A Brief Communication on the Improved Mechanism of Graphene on Zinc-Rich Coatings

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Gallic acid-based epoxy resin monomer was synthesized by the natural extract of gallnut for the efficient dispersion of graphene in epoxy resin. The graphene zinc-rich anticorrosion coatings were further prepared on the basis of the graphene / gallic acid-based epoxy resin monomer dispersion system. Electrochemical experiments and spectral characterization were carried out to study the effect of graphene on zinc-rich coatings and its mechanism. Experiments showed that graphene enhanced the cathodic protection currents of the zinc-rich coatings and prolonged the cathodic protection time. Simultaneously, graphene slowed down the penetration of corrosive media into the coatings. The conductivity of graphene improved electrical contact between zinc particles as well as zinc and iron, and transformed un-activated zinc particles into activated zinc particles. The dispersed and layered structure of the graphene extended the permeation path of the corrosive medium, which resulted in reduced permeation rate and decreased water content of the coatings. It was demonstrated by the tracking of zinc corrosion products by micro-area Raman spectroscopy.

Keywords: Corrosion, Graphene, Zinc-rich coatings, Electrochemistry
1. INTRODUCTION

Since the discoverer of graphene won the Nobel Prize [1], graphene has attracted more and more attention of researchers. Due to the impermeable lamellar structure of graphene [2], one of its practical applications was anticorrosion films [3-5] and coatings [6,7]. However, with the study of graphene anticorrosion technology, there were some different views [8,9]. Some studies found that conductive graphene formed corrosion galvanic couples with metals and accelerated the corrosion [10,11]. Therefore, some researchers even questioned: “Is graphene anti-corrosion reasonable?” [12] Without solving the problem, the research on graphene anticorrosion would not be able to continue. In the zinc-rich coatings, zinc was sacrificial anode and the conductivity of graphene became favorable factor [13]. When zinc formed corrosion galvanic couple with iron, zinc was preferentially corroded [14,15]. The potential of the zinc-iron corrosion galvanic couple was lower than the corrosion potential of iron, so iron was protected as cathode [3,16-18]. In order to ensure charge transfer and the formation of zinc-iron corrosion galvanic [19], the zinc content in zinc-rich coatings was high [20]. This resulted in high porosity of the zinc-rich coatings and low shielding performance [21]. There were many studies trying to doping the conductive materials or optoelectronic materials, such as carbon black [22-25], graphite [15], carbon nanotubes [13,14,26], nano-TiO₂ [27], into the zinc-containing coatings to reduce the zinc content and maintain its cathodic protection, or fillers, such as micaceous iron oxide [28], nanomontmorillonite [16], to improve the shielding performance of the coatings. The addition of graphene was a method for improving the shielding performance of the zinc-rich coatings, reducing the amount of zinc powder and ensuring the zinc-iron corrosion galvanic couple. Prasai et al disclosed that graphene was able to reduce copper and nickel corrosion rate by 7 and 20 times respectively and they credited this to graphene’s barrier ability [29]. The addition of graphene to epoxy resin significantly improved the shielding property of epoxy resin coatings [30]. For zinc-rich coatings, it was not enough to confirm the shielding ability only from the macro-phenomena. Zinc-rich coatings with different graphene content were prepared on the basis of graphene/gallic acid-based epoxy monomer dispersion system. The effect of graphene on the cathodic protection of zinc-rich coatings was investigated from macroscopic point of view. The mesoscopic effect mechanism of graphene on the electrochemical characteristics of zinc distribution in the coatings was studied. The improvement of shielding properties of graphene for zinc rich coatings was described from the kinetic point of view.

