

Characterization of Corrosion Process of Q235 Carbon Steel in Simulated Concrete Pore Solution by EIS and EN Techniques

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The corrosion behavior of Q235 carbon steel in simulated concrete pore solution was investigated by electrochemical impedance spectroscopy (EIS) and electrochemical noise (EN) techniques. The equivalent circuit, statistical analysis, wavelet transform, chaos theory and cluster analysis method were employed to research the EIS and EN data of Q235 carbon steel in simulated concrete pores solution. The results showed that at the initial immersion, Q235 steel had higher charge transfer resistance, film resistance, noise resistance and fractal dimension, but lower standard deviation σ_1 , average charge q and correlation dimension. When the immersion time was larger than 48 hours, the charge transfer resistance, film resistance, noise resistance and fractal dimension of Q235 steel decreased greatly, but the standard deviation σ_1 , average charge q and correlation dimension of Q235 steel increased abruptly. Two distinct stages, i.e. passive state (Cluster 1) and initiation and development of pitting corrosion (Cluster 2), could be classified for Q235 carbon steel in simulated concrete pore solution.

Keywords: Q235 carbon steel; concrete pores solution; electrochemical impedance spectroscopy (EIS); electrochemical noise (EN) techniques

1. INTRODUCTION

The recirculated cooling seawater technology is the important solution of global water crisis, in which the seawater cooling tower constructed by reinforced concrete is the key equipment. Due to the high alkalinity of concrete (with its pH value larger than 13), a stable passive layer was formed on the surface of steel rebar, and thus the reinforcing bar has a higher durability. But when the concrete

structures were performed in the seawater environment, chloride ions in the seawater could penetrate into the reinforcement and make the pH value around the steel bar reduced to a lower value. The protective film on steel surface could be destroyed and the reinforcing steel would be repassivated [1]. As a result, the reinforced concrete structures would be deteriorated, and the premature failure would occur.

In recent years, many methods have been used to explore the corrosion behavior of Q235 carbon steel in solutions simulating concrete pores [2-5]. Dawson [6] firstly investigated the corrosion behavior of reinforced concrete by electrochemical impedance microscopy (EIS) method, and found that the corrosion behavior of reinforced concrete was highly related to the surface film on the steel. Sanchez^[3] proved that the spontaneous growth of passive layers upon steel rebar in alkaline media was associated with the enrichment of Fe (III)-oxides. Hu [7] reported that the charger transfer resistance R_t was decreased after immersion in sodium chloride solution and the active corrosion occurred on the rebar. Qiao [1] found that the capacitive arcs in high frequency and medium frequency regions in the EIS spectrum were responsible for the cement mortar and double layer respectively, and the corrosion process was controlled by the diffusion of oxygen in low frequency region. However, the corrosion process of rebar could not be monitored simultaneously by EIS method.

Electrochemical noise (EN) method is an in situ electrochemical technique, which generates spontaneously by corrosion processes and does not disturb the corrosion system. So EN measurement is becoming one of the most promising methods for detecting corrosion process and exploring the corrosion mechanism. Legat [5] indicated by EN test that the process of corrosion initiation was consisted of a sequence of several events, and metastable pitting happened on the rebar without stable pitting. During the wetting and drying of concrete, the distribution of anodic and cathodic sites could change alternately. By analyzing the EN data with discrete wavelet method, Hu [8] provided a criterion to determine the threshold value controlling the evolution of corrosion state of steel in concrete. By wavelet analysis, Zhao [9] found that during the 20 cyclic immersion and drying tests there were three different corrosion stages of reinforcing steel in cement mortar, including a competition process between breakdown and repassivation of passive film, pitting development and active corrosion.

Apart from statistical and wavelet transform analysis, fractal, phase space reconstruction theory and cluster analysis method could also be applied to resolve the EN data [10-13]. But until now, there was no information about these methods used to analyze the EN data in reinforcement corrosion. The projective of this paper is to determine the corrosion process of Q235 steel bar in simulated concrete pore solution by using EIS and EN techniques. The corrosion parameters of charge transfer resistance, noise resistance, crystal energy, fractal dimension, correlation dimension were calculated to characterize the corrosion process of reinforcing steel.

2. EXPERIMENTAL

2.1 Material and test solution

Q235 carbon steel with diameter of 8 mm was used as reinforcing rebar, and its chemical composition is listed in Table 1. The test samples with an exposed area of 49.6 mm² were connected to

a copper wire at one end to provide electrical contact, and then embedded in epoxy resin. The exposed surface of specimen was abraded with silicon carbide paper (from 240# to 1000#), and then degreased by acetone, washed by distilled water and dried by hot air.

Table 1. Chemical composition of Q235 carbon steel (wt%)

C	Si	Mn	P	S	Fe
0.14-0.22	0.12-0.30	0.30-0.65	0.045	0.050	balance

The simulated concrete pore solution was prepared as follows: firstly 100 grams Portland cement (Brand PS32.5) was added to 1000 ml distilled water, and then the solution was continuously stirred for 10 minutes in order to dissolve all the alkaline substances. After keeping still for 5 min, the obtained solution with the pH value of 13.5 was subsequently filtrated with a vacuum pump. The test solution was composed by this filtrated solution and 0.3 mol/L NaCl solution in a ratio of 1:1 [14].

2.2 Immersion test

The test samples with an exposed area 49.6 mm^2 were immersed in the above simulated concrete pore solution at room temperature. After different immersion periods, the surface morphology of corroded samples was observed by Olympus GX51 optical microscope.

