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Electrochemical Investigation of Corrosion Behavior of Epoxy Modified Silicate Zinc-rich Coatings in 3.5% NaCl Solution

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Abstract: In order to develop waterborne silicate anticorrosive coatings to replace solvent-based anticorrosive coatings used widely in ship's industry, epoxy modified silicate emulsions were synthesized with different content of epoxy resin, then aqueous silicate zinc-rich coatings were prepared with synthesized silicate emulsion, triethylamine and zinc powder. The influence of the content of epoxy on the properties and chemical structure of modified emulsion, mechanical properties of silicate coatings, and the corrosion behavior of silicate zinc-rich coatings in 3.5% NaCl solution were investigated. The coating samples on steel were measured by immersion test, Tafel polarization test and electrochemical impedance spectroscopy (EIS) test with different immersion time. The results showed that epoxy modified silicate emulsions were successfully synthesized. With the increase of epoxy content, the viscosity and the solid content of modified emulsion increases, the impact resistance of the silicate coating raises, the pencil hardness decreases, but the adhesion is not affected. Epoxy modification can reduce to s certain extent the corrosion driving force of zinc rich coating and increase the impedance of the zinc-rich coating decreases with the increase of immersion time in 3.5% NaCl solution. With the increase of the epoxy content, the resistance value of the zinc-rich coating increases, indicating the ability of the coating to resist corrosive media is enhanced.

Keywords: anticorrosive; zinc-rich; coating; epoxy; silicate emulsion

1. Introduction

To prevent the seawater corrosion of ship's hull during its navigation, anticorrosive coatings is always used in the world. The mechanism of the anti-corrosion coating is realized through the isolation shielding effect, the passivation and corrosion inhibition, and the sacrificial anode protection cathode effect [1 ,2]. However, most of the anticorrosive coatings still use solvent-based anticorrosive coatings [3]. Zinc-rich epoxy coatings [4, 5] are usually used as a primer coating, which is very important for general atmosphere and ocean environment has good corrosion resistance [6]. Using zinc powder as a sacrificial anode type filler in zinc rich coating, which with more negative corrosion potential than the protected substrate, it plays a cathodic protection role on the substrate. However such coatings will release a large amount of toxic volatile organic compounds (VOCs) during its application [7]. This organic substance will produce photochemical smog and acid rain under ultraviolet radiation, causing serious pollution and damage to people's lives and the environment. Therefore, with the improvement of people's quality of life and the enhancement of environmental awareness, countries around the world have formulated laws and regulations to limit VOCs emissions, so anticorrosive coatings will inevitably develop in the direction of energy saving, low pollution and high performance. Based on this, water-based ones will become the focus of future development of anticorrosive coatings. This is because water is used as solvent in water-based anticorrosive coatings, and the introduction and emission of VOCs are avoided directly from the

pollution source. There are many types of water-based anticorrosive coatings, mainly including epoxy, acrylic and inorganic zinc silicate coatings, among them, water-based epoxy coatings and water-based inorganic zinc-rich coatings have been successfully industrialized [8]. Water-based inorganic zinc-rich coatings are mainly composed of film-forming base materials (including inorganic polymers such as silicates, phosphates, and dichromate) and zinc powder. It has excellent performance in terms of conductivity, weather resistance and solvent resistance [9,10]. The current research is mainly focused on the silicate series, but water-based silicates have disadvantages such as having more pores on the surface, poor shielding effect, and large brittleness of the coating. In the process of dehydration polycondensation, the cohesion increases with the increase of film thickness, it is easy to cause the coating to crack or even fall off in a large area. And epoxy resin has good flexibility [11], and high permeability can make up for the porosity defects of water silicate coatings [12, 13], and epoxy resin itself has excellent corrosion resistance, therefore, in this paper, epoxy resin is used to modify the silicate emulsion to decrease the brittleness and to improve the impact resistance and the corrosion resistance of the water-based silicate coating.

2. Materials and Methods

2.1 Materials

3-aminopropyltriethoxysilane (LT-550) was obtained from Hubei New Blue Sky Material Co, Ltd. Its purity specification is analytically pure. E777-2 (nano-modified waterborne inorganic zinc-rich resin) was purchased from Wuhan Modern Industrial Technology Research Institute and its purity specification is chemically pure. Epoxy 618(E51) is obtained from Nantong Xingchen Synthetic Material Co, Ltd, and its purity is chemically pure. Zinc powder is purchased from Jiangsu Kechuang Metal New Material Co, Ltd. and its specification is 500 meshes.

2.2 Preparation process and Reaction principle

2.2.1 Synthesis of epoxy modified silicate emulsion

Controlling the content of epoxy resin respectively is 10%, 20%, 30%, 40%, and 50%, to prepare five epoxy modified silicate emulsions (Component A). The content of epoxy resin refers to the ratio of the mass of epoxy resin to the sum of the mass of epoxy resin and water-based silicate resin. Their formulations were listed in Table 1. The first stage is to use LT550 to modify epoxy resin; the second stage is the reaction between the hydroxyl group produced by the hydrolysis of LT550 and the aqueous silicate. The reaction principles of epoxy modified silicate emulsion were shown in Figure 1 and Figure 2[14]. The specific process was as following. First, pour LT550 and E51 into a 500 mL metal mixing tank at a certain ratio, stir with a BGD750 sand mill dispersing and mixing multi-purpose machine for 5 minutes, and after it is evenly dispersed, then add E777-2, and finally dispersed at a speed of 1000 rpm for 15 minutes, after the dispersion is completed, the mixture is poured into a clean white plastic box.

Table 1. Formulation of epoxy modified silicate emulsion

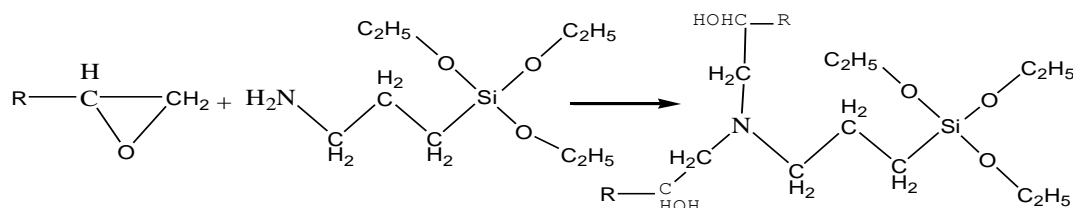| Raw materials / wt.%	G10	G20	G30	G40	G50
E51	9.5	18.1	26	33.3	40
LT550	5.0	9.5	13	16.7	20
E777-2	85.5	72.4	61	50	40

