Preparation and Electrochemical Properties of Graphene/Epoxy Resin Composite Coating

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Abstract. The multilayer graphene powder as filler, epoxy modified silicone resin as film-forming agent, anticorrosion composite coating has been created using sand dispersion method, the electrochemical performance was compared with different content of graphene composite coating and pure epoxy resin coating. The open circuit potential (OCP), potentiodynamic polarization curves (Tafel Plot) and electrochemical impedance spectroscopy (EIS) were tested. The test results showed that the anti-corrosion performance of multilayer graphene added has improved greatly, and the content of the 5% best corrosion performance of graphene composite coating.

1. Introduction

Epoxy resin is a thermosetting resin [1-3] has excellent mechanical, thermal, mechanical, bonding, insulation and anticorrosion performance, widely used in aerospace, automotive, construction and marine chemical industry [4-6], is an indispensable material basis. However, with the modern life and industrial anti-corrosion performance requirements getting higher and higher, the traditional epoxy coating effect of anti-corrosion has been difficult to achieve environmental protection requirements. At present, many studies have found that through the modification of epoxy resin and add high-performance anti-corrosion filler can further enhance its anti-corrosion properties.

Graphene is a single atom layer crystal with a carbon atom bound by sp^2 and was first prepared in 2004 [7]. Graphene has excellent chemical stability, high conductivity, outstanding mechanical properties and corrosion resistance [8,9] has broad application prospects in the field of corrosion protection coatings. The stable layered structure of graphene enables the formation of a stable physical barrier between the base metal and the active medium to prevent diffusion and permeation. Bunch et al [10] in the study of graphene preparation of small sealed "balloon" found that graphene can effectively hinder the passage of gas atoms; Secondly, graphene has good thermal stability and chemical stability, no matter under the condition of high temperature (up to 1500°C [11]) or in the gas corrosive or oxidizing and liquid environment can maintain the stability, which makes graphene as an excellent protective coating material.

In this paper, epoxy resin as film-forming agent, multilayer graphite as auxiliary filler, adjust the graphene prepared in different proportions of graphene/epoxy resin composite coating adding system, improve the graphene in coating the uniformity and stability of dispersing agent. Different proportions of graphene/epoxy resin composite coating were prepared by adjusting the amount of graphene, adding dispersants and other additives to improve the graphene in the coating system uniformity and stability. The homogeneity and stability of graphene in the coating system was improved by adding additives such as dispersants. The coating preparation and coating process was optimized to prepare the finished product on a 304 stainless steel plate to form a coating. The open circuit potential (OCP), the

potentiostatic polarization curve (Tafel Plot) and the electrochemical impedance spectroscopy (EIS) of the coating were measured, the influence of the addition of graphene on the basic properties and corrosion resistance of the coating was discussed and the corrosion mechanism of the coating was discussed.

2. Experimental Part

2.1. Raw Materials and Instruments
Multilayer graphene (>95%) was from Suzhou Hengqiu graphene technology company. Epoxy modified silicone resin (industrial grade) was from Chongqing Hao Chenguang Research Institute of Chemical Industry Co. Ltd.; Texas 202P polyethylene wax anti settling agent (industrial grade) was from Changsha Long Ruixiang Fine Chemical Co., ltd.

PARSTAT 2273 Princeton Applied electrochemical workstation was from America Princeton Applied Research. SFJ-400 sand mixing machine for grinding and dispersion was from Shanghai Modern Environmental Engineering Technology Co. Ltd. ESJ120-4B analytical balance was from Shenyang Longteng Electronic Co. ltd.

2.2. Preparation of Graphene Composite Coating
Multilayer graphene (2 g) was dissolved in the organic solvent xylene (14 g) and n-butanol (6 g) for ultrasonic 2 h. While toluene and n-butanol (7 g, 3 g, respectively) were added to an epoxy resin (200 g), stirred and dissolved. After the ultrasound was finished, the two are mixed and sanded for 1 h (2500 r / min).

20g barium sulfate and 20g talc powder (100 degrees after water treatment) were mixed and milled, and then the mixture was evenly dried and sieved. The treated filler was added to the epoxy resin in the upper step, and the 0.4g 202P anti settling agent, the 0.4g non-ionic dispersant, and the 1g diethylenetriamine were put into the mixture. After that, continue sanding 0.5h (5000r/min).

After high speed sanding, the components were mixed evenly and evenly. The finished coating with 1% graphene content could be obtained by filtration with gauze.

According to the above methods, the coating samples with graphene content of 3%, 5% and 7% were prepared. The content of graphene refers to the percentage of graphene quality to the quality of epoxy resin.