2. EXPERIMENTAL METHODS

The reagents used in the experiments were purchased from Aladdin Co., Ltd. Preparation of the materials and coatings: Gallic acid, epichlorohydrin and tetrabutylammonium bromide were added into a three-necked flask and stirred at room temperature for 30 minutes. And then, the mixture was transferred to oil bath and stirred at 100 °C for 3 hours to allow the ring-opening reaction to proceed sufficiently. When the room temperature was reached, 30 wt% NaOH solution was injected and stirring was continued for another 2 hours. The product was washed 3 times by deionized water. The organic liquid layer was dried for 24 hours by anhydrous sodium sulfate. After the unreacted epichlorohydrin was removed by reduced pressure treatment, gallic acid-based epoxy resin (GEP) was obtained. The epoxy value of GEP was determined to be 0.68 by the hydrochloric acid-pyridine method. The 0.5 g of
GEP was added to 100 mL of tetrahydrofuran (THF) and sonicated for 2 minutes to fully dissolve the GEP. 0.5 g of graphene was added into the GEP-THF solution and ultrasonically dispersed at room temperature for 1 hour, and then graphene dispersion with concentration of 5 mg/mL was obtained. The graphene dispersion prepared by this method was stable and did not agglomerate within 24 hours [31]. Graphene dispersion and zinc powder were added to 10.0 g of epoxy resin E44 and stirred at room temperature for 10 minutes. The amount of graphene dispersion was adjusted to control the mass fraction of graphene in the coatings. The mass content of zinc was 70 wt%. Stirring was continued for 10 minutes after the addition of the curing agent DF1228. The preparation process of the coatings was shown in figure 1. The obtained graphene epoxy coating was applied to the surface of Q235 steel by an automatic coating machine. The coating thickness was 80~100 μm.

**Figure 1.** Molecular structure of gallic acid-based epoxy resin monomer and schematic diagram of the preparation process of the coatings and the cross-sectional structure of the coatings.
Figure 2. The TEM image of graphene and SEM image of zinc powder and the profile of the coatings

The Hitachi S-3400N SEM and Hitachi HT7700 TEM were employed to observe and test the raw materials and the profile of the coatings. Figure 2 demonstrated the micromorphology of the graphene, zinc powder and the profile of the coatings. The size of graphene and zinc powder were about 500 nm and 40 microns respectively. The LRS-5 micro-area Raman spectrometer (Xian Yima Optoelec Co., Ltd., China) was applied to detect and analyze the corrosion products. The ModuLab XM electrochemical workstation was applied to perform electrochemical experiments. The structures of the electrodes for measuring the electrochemical impedance spectroscopy of the dry coatings and cathodic protection currents were shown in figure 3. These two methods were proposed by Marchebois [32] and Abreu [33] respectively.

Figure 3. Electrode structure for electrochemical testing, (a) electrochemical impedance spectroscopy of dry coatings and (b) cathodic protection current of the coatings
3. RESULTS AND DISCUSSION

3.1 Characterization of materials

Figure 4 showed the FTIR image of gallic acid-based epoxy resin (GEP). Bonds of O-H produced a characteristic absorption peak at 440 cm\(^{-1}\). The absorption peaks at 3050 cm\(^{-1}\) and 3000 cm\(^{-1}\) were attributed to C-H bonds in benzene ring of GEP molecules. The absorption peaks of C=C bonds in benzene ring were located at 1600 cm\(^{-1}\) and 865 cm\(^{-1}\). Group -CH2 caused absorption peaks at 2920 cm\(^{-1}\) and 2850 cm\(^{-1}\). The peak at 1725 cm\(^{-1}\) was the stretching vibration peak of the bond of C=O. The peaks at 910 cm\(^{-1}\) and 750 cm\(^{-1}\) were the stretching vibration peak of epoxy group. The results of FTIR indicated that the gallic acid-based epoxy resin was successfully prepared. The \(^1\)H nuclear magnetic resonance was used to examine the molecular structure of GEP as shown in figure 4, and (DMSO, \(\sigma\)) 7.3 ~ 7.5 (m, 2H, benzene ring), 4.0 ~ 4.5 (m, 8H, methylene), 3.0 ~ 3.4 (m, 4H, epoxy), 2.6 ~ 2.9 (m, 8H, epoxy group). The results indicated that the synthesized GEP contained benzene rings, ether bonds, ester bonds and epoxy groups in the molecular structure. The oligomers produced during the synthesis caused a small amount of miscellaneous peaks in the spectrum.

