Improving Corrosion Protection and Friction Resistance of Q235 Steel by Combining Noncovalent Action and Rotating Coating Method

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ABSTRACT: Developing waterborne epoxy (WEP) coatings with excellent corrosion resistance and tribological properties is a key aspect to solve the damage of Q235 steel. In this work, perylene bisimide (PBI) derivatives dispersion graphene (GR) were prepared by a π-π stacking, the highly oriented PBI0.5%/GR0.5%/WEP coating will be prepared by the rotating coating method. Especially, the impedance value reached about 10^9 Ω cm^2 when the PBI and GR ratio is 1:1. The impedance value of PBI0.5%/GR0.5%/WEP coating increased by 3 orders of magnitude compared with that of pure WEP coating (10^6 Ω cm^2). Additionally, the coefficient of friction of the coatings was 0.33; compared with that of WEP, the coefficient of friction decreased by 48%, and the wear resistance increased by 87.6%. The results show that the PBI0.5%/GR0.5%/WEP coatings exhibited excellent corrosion resistance and wear resistance properties due to the good dispersion and high orientation of PBI/GR in WEP. It is anticipated that our current work would guide the ongoing efforts to develop a more efficient method to overcome the poor dispersion of GR in waterborne epoxy resin and provide a green coating with excellent corrosion resistance and wear resistance properties.

1. INTRODUCTION

Q235 steel is widely used in all aspects of life due to its low price, easy processing, excellent comprehensive performance, and other advantages.1,2 It is usually applied directly without heat treatment, so the corrosion resistance and friction resistance are very low.3,4 The coating method has the advantages of low price, simple operation, and good chemical stability; it is one of the most commonly used methods to protect Q235 steel.5-7 Waterborne epoxy (WEP) coating meets the requirements of environmental friendliness and corrosion resistance; it has the potential to replace organic epoxy in the future.8,9 However, due to different dispersants and hydrophilic groups contained in waterborne epoxy resins, holes and defects are likely to develop during film formation. It is easily infiltrated by corrosion factors such as Cl^−, O2^−, SO_4^2−, etc. and reduces corrosion resistance.10,11

A variety of nanofillers are added to the epoxy resin to study the anticorrosion performance, such as ZnO,12 SiO_2,13-15 h-BN,16 graphene,17-19 etc. Because graphene (GR) has a superhigh cross-linking density and a unique layered structure, it can effectively prevent the penetration of corrosion factors and form many new corrosion media diffusion paths.20,21 Ding et al.22 reported the reaction of graphene with biobased epoxy monomer and its application in the anticorrosion of epoxy resin; it was proved that when the content of graphene in epoxy was 0.5%, the coating was nonconductive and had the best anticorrosion performance. However, graphene has a large specific surface area and interlayers are prone to interactions, which are extremely prone to agglomeration.23-25 When GR combined with WEP, graphene agglomerated into large blocks and cracks were easily formed around it; instead of preventing the infiltration of corrosion factors, the corrosion process is accelerated.16,26 This is a major obstacle to the application of graphene in the field of corrosion protection and a lot of work has been done to solve this problem, such as chemical vapor deposition (CVD),27-29 electrodeposition,30,31 and hydrothermal oxidation.32,33 However, these technologies also have some shortcomings, such as the structure of graphene is easily destroyed and the preparation process is complicated and toxic.34-36 Fortunately, noncovalent dispersed graphene was first reported by Xu et al.,37 who provided a dispersion method that retains graphene’s structure. A lot of work has been done to investigate the noncovalent action dispersion of GR and its application in corrosion protection. He et al.38 mentioned that noncovalent and covalent bonds can be combined to improve...
the corrosion property of waterborne epoxy/graphene; the corrosion resistance can work for 30 days. The significant improvement in the performance of the composite coating is attributed to the fact that insulating poly(2-amiathiazole) noncovalently functionalized graphene increases the dispersion of graphene and reduces its electrical conductivity.39