2.3 EIS measurement

The electrochemical impedance spectroscopy tests of Q235 steel in simulated concrete pore solution were carried out at room temperature under different immersion time by using a PARSTAT 2273 electrochemical workstation (Princeton Applied research, USA) and Powersuite software. Two identical Q235 steel with an exposed area 49.6 mm^2 were used as working electrode and counter electrode, and a saturated calomel electrode (SCE) was as reference electrode. The measurements were taken at open circuit potential with a 10 mV amplitude signal and the applied frequency ranged from 10 kHz to 0.01 Hz. After tests, the results obtained were typically fitted to an equivalent circuit by applying ZsimpWin software, and the corresponding electrochemical parameters were calculated.

2.4 EN measurement and analysis

During EN measurement, two identical specimens were used as working electrodes and a SCE was applied as reference electrode. Electrochemical potential and current noise signals were simultaneously measured by PARSTAT 2273 electrochemical workstation through zero resistance ammeter (ZRA) mode. The sampling frequency was 2 Hz, and the test period was 54 hours.

Statistical analysis: After EN test, a 5-order polynomial fitting was applied to remove the direct current component from original EN data. The standard deviation of electrochemical potential noise σ_V and electrochemical current noise σ_I were calculated. The noise resistant R_n and average charge q in each event was obtained by equation $R_n = \sigma_V / \sigma_I$ and $q = (\sigma_V * \sigma_I) / (B * b)$, where B is the Stern-Gearly coefficient, b is the bandwidth of the measurement.

Wavelet analysis: The electrochemical noise signal of Q235 steel in simulated concrete pore solution was decomposed to seven levels ($d1$ - $d7$, and $s7$) by using the wavelet transform technique based on orthogonal db2 wavelet. And the fraction of energy associated with each detail crystal E_j^d was calculated as follows:

$$E_j^d = \frac{1}{E} \sum_{n=1}^{N/2^j} d_{j,n}^2 \quad (j=1, 2, \dots, 7)$$

Where d was the detail crystal and N was the total number of data points for each recording run. E was the total energy, which equaled to the sum of seven detailed crystals ($d1$ - $d7$), discounting the contribution of $s7$ crystal:

$$E = E_1^d + E_2^d + \dots + E_7^d = \sum_{n=1}^{N/2^1} d_{1,n}^2 + \sum_{n=1}^{N/2^2} d_{2,n}^2 + \dots + \sum_{n=1}^{N/2^7} d_{7,n}^2$$

For orthonormal discrete wavelet decomposition, the following power law of $\sigma_j^2 = \frac{\sigma^2}{(2^j)^{-\beta}}$ was obeyed, in which σ_j^2 was the variance of detail crystal d_j . After calculating, the following equation could be obtained:

$$\sigma_j^2 = \frac{1}{N/2^j - 1} \sum_{n=1}^{N/2^j} (d_{j,k} - d_j)^2 \quad (j=1, 2, \dots, 7)$$

The slope β was obtained from the plot $\log_2 \sigma_j^2$ versus level j : $\log_2 \sigma_j^2 = \beta j + \log_2 \sigma^2$.

Finally, the fractal dimension D_{fd} was obtained by $D_{fd} = 2.5 - 0.5\beta$.

Chaos analysis: According to phase space construction theory, the electrochemical noise data were reconstructed into m -dimension state vector with time delay τ and embedding dimension m by mutual information method and Cao's method. The correlation function $C(r)$ (probability of the endpoint distance between two vectors less than r) was calculated, and then the plot of $\ln C(r)$ vs. $\ln(r)$ was obtained. The correlation dimension D_{cd} was determined by the slope of plot with linear squares regression techniques. The details of chaos analysis procedure can be found in Ref. 10.

Cluster analysis: The potential and current signal of each EN data during different immersion time were selected as the variables of cluster analysis, the optimum cluster number (k) was set as 2, i.e. Cluster 1 corresponds to the passive state and Cluster 2 to the stable pitting state. The k -means cluster analysis method was applied, in which the squared Euclidean distance D_k^2 was taken as the similarity measurement and the Ward's method as amalgamation rule. The details of cluster analysis procedure can be found in Ref. 11[11].

3. RESULTS AND DISCUSSION

3.1 Surface morphology

The surface morphology ($\times 500$) of Q235 steel before and after immersion in the simulated concrete pore solution is shown in Fig. 1. Before immersion, Q235 steel was in smooth, flat and bright

surface (Fig. 1a). After immersion in concrete pore solution, no obvious surface change was observed on Q235 steel when the immersion time was less than 47 hours (Fig. 1b). But when the immersion time was larger than 48 hours, there were many corrosion pits with different size on the steel surface (Fig. 1c). These observations indicated that Q235 steel in concrete pore solution was in the passive state with the immersion time less than 47 hours, and changed into pitting corrosion stage with the immersion time larger than 48 hours.

