

Hierarchical lamellar ZIF-8-based epoxy coatings with time-adaptive, pH-triggered stepwise inhibitor release for durable corrosion protection of magnesium alloys

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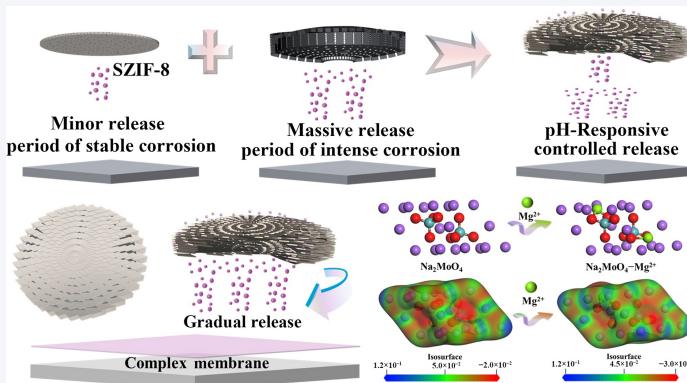
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ABSTRACT: Magnesium alloys are highly susceptible to rapid and non-uniform corrosion in chloride-containing environments. The corrosion process typically evolves from an initially aggressive stage to a relatively stabilized stage during long-term exposure. However, conventional epoxy coatings (EP) and single-stage inhibitor delivery systems cannot effectively adapt to these time-dependent and heterogeneous corrosion conditions, often resulting in premature inhibitor depletion and limited long-term protection. To address this mismatch between corrosion evolution and inhibitor release behavior, a hierarchical porous corrosion inhibitor carrier based on diatomite (DE)-supported sheet-like ZIF-8 loaded with sodium molybdate ($\text{Na}_2\text{MoO}_4@ \text{SZIF-8-DE}$) was rationally designed and incorporated into an E51 epoxy matrix for the protection of AZ31B magnesium alloy. The *in-situ* growth of SZIF-8 on the DE surface effectively suppressed MOF agglomeration while constructing a stable hierarchical porous architecture, which enhanced the inhibitor loading efficiency (12.49%) and structural stability. Ultraviolet-visible (UV-Vis) spectroscopy confirmed the pH-responsive and stepwise release behavior of Na_2MoO_4 from $\text{Na}_2\text{MoO}_4@ \text{SZIF-8-DE}$, enabling rapid inhibitor release during the early aggressive corrosion stage and sustained release during the subsequent stabilized stage. Electrochemical impedance spectroscopy (EIS) results showed that coatings containing $\text{Na}_2\text{MoO}_4@ \text{SZIF-8-DE/EP}$ exhibited significantly higher low-frequency impedance compared with pure EP coatings. Notably, the coating with 10 wt.% $\text{Na}_2\text{MoO}_4@ \text{SZIF-8-DE/EP}$ maintained the highest impedance after 60 days of immersion in 3.5 wt.% NaCl solution, indicating superior long-term corrosion protection. Moreover, simulation analysis demonstrated enhanced interfacial binding between $\text{Na}_2\text{MoO}_4@ \text{SZIF-8-DE}$ and the AZ31B substrate, which facilitated the formation of a dense and stable protective interface.

Complex membrane



Minor release period of stable corrosion

Massive release period of intense corrosion

pH-Responsive controlled release

Gradual release

Complex membrane

1.2x10⁻¹

5.0x10⁻²

2.0x10⁻²

1.2x10⁻¹

3.0x10⁻¹

KEYWORDS: SZIF-8-DE container, smart epoxy coatings (EP) coating, pH-responsive release, Na_2MoO_4 inhibitor, AZ31B corrosion protection

1 Introduction

Magnesium alloys have attracted considerable attention in aerospace, automotive lightweight structures, and electronic

industries due to their low density, high specific strength, effective electromagnetic shielding capability, and excellent vibration damping performance [1–3]. However, their extremely negative standard electrode potential and high chemical reactivity make magnesium alloys highly susceptible to corrosion. This problem becomes particularly severe in chloride-containing environments, which significantly limits their long-term reliability and practical applications [4–6].

Epoxy-based organic coatings are widely used for the protection of magnesium alloys due to their strong adhesion, good mechanical

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properties, and excellent chemical stability [7, 8]. Among them, E51 epoxy resin (EP) has been extensively investigated because of its mature processing technology and superior film-forming ability [9]. However, conventional EP coatings mainly rely on passive barrier protection. During long-term service, micro-defects such as pores, cracks, and interfacial imperfections inevitably form within the coating, facilitating the penetration of corrosive species. This process leads to localized corrosion at the coating-metal interface and ultimately results in coating failure. Therefore, purely passive barrier coatings are insufficient to provide durable protection for magnesium alloys under aggressive environments [10–12].

Importantly, the corrosion of magnesium alloys is a dynamic and non-linear process rather than a steady-state phenomenon. In chloride-containing environments, corrosion typically evolves through an initial aggressive stage, a relatively stabilized stage, and a possible long-term reactivation stage caused by defect evolution or coating degradation. These distinct stages impose different requirements on inhibitor delivery. Rapid inhibitor release is required during the early aggressive stage, whereas sustained and low-rate release is essential for maintaining protection during long-term exposure [13–15]. Therefore, a key scientific challenge lies in achieving corrosion-stage-matched and time-dependent inhibitor release in coating systems. Incorporating corrosion inhibitors into EP coatings can provide active protection; However, direct addition often results in uncontrolled burst release, rapid depletion, and poor dispersion within the coating matrix, which compromises long-term performance [16–18]. Consequently, smart inhibitor carriers capable of controlled and hierarchical release behavior are highly desirable. Metal organic frameworks (MOFs), particularly zeolitic imidazolate framework-8 (ZIF-8), have attracted increasing attention as inhibitor carriers because of their high surface area and tunable pore structures. However, conventional granular ZIF-8 tends to agglomerate in EP matrices and exhibits limited interfacial compatibility, which restricts its effectiveness in coating systems [19–21].

Diatomite (DE) provides an ideal substrate for the *in-situ* growth of MOFs owing to its intrinsic porous structure and abundant surface hydroxyl groups [22]. The *in-situ* construction of sheet-like ZIF-8 (SZIF-8) on DE forms a hierarchical porous carrier with improved structural stability and enhanced inhibitor loading capacity. Compared with conventional granular ZIF-8, the 2D architecture of SZIF-8 acts as a planar diffusion barrier, effectively

prolonging the transport pathways of corrosive species and improving the barrier performance of the coating. More importantly, the hierarchical pore structure enables multi-stage inhibitor release, allowing rapid suppression of early aggressive corrosion while maintaining sustained inhibition during long-term exposure [23–27].

Sodium molybdate (Na_2MoO_4) is an environmentally benign anodic corrosion inhibitor for magnesium alloys; however, its high solubility often leads to rapid depletion when directly incorporated into coatings [28–31]. Encapsulation of Na_2MoO_4 within the hierarchical SZIF-8-DE structure offers an effective approach to control its release behavior, enabling prolonged availability of the inhibitor and achieving sustained long-term corrosion protection.

Based on these considerations, this study presents a corrosion protection strategy guided by corrosion-stage evolution rather than static barrier enhancement. SZIF-8 was *in-situ* grown on DE and loaded with Na_2MoO_4 to construct a hierarchical inhibitor carrier, which was subsequently incorporated into an E51 epoxy matrix for the protection of magnesium alloys. The relationships between carrier microstructure, inhibitor release behavior, and long-term electrochemical performance were systematically investigated, providing mechanistic insight into adaptive, stage-matched corrosion protection for magnesium alloys.

