Electrochemical impedance spectroscopy characteristics of steel corrosion in seawater sea-sand concrete

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Electrochemical impedance spectroscopy characteristics of steel corrosion in seawater sea-sand concrete

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Abstract: In this paper, the electrochemical mechanism and regularity of corrosion of steel bars in seawater sea-sand concrete under different chloride ion erosion styles are studied. Electrochemical impedance spectroscopy (EIS) was used to electrochemically test of steel bars in seawater sea-sand concrete (SSC). By means of analyzing the AC impedance spectra of the steel bars in specimens under two conditions, the conclusions can be gotten that in the EIS diagram of the steel bar in the rust state, the added capacitance arc in medium frequency range is related to pitting corrosion of the steel surface; The chloride ion carried by the aggregate and water decreased the concrete resistivity and transfer resistance of rebar and the anodic oxidation was easier to be carried out. In the equivalent circuit model, the constant phase element (CPE) is taken to replace the capacitor simulation in the equivalent circuit in order to simulate charge and discharge behavior of the electric double layer.

1. Introduction

With the development of marine resources in China, the development and construction of the island is a topic that cannot be bypassed. Considering transportation and time cost, the project on the island using the sea stone and the sea sand has great practical significance. However, the chloride ions contained in the marine aggregates pose a great threat to the steel bars wrapped in the concrete, which makes the steel bars in the concrete blunt, resulting in corrosion of the steel bars and greatly reducing service life of buildings[1, 2]. The corrosion of steel bars is divided into chemical corrosion and electrochemical corrosion and it is mainly electrochemical corrosion in concrete. At present, the electrode process dynamics and corrosion and protection mechanisms of steel corrosion in concrete are mainly dependent on electrochemical testing methods. In recent years, Electrochemical Impedance Spectroscopy (EIS) have been applied to the study of complex material systems, which can effectively characterize the electrochemical reaction mechanism in heterogeneous media[3, 4]. In 1981, Dawson[5] first applied AC impedance spectroscopy to the study of steel corrosion in concrete. Since then, EIS has been widely used in the study of reinforced concrete corrosion[6].

LIU Xiao-min and JI Yong-sheng[7, 8] used the internal salt-mixing method to accelerate the corrosion, and studies the electrochemical law of the steel corrosion process, which is close to our test. But, the current research has found that the aggregate-bearing type and the internal salt-mixing chloride ion are quite different in combination, communication method, efficiency, etc[9, 10]. Therefore, it is still necessary to analyze the electrochemical characteristics of steel bars in seawater sea-sand concrete under different erosion modes.

In this study, the electrochemical impedance spectroscopy (EIS) were used to explore the corrosion

electrochemical properties of steel in seawater sea-sand concrete. The impedance spectra of steel bars under different curing modes were drawn and analyzed. The equivalent circuit models of specimens were established combined with impedance spectrum in different periods and the electrochemical corrosion mechanism of steel bars in seawater sea-sand reinforced concrete was revealed.

2. Experimental Program

2.1 Preparation of specimens

The concrete strength grade of the test piece is C30. The coarse aggregate of the seawater sea-sand reinforced concrete specimen is the sea stone which has not been desalinized and the particle size range is 5~20mm. The fine aggregate is sea sand whose fineness modulus M_x is 2.8 and chloride ion content of 0.24%. Water of mixing in concrete is artificially prepared seawater[11]. Concrete mix ratio is shown in Table 1. The specimen is in the form of length × width × height = 100mm × 100mm × 100mm. The steel bar is embedded in the concrete as the working electrode and 304 stainless steel is used as the auxiliary electrode. The container is fixed on one side to erode the surface of the artificial seawater (Figure 1).

Table 1. Mixture proportions of concrete (kg/m^3).