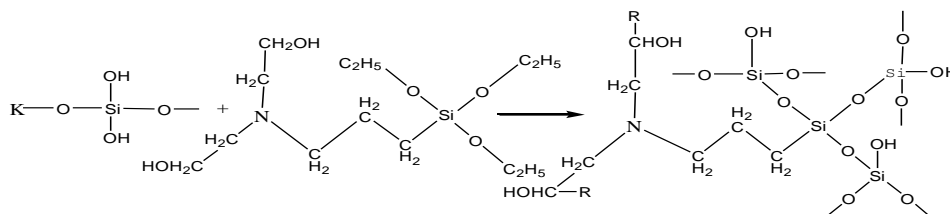**Figure 1** Epoxy reacts with LT550

Figure 2 Reaction of silicate with grafted epoxy

2.2.2 Formulation and preparation of zinc-rich coating

To ensure a good electrical contact between zinc particles and cathodic protection for steel substrate, 1 high pigment concentration of 92 wt% zinc powder is required in the dry film [15]. The anticorrosive zinc-rich paint was prepared as following composition. It consists of three components. Component A is silicate emulsion E777-2 or epoxy modified silicate emulsion prepared as above-mentioned. Component B is triethylamine. Component C is 500 mesh zinc powder. The mixture ratio of three components is Component A: Component B: Component C=100:1.25:233 according to the mass ratio. They were mixed and then coated and cured on steel plate for 60 μm dry film thick (DFT). The preparation process of the coating was performed with BGD 750 multifunction high speed dispersing machine. Add component A and component B to a 500 mL metal stirring tank at a speed of 500 r / min, add zinc powder to the stirring tank according to the amount in the formula, then increase the speed to 1500 r / min and stir for 15 min. Finally, the prepared coating was brushed on the surface of a steel plate with a size of 150 mm × 70 mm × 1 mm which was polished with 100 mesh sandpaper and washed with absolute ethanol. N0 represents water-based silicate zinc-rich coatings, and the coatings prepared with the epoxy modified silicate emulsions listed in table 1 were denoted by G10, G20, G30, G40 and G50.

2.3. Measurement and Characterization

2.3.1 Fourier transform infrared spectroscopy

The emulsion samples were tested by the attenuation total reflection (ATR) method with FTIR from PERKINELMER, USA. The scanning range is 4000-650 cm^{-1}, the resolution is 2 cm^{-1}, and the number of scans is 32 times.

2.3.2 Determination of solid content

The aluminum foil box was dried in a 140°C vacuum drying box for 20 minutes and cooled to room temperature, the box is weighed and its mass was recorded as m_1. Then the modified emulsion was added to the box, weighed it and recorded the mass as m_2, and placed it in a 140°C vacuum drying box, dry it for 1h, and then cooled again to room temperature, weigh the box with dried modified emulsion, record it as m_3, then the solid content =100%× $(m_3-m_1) / (m_2-m_1)$.

2.3.3 Basic mechanical properties

According to GB/T 1720-89, the adhesion of anticorrosion coatings was evaluated by spiral scoring method and the film adhesion tester (QFZ-II). According to GB/T6379-2006 and GB/T1732-93,

the pencil hardness and impact strength of anticorrosion coatings were evaluated by pencil-scratch hardness tester (QHQ-A) and paint film impactor (QCJ) respectively.

2.3.4 Film thickness measurement

The thickness of each sample was measured using a QuaNix 7500 coating meter, and each sample was tested at 5 points, the mean was reported in this paper.

2.3.5 Immersion test in 3.5% NaCl solution

The surface of the steel plate with a size of 150 mm × 70 mm × 1 mm was polished with 100-mesh sandpaper and washed with absolute ethanol, then it was painted with the prepared aqueous silicate zinc-rich coating and edge-sealed with epoxy resin. Then it was immersed in 3.5% NaCl solution, the test temperature is $23 \pm 2\,℃$. On the third day, the seventh day, the tenth day and the fourteenth day, the samples were taken for observation and electrochemical measurement.

2.3.6 Electrochemical test

The polarization curve and electrochemical impedance spectroscopy (EIS) were performed using a ZAHNER IM6ex electrochemical workstation with a Coating & Laminate Tester (COLT) module under a two-electrode system, the sample plate is the working electrode and the a shielded cylinder copper electrode is the counter. The detailed test operation can be found in Reference [16].The contact area between the coating and the corrosive medium (3.5% NaCl solution) was 19.625 cm^2, and the measurement range of the polarization curve was -200 mV to 200 mV, scanning speed is 1 mV/s, EIS with a perturbation potential of 10 mv and a frequency range of 100 mHz to 100 kHz. The test results were treated using Z2.03 USB software and then analyzed using ZSimp Win3.2.1 software.

3. Results

3.1 Emulsion properties

All silicate emulsions present cream color, as shown in Figure 4. Their viscosity was measured by NDJ-1 rotational viscometer. The viscosity of the silicate emulsion purchased is 10 mPa·s, the viscosity of the epoxy modified silicate emulsion with 10%, 20%, 30%, 40% and 50% epoxy content is respectively 19.5 mPa·s, 40.5 mPa·s, 54 mPa·s, 60 mPa·s and 70 mPa·s. It clearly shows that the viscosity of the modified emulsion increases due to the introduction of epoxy resin. The pH value before and after modification was measured with a precision pH test paper. The results showed that the pH of the emulsion before and after the modification hardly changed, and both showed alkaline. In addition, the solid content of modified emulsion increases linearly with epoxy content and higher than that of silicate emulsion. The solid content of silicate emulsion is above 27%. While the solid content of modified emulsion with epoxy content 10%, 20%, 30%, 40% and 50% is respectively more than 28%, 33%, 37%, 40% and 43%.