![Figure 4](image_url)

**Figure 4.** The images of fourier transform infrared spectroscopy and Nuclear magnetic resonance spectroscopy of gallic acid-based epoxy resin monomer
3.2 Effect of graphene on cathodic protection performance of coatings

Figure 5 showed the cathodic protection currents of zinc-rich coatings with different graphene contents. In the figure, the increase of graphene content increased the values and prolonged the duration of cathodic protection currents. Marchebois found a similar phenomenon through conductive graphite fillers, but its promotion effect was lower than that of graphene [24]. The optimum mass content of graphene was 0.3 wt% for 70 wt% Zn coatings.

In order to further investigate the effect of graphene on zinc-rich coatings, a series of electrochemical impedance spectroscopy (EIS) experiments were carried out. The EIS of zinc-rich coatings with different graphene contents showed similar evolution process. The 0.3 wt% graphene – 70 wt% zinc coatings were taken as an example for illustration. Figure 6 showed the EIS of 0.3 wt% graphene – 70 wt% zinc coatings immersed in 3.5 wt% NaCl solution for different times. At the initial stage of immersion, EIS exhibited one time-constant, and the corresponding equivalent circuit was a three-element circuit. In this stage, the electrolyte solution penetrated into the coatings. Because one time-constant corresponds to one electrode process, and the dielectric process of the coatings was its own physical characteristics and was certainly present [34,35]. At the later stage of immersion, EIS exhibited two time-constants, and the corresponding equivalent circuit was a five-element circuit. The second time constant here represented the electrochemical process of zinc, which was more active than iron, relative to the previous stage [36]. In this stage, sacrificial corrosion of zinc occurred and cathodic protection on iron was produced.

![Figure 5. Cathodic protection currents of 70 wt% zinc-rich coatings without and with 0.3 wt% and 0.1 wt% graphene immersed in 3.5 wt% NaCl solution for 12 to 800 hours](image)
By fitting the EIS, the charge transfer resistance of the corrosion of zinc $R_{\text{t,Zn}}$ was showed in figure 7. The $R_{\text{t,Zn}}$ reflected the sacrificial corrosion resistance of zinc [18,37] and graphene decreased the sacrificial corrosion resistance of zinc. It was conducive to the cathodic protection on iron. The reason was that conductive graphene enhanced the galvanic interaction between zinc and iron. Ramezanzadeh achieved similar results with conductive polyaniline fibers, and attributed it to the promotion of galvanic couples and the reduction of charge transfer resistance of zinc [17].

Figure 6. Electrochemical impedance spectroscopy of 0.3 wt% graphene – 70 wt% zinc coatings immersed in 3.5 wt% NaCl solution for 12 to 800 hours

Figure 7. Charge-transfer resistance of zinc corrosion in the 70 wt% zinc coatings without and with 0.3 wt% and 0.1 wt% graphene immersed in 3.5 wt% NaCl solution for 12 to 400 hours
Figure 8. Electrochemical impedance spectroscopy of dry 50 wt% and 70 wt% zinc coatings without and with 0.3 wt% graphene

Table 1. The ratio of active zinc particles and cathodic protection currents of 50 wt% and 70 wt% zinc coatings without and with 0.3 wt% graphene

<table>
<thead>
<tr>
<th>Graphen wt%</th>
<th>Zn wt%</th>
<th>$\alpha$</th>
<th>$i_{cp}$ ($\mu$A$\cdot$cm$^{-2}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>50</td>
<td>0.472</td>
<td>—</td>
</tr>
<tr>
<td>0</td>
<td>70</td>
<td>0.581</td>
<td>257.29</td>
</tr>
<tr>
<td>0.3</td>
<td>50</td>
<td>0.802</td>
<td>—</td>
</tr>
<tr>
<td>0.3</td>
<td>70</td>
<td>0.833</td>
<td>400.97</td>
</tr>
</tbody>
</table>