2 Experimental

2.1 Materials

Zinc nitrate hexahydrate ($\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) was from Shanghai Aladdin Reagent Co. Ethyl alcohol and ethyl acetate were from Chongqing Huanghui Chemical Dangerous Goods Sales Co., Ltd. Diatomite (DE), 2-methylimidazole (2-Mim), and Na_2MoO_4 were purchased from Shanghai Maclin Biochemical Technology Co., Ltd. Epoxy resin and curing agent were purchased from Wuxi Qianguang Chemical Raw Materials Co., Ltd. The AZ31B magnesium alloy (10 mm × 10 mm × 2 mm) was purchased from Deno Steel, and the deionized water was homemade by the laboratory.

2.2 Preparation of active fillers

2.2.1 Preparation of SZIF-8-DE filler

As shown in Fig. 1, 0.5 g of DE was dispersed in 70 mL of deionized water and ultrasonicated at room temperature for 30 min to form a

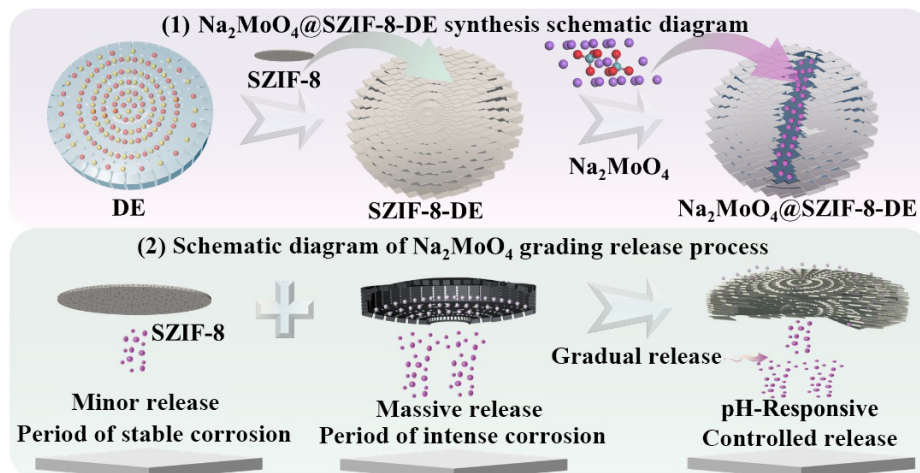


Figure 1 Schematic diagram of SZIF-8-DE synthesis and gradual release characteristics of Na_2MoO_4 @SZIF-8-DE.

uniform suspension. Then, 3.45 g of 2-Mim was added, and the mixture was ultrasonicated for an additional 15 min to ensure homogeneous distribution. Meanwhile, 1.25 g of $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ was dissolved in 30 mL of deionized water under continuous stirring. The Zn precursor solution was added dropwise to the DE and 2-Mim suspension, followed by magnetic stirring at room temperature for 2 h to promote the *in-situ* growth of SZIF-8 on the DE surface. After the reaction, the resulting suspension was centrifuged at 8000 rpm for 10 min, and the collected precipitate was washed twice with deionized water to remove unreacted species. Finally, the product was dried at 60 °C for 6 h to obtain the SZIF-8-DE composite material.

For the control experiment, 4.48 g of 2-Mim was dissolved in 70 mL of methyl alcohol and ultrasonicated for 15 min to obtain a clear and homogeneous solution. Meanwhile, 1.25 g of $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ was dissolved in 30 mL of methyl alcohol under continuous stirring. The $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ solution was then added dropwise to the 2-Mim solution, followed by magnetic stirring at room temperature for 2 h to complete the reaction. The resulting precipitate was collected by centrifugation at 8000 rpm for 10 min, washed twice with deionized water, and dried at 60 °C for 6 h to yield the SZIF-8-DE sample.

2.2.2 Preparation of Na_2MoO_4 @SZIF-8-DE filler

The synthesized SZIF-8-DE was used as a carrier to prepare the Na_2MoO_4 @SZIF-8-DE composite material. Equal masses of Na_2MoO_4 and SZIF-8-DE (typically 0.5–1.0 g each, depending on the desired yield) were accurately weighed and dispersed in 50–100 mL of distilled water. The mixture was magnetically stirred at 600–800 rpm for 30–60 min to form a uniform suspension, followed by ultrasonication for 10–15 min to enhance dispersion and promote adsorption of Na_2MoO_4 within the porous structure of SZIF-8-DE. The resulting suspension was then dried in a

vacuum oven at 60 °C under reduced pressure (0.08 MPa) for 12 h. After drying, the pressure was slowly returned to atmospheric conditions, and the sample was equilibrated for 1 h to stabilize the composite structure. Finally, the dried solid was gently ground in a mortar to break up agglomerates, yielding a fine powder, which was stored in a dry environment for subsequent use.

2.3 Simulation of barrier properties

Molecular dynamics (MD) simulations were conducted using the Materials Studio software to systematically investigate the barrier properties of Na_2MoO_4 @SZIF-8-DE/EP composite coatings. Amorphous coating models were constructed with the Amorphous Cell module, and periodic boundary conditions were applied along all three spatial directions. The simulation cells were defined as orthorhombic systems with lattice parameters $\alpha = \beta = \gamma = 90^\circ$, ensuring structural consistency and computational reliability (schematic representations are shown in Fig. 2).

Eight coating models with varying compositions were constructed: (i) EP coating ($24.8 \text{ \AA} \times 24.8 \text{ \AA} \times 24.8 \text{ \AA}$) containing 20 EP molecules, 3 Cl^- , 3 H_2O molecules, and 1 O_2 molecule; (ii) $\text{DE}_{10 \text{ wt\%}}/\text{EP}$ coating ($25.0 \text{ \AA} \times 25.0 \text{ \AA} \times 25.0 \text{ \AA}$) comprising 18 EP molecules, 2 DE units, 3 Cl^- , 3 H_2O molecules, and 1 O_2 molecule; (iii) $\text{Na}_2\text{MoO}_4/\text{DE}_{5 \text{ wt\%}}/\text{EP}$ coating ($25.6 \text{ \AA} \times 25.6 \text{ \AA} \times 25.6 \text{ \AA}$) including 19 EP molecules, 1 $\text{Na}_2\text{MoO}_4/\text{DE}$ unit, 3 Cl^- , 3 H_2O molecules, and 1 O_2 molecule; (iv) $\text{Na}_2\text{MoO}_4/\text{DE}_{10 \text{ wt\%}}/\text{EP}$ coating ($26.2 \text{ \AA} \times 26.2 \text{ \AA} \times 26.2 \text{ \AA}$) containing 18 EP molecules and 2 $\text{Na}_2\text{MoO}_4/\text{DE}$ units, 3 Cl^- , 3 H_2O molecules, and 1 O_2 molecule; (v) $\text{Na}_2\text{MoO}_4/\text{DE}_{20 \text{ wt\%}}/\text{EP}$ coating ($26.9 \text{ \AA} \times 26.9 \text{ \AA} \times 26.9 \text{ \AA}$) with 17 EP molecules and 3 $\text{Na}_2\text{MoO}_4/\text{DE}$ units, 3 Cl^- , 3 H_2O molecules, and 1 O_2 molecule; (vi) (Na_2MoO_4 @SZIF-8-DE) Filler_{5 wt%}/EP coating ($26.0 \text{ \AA} \times 26.0 \text{ \AA} \times 26.0 \text{ \AA}$) including 19 EP molecules and 1 Na_2MoO_4 @SZIF-8-DE unit, 3 Cl^- , 3 H_2O molecules, and 1 O_2 molecule; (vii) Filler_{10 wt%}/EP coating ($27.0 \text{ \AA} \times 27.0 \text{ \AA} \times 27.0 \text{ \AA}$)