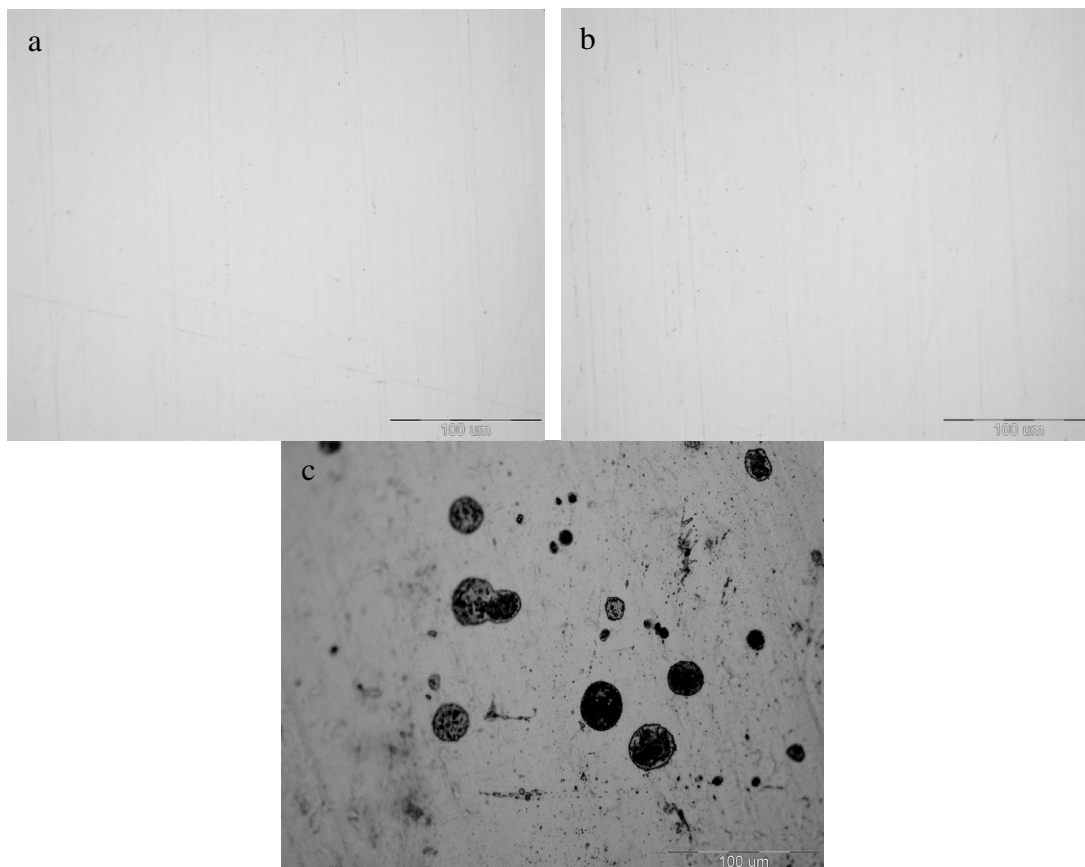


Figure 1. Surface morphology of Q235 steel before and after immersion in simulated concrete pore solution (a) before immersion, (b) after immersion of 47.0 hours, (c) after immersion of 53.5 hours $\times 500$

3.2 EIS spectrum

Fig. 2 and Fig. 3 are the electrochemical impedance spectrum of Q235 carbon steel in simulated concrete pore solution. During the immersion time in 3.5- 47 hours, there were two capacitance loops in Nyquist plot, and the diameter of capacitance loop increased with the immersion time from 3.5 to 47 hours (Fig. 2a). The two capacitance impedances should be associated to the passive film surface and steel rebar surface respectively. With the immersion time larger than 48 hours, EIS spectrum of Q235 steel consisted of two capacitance loops in high frequency range and a straight line in low frequency range, the diameter of capacitance loop increased with the immersion time (Fig. 3a). However, the diameter of capacitance loop with the immersion time larger than 48 hours was

almost two orders lower than that with immersion time less than 47 hours [7, 16]. This indicated that pitting corrosion was occurred.

By considering the above characteristics of EIS spectrum, the electrochemical equivalent circuits in Fig. 4 were used to correspond to Fig. 2 and Fig. 3, in which R_s is the solution resistance, R_t is the charge transfer resistance between steel rebar and concrete pore solution, Q_t (or C_t) is the constant phase element (or capacitance) between steel bar and concrete pore solution, R_f is the passive film resistance, Q_f is the capacitance between passive film and concrete pore solution, W is the Warburg resistance indicating the diffusion process across the corrosion pit [7]. The fitting parameters were calculated and listed in Table 2 and Table 3.

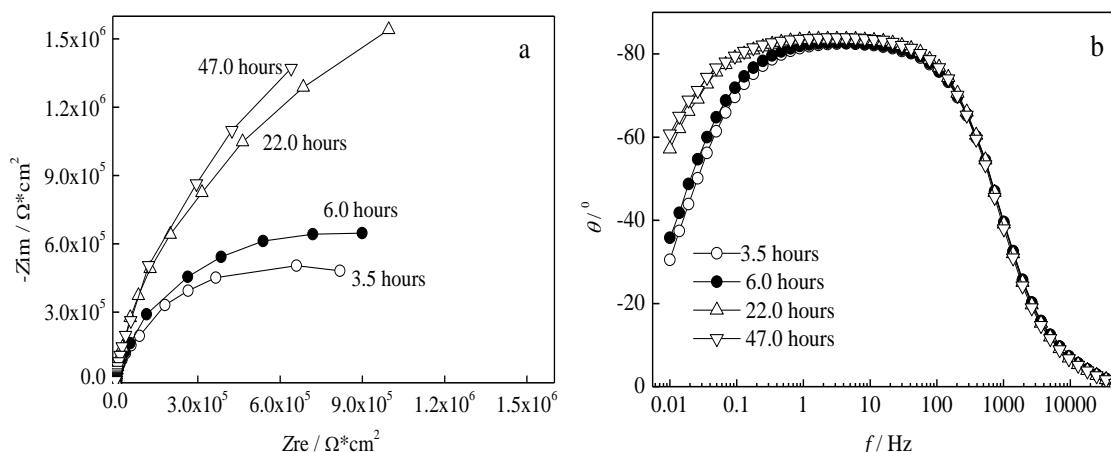


Figure 2. EIS spectrum of Q235 steel in simulated concrete pore solution with the immersion time less than 47 hours, (a) Nyquist plot and (b) Bode plot