2.3. Electrochemical Performance Test of Coating
PARSTAT 2273 electrochemical workstation made by Princeton Applied Research Company, Power Suite was used as the operating software. The electrochemical three electrode system was adopted, the working electrode was the sample coating, the platinum film electrode was the opposite electrode and the reference electrode was saturated calomel electrode, using 3.5wt%NaCl solution as the corrosion liquid electrolyte, the test environment temperature was kept at room temperature ($20 \pm 2°C$). The workstation should be preheated 10min before electrochemical testing.

2.3.1. Open circuit potential (OCP) test. To ensure the stability of the test, The working electrode was immersed in electrolyte solution for 24h before the test. The scanning speed was set as1s/point, and the scanning time was temporarily set as 3600s (after the value stable, the scanning can be stopped manually). the change of open circuit potential at the last 300s was observed, if the value was less than 5mV, the open circuit potential value of the time period was taken as the average value, and the trend of the open circuit potential with the immersion time was calculated by using Origin software.

2.3.2. Tafel Plot test. Set the electrokinetic potential scanning range of -0.3V (vs OCP) to 1.5V (vs OCP), scanning speed of 1.0mV/s, the working area of the sample was 1cm^2. After a complete polarization curve was calculated, the corrosion current density and corrosion potential were calculated using Power Suite software.

2.3.3. Electrochemical impedance spectroscopy (EIS) test. The sample was soaked in 3.5wt% NaCl solution for 50 days. Then the electrochemical impedance spectra of the sample were determined. the
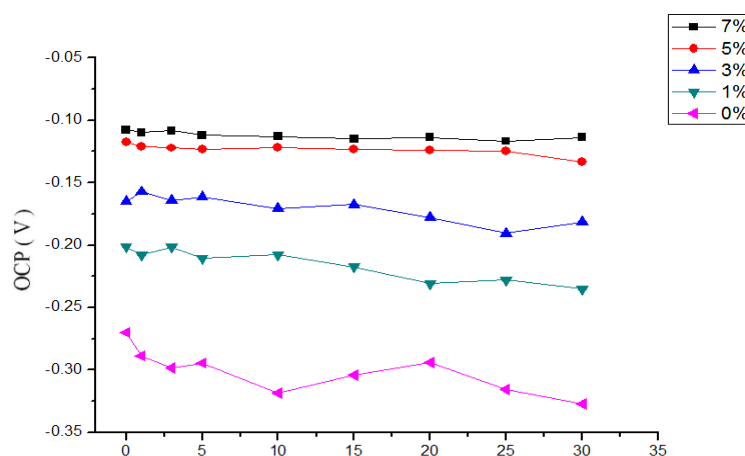
amplitude of applied sine wave signal was 10mV, frequency scanning range was 100mHz-100kHz, the measured impedance spectrum of Nyquist map and Bode map were fitted for analysis using ZSimpWin software and the impedance spectrum fitting parameters were got.

3. Results and Discussion

3.1. Open circuit potential (OCP) analysis

As the value of the open circuit potential changed continuously with the immersion time, the open circuit potential test of the coated sample for a long time in 3.5wt%NaCl solution was shown in Figure1. From the above experimental results can be seen, when the test system was stable, open circuit potential
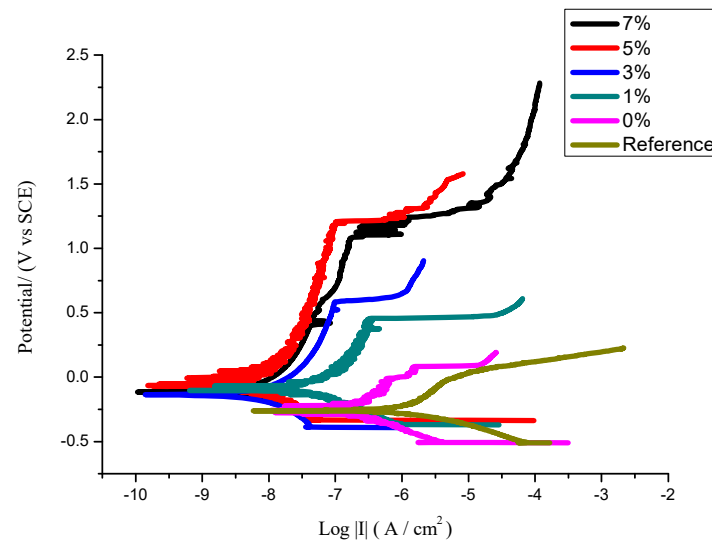

Figure 1. The open circuit potential test for immersion coating at different times

value increased with the graphene content increasing, and with the increase of immersion time, the coating of with high content graphene maintained a relatively highly OCP ability.

According to the basic knowledge of metal corrosion, if the equilibrium potential metal oxidation is below the electrolyte balance potential reduction reaction, then the electrochemical corrosion can occur. the greater the potential difference corrosion tendency was, the higher open circuit potential was, it can maintain the stability of its electrochemical properties. From the thermodynamic analysis of the corrosion reaction, graphene coating can reduce the probability of electrochemical corrosion.