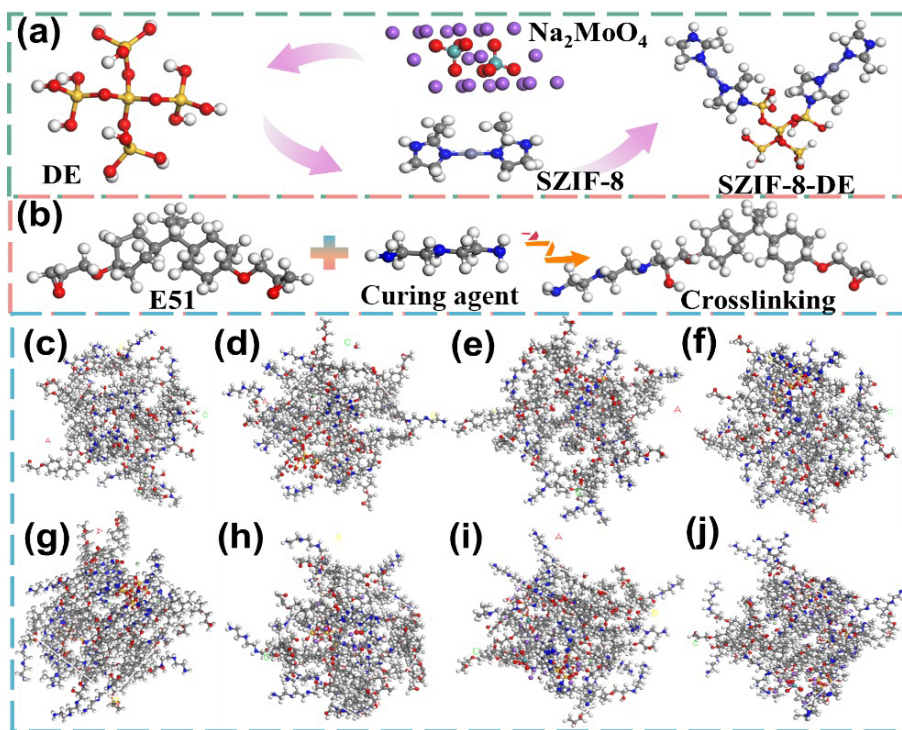


Figure 2 (a) The molecular structures of the fillers and intermediate products. (b) The molecular structure of EP resin and curing agent. MD modeling of (c) EP, (d) $\text{DE}_{10 \text{ wt\%}}/\text{EP}$, (e) $\text{Na}_2\text{MoO}_4/\text{DE}_{5 \text{ wt\%}}/\text{EP}$, (f) $\text{Na}_2\text{MoO}_4/\text{DE}_{10 \text{ wt\%}}/\text{EP}$, (g) $\text{Na}_2\text{MoO}_4/\text{DE}_{20 \text{ wt\%}}/\text{EP}$, (h) Filler_{5 wt%}/EP, (i) Filler_{10 wt%}/EP, and (j) Filler_{20 wt%}/EP coatings.

containing 18 EP molecules and 2 Na_2MoO_4 @SZIF-8-DE units, 3 Cl^- , 3 H_2O molecules, and 1 O_2 molecule; (viii) Filler_{20 wt. %}/EP coating ($27.9 \text{ \AA} \times 27.9 \text{ \AA} \times 27.9 \text{ \AA}$) consisting of 17 EP molecules and 3 Na_2MoO_4 @SZIF-8-DE units, 3 Cl^- , 3 H_2O molecules, and 1 O_2 molecule.

All coating systems contained identical amounts of corrosive species 3 Cl^- , 3 H_2O molecules, and 1 O_2 molecule to ensure comparability. Prior to molecular dynamics simulations, energy minimization was performed for all models to remove unfavorable contacts and reduce internal stress. A combination of the smart minimizer algorithm and the conjugate gradient method was employed to achieve full energy convergence. Subsequently, MD simulations were performed using the COMPASS II force field under isothermal-isobaric (NPT) conditions at 298 K and 1 atm. Both van der Waals and long-range electrostatic interactions were considered, with an electrostatic cutoff distance of 10 $\text{\AA}$.

To ensure adequate equilibration, each system was relaxed for 300 ps under the NPT ensemble until a stable thermodynamic state was reached. The barrier performance and anticorrosion mechanisms of the coatings were subsequently assessed by analyzing the mean square displacement (MSD) of aggressive species (H_2O , O_2 , and Cl^-) and the evolution of fractional free volume (FFV) within the coating matrices. These analyses provide molecular-level insights into the enhanced barrier effects imparted by Na_2MoO_4 /DE and Na_2MoO_4 @SZIF-8-DE fillers in EP coatings.

2.4 Preparation of composite coatings

AZ31B magnesium alloy substrates were sequentially polished using 600, 800, and 1000-grit silicon carbide sandpapers, ultrasonically cleaned in anhydrous ethanol to remove surface contaminants, and subsequently preheated on a heating plate at 120 °C. The EP-based coating solution was prepared by dissolving 1.5 g of E51 epoxy resin and 1.5 g of curing agent in 15 mL of ethyl acetate. The prepared solution was uniformly deposited onto the magnesium substrates by high-pressure spraying, followed by curing at 150 °C for 2 h to obtain the pure EP coating. For composite coatings, functional fillers (0.15, 0.30, and 0.60 g of Na_2MoO_4 @SZIF-8-DE) were incorporated into the base solution under mechanical stirring to ensure homogeneous dispersion. The spraying and curing procedures were identical to those used for the pure EP system, resulting in DE/EP, SZIF-8-DE/EP, and Na_2MoO_4 @SZIF-8-DE/EP composite coatings. To exclude the influence of thickness on corrosion performance, all coatings were carefully controlled under identical spraying parameters and solid contents. The dry film thickness was measured at no fewer than five randomly selected positions on each sample using a coating thickness gauge, and the average value was calculated. The results indicate that the thickness of all coatings was maintained at approximately $120 \pm 5 \text{ \mu m}$, with no significant difference among the samples, ensuring that the variations in corrosion behavior arise primarily from compositional differences rather than thickness effects.

2.5 Characterization of the active filler

The molecular structures of Na_2MoO_4 , SZIF-8, DE, SZIF-8-DE, and Na_2MoO_4 @SZIF-8-DE were examined by Fourier-transform infrared (FTIR) spectroscopy. Their crystalline phases were identified by X-ray diffraction (XRD) using a SHIMADZU XRD-7000 diffractometer equipped with Cu K α radiation, operated at a scan rate of 5 °C/min over a 2θ range of 5°–80°. The surface elemental composition and corresponding chemical states of

Na_2MoO_4 , SZIF-8, DE, and Na_2MoO_4 @SZIF-8-DE were further analyzed by X-ray photoelectron spectroscopy (XPS). In addition, the surface morphology, internal structure, and elemental distribution of the modified DE microcapsules were systematically characterized using field-emission scanning electron microscopy (SEM), transmission electron microscopy (TEM), and high-angle annular dark-field energy-dispersive spectroscopy (HAADF-EDS). The corrosion inhibitor loading content was determined by thermogravimetric analysis (TGA, LS00-HS-TGA-101) under a N_2 atmosphere at a heating rate of 10 °C/min. The cumulative release of Na_2MoO_4 was calculated using the standard curve method, revealing the release profile of the corrosion inhibitor in solutions with different pH values over time.