Furthermore, Wang et al.40 reported that the rotating coating method improves the horizontal orientation of graphene in epoxy resin. The GR was arranged along the horizontal direction to the greatest extent to obstruct the penetration of corrosive media from the vertical direction. On the basis of the above discussion, we combined π–π noncovalent bonds and the rotating coating method not only to promote the dispersion of GR in the WEP matrix but also to enhance the orientation in the horizontal direction to get coating with excellent corrosion resistance and wear resistance properties. For the π–π stack, perylene bisimide (PBI) derivatives has a very powerful conjugated system, the π–π stack action between the molecule with the orbital and the graphene electron cloud, which is adsorbed on the graphene nanocrystals to disperse graphene.41–43 Meanwhile, because a nonconducting polymer can interrupt the conductive path of graphene to prevent electrochemical corrosion, good dispersion of graphene improves the barrier property and lubricity of the coating. Cui et al.44 prepared poly(dopamine) by noncovalent bond dispersion of graphene oxide, with the impedance value of 1.16 × 10⁸. Zhang et al.36 prepared graphene oxide (GO) containing any zinc phosphate (ZnP) coating with a corrosion rate of 68.5 μm/year and resistance of 1424.5 Ω.cm². Our results show that PBI0.5%/GR0.5%/WEP coatings with the impedance value of 10⁸ Ω⋅cm² and coefficient of friction of 0.33 exhibited excellent corrosion resistance and wear resistance properties. A green and pollution-free waterborne epoxy resin coating with excellent anticorrosion and antifriction properties was proposed, which provided the possibility to expand the practical application range of waterborne epoxy resin.

2. EXPERIMENTAL SECTION

2.1. Material. F0704 waterborne epoxy resin and curing agent (WEP, the solid content is 50%) was supplied from Shenzhen Jitian Chemical Co., Ltd., China. SE1132 commercial graphene (GR, layer number: 5–10, layer thickness: 3–8 nm) were purchased from the Changzhou Sixth Element Material Technology Co., Ltd., China. 3,4,9,10-Perylenetetracarb dianhydride (PTCDI), poly(ethylene polyamine) (PEPA), ethanol, dimethylbenzene, and potassium hydroxide were purchased from Aladdin Industrial Corporation; all chemicals were used without further purification.

2.2. Synthesis of Perylene Bisimide (PBI) Derivatives. One gram of perylene-3,4,9,10-tetracarboxylic dianhydride (PTCDA), 11 g of PEPA, and 40 mL of dimethylbenzene were ultrasonically mixed for 0.5 h. Then, the reaction was performed under nitrogen for 10 h at 100 °C. The crude product was added to 80 mL of potassium hydroxide solution with a mass fraction of 10% and stirred at room temperature for 5 h to remove unreacted PTCDA. Finally, the product PBI was obtained by washing with deionized water and ethanol until the solution became neutral and then dried in a vacuum at 60 °C for 12 h; the preparation process of PBI is shown in Figure S1.

2.3. Preparation of PBI/GR Dispersion. PBI with 0.25%, 0.5%, and 1% ratios was dissolved in deionized water by ultrasonication for 1 h to obtain a uniform purple solution. Then 0.5% recalculated graphene was then added to the PBI solution, and the PBI/GR suspension was obtained after 2 h of ultrasonication. We compared two samples PBI and GR, both of 0.5%. A total of five different proportion solutions were added, PBI, PBI0.25%/GR0.5% (2:1), PBI0.5%/GR0.5% (1:1), PBI1%/GR0.5% (1:2), and GR. In this study, the optimum weight ratio of GR0.5%/PBI0.5% was 1:1; it could be kept for 5 days without precipitation and dispersion effect as shown in Figure 1a.

2.4. Fabrication of Waterborne Epoxy Composite Coatings. The above solutions were dried in a vacuum at 60 °C to a constant weight and then a certain amount of epoxy resin was added. After magnetic stirring for 30 min, the hardener was added and the mixture stirred for 10 min. The Q235 carbon steels were polished with 100–1000 mesh sandpaper, then cleaned with distilled water, after that ultrasonic in acetone solution being degreased, finally, dried at 60 °C to remove water. Finally, coating to the surface of Q235 carbon steel. The mixed solutions are coated on the Q235 steel by spin coating method at 500 rpm for 5 min the cured reaction was conducted at room temperature for 3 days and then dried at 40 °C for 12 h, the thickness was 40 ± 2 μm. The preparation processes of WEP, GR0.5%/WEP, PBI0.25%/ GR0.5%/WEP, PBI0.5%/GR0.5%/WEP, PBI1%/GR0.5%/WEP, and PBI/GR/EP coatings are shown in Figure 1a,b.