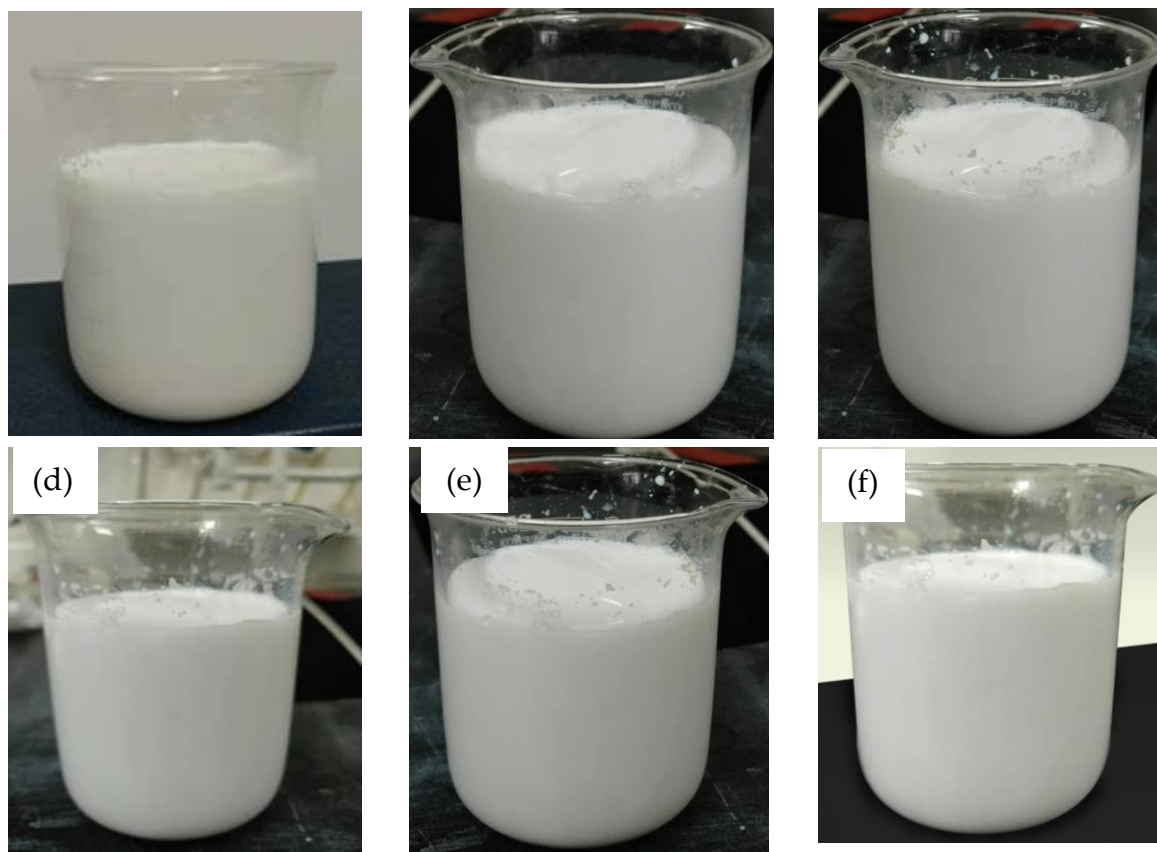(a)   (b)   (c)

Figure 4 Photos of studied emulsions with different epoxy contents (a) 0; (b) 10%; (c) 20%; (d) 30%; (e) 40%; (f) 50%

3.2 Chemical structure

Measured FTIR spectrum were showed in Figure 5(a) for silicate emulsion, Figure 5(b) for the reaction product of LT550 and E51, and Figure 5(c) for the epoxy modified silicate emulsion. It can be seen that there are Si-OH peaks in the intermediate product of the reaction between the silicate emulsion and LT550 and epoxy resin, and the Si-OH peak disappears in the modified silicate emulsion, indicating that Si-OH participates in the reaction and was consumed, and the peak position of the modified silicate at 1108 cm^{-1}, which is because the Si-O-Et (near 963 cm^{-1}) in the LT500 added during the modification became a Si -O-Si bond. Therefore, it is proved that epoxy modified silicate emulsion has been successfully synthesized.
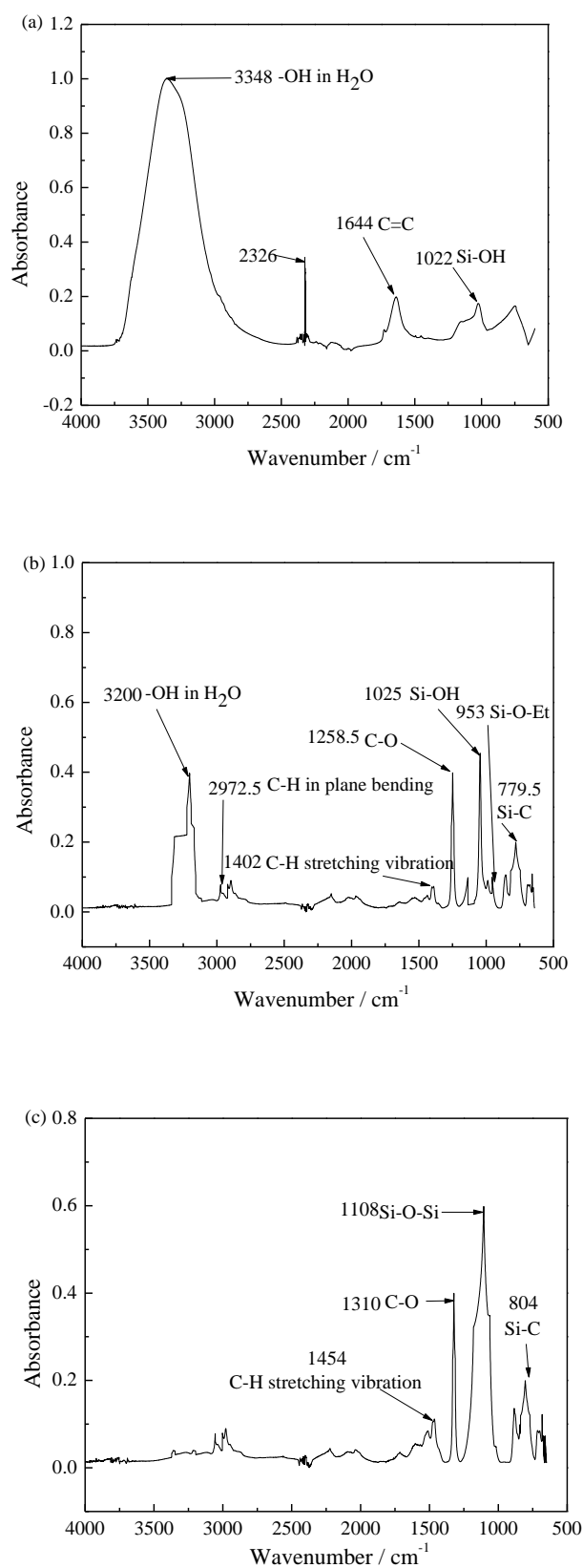
Figure 5 FTIR spectrum (a) Silicate emulsion E777-2; (b) Product of LT550 modified E51; (c) Modified silicate emulsion with 20% epoxy

3.3 Basical properties of the silicate coatings

Measured results showed that the average dry film thickness of each coating is between 58-65 μm，all coatings have the best adhesion (grade 1). With the increase of epoxy content from 10% to 50%, the hardness decreases from 6H to 4H. The impact resistance of epoxy modified silicate coating higher than that of silicate coating (30 kg·cm) and it increases with epoxy content. Once the epoxy content reaches 20%, as shown in Figure 6, the impact resistance of epoxy modified silicate coating can reach the maximum measurement value (50 kg·cm). This shows that the introduction of epoxy resin can improve the impact resistance of silicate coating.
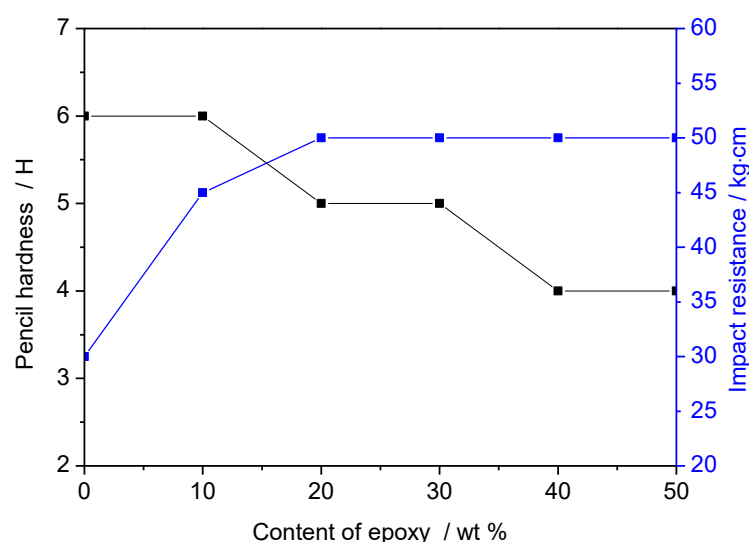
Figure 6 Hardness and impact resistance of studied coatings with epoxy content