2.6 Corrosion test

The corrosion resistance of the coatings was evaluated by electrochemical impedance spectroscopy (EIS) using a CS310M electrochemical workstation in a conventional three-electrode setup. The coated specimen was used as the working electrode, with a saturated calomel electrode (SCE) and a platinum sheet serving as the reference and counter electrodes, respectively. All measurements were carried out in a 3.5 wt.% NaCl solution at 25 °C and 65% relative humidity. EIS spectra were recorded at the open-circuit potential with a sinusoidal perturbation amplitude of 10 mV over a frequency range from 10^5 to 10^{-2} Hz, ensuring reliable and comparable electrochemical data.

2.6.1 Research on the corrosion inhibiting performance of fillers

The corrosive media for the different systems were prepared by dispersing 0.1 g of each active filler (DE, SZIF-8-DE, and Na_2MoO_4 @SZIF-8-DE) into 50 mL of 3.5 wt.% NaCl solution. Polished metal substrates were immersed in each dispersion, and their low-frequency impedance modulus ($|Z|_{0.01\text{Hz}}$) was determined using EIS. Electrochemical measurements were performed after 1 and 7 days of immersion to assess the effect of different active fillers on the long-term corrosion behavior of the metal substrates.

2.6.2 Comprehensive coating anti-corrosion performance test

The coated samples were then subjected to electrochemical testing by immersion in a 3.5 wt.% NaCl solution at room temperature. The complex impedance at 0.01 Hz was measured at multiple exposure times, including 5, 15, 30, 45, and 60 days. To evaluate the long-term corrosion protection stability. All electrochemical tests were performed at 25 °C to ensure consistent experimental conditions, and the effective exposed area of the metal substrate was $4\pi \text{ cm}^2$. EIS measurements were conducted over a frequency range of 10^5 to 10^{-2} Hz, with an applied alternating current perturbation voltage of 10 mV.

To evaluate the corrosion inhibition and self-healing performance of the coatings under service-damage conditions, artificial scratches with a length of approximately 2 cm were introduced on the coating surface. The scratched samples were then continuously exposed to a 5 wt.% NaCl salt spray environment at 50 °C for 7 days. The corrosion evolution was monitored by observing the changes in surface morphology during the exposure process. After the corrosion test, a three-dimensional (3D) white-light interferometric microscope was employed to quantitatively evaluate the corrosion extent by measuring the surface morphology and roughness parameters of the magnesium alloy substrate. Finally, the composition and structure of the corrosion products

were analyzed by Raman mapping, XPS, and XRD to verify the formation of passivation films and to further elucidate their formation mechanism.

2.7 Wear resistance test

Wear resistance is an important parameter for evaluating the overall protective performance of coatings. In this study, a Taber abrasion tester was used to investigate the wear behavior of pure EP coatings and composite coatings containing different amounts of $\text{Na}_2\text{MoO}_4/\text{SZIF-8-DE}$. During the test, a 1000-grit silicon carbide abrasive wheel was used as the wear medium and operated at a rotational speed of 60 rpm. All abrasion tests were carried out at room temperature with a relative humidity of approximately 65%. During the testing process, the coated samples were subjected to continuous contact and sliding against the silicon carbide abrasive wheel under a standard load of 5 N. The wear resistance and mechanical stability of the coatings were evaluated by comparing the surface wear characteristics before and after the abrasion tests.

3 Results and discussion

3.1 Analysis of the surface morphology of active fillers

The morphology and compositional characteristics of natural DE are clearly presented in Figs. 3(a)–3(c). The material exhibits a regular spherical structure resembling a round sieve, with a diameter of approximately 30 μm , uniformly distributed surface pores, and an intact framework, reflecting the naturally ordered porous nature of DE. EDS mapping (Figs. 3(b) and 3(c)) and elemental analysis (Fig. 3(m)) further confirm that pure DE consists

solely of Si and O elements, with atomic percentages of 34.71% and 65.29%, respectively [32]. This composition is consistent with the Si-O framework of DE. The modified SZIF-8-DE material retains the spherical morphology of DE at the macroscale (Fig. 3(d)) but exhibits significant modifications in surface microstructure. High-magnification SEM images (Figs. 3(e) and 3(f)) reveal that the surface of DE is densely covered by numerous nanosheets with a thickness of approximately 200 nm and lateral dimensions of 1–2 μm . These nanosheets are closely stacked, forming a lamellar-assembled, multilevel structure. This architecture not only preserves the macroscopic spherical morphology of DE but also establishes a rich hierarchical pore network through nanosheet stacking, effectively enhancing the specific surface area and the number of interfacial reaction sites of the material.

Regarding the distribution of components, the EDS mapping results presented in Figs. 3(h)–3(l) indicate that Si and O, originating from the DE substrate, together with Zn, N, and C, corresponding to the SZIF-8 components, are homogeneously distributed across the surface of the SZIF-8-DE material, with no noticeable elemental agglomeration. The quantitative EDS analysis shown in Fig. 3(n) further confirms this observation, with measured atomic percentages of Si (6.63%), O (7.73%), Zn (22.10%), N (8.29%), and C (55.25%). These results confirm the successful anchoring and uniform growth of the characteristic Zn-N₄ coordination units of SZIF-8 on the surface of the DE carrier, evidencing the formation of a well-defined composite between SZIF-8 and the DE substrate. Moreover, the density functional theory (DFT)-simulated structural model depicted in Fig. 3(o) illustrates the microscopic coordination configuration of SZIF-8-DE. In this model, Si atoms, serving as the core units of the DE