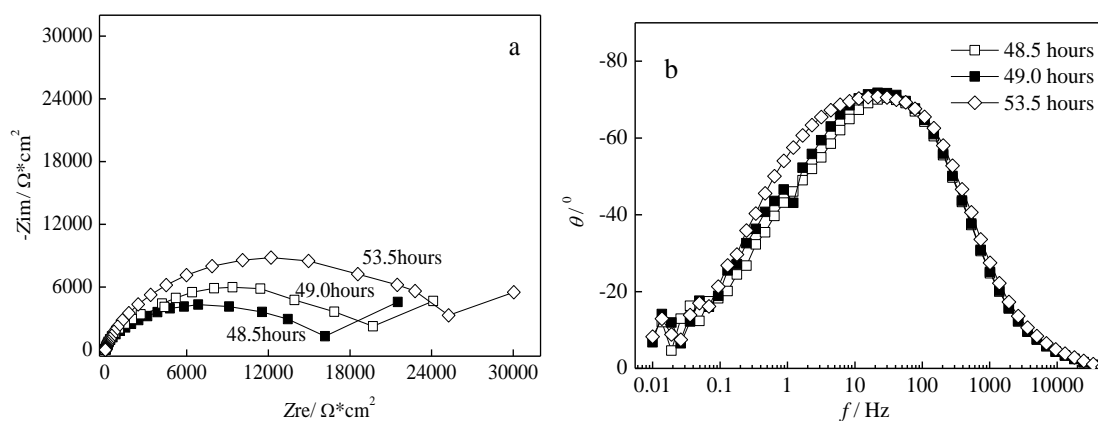


Figure 3. EIS spectrum of Q235 steel in simulated concrete pore solution with the immersion time larger than 47 hours, (a) Nyquist plot and (b) Bode plot

It can be seen that during the immersion in 3.5-47 hours the charge transfer resistance R_t was located between $2786\sim 5310\Omega\cdot\text{cm}^2$, but the passive film resistance R_f increased from 5.45×10^5 to $1.77\times 10^6\Omega\cdot\text{cm}^2$ with the increasing of immersion time (Table 2). This result implied that Q235 steel in

simulated concrete pore solution was in the passive state, and the corrosion resistance of steel increased with the immersion time. After the immersion time larger than 48 hours, the charge transfer resistance R_t and passive film resistance R_f decreased to $398\sim 1131\Omega\cdot\text{cm}^2$ and $6165\sim 11970\Omega\cdot\text{cm}^2$ respectively (Table 3), which were obviously lower than that with the immersion time less than 47 hours. Meanwhile, there was a Warburg resistance W occurred in the EIS spectrum. These observations proved that the passive film on Q235 steel started to be destroyed because of the penetration and diffusion of Cl^- ions in the passive film [17], and then the corrosion pits were initiated and developed gradually.

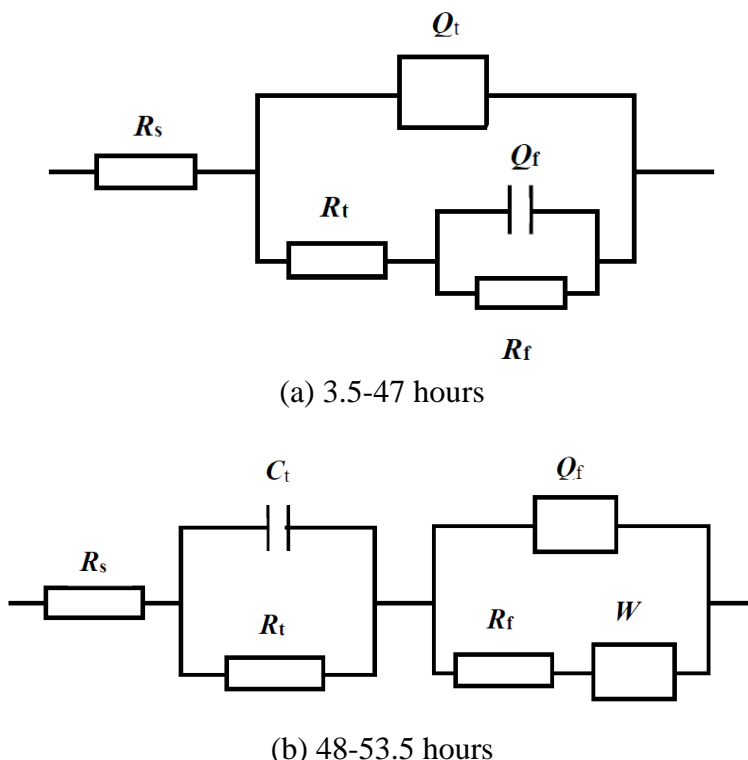


Figure 4. Equivalent circuit diagram of Q235 steel in simulated concrete pore solution with the immersion time (a) less than 47 hours and (b) larger than 48 hours

Table 2. EIS fitting results of Q235 carbon steel in simulated concrete pore solutions with the immersion time less than 47hours