3.4 Corrosion performance of the coatings

3.4.1 Effect of epoxy content on corrosive performance

Figure 7 shows the photos of the six coatings before immersion in 3.5% NaCl solution. The results of Tafel polarization curves were shown in Figure 8(a). The self-corrosion potential of the silicate zinc-rich coating is -0.427 V. The open potential of the modified coating G50 is about -0.4 V. As the epoxy content increases, the open potential of modified coating shows overall an increasing trend (Figure 8(b)), this is because the surface of the silicate coating is porous, and the adding epoxy resin results in increasing the solid content of modified emulsion and a denser coating. It makes less hollow in modified coating. With the increase of epoxy content, more and more micropores are covered by epoxy resin, which increases the self-corrosion potential of the coating. It also leads to an increase in the impedance of modified coating, as shown in Figure 9. With the increase of the epoxy content, although the resistance value of the coating shows an overall upward trend, Z_{G50}> Z_{G40}> Z_{G30}> Z_{G20}> Z_{G10}> $Z_{N0,}$ indicating the ability of the coating to resist corrosive media is enhanced. The main reason for this difference is that the solid content of epoxy modified emulsion increases with epoxy content, higher the solid content of the emulsion is, higher the compactness of the coating is under the same composition. Because the solid content of modified emulsion increases with epoxy content and higher than that of silicate emulsion. The solid content of silicate emulsion is above 27%. While the solid content of modified emulsion with epoxy content 10%, 20%, 30%, 40% and 50% is respectively more than 28%, 33%, 37%, 40% and 43%. However, the impedance of the coating is only about 10^5 Ω·cm², which indicates that the zinc rich coating does not have good shielding and isolation performance, and has good conductivity characteristics, that is to say, the zinc powder has good contact conductivity and acts as sacrificial anode. Two-time constants exist immediately in Bode and Nyquist diagram of the zinc-rich coatings after the immersion test for 0.5 h, as shown in Figure 10, it indicates that it shows that after

the coating is immersed in 3.5% NaCl solution, the anodic dissolution reaction immediately occur in zinc powder on the surface of the zinc-rich coating, which plays the role of sacrificial anode to protect the steel. The radius of capacitive arc of N0 coating in Nyquist diagram is least, which indicates that the impedance of the coating is low and the barrier effect on the medium is poor. The radius of capacitive arc and the impedance of epoxy modified coating become more and more with the increase of epoxy content, which indicates that the barrier effect of G50 coating is best on 3.5% NaCl solution.

Figure 7 The photos of the coatings before immersion test
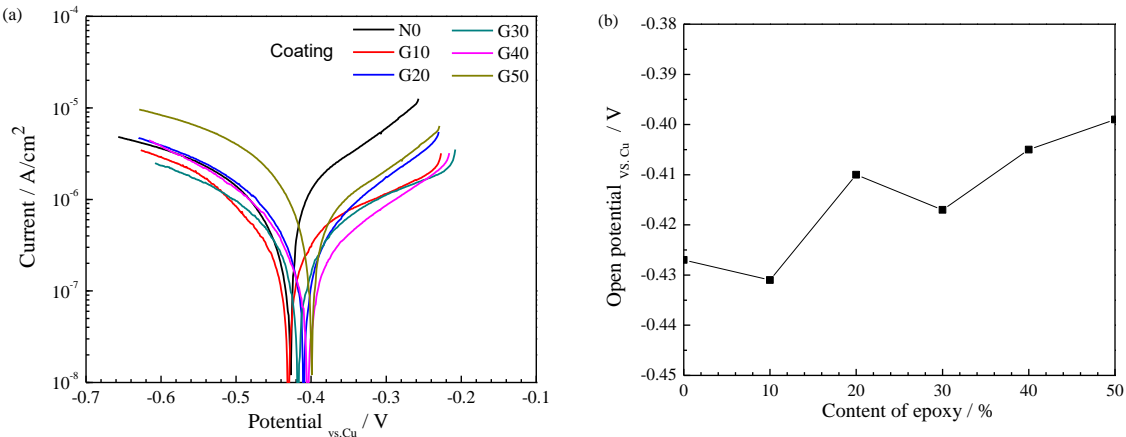
Figure 8 Polarization test results (a) Open potential of coatings (b) Tafel curves of zinc-rich coatings
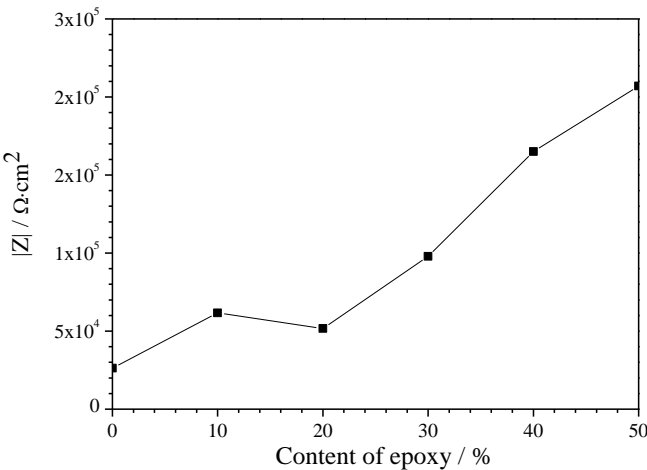
Figure 9 Impedance of zinc-rich coatings with epoxy content
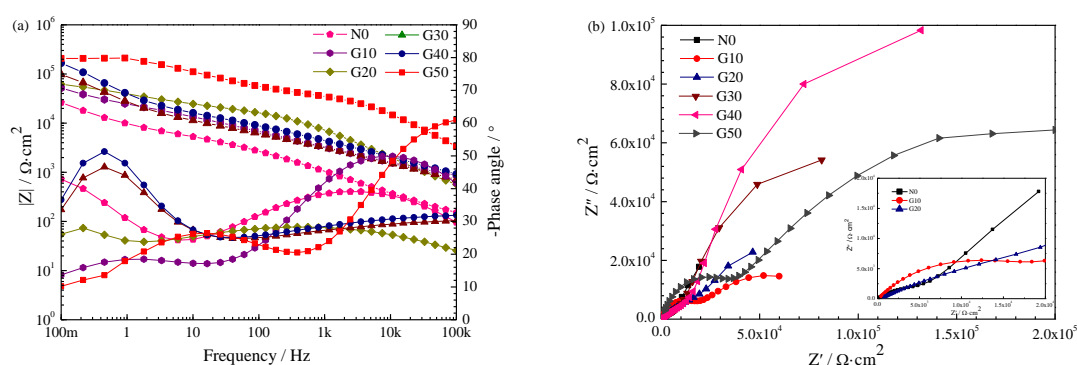
Figure 10 EIS plots of the coatings (a) Bode (b) Nyquist