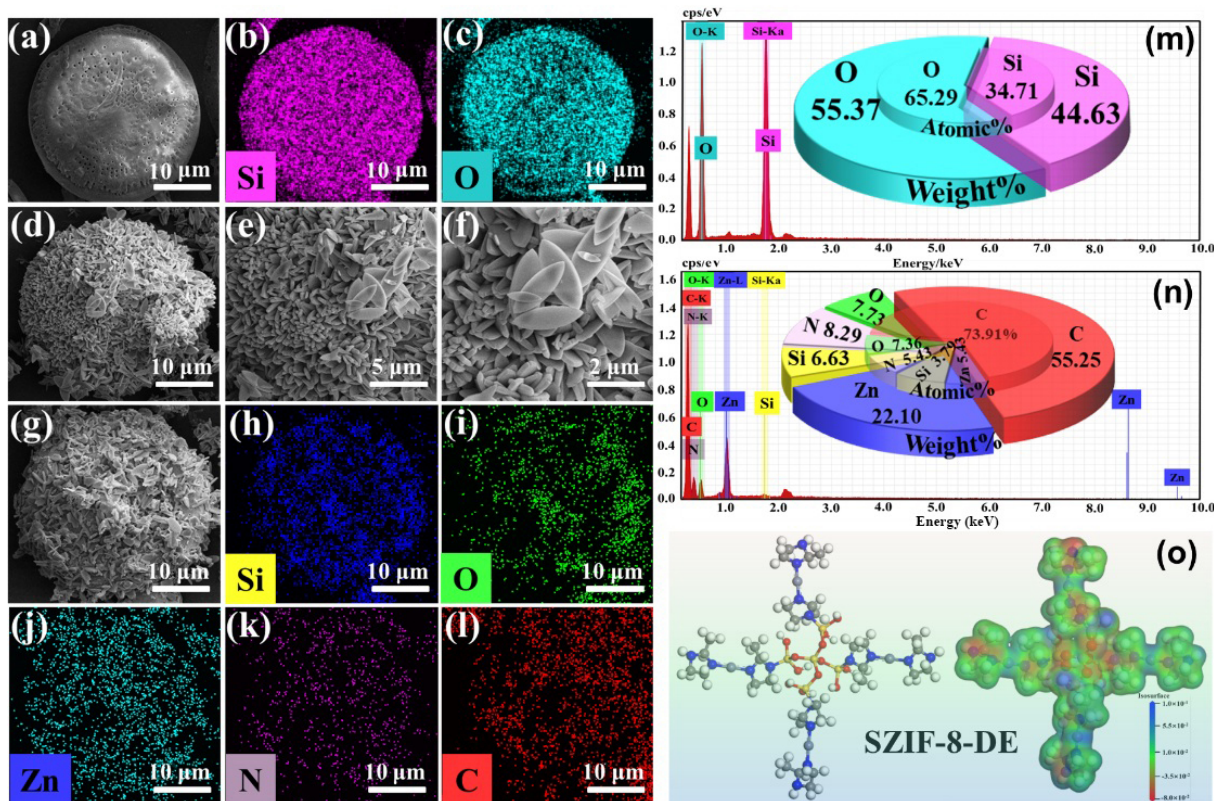


Figure 3 (a) SEM image of DE, (b) and (c) element distribution maps with the spatial distribution of Si and O. (d)–(f) SZIF-8-DE images at different magnifications, (g)–(l) SZIF-8-DE image and corresponding element distribution maps with the spatial distribution of Si, O, Zn, N, and C. Statistical map of elemental contents of (m) DE and (n) SZIF-8-DE. (o) DFT of SZIF-8.

substrate, interact with the Zn-N coordination framework of SZIF-8 through interfacial interactions, thereby preserving the structural stability of the Si backbone and maintaining the characteristic porous coordination network of SZIF-8. The combination of the sheet-like assembly morphology and uniform elemental distribution synergistically provides abundant active sites and efficient mass-transfer pathways, which are favorable for subsequent functional applications.

As shown in Fig. 4, the morphology, elemental distribution, structural characteristics, and growth mechanism of the $\text{Na}_2\text{MoO}_4/\text{SZIF-8-DE}$ composite materials were systematically analyzed. TEM images and EDS mapping of SZIF-8 monomers, with sizes ranging from 1 to 2 μm , reveal a homogeneous distribution of N, O, C, and Zn, confirming that the prepared sheet-like material corresponds to SZIF-8 [33]. At the macroscale, $\text{Na}_2\text{MoO}_4/\text{SZIF-8-DE}$ retains the circular sieve-like morphology of the DE substrate, with an approximate diameter of 30 μm . EDS mapping further demonstrates that Zn and N (characteristic elements of SZIF-8), Na and Mo (associated with the Na_2MoO_4 loading), and Si and O (originating from the DE substrate) are uniformly distributed throughout the composite without noticeable agglomeration. These results indicate that Na_2MoO_4 was successfully loaded while maintaining the elemental homogeneity of the material. Moreover, the overall morphology of $\text{Na}_2\text{MoO}_4/\text{SZIF-8-DE}$ shows no significant changes compared with SZIF-8-DE following the loading process.

As illustrated in Fig. 4(l), DFT calculation results based on electron density differences (isosurface) visually reveal the charge distribution and interfacial interaction patterns in the DE, SZIF-8,

and SZIF-8-DE systems. In the DE system on the left, the charge accumulation regions, indicated in red with a value of 1.4×10^{-1} , are concentrated at surface oxygen-containing functional groups, whereas the charge depletion regions, indicated in blue with a value of -7.0×10^{-2} , correspond to the Si-O backbone, reflecting the electronegative nature of the DE surface groups. In the central SZIF-8 system, the charge accumulation regions, indicated in red with a value of 8.0×10^{-2} , cluster around the N atoms of the imidazole rings, while the C framework acts as the charge depletion region, reflecting the electron-rich nature of the SZIF-8 ligands. In the SZIF-8-DE composite system, the charge accumulation region, indicated in red with a value of 1.2×10^{-1} , simultaneously covers the oxygen-containing groups of DE and the N atoms of SZIF-8. The interface region exhibits a continuous charge gradient from red to green to blue, while the charge depletion zone bridges the two frameworks. This distribution pattern indicates significant interfacial charge transfer between DE and SZIF-8, representing not simple physical mixing but chemical bonding achieved through electron interactions between oxygen-containing groups and N atoms. This provides electronic structural support for the composite system, enhancing both its structural stability and functional synergy [34, 35].

As shown in Fig. 4(m), the *in-situ* growth of SZIF-8 on DE, as well as the control of its morphology through the solvent system (methanol and water) and the Zn^{2+} -2-Mim molar ratio, is fundamentally governed by the modulation of nucleation rate, coordination equilibrium, and anisotropic crystal growth behavior. When water is used as the solvent, enhanced solubilization and hydrolysis of Zn^{2+} partially inhibit Zn-N coordination, thereby

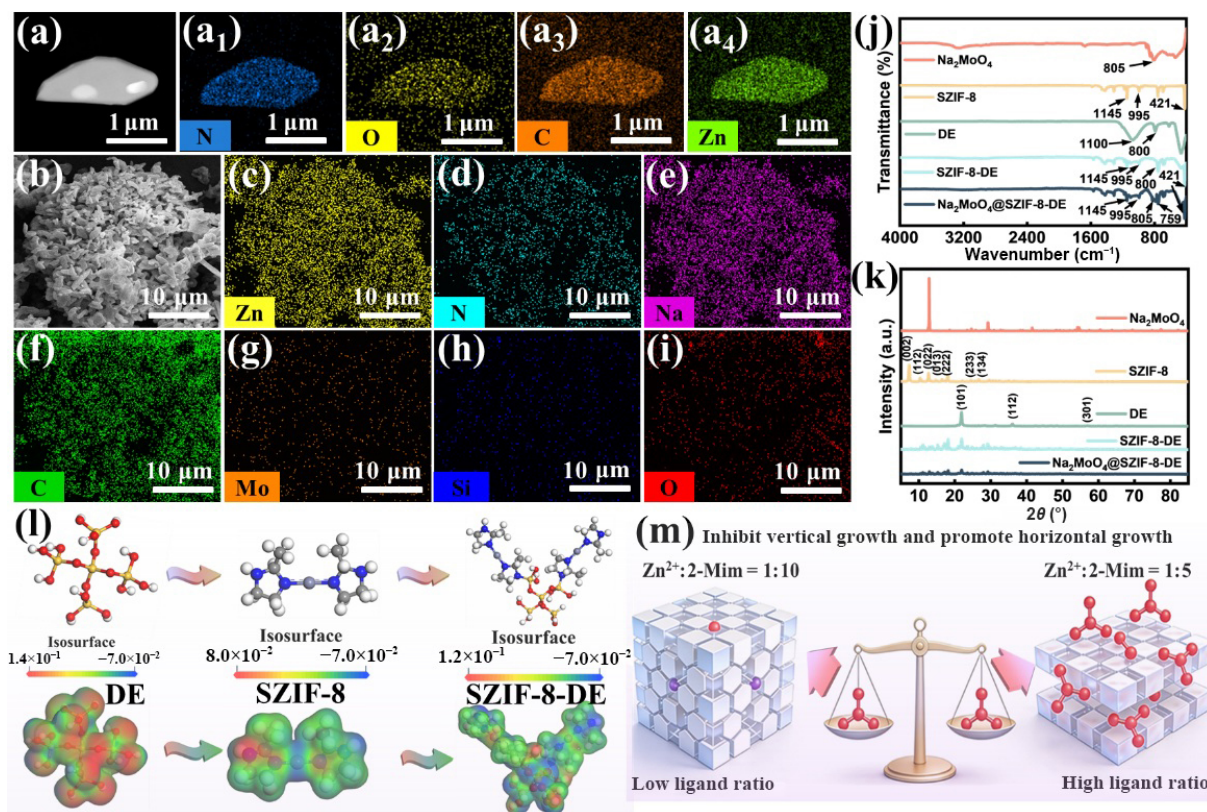


Figure 4 (a)–(a₄) TEM image of SZIF-8 and main element distribution diagrams. (b) SEM image of $\text{Na}_2\text{MoO}_4/\text{SZIF-8-DE}$, (c)–(i) elemental distribution maps with the spatial distribution of Zn, N, Na, C, Mo, Si, and O elements, respectively. (j) FTIR spectra and (k) XRD patterns of Na_2MoO_4 , SZIF-8, DE, SZIF-8-DE, and $\text{Na}_2\text{MoO}_4/\text{SZIF-8-DE}$. (l) DFT process of the complexation of SZIF-8 and DE. (m) SZIF-8 growth mechanism diagram.