Figure 9. Transmission line model of the electrochemical impedance spectroscopy of dry 50 wt% and 70 wt% zinc coatings without and with 0.3 wt% graphene
In order to study the electrochemical improved mechanism of graphene on zinc-rich coatings in depth, the EIS of dry coatings was measured and analyzed by transmission line model [32]. Figure 8 demonstrated the EIS of dry graphene – zinc coatings. The EIS exhibited three time-constants, and the time constant representing the coating capacitance in low frequency region was not obvious. In order to analyze EIS, the transmission line model was established. The transmission line model regarded the currents as the electromagnetic field oscillation between parallel double conductors [24,38]. There were three electromagnetic oscillation paths in graphene zinc-rich coatings as shown in figure 9. They were the capacitive properties of the coatings, the path of activated zinc particle and the path of un-activated zinc particle, respectively. If the zinc-related electromagnetic oscillation path was set to 1 and the ratio of activated zinc particle path was set to α, then the ratio of un-activated zinc particle path was 1-α. The EIS was fitted by transmission line model, and the value of α was obtained and displayed in table 1. The presence of graphene increased the proportion of activated zinc particles as shown in figure 10. It was conducive to sacrificial corrosion of zinc and cathodic protection on iron. Conductive graphene transformed un-activated zinc particles into activated zinc particles. This was the mesoscopic electrochemical mechanism of graphene improving the cathodic protection performance of zinc-rich coatings. The explanation of cathodic protection promotion of graphene from the perspective of electrodynamics and quantum mechanics [39] was consistent with the conclusion of transmission line model in this paper.

![Figure 10](image-url)

**Figure 10.** The brief schematic of graphene changed the activity characteristics of zinc particles in the graphene zinc-rich coatings.
3.3 Effect of graphene on shielding properties of coatings

The cathodic protection on steel by zinc-rich coatings was usually measured by whether the potential was below -0.8V [23]. Figure 11 showed the potential-time curves of zinc-rich coatings with different graphene contents. The zinc-rich coatings generally possessed relatively high porosity, which resulted in easy penetration of the electrolyte solution. Therefore, the potential of zinc-rich coatings without graphene dropped below -0.8V quickly, and cathodic protection effect was achieved. The potential of zinc-rich coatings containing graphene dropped below -0.8V after maintaining high potential for a period of time. This meant that graphene imparted a degree of shielding protection to the zinc-rich coatings prior to cathodic protection. This initial shielding phenomenon did not occur in the graphene-free zinc-rich coating [17,18]. This reflected that the layered distribution of graphene in the coatings extended the permeation path of corrosive media and increased its diffusion resistance. As shown in figure 12, graphene significantly improved the microporous resistance of the coatings $R_{po}$. The $R_{po}$ reflected the diffusion and penetration resistance of the corrosive medium into the coatings [40]. It facilitated the shielding protection on the steel substrate.
Figure 12. Coating microporous resistance of the 70 wt% zinc coatings without and with 0.1 wt% and 0.3 wt% graphene immersed in 3.5 wt% NaCl solution for 0 to 1000 hours.

The water content of the coatings (V(t) and M(t)) showed quantitative relationship with the coating capacitance $C_c$ [34,35]:

$$V(t) = \frac{\ln C_c(t)}{\ln C_d} \quad (1)$$

$$M(t) = S L \rho_w V(t) \quad (2)$$

$V(t)$ was water volume fraction in the coatings, $C_c(t)$ was coating capacitance, $C_d$ was coating capacitance of dry coatings, and $\varepsilon_w$ was relative permittivity of water. The coating capacitance $C_c$ was calculated by the formula 3 [41] and admittance coefficient $Y_0$ of the constant phase angle element $Q_c$ (figure 6) obtained by fitting the EIS.