3.4.2 Corrosive performance of coatings with immersion time

The pictures of six samples immersed in 3.5% NaCl solution for 336 hours were shown in Figure 11. Some red-brown rust spots began to appear on the surface of the silicate coating N0 and G10, in which a small amount of white flocculent corrosion products began to appear in the saline-soaked area. The evolution of self corrosion potential of each coating sample with immersion time is shown in Figure 12. For unmodified silicate coating N0, its open potential increases with immersion time. However, the open potential of the epoxy modified silicate coating decreases during 72 h, then increases continuously. The increase of potential decreased with the increase of epoxy content. This shows that epoxy modification can reduce to a certain extent the corrosion driving force of zinc rich coating. Similarly, as shown in Figure 13, the impedance of unmodified silicate coating N0 decreases hardly, however the impedance of the epoxy modified coating decreases obviously with the increase of immersion time. For example, the impedance of unmodified silicate coating N0 decreases from 10^4 $\Omega \cdot cm^2$ at the beginning of 0.5 h to 10^4 $\Omega \cdot cm^2$ after 72 h immersion; the impedance of G30 coating decreases from 10^5 $\Omega \cdot cm^2$ at the beginning of 0.5 h to 6×10^4 $\Omega \cdot cm^2$ after 72 h immersion. the impedance of G50 coating decreases from 2×10^5 $\Omega \cdot cm^2$ at the beginning of 0.5 h to 10^5 $\Omega \cdot cm^2$ after 72 h immersion. The coating's impedance decreased rapidly at the beginning of immersion test and then slowed down. The degree of decline increases with the increase of epoxy content. With the further prolongation of immersion time, the impedance of the coating is gradually decreasing. After 168 h, the impedance of G30 coating is maintained at 10^4 $\Omega \cdot cm^2$. The impedance of G50 coating decreased continously from 2.5×10^4 $\Omega \cdot cm^2$ after 168 h immersion to 2.2×10^4 $\Omega \cdot cm^2$ after 240 h immersion, and then remained unchanged. It shows that epoxy modification can increase to a certain extent the isolation effect of zinc rich coating on corrosion medium.

Bode and Nyquist diagram of all coatings with different immersion time were shown in Figure 14. From the beginning of immersion test to 168 hours, the Nyquist diagram of each coating shows two time constants, the zinc powder in the coating starts to react with NaCl solution and provides cathodic protection for the steel. The semicircle in the high frequency domain represents the impedance and capacitance of the coating, and the semicircle in the low frequency domain represents the impedance and capacitance of the zinc dissolution reaction. The impedance arc radius of each coating decreases rapidly with the increase of immersion time.
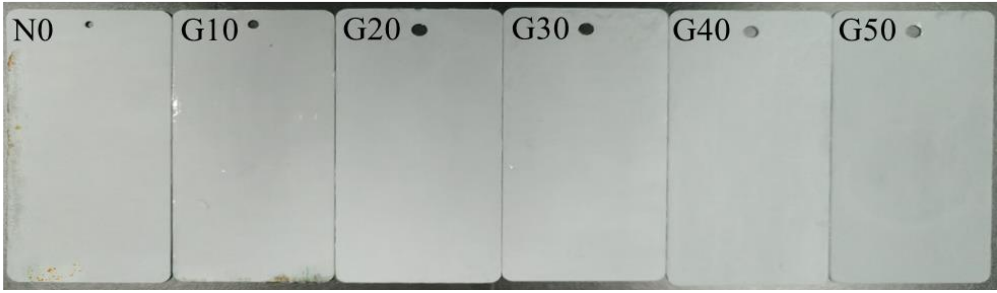
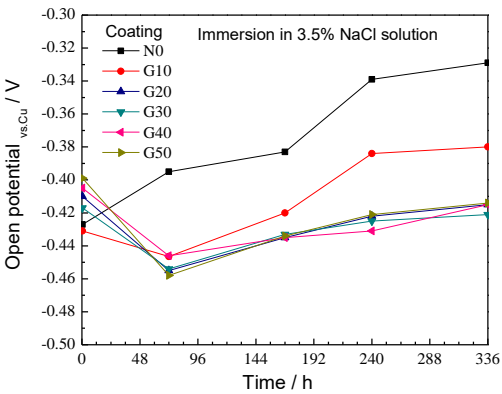**Figure 11** Photos of the coatings immersed in 3.5% NaCl solution for 336 hours