slowing the overall crystal growth rate. However, this also promotes heterogeneous nucleation on the DE surface. Concurrently, the selective adsorption of water molecules onto specific crystal planes suppresses vertical growth, favoring the formation of 2D sheet-like or thin-film structures. In contrast, methanol accelerates Zn^{2+} -2-Mim coordination, which facilitates the formation of isotropic polyhedral crystals [36, 37]. Moreover, increasing the concentration of Zn^{2+} accelerates the initial nucleation process and enhances local Zn enrichment, leading to relative ligand deficiency or incomplete coordination. This condition promotes lateral expansion along low-energy crystal planes, thereby facilitating the formation of lamellar structures. Consequently, the observed trend that using water as the solvent and increasing Zn content favors the formation of sheet-like materials arises from the combined effects of reduced driving force for 3D isotropic growth and the promotion of interface-induced and crystal plane-selective growth mechanisms.

3.2 Analysis of the chemical structure of active fillers

3.2.1 FTIR analysis

As illustrated in Fig. 4(j), the FTIR spectra of Na_2MoO_4 , SZIF-8, DE, and their composites, SZIF-8-DE and $\text{Na}_2\text{MoO}_4@\text{SZIF-8-DE}$, were analyzed. The pure Na_2MoO_4 sample exhibits strong absorption in the 700–900 cm^{-1} range, characteristic of tetrahedral or octahedral Mo–O or MoO_4^{2-} groups [38]. Similar absorption is observed at the same position in the FTIR spectrum of $\text{Na}_2\text{MoO}_4@\text{SZIF-8-DE}$, confirming the retention of the MoO_4^{2-} vibrational peak and indicating that Na_2MoO_4 was successfully incorporated into the composite. The FTIR spectrum of DE shows characteristic absorption peaks of the siloxane backbone, including the asymmetric Si–O–Si stretching at 1100 cm^{-1} and the bending vibration at 759 cm^{-1} . These Si–O absorptions are preserved in both SZIF-8-DE and $\text{Na}_2\text{MoO}_4@\text{SZIF-8-DE}$, demonstrating that the DE framework remains intact within the composites [39, 40]. SZIF-8 exhibits absorption peaks at 995 and 1145 cm^{-1} , corresponding to C–N and C=N stretching vibrations, respectively, as well as Zn–N stretching vibrations at 421 cm^{-1} in the low-wavenumber region [41]. In $\text{Na}_2\text{MoO}_4@\text{SZIF-8-DE}$, these imidazole-related absorptions are maintained, confirming that the SZIF-8 structure is preserved and effectively interacts with both Na_2MoO_4 and DE. Collectively, these observations verify the successful synthesis of the $\text{Na}_2\text{MoO}_4@\text{SZIF-8-DE}$ composite material.

3.2.2 XRD analysis

As shown in Fig. 4(k), the XRD patterns of Na_2MoO_4 , SZIF-8, DE, and their composites, SZIF-8-DE and $\text{Na}_2\text{MoO}_4@\text{SZIF-8-DE}$, were analyzed. The diffraction peaks observed at $2\theta = 21.9^\circ$, 36.1° , and 56.9° correspond to the (101), (112), and (301) crystal planes of crystalline SiO_2 , respectively, which are characteristic of the SiO_2 framework in DE [39]. Pure Na_2MoO_4 exhibits a series of sharp and intense diffraction peaks, particularly prominent in the low-angle region [42], indicative of its high crystallinity. SZIF-8 displays diffraction peaks at $2\theta = 7.3^\circ$, 10.3° , 12.7° , 14.6° , 16.4° , 24.4° , and 26.6° , corresponding to the (002), (112), (022), (013), (222), (233), and (134) reflection planes. These peaks arise from the planar diffraction of the rhombic dodecahedral units that constitute the SZIF-8 framework, confirming its well-defined crystalline structure.

In the composite material, the characteristic low-angle diffraction peaks of SZIF-8 are clearly preserved, indicating that the framework structure of SZIF-8 remained intact during the composite

formation. The broad diffuse diffraction background of DE is also evident, demonstrating that DE effectively served as a carrier in constructing the composite system. In contrast, the diffraction peaks of pure Na_2MoO_4 show a substantial reduction in intensity and sharpness upon incorporation into $\text{Na}_2\text{MoO}_4@\text{SZIF-8-DE}$, suggesting that Na_2MoO_4 exists in a highly dispersed, nanoscale, or encapsulated state within the composite, no longer forming large crystalline domains, which renders its characteristic diffraction peaks less distinguishable. The combined observation of preserved SZIF-8 peaks, diffuse DE background, and the attenuated Na_2MoO_4 reflections confirms that Na_2MoO_4 was successfully loaded into the SZIF-8-DE framework rather than simply physically mixed. These results collectively verify the successful integration of Na_2MoO_4 , SZIF-8, and DE into a well-defined composite system, confirming the successful synthesis of $\text{Na}_2\text{MoO}_4@\text{SZIF-8-DE}$.

3.2.3 XPS analysis

Further analysis of the chemical composition and bonding environment of the synthesized materials was carried out using XPS on Na_2MoO_4 , DE, SZIF-8, and $\text{Na}_2\text{MoO}_4@\text{SZIF-8-DE}$ samples. As shown in Fig. 5, the XPS survey spectra of Na_2MoO_4 clearly reveals the presence of Na, Mo, and O, consistent with its chemical composition. The high-resolution Mo 3d spectrum displays a characteristic doublet for Mo^{6+} , with binding energies of 232.3 (Mo 3d_{5/2}) and 235.6 eV (Mo 3d_{3/2}), corresponding to Mo^{6+} in MoO_4^{2-} . The Na 1s spectrum exhibits a strong peak at 1070.8 eV, characteristic of Na^+ , while the O 1s spectrum shows a broad peak at 531.2 eV, attributable to O in Mo–O bonds [43].

The XPS spectrum of pure DE shows characteristic peaks for Si 2p and O 1s, consistent with the SiO_2 framework of the DE substrate [40]. SZIF-8 exhibits peaks for C, N, O, and Zn, in agreement with the expected elemental composition of SZIF-8. In the high-resolution C 1s spectrum, the peak at 284.4 eV corresponds to C atoms in C–C/C=C bonds of the organic ligands, representing the typical C binding energy of SZIF-8 ligands. The N 1s spectrum shows a peak at 398.7 eV, attributed to N atoms in the imidazole rings coordinated with Zn^{2+} , confirming the formation of the SZIF-8 coordination framework. The broad O 1s peak at 531.4 eV is assigned to adsorbed O or OH^- species on the surface. The Zn 2p spectrum exhibits the characteristic spin-orbit split doublet, with Zn 2p_{3/2} and Zn 2p_{1/2} peaks at 1021.6 and 1044.6 eV, respectively, corresponding to Zn^{2+} coordinated with N atoms in the ZIF-8 framework. These binding energies fall within the expected range for Zn^{2+} in SZIF-8 materials, confirming both the chemical state and coordination environment of Zn^{2+} [44, 45].

