Study on diffusion of NaOH solution in zinc-rich epoxy coating using EIS

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Abstract. In order to explore the diffusion process of NaOH solution in zinc-rich epoxy coating, in this paper, conventional three-electrode system was used to test the open circuit potential and electrochemical impedance spectrum, and equivalent electric circuit was fitted to get the related parameters including capacitance, resistance, phase angle and et al to reveal the diffusion process. The results show that three stages are divided including diffusion in coating, finite layer diffusion and double layer diffusion, and two criterions are put forward.

1. Introduction

Due to the high density and bonding strength between the coating and metal, zinc-rich epoxy coating is widely used in metal anticorrosion. On the other hand, the zinc also provides cathodic protection for the metal substrate. However, with the increase of usage time, the diffusion of water/electrolyte solution in the coating and the electrochemical reaction process on the coating/metal interface will inevitably occur [1]. Therefore, it is of great significance for the study of clarifying the change of coating properties caused by water/electrolyte diffusion in zinc-rich epoxy coating and the electrochemical reaction process at the interface.

For a long time, a large number of scholars have discussed the diffusion process of NaCl solution and deionized water in epoxy coating on the basis of Fick diffusion, and established EIS (electrochemical impedance spectrum) models of water diffusion at different stages [2]. In terms of water/electrolyte diffusion of zinc-rich epoxy coatings, relevant scholars have studied the preparation, appearance and related morphologies of different types of zinc-rich epoxy coatings, but there are few reports on the EIS characteristics of zinc-rich epoxy coatings under alkaline conditions. Therefore, this article adopts the traditional three electrode system to research the diffusion process of zinc-rich epoxy coatings using electrochemical test, including OCP (open circuit potential) and EIS, to establish the models of diffusion and electrochemical reaction.

2. Formatting the title, authors and affiliations

The standard three-electrode system was adopted in the experiment, in which the working electrode was a piece with zinc-rich epoxy coating with a thickness of 30±5μm and an area of 6.25cm², reference electrode was saturated calomel electrode (SCE). Pt electrode worked as auxiliary electrode. Preparation of working electrode: the metal matrix was X80 steel in 25×25x2mm³. After the process of acetone degreasing - deionized water cleaning - anhydrous ethanol degreasing, the electrode was dried for 24h. Specimens was welded copper wires with epoxy resin encapsulation leaving exposed
area of 6.25cm² [3], then artificial coated with 70% zinc rich epoxy coating, tested the thickness of the normal temperature cooling after 48h.

Experimental conditions: Experimental solution was prepared by analytical pure NaOH and deionized water with a mass fraction of 3% was prepared, and the all experiment were carried out at a constant temperature of 25℃.

Electrochemical test was conducted using electrochemical workstation PARSTST2273. Firstly, the OCP test was conducted. When the OCP fluctuation did not exceed 3mV within 300s, the whole system was considered to be in equilibrium state for EIS test. In this paper, the average value under the equilibrium state is taken as the OCP in different time periods.

The range of test frequency in EIS was set as 100kHz~10mHz, and the disturbance voltage is 10mV. One set of experimental data was tested every 15 minutes. The data analysis was adopted by the PowerSuite and ZSimpWin software that came with the system. The experiment was repeated three times to ensure the accuracy. However, due to the complexity of the coating system, the data fitting results could not be completely consistent, but their change rules were highly consistent. Therefore, one group of experimental data was selected for analysis [4].

3. Results and discussion

3.1. Open circuit potential

Fig.1 shows the change curve of the OCP of the test sample with time. As can be seen from the figure, the OCP of the bare steel and coated samples was -0.38V vs.SCE and -1.24V vs.SCE, respectively, showing a great decrease. From the perspective of thermodynamics, the zinc-rich epoxy coating greatly reduced the driving force of metal corrosion, reflecting the corrosion protection of the coating on the metal. At the same time, along with time of the experiment in 15 min, the OCP decreased to -1.30V vs.SCE with a decrease of 0.6V vs.SCE, suggesting that the corrosive medium gradually diffused into the coating. However, the OCP moved positively with time, illustrating a decrease of protecting corrosion with an increasing OCP. When the experiment reached 45min, the rise trend of its OCP became significantly slow, which suggested that the solution might have reached the coating/metal interface and electrochemical reaction occurred.