$$C_c = Y_0 \left(\omega''_{\text{max}}\right)^{n-1} \quad (3)$$

$\omega''_{\text{max}}$ was the frequency at which the imaginary part of the impedance ($Z''$) had a maximum. $n$ was dispersion coefficient of $Q_c$. As shown in figure 13, the logarithm of coating capacitance was linear with the square root of time. It indicated that the infiltration process of water in the coatings compounded Fick law [42]. The diffusion rate of water in the coatings was calculated by formula 4 [39] and the slope of the linear relationship in figure 13.
\[
\frac{d \ln C_c}{d \sqrt{t}} = \frac{2\sqrt{D}(\ln C_\infty - \ln C_d)}{L\sqrt{\pi}} \quad (4)
\]

\(C_\infty\) was water-saturated coating capacitance, \(D\) was diffusion rate coefficient of water, and \(L\) was coating thickness.

Figure 13. Coating capacitance of the 70 wt% zinc coatings without and with 0.1 wt%, 0.3 wt% and 0.5 wt% graphene immersed in 3.5 wt% NaCl solution for 0 to 36 hours

Therefore, the larger slope meant the faster penetration rate of water [43]. Figure 13 showed that graphene reduced the slope of the linear relationship. Accordingly, table 2 showed that graphene significantly reduced the penetration rate of corrosive media in the coatings and water content in the coating. Micro-area Raman spectroscopy experiments on the profile of the coatings were carried out to further confirm the impermeability. Raman spectroscopy of corrosion products of zinc were shown in figure 14. The corrosion products of zinc were mainly \(\text{ZnO}\) and \(\text{ZnCl}_2 \cdot \text{Zn(OH)}_2\). Figure 14 showed the maximum depth of zinc corrosion products as a function of time. Graphene significantly delayed the appearance of corrosion products of zinc by hindering the penetration of corrosive media into the coatings.
Table 2. Water diffusion and water content parameters of the 0 wt% zinc coatings without and with 0.1 wt%, 0.3 wt% and 0.5 wt% graphene immersed in 3.5 wt% NaCl solution

<table>
<thead>
<tr>
<th>Graphene wt%</th>
<th>Slope</th>
<th>D ($10^{-10}$ cm$^2$·s$^{-1}$)</th>
<th>V (%)</th>
<th>M (mg·cm$^{-2}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>0.057</td>
<td>6.25</td>
<td>7.07</td>
<td>619.06</td>
</tr>
<tr>
<td>0.1</td>
<td>0.041</td>
<td>2.01</td>
<td>5.10</td>
<td>446.62</td>
</tr>
<tr>
<td>0.3</td>
<td>0.038</td>
<td>1.76</td>
<td>4.52</td>
<td>396.31</td>
</tr>
<tr>
<td>0.5</td>
<td>0.040</td>
<td>2.07</td>
<td>5.79</td>
<td>506.35</td>
</tr>
</tbody>
</table>

Figure 14. Raman spectroscopy of zinc corrosion products and the maximum depth of zinc corrosion products as a function of time in 70 wt% zinc coatings without and with 0.3 wt% graphene immersed in 3.5 wt% NaCl solution for 0 to 55 hours

4. CONCLUSION

The conductivity of graphene facilitated cathodic protection of zinc-rich coatings on steel substrate. Graphene enhanced the electrical contact and galvanic interaction between zinc particles and steel substrate. The improvement mechanism was that graphene converted un-activated zinc particles into activated zinc particles. The layered distribution of graphene improved the shielding protection of the zinc-rich coatings. As a result, the zinc-rich coatings achieved a certain degree of shielding protection before cathodic protection. The mechanism was that graphene reduced the permeation rate by extending the permeation path of the corrosive medium and decreased the water content of the coatings. The infiltration process of corrosive media in graphene zinc-rich coatings was the Fick diffusion process. For coatings with 70 wt% zinc, the optimum content of graphene was 0.3 wt%.

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