Following the loading of the corrosion inhibitor Na_2MoO_4 , XPS characterization was employed to confirm the composition and structural integrity of the $\text{Na}_2\text{MoO}_4@\text{SZIF-8-DE}$ composite. The survey spectrum reveals the presence of seven elements: C, N, Si, Na, Zn, Mo, and O. C, N, and Zn are attributed to the SZIF-8 coordination framework, Si originates from the DE substrate (SiO_2), and Na and Mo derive from the loaded Na_2MoO_4 . O is distributed among Si–O bonds, the oxygen-containing functional groups of SZIF-8, and Mo–O bonds. In the high-resolution spectra, the C 1s peak at 284.4 eV corresponds to C–C and C=C bonds in the SZIF-8 ligand. The Mo 3d spectrum displays a doublet at 232.3 and 235.6 eV, consistent with the Mo^{6+} oxidation state in MoO_4^{2-} . The N 1s peak at 398.7 eV is attributed to Zn–N coordination bonds in SZIF-8, while the Na 1s peak at 1070.8 eV corresponds to Na^+ . The broad O 1s peak at 531.2 eV represents contributions from Si–O bonds,

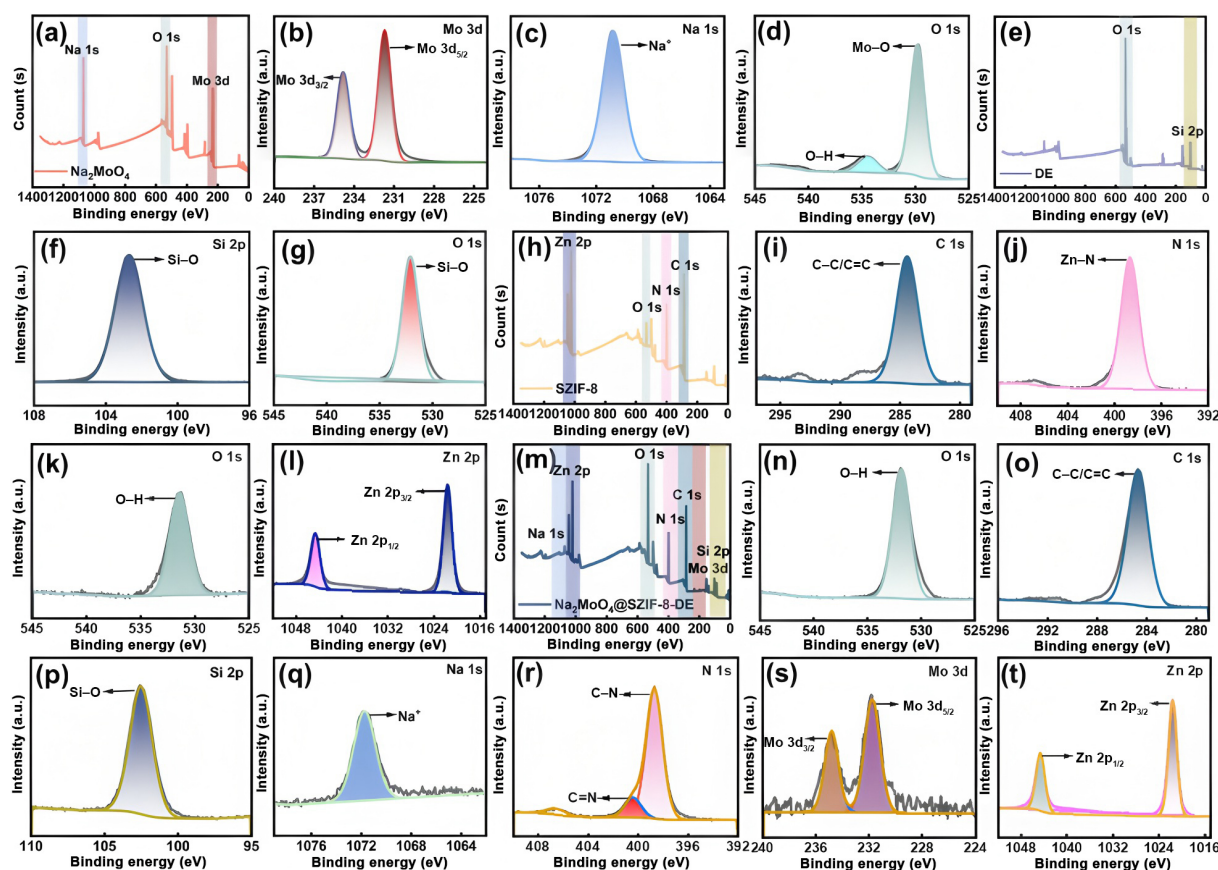


Figure 5 (a) XPS survey spectrum of Na_2MoO_4 and high-resolution XPS spectra of (b) Mo 3d, (c) Na 1s, and (d) O 1s. (e) XPS survey spectrum of DE and high-resolution XPS spectra of (f) Si 2p and (g) O 1s. (h) XPS survey spectrum of SZIF-8 and high-resolution XPS spectra of (i) C 1s, (j) N 1s, (k) O 1s, (l) Zn 2p. (m) XPS survey spectrum of Na_2MoO_4 @SZIF-8-DE and high-resolution XPS spectra of (n) O 1s, (o) C 1s, (p) Si 2p, (q) Na 1s, (r) N 1s, (s) Mo 3d, and (t) Zn 2p.

OH⁻ species, and Mo–O bonds. The Si 2p peak at 103.5 eV is assigned to Si in SiO_2 , and the Zn 2p spectrum shows the characteristic spin-orbit doublet at 1021.6 (Zn 2p_{3/2}) and 1044.6 eV (Zn 2p_{1/2}), consistent with Zn²⁺ in SZIF-8. Collectively, these results confirm the successful growth of SZIF-8 on the DE surface and the effective incorporation of Na_2MoO_4 . Notably, the chemical states and structural integrity of all components remain stable, providing compositional and structural support for the corrosion-protection functionality of the composite.

3.3 Analysis of the pore structure and thermal stability of active fillers

Figures 6(a)–6(e) present the N_2 adsorption–desorption isotherms of SZIF-8, DE, SZIF-8-DE, and Na_2MoO_4 @SZIF-8-DE, along with the corresponding data summarized in Table S1 in the Electronic Supplementary Material (ESM). SZIF-8 exhibits rapid adsorption at low relative pressures, characteristic of a Type I isotherm, consistent with its micropore-dominated structure [46]. In contrast, DE shows a low adsorption capacity without a distinct plateau, in agreement with its mesoporous nature. The pore size distribution of Na_2MoO_4 @SZIF-8-DE reveals a diminished mesoporous peak and an increased proportion of micropores, suggesting that some mesopores were partially filled and additional micropore sites were generated upon loading. Pure SZIF-8 displays typical microporous behavior, with a high Brunauer–Emmett–Teller (BET) specific surface area of 624.505 m²/g, a pore volume of 0.2413 cm³/g, and an average pore diameter of 1.9042 nm, reflecting its intrinsically high

surface area and micropore-dominated architecture.