Figure 12 Evolution of coating sample self-corrosion potential with immersion time in 3.5% NaCl solution
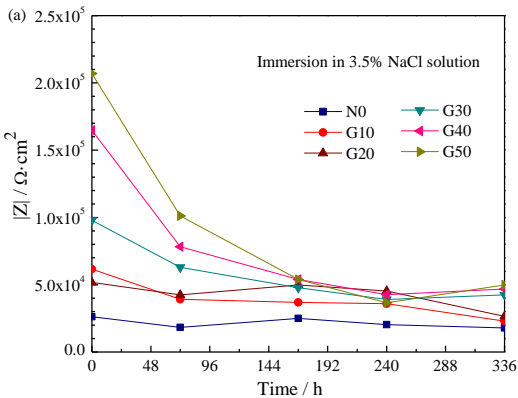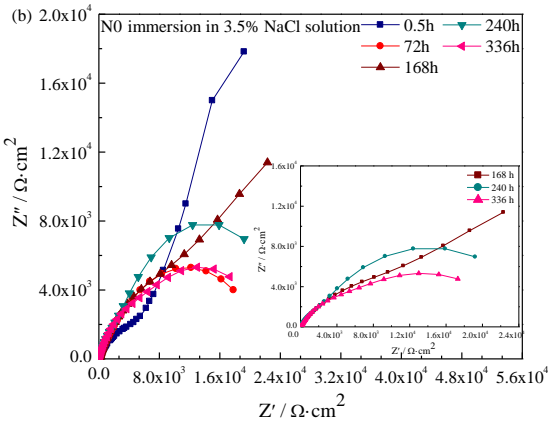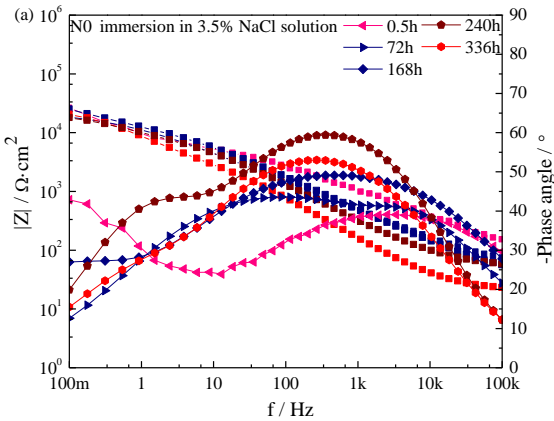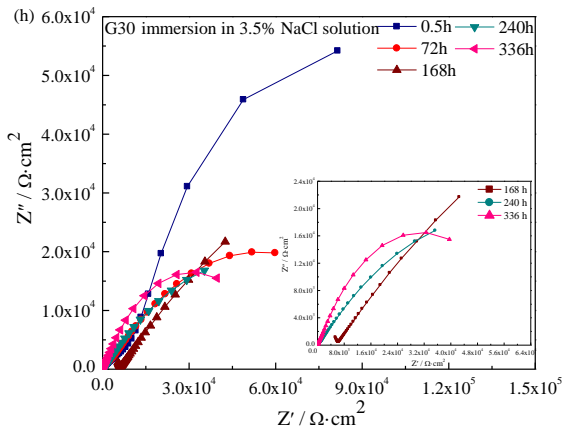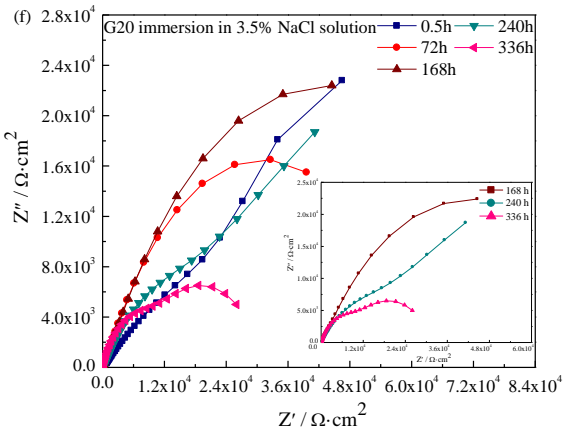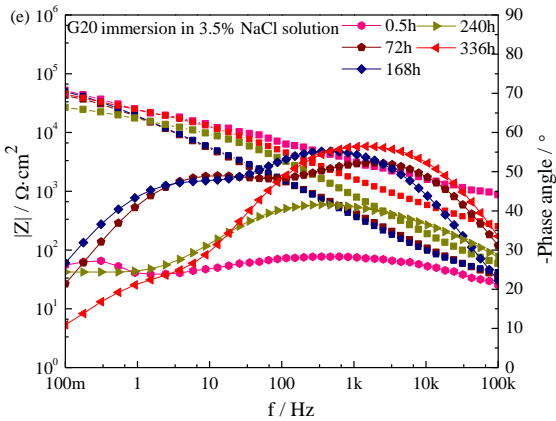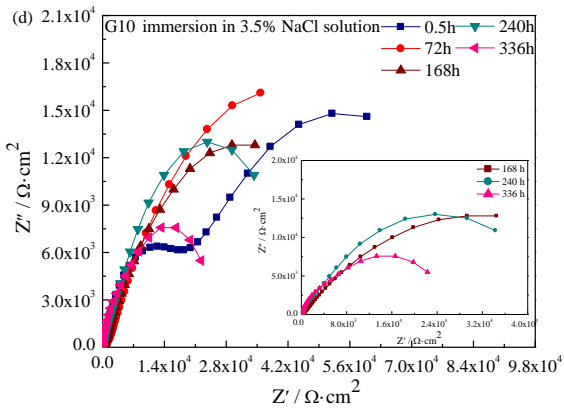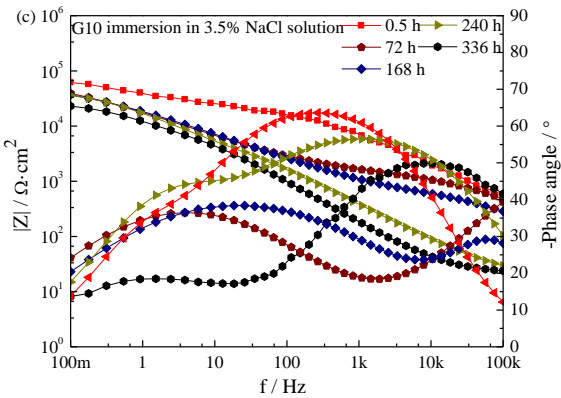