Figure 1. Dispersion of PBI, GR0.5%/PBI0.25% (1:2), GR0.5%/PBI0.5% (1:1), and GR0.5%/PBI1% (2:1) and GR in aqueous solution (a). Preparation process of PBI/GR/WEP coating (b).
2.5. Measurement and Characterization. A Fourier transform infrared spectrometer (FTIR, Thermo Nexus 470FT-IR) and a thermogravimetric analyzer (TGA, TGA Q500) were used to characterize the synthesis of PBI. The noncovalent action is dispersed through the ultraviolet–visible (UV−vis) spectrum (UV spectrometer, lambda750) and X-ray photoelectron spectroscopy (XPS, ESCALAB 250xi) characterization. The microstructure and morphology of GR, PBI/GR hybrid, and the crossfriction of composites coating were examined by a field emission scanning electron microscope (SEM, S4800) and a field emission transmission electron microscope (TEM, JEM-2100F). The friction and wear tests were performed on MRH-3A high-speed ring block friction and wear tester; the test conditions were a load of 20 N, a sliding speed of 1.03 m/s, and a sliding duration of 10 min. All electrochemical measurements were conducted in a three-electrode cell with a saturated calomel electrode (SCE) by CHI660-E electrochemistry workstation at room temperature (298 K). The coatings (coating soaking area is 1 × 1 cm²) were immersed in the 3.5% NaCl solution. When the open-circuit potential (OCPT) evaluates the sample as stable, then the electrochemical impedance spectroscopy (EIS) was performed and polarization curves were plotted. The polarization curves were recorded from −250 to +250 mV at the
scan rate of 10 mV/s. For the EIS test, the frequency ranged from $10^5$ to $10^{-2}$ Hz and the amplitude is 10 mV. The EIS data was fitted using ZView2 software with an equivalent circuit.

### 3. RESULTS AND DISCUSSION

#### 3.1. Characterization of PBI

The FTIR spectra (Figure 2a) were recorded to investigate the synthesis of PBI. For PTCDA, the characteristic peaks are as follows: 3488 cm$^{-1}$ (−OH), 1750 cm$^{-1}$ (−C=O stretching), 1680 cm$^{-1}$ (−C=C−), 1310 cm$^{-1}$ (C−H stretching), and 1020 cm$^{-1}$ (−O−). For PBI, the characteristic peaks appeared at 1593 cm$^{-1}$ (N−H) and 1360 cm$^{-1}$ (tertiary amine). The comparison between PTCDA and PBI shows that the peaks of 1750 cm$^{-1}$ (−C=O stretching) and 1020 cm$^{-1}$ (−O−) disappear, producing 1593 cm$^{-1}$ (N−H) and 1360 cm$^{-1}$ (tertiary amine), respectively, suggesting the successful preparation of PBI. In order to study the decomposition of PBI and PTCDA at high temperature, TGA as shown in Figure 2b, the temperature range between 100 and 800 °C, PTCDA gradual weight loss approximately 75 wt %. However, PBI lost about 51.5 wt %, which proved that PBI is more stable than PTCDA. The peak of about 300 °C is assigned to the oxygen-containing functional groups of PTCDA. The decomposition of amide bonds in PBI occurs at about 550 °C, which further demonstrates the successful preparation of PBI.

Figure 3a shows the comparison of the UV−vis absorption spectra of PBI and PBI/GR hybrid in deionized water. The peak of n−π* transition of the benzene ring was blue-shifted from 595 to 578 nm; the blue shift of 285 to 275 nm was caused by the π−π* transition of benzenoid to quinoid, which directly indicated the π−π* interaction between PBI and GR. The valence bond changes in PTCTA, PBI, and PBI/GR were further analyzed by XPS. Figure 3b shows the elements of C, N, and O, that the N atom comes from the PBI amine, and that the O atom was the residue of PTCDA. In Figure S2a,b, the peaks of 284, 284.5, 285.3, and 287.3 eV in the C 1s spectra of PTCDA and PBI, respectively, belong to
C–C, C–O, O=C–O, and C=C; for PTCDa, the C=C disappears, while C–O is generated in PBI. In the O 1s spectra of PTCDa and PBI (Figure 3c,d), the two peaks centered at 531.2 and 533.1 eV correspond to C–O and C=C; compared with PTCDa, the C=C of PBI is significantly reduced. The successful preparation of PBI was proved by C 1s and O 1s. Figure 3ef exhibits the N 1s core level spectrum of PBI and PBI-GR. One peak located at 399.6 eV was attributed to the bond of −NH−, while another peak centered at 401 eV corresponded to the bond of the π−π* shakeup between graphene and PBI.45

