whole, it is clear that the coating pore resistance, charge transfer resistance, and the diffusion impedance together determine the polarization resistance of epoxy coated reinforced steel. As the technique is valid only when metal oxidation occurs at anode, the corrosion rates obtained may not be true. The corrosion mechanism to study the steel reinforced in concrete is more complex than a general metal oxidation process.

4. CONCLUSIONS

Bridge construction and concrete properties that undergoes chloride infiltration makes use of epoxy coated rebar. EIS testing was performed between the embedded steel by applying different potentials at various frequencies to evaluate the chloride ion effect and coating condition. The value of impedance at 1 mHz shows that epoxy-coating has a major influence on impedance values. This behaviour may be due to the combination of coating and corrosion related impedance factors. It is also

clear that the coating pore resistance, charge transfer resistance, and the diffusion impedance together determine the polarization resistance of epoxy coated reinforced steel.

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