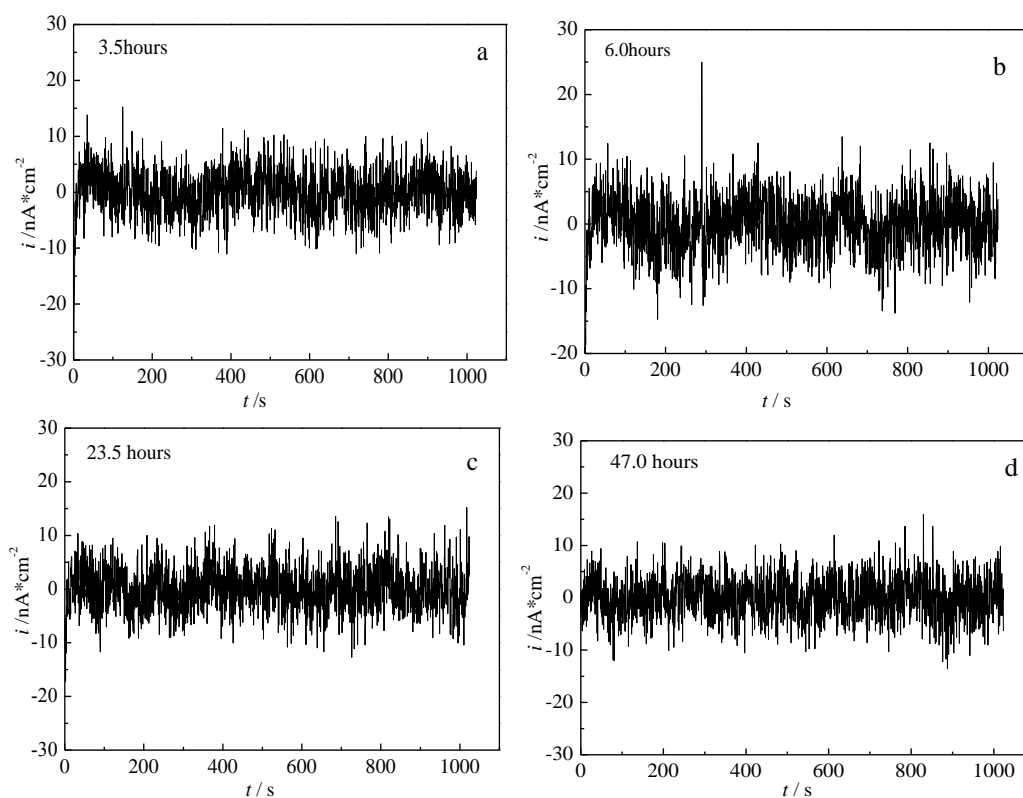
t/h	$R_s / \Omega\cdot\text{cm}^2$	$R_t / \Omega\cdot\text{cm}^2$	$Q_t / \Omega^{-1}\cdot\text{cm}^{-2}\cdot\text{s}^{-1}$	n_t	$R_f / \Omega\cdot\text{cm}^2$	$Q_f / \Omega^{-1}\cdot\text{cm}^{-2}\cdot\text{s}^{-1}$	n_f	Chisq
3.5	17.63	3387	1.48×10^{-5}	0.94	5.455×10^5	2.650×10^{-6}	0.9	5.13×10^{-3}
6.0	18.01	4126	1.487×10^{-5}	0.95	6.614×10^5	1.419×10^{-6}	1	6.75×10^{-3}
22.0	19.30	2786	1.199×10^{-5}	0.97	1.561×10^6	1.852×10^{-6}	1	8.55×10^{-3}
23.5	19.00	5017	1.340×10^{-5}	0.96	1.56×10^6	1.342×10^{-6}	1	6.94×10^{-3}
28.0	18.78	7929	1.422×10^{-5}	0.95	1.412×10^6	7.825×10^{-7}	1	8.78×10^{-3}
29.5	19.83	5180	1.301×10^{-5}	0.95	1.631×10^6	1.918×10^{-6}	0.94	8.17×10^{-3}
47.0	20.05	5310	1.330×10^{-5}	0.96	1.775×10^6	1.227×10^{-6}	1	7.41×10^{-3}

Table 3. EIS fitting results of Q235 carbon steel in simulated concrete pore solutions with the immersion time larger than 47 hours

<i>t/h</i>	R_s / $\Omega \cdot \text{cm}^2$	R_t / $\Omega \cdot \text{cm}^2$	C_t / $\text{F} \cdot \text{cm}^{-2}$	R_f / $\Omega \cdot \text{cm}^2$	Q_f / $\Omega^{-1} \cdot \text{cm}^{-2} \cdot \text{s}^{-1}$	<i>n</i>	W / $\Omega \cdot \text{cm}^2 \cdot \text{s}^{-1/2}$	Chisp
48.5	19.36	710	6.245×10^{-5}	6165	1.0×10^{-4}	0.8	1.6×10^{-3}	6.83×10^{-3}
49.0	19.06	1131	6.197×10^{-5}	8390	1.0×10^{-4}	0.8	2.5×10^{-3}	3.75×10^{-3}
53.5	18.87	398	14.50×10^{-5}	11970	6.0×10^{-5}	0.8	1.8×10^{-3}	1.90×10^{-3}

3.3 EN analysis

The electrochemical current noise of Q235 steel in simulated concrete pore solution is shown in Fig. 5. During the immersion time less than 47 hours, the current fluctuations were in high frequency with the amplitude less than $15 \text{ nA} \cdot \text{cm}^{-2}$, and large isolated transients were hardly observed (Fig. 5a-5d), which indicating that Q235 steel was undergoing a passive state with a lower corrosion rate. For the immersion time larger than 48 hours, larger transients with larger amplitude ($80 \text{ nA} \cdot \text{cm}^{-2}$ in Fig. 5e or $1500 \text{ nA} \cdot \text{cm}^{-2}$ in Fig. 5f) and low frequency were observed in the current fluctuations, which indicated that pitting corrosion with higher corrosion rate occurred on the surface of Q235 steel. These results accord with the surface morphology of Q235 steel in Fig. 1.