3.2. Morphology of Composite Coatings. The morphology and texture structure of GR and PBI/GR hybrid were investigated by SEM, respectively. As shown in Figure 4a, graphene exhibits a typical exfoliated layer structure, and it agglomerates into about 10 μm block stacking to severity. As shown in Figure 4b, PBI presents a uniform rodlike structure with a length of approximately 2 μm, the process of graphene agglomeration is interrupted by PBI, which is inserted into the gap between graphene to prevent the agglomeration of graphene. PBI can solve the problem of easy agglomeration of graphene from the root because it is not conductive, breaks the conductive pathway of graphene, and reduces the electrochemical corrosion of graphene.

The dispersion of graphene would be directly observed by TEM. Figure 4c,d shows the typical TEM images of GR and PBI/GR. It is seen that the graphene has many folds and grooves, indicating that it is stacked up in many layers. For PBI/GR, the bar in the shadow is PBI. In general, there are fewer folds and gullies, and the number of graphene layers is significantly lower. This is because PBI disperses graphene through noncovalent action, preventing it from agglomeration.

The cross-sectional morphology shows the dispersion of graphene in epoxy resin. Figure 5a shows the cross-sectional views of epoxy resin at large magnification; it is found that the resin contains a large number of pores formed by solvent evaporation; this factor makes the resin extremely permeable to the metal base plate, making the epoxy resin not very resistant to corrosion. As shown in Figure 5b, the cross-sectional pores of graphene coating are reduced, proving that the addition of graphene could indeed reduce the penetration of corrosion factors, but its agglomeration was too severe so that they were not compatible with the epoxy and cracks and pores formed around them, which leads to an accelerated corrosion process. As shown in Figure 5c,d, the GR is evenly distributed in the WEP because PBI was adsorbed on the surface of graphene through noncovalent action, preventing the agglomeration of graphene, and the rotary coating method improved the horizontal alignment of graphene. The direction is horizontal and perpendicular to the direction of corrosion factor infiltration, which completely blocks the corrosion path.46

3.3. Electrochemical and Mechanism Analysis of the Coating Systems. The open-circuit potential (OCPT) value is a test method to characterize the stability of coating with the value of voltage changing with time. Figure 6a exhibits the OCPT value for different coatings during 30 days in 3.5% NaCl solution at room temperature (298 K). As can be seen, the OCPT value of the coating system showed a downward trend with the passage of time. After 30 days, the OCPT values of WEP, GR0.5%/WEP, PBI0.25%/GR0.5%/WEP, PBI0.5%/GR0.5%/WEP, and PBI1%/GR0.5%/WEP were about −0.63, −0.71, −0.53, −0.38, and −0.51 V, respectively. The GR0.5%/WEP coating dropped the most, about 0.35 V, and the reason for the rapid drop from 20 to 25 days was probably the electrochemical corrosion caused by graphene. Moreover, the OCPT value of PBI0.5%/GR0.5%/WEP is more positive than those of the others, which proves that the addition of graphene can effectively increase the stability of the coating.

Table 1 shows the polarization curve of the composite coatings after 30 days. In general, a lower corrosion current density (Icorr) and a higher corrosion potential (Ecorr) indicated better corrosion protection for polymer coating.47 The Ecorr of the pure waterborne epoxy coating was −0.71 V vs SCE and the corrosion current density was the highest (7.84 × 10−8 A/cm²), while the corrosion potential of graphene was higher (−0.53 V vs SCE) than that of WEP coating, suggesting that the addition of graphene could delay the corrosion process. Particularly, PE is the protection efficiency of other coatings relative to the blank samples (WEP). The protection efficiency of GR only reaches 54.8%, but that of PBI0.5%/
GR₀.5%/WEP reaches 98.9%, exhibiting the lowest corrosion current (7.94 × 10⁻¹⁰ A/cm²) with the highest \( E_{\text{corr}} \) (−0.368 V vs SCE); the result indicates that graphene plays a shielding role in corrosion protection to enhance the impermeability, with highly dispersed graphene inhibiting the penetration of corrosion factors. \( d^{22} \) is the value used to characterize the corrosion rate. According to the formula of corrosion depth, the corrosion rate of composite coating is calculated as shown in Table 1. The corrosion rate (\( d \)) of pure epoxy resin was 907 nm/year, and the corrosion rate of PBI₀.5%/GR₀.5%/WEP was only 9 nm/year, which greatly reduced the corrosion rate.