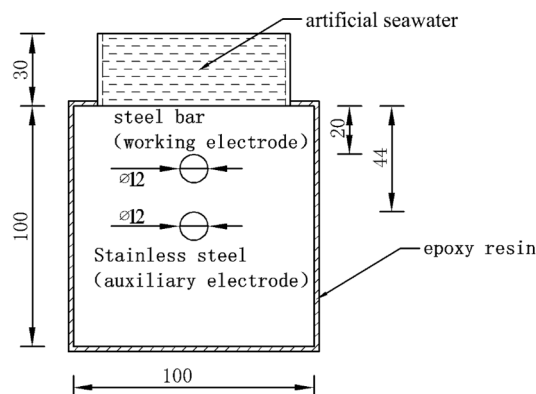| Cement	Water	Sand	Gravel	Water Cement Ratio
496.03	203.37	520.83	1 279.76	0.41

Fig. 1. Detail drawing of the specimen.

After the specimen was finished for 28 days, artificial seawater was injected. Group L1 was continuously immersed to simulate the underwater environment of the ocean; Group L2 was set up as wetting-drying seawater exposure cycles[12]. The experiment environment was 20±5 °C.

2.2 Electrochemical test

The electrochemical test uses a three-electrode system tested by an AUTOLAB-AUT86742 electrochemical workstation manufactured by the Metrohm. A saturated calomel electrode is adopted to be the reference electrode. In the EIS test, Measured amplitude of the electrochemical impedance spectrum is 10 mV, and the frequency range is 10^6~10^{-3} Hz. The resistance of the steel bar is controlled to be an open circuit potential during the test. Impedance data was processed by the ZSimpWin software. The average temperature of the solution was 20 °C.

3. Results and Discussion

3.1 Electrochemical impedance spectroscopy test

In impedance spectroscopy, we often use two kinds of analysis charts. One is called the Nyquist, the other is called the Bode. The vertical axis of the Nyquist graph is the imaginary part Z_{Im} and the horizontal axis is the real part Z_{Re} of the linear circuit impedance in the polarization system. From the basic principle of EIS, we can get that the real part Z_{Re} and the imaginary part Z_{Im} satisfy the following relationship[4]:

$$\left(Z_{Re} - \frac{R_t}{2}\right)^2 + Z_{Im}^2 = \left(\frac{R_t}{2}\right)^2 \qquad (1)$$

Where R_t is the resistance describing the equivalent element of the Faraday process on the surface of electrode. It can be seen that in the Nyquist diagram, this is a circle with $\left(\frac{R_t}{2}, 0\right)$ as the center and $\frac{R_t}{2}$ as the radius. Obviously, the impedance of the equivalent capacitive element can be initially compared by the radius of the semicircle characterized in the impedance spectrum.

Figure 2 shows the EIS diagram of the carbon steel electrode of specimen L2 in different periods. After comparison, we found that there is no difference between L1 and L2 in a relatively short period of time. With the continuation of the experiment, the capacitance arc of L1 and L2 in the low frequency region produced a large difference at 12 weeks, which indicating that the influence of different erosion modes began to appear gradually. The specific performance is that the radius of the capacitance arc of L2 in low-frequency zone is always greater than L1. It indicated that the transfer resistance of the double-layer on the steel surface is extremely large and the surface of the steel bar is seriously corroded. Since the L1 and L2's concretes are of the same type and only the seawater erosion method is different, we believe that the difference in oxygen concentration causes this situation. Compared with the specimens in the immersed state, the oxygen is more easily to reach the surface of steel in L2 and participate in the reduction reaction of the cathode, accelerating the accumulation of corrosion products. Since the fluidity of the entire system and the ability of the material to migrate are far less than in the solution, the diffusion of the generated corrosion products became into a control step of the entire process.
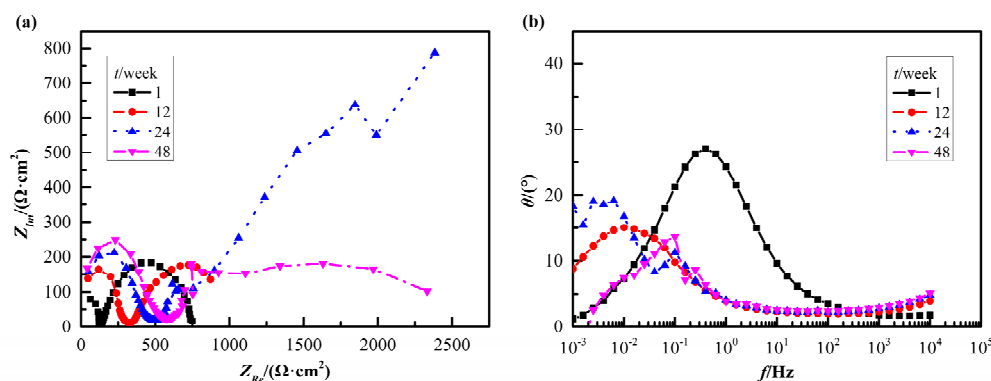