![Fig.1 Open circuit potential over time](image)

3.2. Nyquist diagrams

Fig.2 shows the test results of EIS behaviour of coating at different diffusion stages. Tab.1 shows the fitting results [5].The solid line in the figure was the fitting curve, and the discrete point was the test data. As can be seen from the figure, the Nyquist plots were divided into three stages.

At the initial stage of solution diffusion (0~30min), the EIS characteristics of the coating showed a complete capacitive reactance arc, that is to say, its equivalent circuit was solution resistance in series with characteristic parameters, therefore, fitting circuit was chosen as \( R_c(R_cC_e) \). Considering the dispersion characteristics of the coating system, CPE(\( Q \)) is generally used to replace coating capacitor \( C_e \). As can be seen from the figure, with the development of diffusion, the radius of the capacitive reactance arc decreased gradually, presenting the \( R_c \) decreased gradually while the \( Q \) increased. Generally speaking, in relevant studies, the resistance of epoxy coating is generally \( 10^8 \sim 10^{10} \) orders of
magnitude, and when it drops to $10^6$ orders of magnitude, the coating has failed [6]. However, with the addition of zinc, the electrical conductivity of the coating was significantly enhanced, and the resistance of the coating was also significantly reduced. As can be seen from the data in the table, at the beginning of the spread, the resistance of the coating itself was $3.435\times10^4\Omega\cdot$cm$^2$, and gradually reduce to $1.161\times10^4\Omega\cdot$cm$^2$, because of the diffusion of NaOH solution. Meanwhile, it can be seen that the $Q$ for coating capacitance increased from $1.399\times10^5$F/cm to $4.256\times10^5$F/cm, while the dispersion coefficient of $n=0.51\sim0.59$ remained basically unchanged, indicating that the roughness of the electrode surface was equal to the uniformity of the distribution of corrosion current density in different test times [7], which had no impact on the test results.

When the experiment was carried out for 45min, the EIS showed obvious characteristics of double capacitive reactance arc and there were two time constants, which indicated that the solution had diffused to reach the coating/metal interface for electrochemical reaction and there was an obvious limited layer diffusion process. Therefore, the equivalent circuit was described by $R_c(Q(R_cO(C_{dlR_{ct}})))$ : the first time constant of $\tau_1=R_s-R_c$, representing the nature of the coating system, the second time constant $\tau_2=C_{dl}-R_{ct}$, reflecting the information on the coating/metal interface, and the element O in the fitting circuit represented the diffusion process of finite layers. At this point, it can be seen that the solution had diffused to the coating/metal interface and the electrochemical reaction has begun. However, it can be seen from the limited layer diffusion characteristics of dual capacitive reactance that the electrochemical reaction had just taken place at this time, and there was still no complete double electric layer formed on the metal surface, that is to say, no new concentration gradient layer was formed on the metal surface.

With experiment lasted for 60 min, the finite layer diffusion impedance characteristics disappeared, while there was an obvious Warburg impedance with $n=0.5$, illustrating a complete double electric layer on metal surface has formed. At this time, diffusion process on interface was controlled by the concentration gradient of the new layer, presenting that capacitance of electric double layer firstly increased quickly and then basically remained the same, while the charge transfer resistance greatly increased. In fact, when the solution diffuses in the epoxy coating without zinc, once the solution arrived at the coating/metal interface, the electrochemical reaction occurred: in cathode $O_2+2H_2O+4e^-\rightarrow4OH^-$, and in anode $Fe\rightarrowFe^{2+}+2e^-$. When the diffusion in the coating has been completed, the coating capacitance basically remain unchanged, and the coating stripping because of the accumulation of corrosion products to lead to the loss of adhesion between coating/metal. However, based on the fitted results of 45min~75min in this paper, it can be found that when the solution reached the coating interface, the coating capacitance first decreased and then increased. This was because a cathodic protection of Zn-Fe was formed: in anode $Zn\rightarrowZn^{2+}+2e^-$. On the other hand, the addition of zinc in coating system changed its nature, thus made the coating capacitance reduce, and with the consumption of zinc, the coating capacitance gradually increased [8].