\[
\text{PE} = \frac{i_{\text{corr}}^{\text{black}} - i_{\text{corr}}} {i_{\text{corr}}^{\text{black}}}
\]

where PE is the protection efficiency of other coatings relative to the blank samples, \( i_{\text{corr}}^{\text{black}} \) is the corrosion current density of WEP, and \( i_{\text{corr}} \) is the corrosion current of composite coatings.\(^{35}\)

\[
d = \frac{v} {\rho} = 3.28 \times 10^{-3} \frac{M}{nF} i_{\text{corr}}
\]

where \( d \) is the corrosion depth (mm/year), \( i_{\text{corr}} \) is the corrosion current density (\( \mu A/cm² \)), \( M \) is the gram atomic weight of the metal (g), \( n \) is the valence of the metal, \( F \) is Faraday’s constant, and \( \rho \) is metal density (g/cm³).\(^{22,27}\)

Electrochemical impedance spectroscopy (EIS) is one of the commonly used methods to evaluate the corrosion resistance of the coatings. Figure 7a,b is the bode and the phase angle plot of WEP in 10 days. As can be seen from Figure 7a, after 10 days, the impedance value is less than 10⁸ Ω·cm² and the two-time constants are generated in Figure 7b. The Nyquist plot (Figure S3a) shows two semicircles, characterized by two capacitive loops; as the metal produces a pitting reaction, a new time constant appears at 10³ Hz,\(^{38}\) the above data indicates that water molecules and other corrosion factors penetrated the layer in 10 days. Compared with WEP, GR₀.5%/WEP (Figure 7b,d) was tested for 30 days before the occurrence of two-time constants, but the impedance was not very high, only 10⁷ Ω·cm² (Figure 7d), indicating that GR had a certain anticorrosion effect but the anticorrosion effect was not greatly improved.

The impedance values are 7.4 × 10⁷ Ω·cm² for PBI₀.25%/GR₀.5%/WEP (Figure S4a), 2.2 × 10⁹ Ω·cm² for PBI₀.5%/GR₀.5%/WEP (Figure 7e), and 2.1 × 10⁸ Ω·cm² for PBI₁%/GR₀.5%/WEP (Figure S4b) in 10 days. After 30 days, the impedance values were 7.4 × 10⁶ Ω·cm² for PBI₀.25%/GR₀.5%/WEP, 8.2 × 10⁸ Ω·cm² for PBI₀.5%/GR₀.5%/WEP, and 3.5 × 10⁸ Ω·cm² for PBI₁%/GR₀.5%/WEP, which demonstrate that with PBI₀.5%/GR₀.5%/WEP coating acting as excellent barrier, the phase angle decrease from 142 to 80° is much higher than that for WEP and GR₀.5%/WEP.

The equivalent circuit conforms to Figure 8a,b and Table S1, which show the electrochemical fitting data based on the equivalent electrical circuit model. \( R_s \) represents the difficulty of the solution entering the coating as the growth of the time, the easier corrosive medium into the coating, the \( R_p \) is coated on the surface of the micro-hole resistance, represents the
corrosive medium to the metal coating with the ease of interface.26,48 In Table S1, the PBI0.5%/GR0.5%/WEP with maximum corrosion resistance before 20 days. Due to insufficient PBI dispersed graphene, the PBI0.5%/GR0.5%/WEP impedance is higher from 25 to 30 days, so some of it is deposited at the bottom, leading to an increase in the impedance value. \( R_s \) is the polarization resistance of the reaction of metal corrosion; \( CPE_{coat} \) is the coating capacitance; and \( CPE_{dl} \) is the double-layer capacitance.49,50

Figure 9 is the schematic representation of the corrosion resistance mechanisms of WEP, GR/WEP, and PBI/GR/WEP. For WEP (Figure 9a), corrosion factors reach the interface between the coating and the metal along the pores, leading to the corrosion of the metal. Regarding GR/WEP (Figure 9b), graphene has a certain barrier effect; however, due to agglomeration, the barrier effect is uneven, causing corrosive substances in some areas to easily enter the substrate and cause corrosion. For the PBI/GR/WEP composite Figure 9 coating, PBI has a very powerful conjugated system, the \( \pi - \pi \) stacking action between the molecule with the orbital and the graphene electron cloud, which is adsorbed on the graphene nanocrystals to disperse graphene, combined with the rotational coating method, the transverse barrier property of graphene is maximized.3,50 The graphene is evenly dispersed in the water-based epoxy resin, and the corrosive substances need to pass through heavy barriers to enter the substrate to achieve corrosion prevention.