3.2. Tafel Plot analysis

Figure 2 was comparison of different graphene content coatings for polarization curves, the stable passivation region appeared in the anodic polarization curve, which indicated that the compact oxidation protective film was formed on the surface of stainless steel, the anodic dissolution reaction was inhibited greatly, and the corrosion rate was slowed down. Therefore, the corrosion resistance of the coating can be evaluated by comparing the electrochemical parameters of the coating, and the results were shown in Table 1.

Figure 2. Comparison of different graphene content coatings for polarization curves

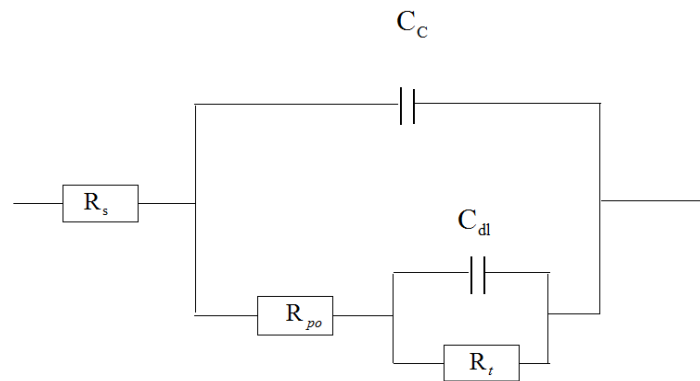**Table 1.** Test results for different coating polarization curves

	Reference	0%	1%	3%	5%	7%
E_{corr} (V)	-0.264	-0.261	-0.092	-0.112	-0.083	-0.101
I_{corr} (A/cm^2)	8.13×10^{-7}	1.74×10^{-7}	8.91×10^{-8}	3.16×10^{-8}	1.78×10^{-8}	1.65×10^{-8}
E_b (V)	—	0.083	0.448	0.584	1.211	1.22
I_p (A/cm^2)	—	1.66×10^{-6}	3.02×10^{-7}	1.11×10^{-7}	9.55×10^{-8}	1.41×10^{-7}

By the polarization results, coating can effectively reduce the corrosion current of steel substrates (I_{corr}). With the increase of the content of graphene, the corrosion potential of steel substrates (E_{corr}) gradually shifted positively and the corrosion current decreased gradually. The self-corrosion current of 7% content drops by two orders of magnitude than that of the blank steel substrate by 8.13×10^{-7}A/cm^2. The blunted current density (I_p) decreased with increase of graphene content, and the dull current density of 5% coating was 9.55×10^{-8}A/cm^2, which was more than 10 times lower than that of 1.66×10^{-6}A/cm^2 of 0% contentpassive current density. The result indicated that the passivation capacity of the passive film on the base metal surface was stronger than that of the anodic passivation reaction.

In a word, the addition of graphene could effectively improve the corrosion resistance of base metal, and the coating with the 5% content had the best corrosion resistance.

3.3. Electrochemical impedance spectra (EIS) analysis
Considering the penetration of electrolyte solution to base metal interface could cause corrosion reaction. It is assumed that the electrolyte solution in the coating system was uniform and the electrochemical corrosion reaction at the base metal interface was even distributed, the equivalent circuit diagram shown in Figure 3 was chosen, the coating Nyquist diagram was fitted with Zsinwin software. C_C was coating capacitance, R_{po} was hole resistance, C_{dl} was electrical double-layer capacitance, R_t was numerical values of linear polarization resistance of corrosion reactions, and Zsinwin software was used to fit the Nyquist diagram, as shown in Table 2.

C_C

Figure 3. Equivalent circuit of EIS for the composite coating in the early in the middle

Table 2. Fitted parameters of EIS for the composite coating

sample	0%	1%	3%	5%	7%
R_S (Ω)	3.42×10^2	1.21×10^3	6.32×10^2	1.23×10^3	7.89×10^2
C_C (F/cm)	2.05×10^{-9}	3.12×10^{-9}	4.75×10^{-9}	7.56×10^{-10}	1.25×10^{-9}
R_{po} (Ω)	2.45×10^3	7.23×10^3	4.06×10^3	2.12×10^4	9.54×10^3
C_{dl} (F/cm)	1.24×10^{-8}	2.54×10^{-8}	1.54×10^{-8}	2.41×10^{-8}	2.01×10^{-8}
R_t (Ω)	1.24×10^4	2.43×10^4	2.44×10^4	7.45×10^4	7.52×10^4