![Fig.2 Nyquist diagrams over time](image)
### Tab.1 Fitted results of equivalent electric circuits

| Element | 0     | 15min | 30min | 45min | 60min | 75min |
|---------|-------|-------|-------|-------|-------|-------|
| $R_s$   | 269.9 | 184.7 | 157.5 | 141   | 129.5 | 117.7 |
| $Q/10^5$| 1.399 | 3.303 | 4.256 | 2.48  | 3.443 | 3.966 |
| $n$     | 0.5918| 0.5587| 0.5122| 0.5633| 0.5457| 0.5146|
| $R_c/10^4$| 3.435| 1.54  | 1.161 | 0.2035| 1.273 | 1.413 |
| $O/10^5$| -     | -     | -     | 2.588 | -     | -     |
| $B$     | -     | -     | -     | 0.142 | -     | -     |
| $W/10^3$| -     | -     | -     | -     | 1.162 | 2.98  |
| $C_{dl}/10^5$| - | - | - | 8.601 | 87.48 | 75.28 |
| $R_{ct}/10^4$| - | - | - | 1.554 | 2.714 | 5.115 |

#### 3.3. Bode plots

Fig.3 shows the change curve of phase Angle of coating with time. As can be seen from the figure, the phase Angle change can be divided into three distinct stages, meeting with the analysed results of Nyquist diagrams. In the first stage (0~30 min), the curve was only one peak, showing the characteristics of coating system, and its biggest phase Angle slightly decreased (44.7°→41°→39.9°) with time. Due to the addition of Zn, the phase Angle did not show the obvious characteristics of capacitive reactance (90°). In this stage, the maximal phase Angle frequency increased slightly (7.9Hz→13.7Hz→24Hz). As the experiment progressed to 45min, two significant time constants (two peaks) appeared, which indicated that the solution diffused to the interface and the electrochemical reaction began to occur. As the experiment reached the third stage (60min~75min), it indicated that the “peak” of the double electric layer was significantly shifted to the low frequency, and the maximal phase Angle and frequency basically remained unchanged in the third stage. At the same time, in the second and third stages, the maximal phase Angle and frequency representing the coating characteristics were also basically unchanged. The results were the same as those of Nyquist plots.

Thus, according to the above analysis, process of solution diffusion in zinc-rich epoxy coating are divided into three distinct phases: in the first stage with only one peak in Bode plots, its capacitance increases and the resistance is reduced, therefore time constant ($\tau_1=Q_c R_c=0.5$) keeps mostly unchanged. The second stage is the finite layer diffusion process on the coating/metal interface, which is manifested as the appearance of diffusion impedance $O$, and two obvious time constants appear in the Bode figure. The third stage is the electrochemical reaction process on the interface, which shows an obvious Warburg diffusion impedance. In the Bode figure, it shows that the peak value of the dual-electrical measurement features gradually moves to the low frequency, and basically does not change with time. However, due to the cathodic protection effect of zinc, the coating capacitance shows a characteristic of first decreasing and then increasing.

In conclusion, the appearance of limited layer diffusion impedance $O$ can be used as the judgment basis for the solution reaching the coating/interface, while the appearance of Warburg impedance can be used as the judgment basis for the complete formation of new concentration diffusion layer (double electric layer) on the metal interface.
4. Conclusion
The diffusion process of NaOH solution in zinc-rich epoxy coating is studied by electrochemical method, and two conclusions are drawn as follows.

(1) The diffusion process of NaOH solution in zinc-rich epoxy coating is divided into three stages: the first stage is the diffusion process of solution in the coating, which shows that the coating capacitance increases, the impedance decreases, and the time constant is basically unchanged. The second process is the finite layer diffusion process on the coating/metal interface, which shows that the Nyquist plot shows two apparent capacitive reactivity arcs and the Bode plot shows two peaks. The third process is the diffusion in the double-layer capacitor, which represents the maximal phase Angle of the double-layer capacitor moves to the low-frequency area. Due to the addition of zinc, the electrochemical reaction process with zinc as the anode mainly occurs.

(2) In this paper, it points out that the appearance of limited layer diffusion impedance O could be used as the judgment basis for the solution reaching the coating/interface, while the appearance of Warburg impedance could be used as the judgment basis for the complete formation of new concentration diffusion layer (double electric layer) on the metal interface.

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