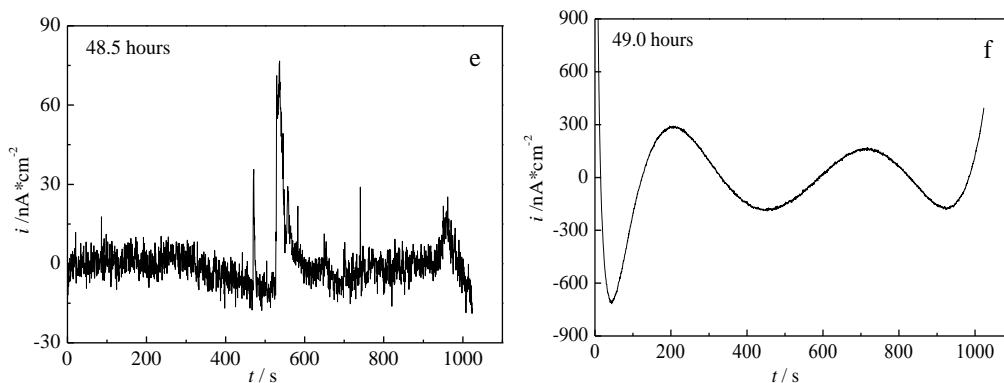


Figure 5. Electrochemical current noise of Q235 steel in simulated concrete pore solution at different immersion time (a)3.5h, (b)6.0h, (c)23.5h, (d)47.0h, (e)48.5h, (f)49.0h

By statistical calculation, the standard deviation of current noise σ_I , average charge q in every event and noise resistance R_n of Q235 carbon steel is shown in Table 4 and Fig. 6. When the immersion time was less than 47 hours, the standard deviation of current noise σ_I and average charge q of Q235 carbon steel were kept in a lower value with the order of $3\sim 5 \text{ nA}\cdot\text{cm}^{-2}$ and 10^{-13} C , and the noise resistance R_n was located in order of $10^4 \Omega\cdot\text{cm}^2$. After the immersion time larger than 48 hours, σ_I and q values suddenly increased to the order of $10^1\sim 10^2 \text{ nA}\cdot\text{cm}^{-2}$ and $10^{-12}\sim 10^{-11} \text{ C}$, and the noise resistance R_n decreased to $10^2\sim 10^3 \Omega\cdot\text{cm}^2$. All these results meant that two distinct processes could be classified for the corrosion behavior of Q235 steel in simulated concrete pore solution.

Table 4. Standard deviation of current noise σ_I , average event charge q and noise resistance R_n of Q235 carbon steel at different immersion time

Time/h	3.5	6.0	22.0	23.5	28.0	29.5	47.0	48.5	49.0	53.5
$\sigma_I/\text{nA}\cdot\text{cm}^{-2}$	4.05	4.27	3.90	3.96	3.93	3.95	3.85	9.94	343.0	429.0
$q/10^{-13}\text{C}$	0.896	0.826	0.925	0.801	2.59	2.58	1.75	20.4	197.0	836.0
$R_n/\Omega\cdot\text{cm}^2$	39178	30862	12099	18043	25510	26032	15922	2980	122	427

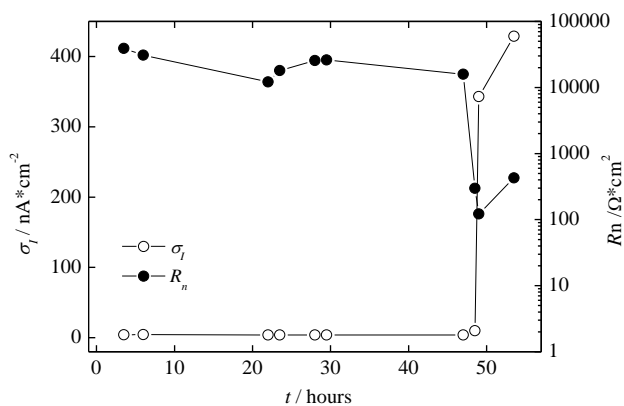


Figure 6. Standard deviation of current noise σ_I and noise resistance R_n of Q235 carbon steel in simulated concrete pore solution at different immersion time

The distribution of crystal energy of Q235 carbon steel in simulated concrete pores solution under different immersion time is shown in Fig. 7. During the immersion time less than 47 hours, the maximum crystal energy was located in *d1* crystal, which indicating the current noise mainly fluctuated in a higher frequency range. This characteristic is corresponded with Fig. 5a-5d, and means that Q235 steel is in a passive state [15]. After the immersion time larger than 47 hours, the maximum crystal energy was changed to *d7* crystal, which indicating the current noise fluctuated in a lower frequency range. This observation accords with the result of Fig. 5e and Fig. 5f, and implies that a localized corrosion is occurred on the steel [1].