Figure 13 Impedance change of the coatings immersed in 3.5% NaCl solution
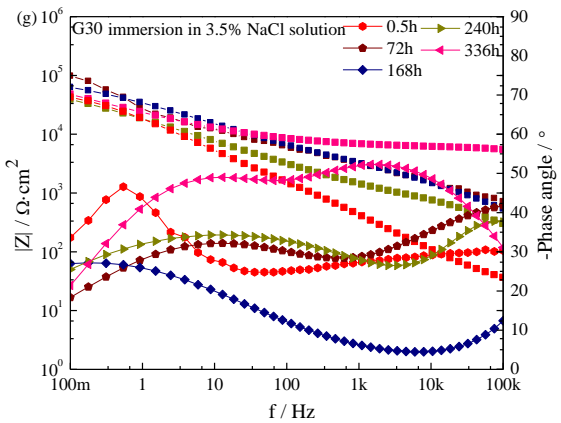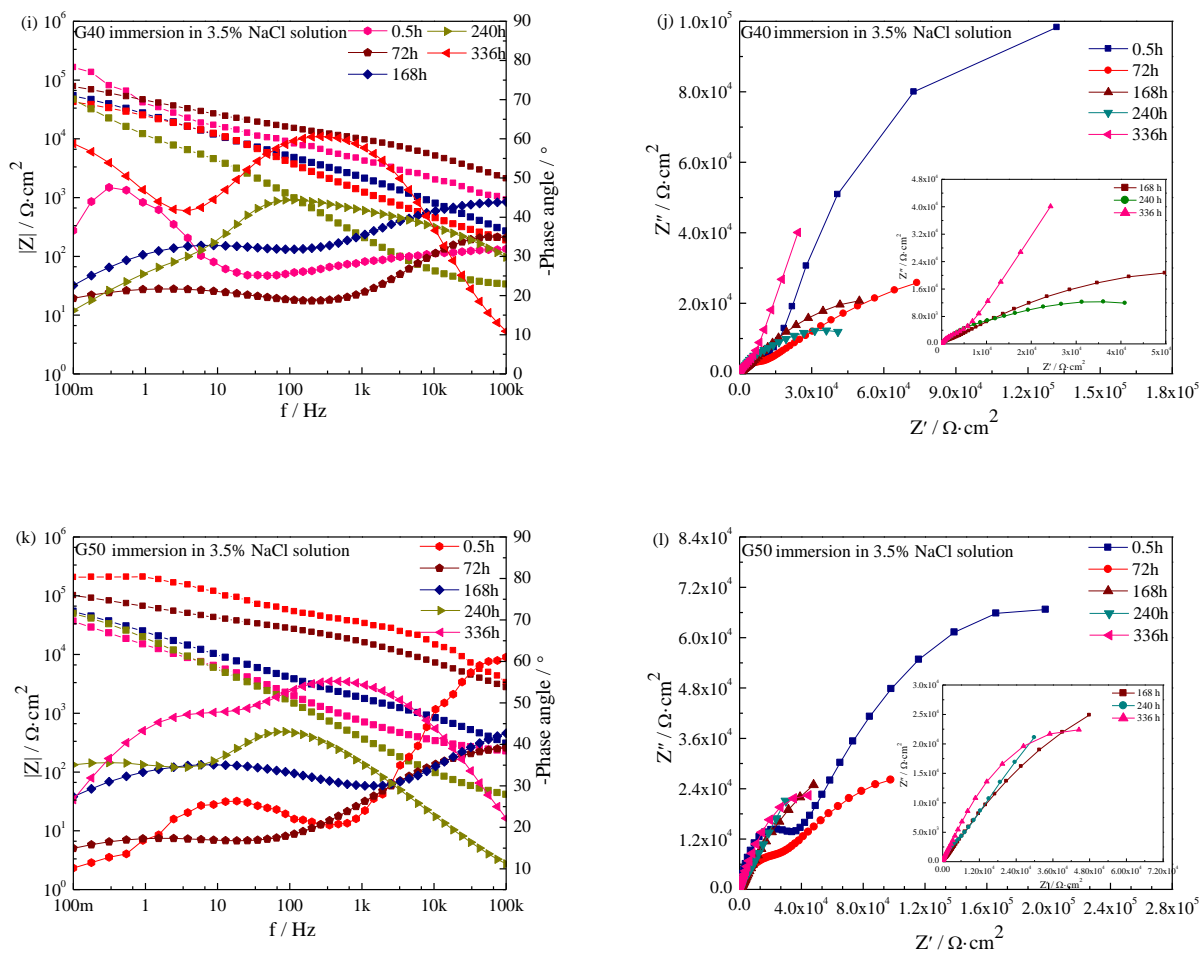
Figure 14 Bode and Nyquist diagram of the coating immersed in 3.5% NaCl solution at different times

3.4.4 Analysis of electrochemical parameters of coating equivalent circuit

Based on above results, the Nyquist and Bode diagrams in Figure 14 of the coating samples immersed in 3.5% NaCl solution for different times, the impedances of the six sample coatings are about 10^5 $\Omega\cdot cm^2$ at the initial stage of corrosion, and their impedance is in turn $Z_{G50} > Z_{G40} > Z_{G30} > Z_{G20} > Z_{G10} > Z_{N0}$. There are two time constants in Nyquist diagram, one related to the resistance (R_c) and capacitance (Q_c) of the coating, appear at the high frequency end; the other is related to the corrosion reaction resistance (R_P) and the capacitance (Q_{dl}) of electric double layer on zinc, which appear at the low frequency end, and n_1 and n_2 are constant phase angle indexes, which indicate the degree of dispersion effect [17].

With the prolongation of immersion time, as shown in Figure 13 and Figure 14, the impedance of the coatings continues to decrease. In order to better explain the corrosion process of the coating, this paper uses R (QR) (QR) (Figure 15) equivalent circuit diagram to fit the electrochemical impedance data till the steel begins to corrode. Typical fitting results were shown in Figure 16. The results show that the equivalent circuit can reproduce the measurement results and capacitive reactance characteristics of EIS. Figure 17 is the change curve of coating resistance, coating capacitance and product resistance and capacitance of Zn powder reaction with immersion time. Both R_C in Figure 17(a) and R_p in Figure 17(b) of the coating decreases with the increase of immersion time, it shows that one hand the substrate steel is always at the state of cathodic protection by zinc powder, on the other hand the corrosion products of zinc reaction fail to form a

compact and continuous passivation layer and will not block the passage of corrosive medium into zinc rich coating during immersion test.

The double layer capacitance (Q_{dl}) can reflect the degree of zinc reaction in coating. The larger the degree of zinc reaction is, the greater the double layer capacitance. Figure 17(c) shows that the degree of zinc reaction increases during immersion. Compared with N0 silicate coating, epoxy modified coatings have lower Q_{dl}, i.e. lower zinc reaction and Q_{dl} of the epoxy modified coatings decreases with epoxy content.

Similarly, the coating's capacitance (Q_C) can reflect the water absorption of the coating. The larger the water absorption of the coating is, the greater the coating capacitance, the worse the protective performance of the coating. Figure 17(d) shows that the water absorption of the coating increases during immersion. Compared with N0 silicate coating, epoxy modified coatings have lower Q_c, i.e. water absorption and better protective performance, and Q_c decreases with epoxy content.
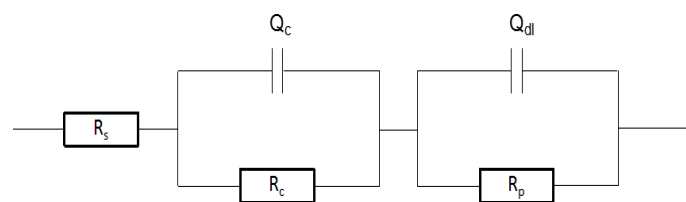
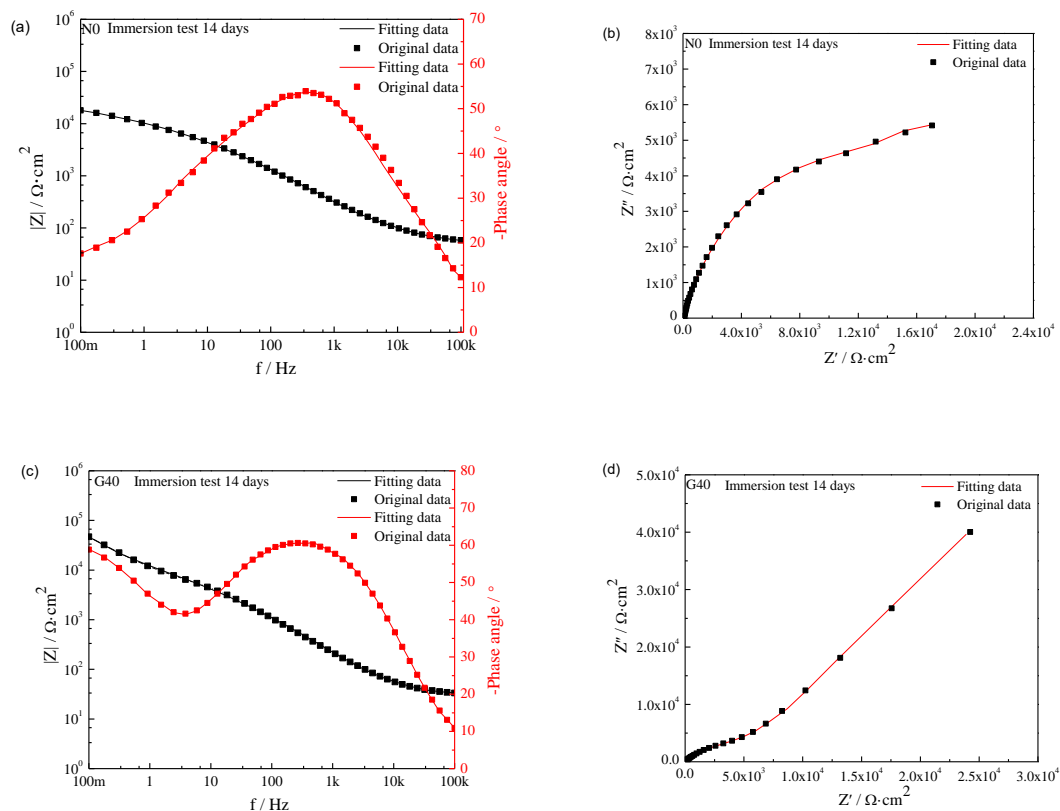**Figure 15** Equivalent circuit for fitting the EIS data