Fig. 2. Nyquist (a) and Bode (b) plots of specimen L2.

3.2 Equivalent circuit model

It can be seen from the EIS diagram that when the steel bar is in a passivated state (week 1), there are two capacitance arcs in the Nyquist diagram, that is, there are two time constants; when the steel bars are in an activated state (week 12), There are three capacitance arcs in the Nyquist diagram, that is, there are three time constants. From this, we infer the corresponding equivalent circuit model, as shown in Figure 3 (a), (b). These two equivalent circuit models are also one of the most commonly used models in academic circles.
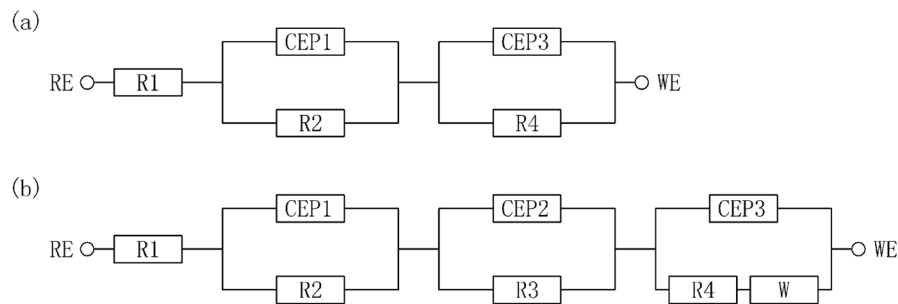
(a)

(b)

Fig. 3. Simplified equivalent circuit model: (a) passivation and (b) corrosion.

Considering the form of specimens, we hold that in the equivalent circuit diagram, R1 represents the solution resistance, R2 represents the concrete protective layer resistance and R3 represents the charge transfer resistance of the steel bar dissolution process at the bottom of the pitting hole. R4 represents the transfer resistance of the electric double layer on the steel surface and W represents the diffusion-related element (Warburg impedance) in the equivalent circuit to simulate the diffusion control effect. The capacitance arc has deviated from the semicircle exhibited by the ideal capacitor, but a flattened semicircle. This phenomenon is called the dispersion effect[4]. For reinforced concrete systems, this phenomenon is caused by the unevenness of the steel surface and the non-uniform multiphase structure of the concrete itself. Therefore, the constant phase element (CPE) is taken to replace the capacitor simulation in the equivalent circuit in order to simulate charge and discharge behavior of the electric double layer.

4. Conclusion
In order to explore the electrochemical process of steel corrosion in seawater sea-sand concrete under marine environment, this study illustrates the electrochemical mechanism and rate of steel corrosion in seawater sea-sand concrete by linear sweep voltammetry (LSV) and electrochemical impedance spectroscopy (EIS). Conclusions followed are obtained:

(1) In the dry and wet cycle, the radius of capacitance arcs of specimens are smaller, indicating that the oxygen is participating in the cathodic reduction reaction, accelerating the anodic reaction. The reaction is that the transfer resistance's reduction on the surface of the steel bar.

(2) It can be seen from the EIS diagram that when the steel bar is in a passivated state, there are two capacitive reactance arcs in the Nyquist diagram, which means two time constants; when the steel bars are in an activated state, there are three capacitive reactance arcs in the Nyquist diagram which means three time constants.

(3) In the equivalent circuit model, the constant phase element (CPE) is taken to replace the capacitor simulation in the equivalent circuit in order to simulate charge and discharge behavior of the electric double layer.

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