3.4. Tribological Properties of the PBI0.5%/GR0.5%/WEP Composite Coating. To get close to practical application, the friction resistance of the coating was tested; the test conditions were a load of 20 N, a sliding speed of 1.03 m/s, and a sliding duration of 10 min. The representative curves of the coefficient of friction vs sliding time for the samples are shown in Figure 10a,b; at the beginning of the sliding wear, the friction coefficient of the coating increases rapidly (Figure 10a), which is caused by the gradual increase in the actual area of friction.45 After the run-in phase, the friction coefficient fluctuates around a value, this is because of the transfer film and debris generated. Figure 10b shows the average friction coefficient and wear rate; the values of average friction for WEP, GR0.5%/WEP, and PBI0.5%/GR0.5%/WEP are 0.65, 0.53, and 0.33, respectively, and those of the wear rate for WEP, GR0.5%/WEP, and PBI0.5%/GR0.5%/WEP were 6.38 \( \times 10^{-5} \), 1.88 \( \times 10^{-5} \), and 0.79 \( \times 10^{-5} \) mm\(^3\)/(N·m), respectively; for PBI0.5%/GR0.5%/WEP compared with that for WEP, the coefficient of friction decreased by 48% and the wear resistance increased by 87.6%. According to the above data, graphene could reduce the friction coefficient and wear rate; however, due to the agglomeration problem, the reduction was not significant. As a result, PBI improved the dispersion of graphene in epoxy resin and the friction coefficient and reduced the wear rate.

SEM was used to investigate the morphologies of WEP, GR0.5%/WEP, and PBI0.5%/GR0.5%/WEP wear surface. In Figure 11a, WEP has obvious scratches and the surface develops many holes after friction, indicating that the binding between WEP coatings is not strong. The abrasion marks of GR0.5%/WEP (Figure 11b) are less than that of WEP. However, due to the agglomeration of graphene, the number of holes is not significantly reduced. For PBI0.5%/GR0.5%/WEP (Figure 11c), the scratches are almost invisible, with only a few small holes. The results show that the dispersion of graphene combined with the noncovalent and rotating coating method can improve the surface lubricity and reduce the damage caused by friction to the coating.22

4. CONCLUSIONS

The epoxy/graphene composite coating was prepared by a combined noncovalent and rotating coating method with excellent corrosion and friction protection for the Q235 steel. When the ratio of PBI and GR is 1:1, the dispersion effect in the aqueous solution is the best. The SEM results show that graphene is uniformly dispersed and perpendicular to the corrosion factor infiltration in the cross-sectional morphology of PBI0.5%/GR0.5%/WEP coating, which prevents the penetration of corrosive substances. The EIS analysis shows that PBI0.5%/GR0.5%/WEP with the highest impedance is 2.2 \( \times 10^9 \) \( \Omega \)·cm\(^2\), far more than that of GR0.5%/WEP (10\(^7 \) \( \Omega \)·cm\(^2\)) and WEP (10\(^8 \) \( \Omega \)·cm\(^2\)); it is significant for improving the corrosion resistance. For PBI0.5%/GR0.5%/WEP compared with WEP, the coefficient of friction decreased by 48% and the wear resistance increased by 87.6%, which is superior to other composite
coatings. The improvement of the properties broadens the application range of waterborne epoxy resin and provides potential applications for waterborne epoxy resin.

ASSOCIATED CONTENT
* Supporting Information
The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.0c05866.

Preparation process of PBI, the C 1s core level spectrum of PTCDA; the C 1s core level spectrum of PB; the Nyquist plot of WEP, GR_{0.5%}/EP, and PBI_{0.5%}/GR_{0.5%}/WEP; the EIS plots of PBI_{0.25%}/GR_{0.5%}/WEP and PBI_{1%}/GR_{0.5%}/WEP; and the electrochemical corrosion parameter fitted from the equivalent circuit (PDF)

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Author Contributions
L.L. performed the investigation and formal analysis and wrote the original draft. K.L. and L.R. did the investigation and formal analysis. J.Y. and J.C. did the investigation. L.L., K.L., L.R., J.Y., J.C., and Y.L. did the writing, reviewing, and editing. S.L. performed the conceptualization and supervision.

Notes
The authors declare no competing financial interest.

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