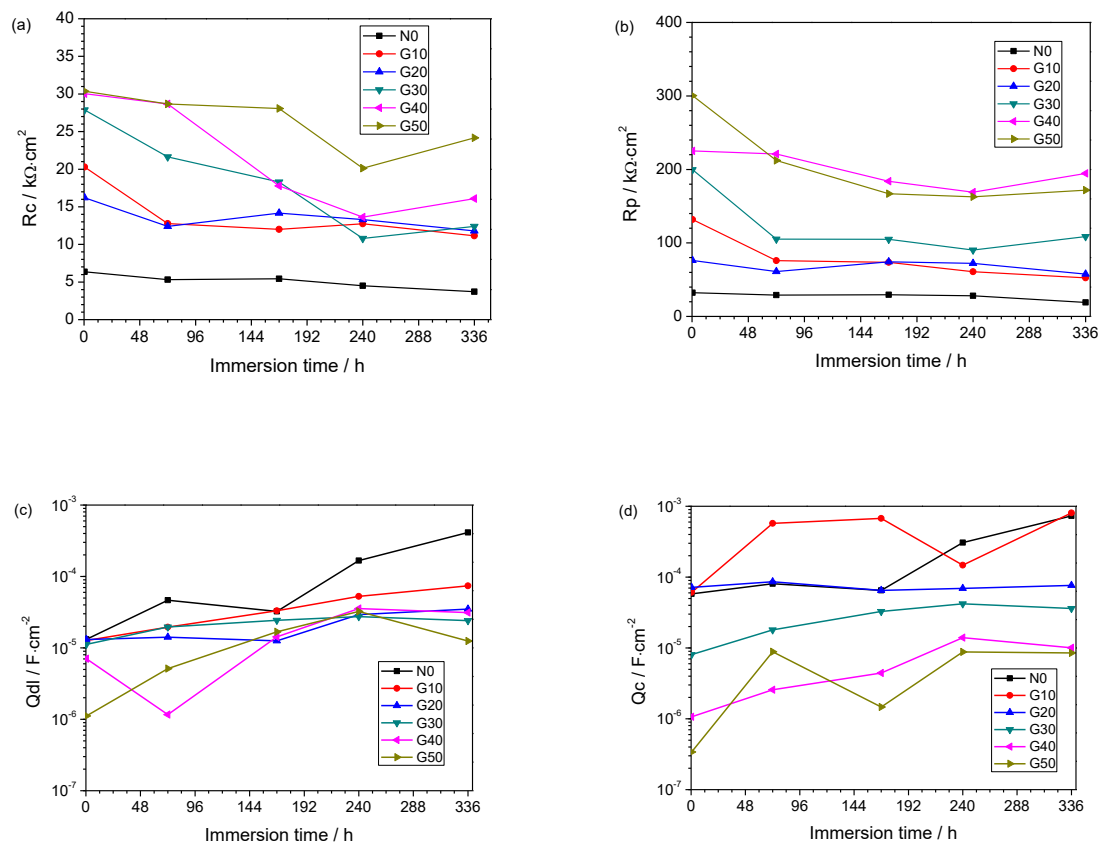**Figure 16** Comparison of typical EIS and fitting results

Figure 17 Variation of resistance and capacitance with immersion time in 3.5% NaCl solution

3.5 Anticorrosive mechanism of zinc rich coatings

The data from static immersion and electrochemical tests show that compared to silicate zinc-rich coating N0, epoxy-modified silicate coatings have good compactness, long cathodic protection time to the steel, and good corrosion resistance.

The corrosion failure process of the N0 coating is as follows: during early immersion to 72h, the corrosive medium quickly entered the coating and reached the surface of the steel. The steel get mainly cathodic protection by zinc powder. With the increase of immersion time, the corrosion products of zinc powder block the medium into the channel. At this time, the cathodic protection and the shielding effect of the coating corrosion products together protect the substrate effect [18]. The presence of an appropriate amount of epoxy resin can delay the process of corrosive media penetrating of zinc rich coating and to the interface between coating and steel substrate, and prolong the cathodic protection time of zinc-rich coatings. Compared with silicate zinc-rich coating, epoxy-modified silicate zinc-rich coatings have better compactness, more significant shielding effects and cathodic protection effects, and better protection against corrosive media.

4. Conclusions

In this paper, epoxy modified silicate anticorrosive coatings have been prepared and their properties were studied. The conclusions can be summarized as follows:
  (1) Epoxy modified silicate emulsions have been successfully synthesized. The viscosity and solid content of modified emulsion increases with epoxy content.
  (2) Compared with silicate coating, epoxy modified silicate coatings have the best adhesion (grade 1), lower hardness and higher impact resistance, more compact and better durability.

(3) The impedance of the silicate zinc-rich coating is 3×10^4 $\Omega\cdot cm^2$, it increases with epoxy content in modified silicate zinc-rich coating, that of G50 coating is only about 2×10^5 $\Omega\cdot cm^2$. Modification with epoxy does not harm the sacrificial anode effect of zinc powder in the coating.

(4) Epoxy modified silicate zinc-rich coatings have better shielding and isolation performance, and can provide longer protection lifetime than that of silicate ones.

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Conflicts of Interest: The authors declare no conflict of interest.

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