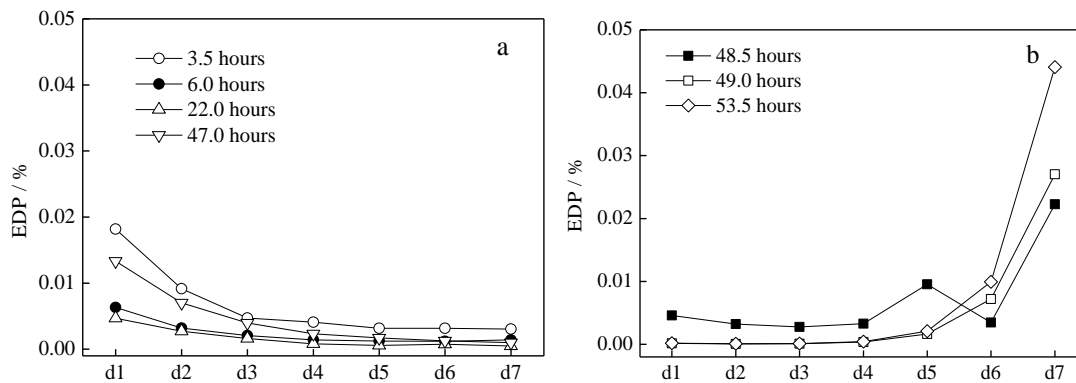


Figure 7. Energy distribution plots of Q235 carbon steel in simulated concrete pore solution at different immersion time (a) 3.5-47.0 hours (b) 48.0-53.5hours

Fig. 8 is the fractal dimension D_{fd} of Q235 carbon steel in simulated concrete pores solution under different immersion time. When the immersion time was less than 47 hours, the fractal dimension was kept almost invariable around 2.0, which meant the steel surface was in general corrosion or passive state. After the immersion time larger than 48 hours, the fractal dimension was decreased abruptly and fixed at 1.0, indicating the pitting corrosion was occurred on the steel[10,13].

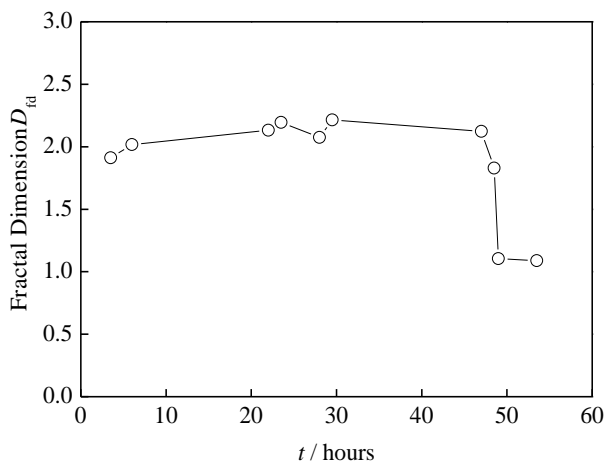


Figure 8. Dependence of Fractal dimension of Q235 carbon steel in simulated concrete pore solution on immersion time