After prolonged immersion, the corrosion electrolyte penetrated into the metal substrate and underwent electrochemical etching to some extent. The corrosion pore produced by corrosion reaction is not visible to the naked eye, but it can be directly reflected by the electrochemical parameters. Assuming that the porosity is F[12], then parameters such as C_C, R_{po} and C_{dl} should be given in the following categories:

$$C_C = C_C^0 \cdot (1 - F) \cdot S$$

$$R_{po} = \frac{R_{po}^0}{F \cdot S}$$

$$C_{dl} = C_{dl}^0 \cdot F$$

$$R_t = \frac{R_t^0}{F \cdot S}$$

Because the time constant at the high frequency is related to the charge discharge process of the organic coating, The reciprocal of the time constant is the characteristic angular frequency of the high-frequency end，which is ω_h
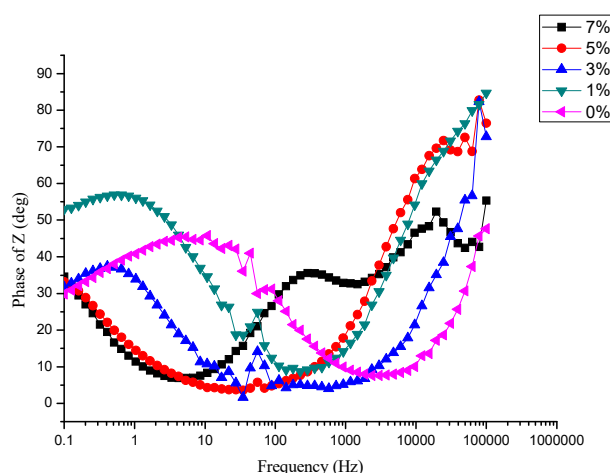
$$\omega_h = 2\pi f_h = \frac{1}{R_{po} \cdot C_C}$$

$$\omega_h = 2\pi f_h = \frac{1}{R_{po}^0 \cdot C_C^0 \cdot \frac{1-F}{F}}$$

In the case of small porosity F, F<<1, the follow can be obtained,
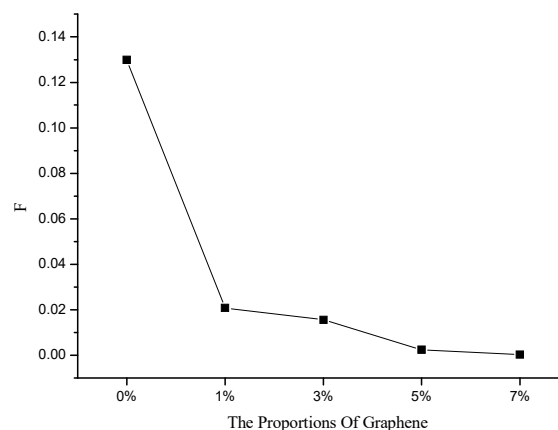
$$\omega_h = 2\pi f_h = \frac{F}{R_{po}^0 \cdot C_C^0}$$

After fitting, it was shown that Rpo and CC do not change with time. It was found that the porosity

F was proportional to the characteristic frequency f_h [12]. According to the above conclusions, the electrochemical impedance spectroscopy analysis of the sample soaked for 50 days, the phase angle and frequency of the Bode diagram was shown in Figure 4. According to the Figure 4, the characteristic frequency was found out and the result was brought into the formula. The porosity of the coating is F. The contrast drawing was shown in Figure 5.

Figure 4. Impedance Bode diagram of 50 days sample immersion

Figure 5. The porosity of the coated samples for 50 days after soaking

As we can see from Figure 5, compared with the pure epoxy coating, graphene addition can effectively reduce the porosity of the coatings of F, As the content of graphene increases, the porosity decreases gradually, and the porosity of the 7% coating is lower than that of the pure epoxy coating, which is nearly three orders of magnitude, and the corrosion resistance is remarkable.

According to electrochemical impedance spectroscopy analysis, the composite coating effectively blocked the invasion of corrosive electrolyte, reduced the corrosion porosity of the base material and had better corrosion resistance after adding graphene.

4. Conclusion

The OCP measurement of different content graphene coating showed that with the increase of the content graphene, the OCP number of the coating numerical was more and more high. It showed that the smaller the thermodynamic trend of electrochemical corrosion reaction was, the less likely the coating was to corrode. The Tafel curve of stainless steel and five kinds of the content graphene coatings in 3.5wt% NaCl solution was measured. Compared with the coating with no additional content and other content of graphene, the 5% content coating had better corrosion resistance. Although the coating with 7% content was slightly better, the lifting space was relatively limited. According to the EIS fitting results, it was seen that the impermeability of the composite coating increased with the addition of graphene. Using characteristic frequency method to evaluate the coating properties, it was found that the incorporation of graphene effectively reduced the corrosion porosity and improved the corrosion resistance of the coating. The test results of AC impedance agree with those of polarization curves.

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