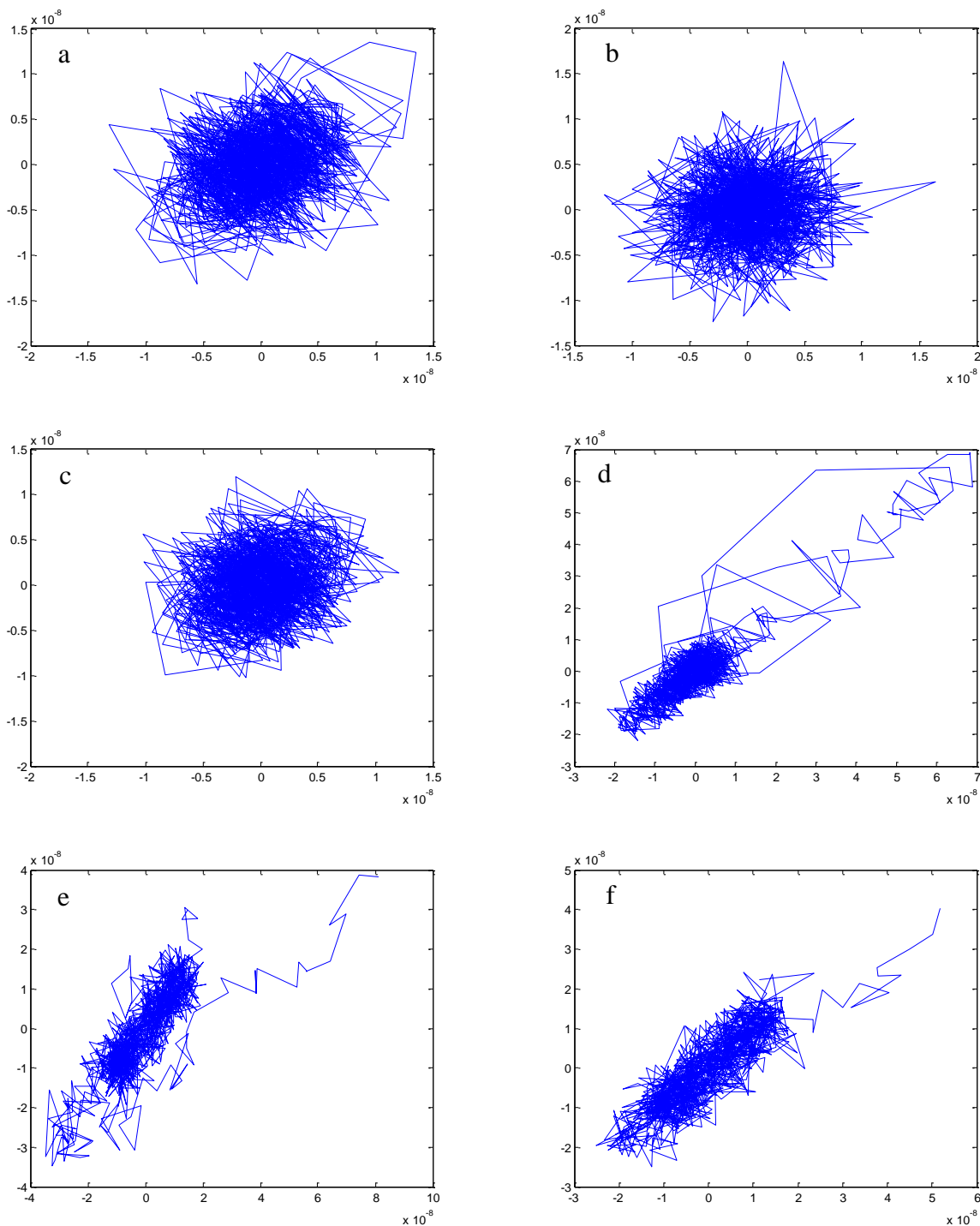


Figure 9. Phase space construction diagram of electrochemical potential noise of Q235 carbon steel in simulated concrete pore solution at different immersion time (a)3.5h, (b)6.0h, (c)47.0h, (d)48.5h, (e)49.0h, (f)53.5h

The phase space diagram of electrochemical current noise of Q235 steel in simulated concrete pore solution is shown in Fig. 9, and the calculated correlation dimension D_{cd} is shown in Fig. 10. From Fig. 9 and Fig. 10, it can be seen that with the immersion time less than 47 hours the phase space

diagram of Q235 steel was in a “spherical shape”(Fig. 9a-9c), and the correlation dimension D_{cd} was around 1.0(Fig. 10), indicating the passivation or uniform corrosion was occurred on Q235 steel surface. Whereas with the immersion time larger than 48 hours, the phase space diagram was in a “rod-like shape” (Fig. 9d-9f), and the correlation dimension D_{cd} was around 2.60~2.80(Fig.10), indicating the local corrosion or pitting corrosion was occurred on Q235 steel surface [10].

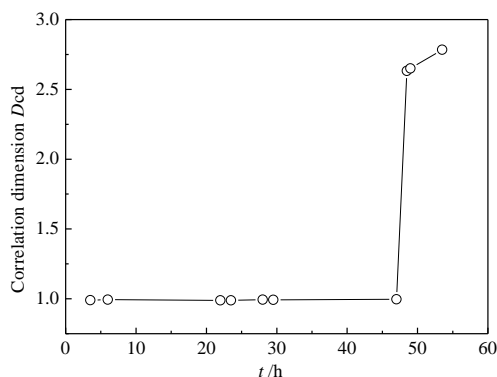


Figure 10. Dependence of correlation dimension of Q235 carbon steel in simulated concrete pore solution on immersion time

The cluster distribution of Q235 carbon steel in simulated concrete pore solution as the function of immersion time is shown in Fig. 11. It can be seen that there are two distinct distributions: 3.5–47 hours belonging to Cluster 1, 48.5–53.5 hours belonging to Cluster 2. It means that Q235 steel in simulated concrete pore solution was in passive state before the immersion less than 47 hours. After 48 hours of immersion, it is changed into stable pitting corrosion stage. This conclusion is accorded with that of Fig. 6, Fig. 7, Fig. 8 and Fig. 10.

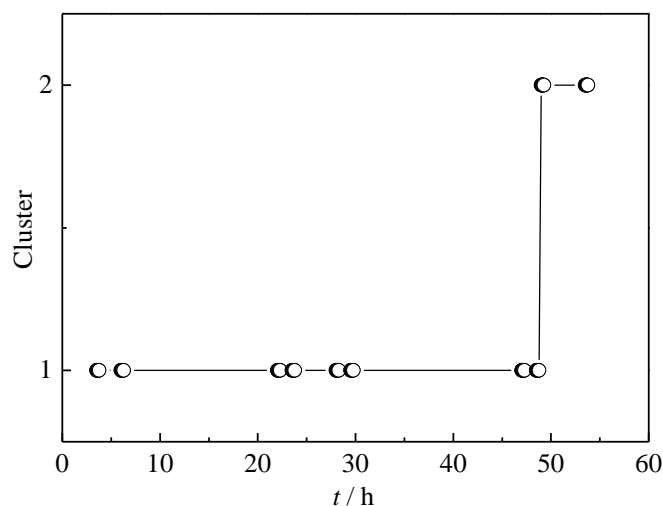


Figure 11. Cluster distribution of Q235 carbon steel in simulated concrete pore solution as the function of immersion time

From the above results, it can be concluded that there are two distinct stages existed on the corrosion process of Q235 steel in simulated concrete pore solution. The first step is the passivation state of Q235 steel in the initial immersion. In this stage, a passive film is formed and growth on the steel surface because of the alkalinity of concrete pore solution with pH value greater than 13. The second step is the initiation and development of pitting corrosion of Q235 steel because of the rupture of passive film by the penetration and diffusion of Cl⁻ ions in the concrete pore solution.

4. CONCLUSIONS

(1) During the initial immersion in simulated concrete pore solution, Q235 steel has a higher charge transfer resistance, film resistance, noise resistance and fractal dimension. Whereas with the immersion time larger than 48 hours, the charge transfer resistance, film resistance, noise resistance and fractal dimension of Q235 steel decrease greatly.

(2) During the initial immersion in simulated concrete pore solution, Q235 steel has a lower standard deviation σ_I , average charge q and correlation dimension. After the immersion time larger than 48 hours, the standard deviation σ_I , average charge q and correlation dimension of Q235 steel increase abruptly.

(3) Two distinct stages could be classified for the corrosion of Q235 carbon steel in simulated concrete pore solution, i.e. formation and growth of passive film (Cluster 1), breakdown of passive film and development of pitting corrosion (Cluster 2).

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