DE exhibits a BET specific surface area of 1.9174 m²/g and an average pore diameter of 19.364 nm, reflecting its intrinsically porous framework dominated by large mesopores, along with a relatively low pore volume of 0.0214 cm³/g. After composite modification, the surface area of SZIF-8-DE increased to 8.5698 m²/g, while the average pore diameter decreased to 4.7768 nm, indicating that the SZIF-8 component grown on the DE surface introduced additional micropore sites while partially retaining the original mesoporous structure. Consequently, a hierarchical micropore-mesoporous system is formed, which increases the composite's specific surface area and alleviates the mass transfer limitations associated with the extremely small pores of pure SZIF-8. Upon loading with Na_2MoO_4 , the BET surface area of Na_2MoO_4 @SZIF-8-DE further increased to 9.7615 m²/g, while the average pore diameter decreased to 1.7469 nm, approaching the micropore size of SZIF-8. Simultaneously, the pore volume decreased markedly to 0.0013 cm³/g, as Na_2MoO_4 particles partially occupied the mesoporous channels of SZIF-8-DE. The dispersion and loading process also exposes more active sites within the SZIF-8 framework, resulting in a structure predominantly composed of micropores with mesopores as a supplementary feature. This hierarchical pore architecture provides abundant reactive sites and moderate mass transfer pathways, enhancing the composite's performance and suitability for subsequent functional applications.

The BET specific surface area of Na_2MoO_4 @SZIF-8-DE, after loading with Na_2MoO_4 , further increased to 9.7615 m²/g.

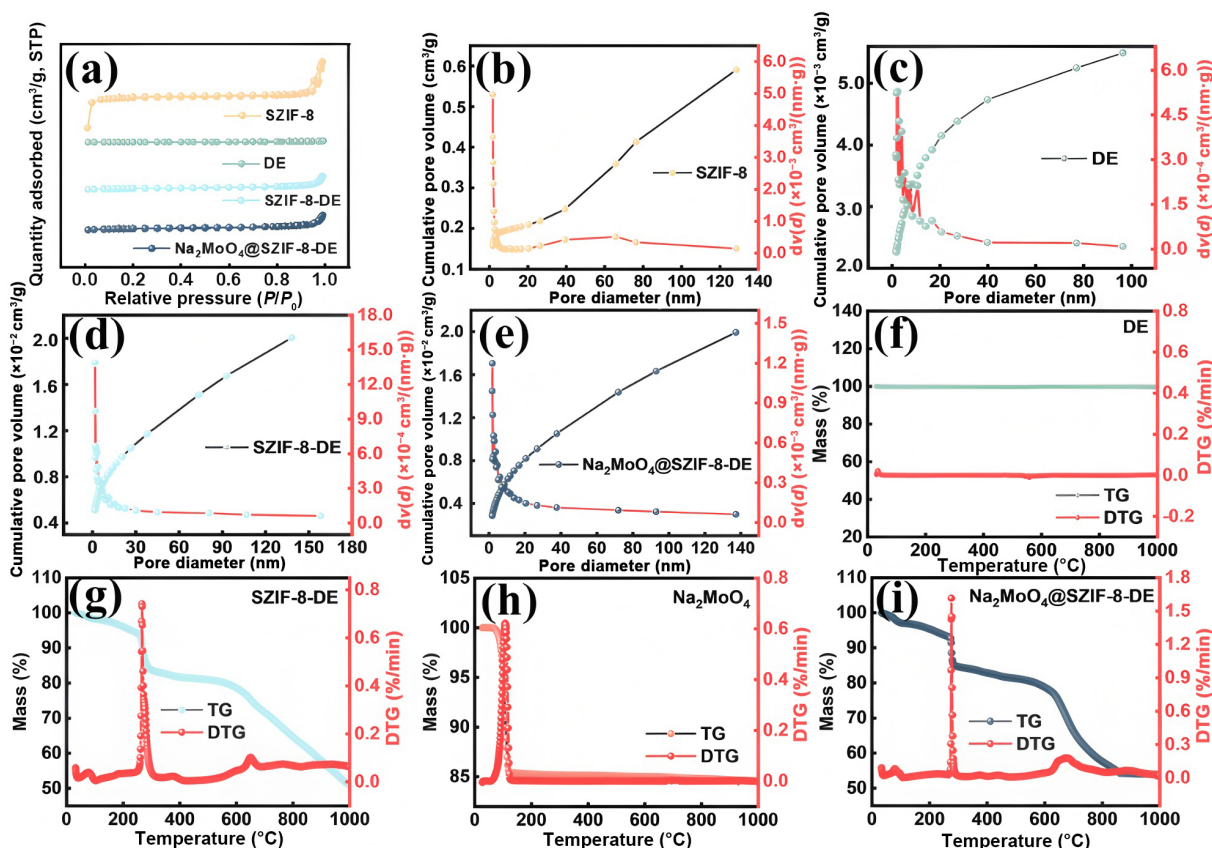


Figure 6 (a) N_2 adsorption/desorption isotherms of SZIF-8, DE, SZIF-8-DE, and $Na_2MoO_4@SZIF-8-DE$. Pore size distribution of (b) SZIF-8, (c) DE, (d) SZIF-8-DE, and (e) $Na_2MoO_4@SZIF-8-DE$ based on adsorption branches by BJH algorithm. TG and DTG curves of (f) DE, (g) SZIF-8-DE, (h) Na_2MoO_4 , and (i) $Na_2MoO_4@SZIF-8-DE$.

Simultaneously, the average pore diameter decreased to 1.7469 nm, approaching the micropore size of SZIF-8. However, the pore volume decreased significantly to 0.0013 cm^3/g , owing to partial filling of the mesoporous channels of SZIF-8-DE by Na_2MoO_4 . The dispersion and loading process also exposes additional active sites within the SZIF-8 framework, ultimately producing a structure dominated by micropores with mesopores as a supplement. This hierarchical configuration provides abundant reaction sites and moderate mass transfer pathways, enhancing the material's suitability for subsequent functional applications.

To evaluate the thermal stability of $Na_2MoO_4@SZIF-8-DE$ and to estimate the loading content of the corrosion inhibitor Na_2MoO_4 , thermogravimetric analysis (TG) was performed on DE, ZIF-8-DE, and Na_2MoO_4 . As shown in Figs. 6(f)–6(i), the mass of DE exhibits almost no noticeable change within the temperature range of 25–1000 $^{\circ}C$, indicating that DE possesses excellent thermal stability. In contrast, the mass of SZIF-8-DE gradually decreases after 100 $^{\circ}C$, which can be attributed to the removal of adsorbed and coordinated water molecules within the SZIF-8 framework. With further temperature increase, a more pronounced weight loss occurs above approximately 600 $^{\circ}C$, which is associated with the thermal decomposition and structural collapse of the SZIF-8 framework. Na_2MoO_4 begins to decompose at around 100 $^{\circ}C$ and reaches a maximum weight-loss peak at approximately 150 $^{\circ}C$, after which the mass remains nearly constant. This behavior can be clearly attributed to the loss of crystal water from Na_2MoO_4 . Notably, the composite filler $Na_2MoO_4@SZIF-8-DE$, assembled from these individual components, exhibits similar decomposition features in its thermogravimetric curve, confirming the presence of

Na_2MoO_4 within the composite structure.

Additionally, Table S2 in the ESM presents the initial mass, residual mass, and decomposition rates of each substance. The decomposition rates of Na_2MoO_4 and SZIF-8-DE are 14.98% and 49.80%, respectively. By comparing the decomposition rates of ZIF-8-DE, Na_2MoO_4 , and $Na_2MoO_4@SZIF-8-DE$, the loading amount of Na_2MoO_4 within $Na_2MoO_4@SZIF-8-DE$ can be determined. The calculations were performed using Eqs. (1) and (2) [47]

$$85.02\% \times M_{SZIF-8-DE} + 49.80\% \times M_{Na_2MoO_4} = 54.20\% \times M_{Na_2MoO_4@SZIF-8-DE} \quad (1)$$

$$M_{SZIF-8-DE} + M_{Na_2MoO_4} = M_{Na_2MoO_4@SZIF-8-DE} \quad (2)$$

The contents of Na_2MoO_4 and SZIF-8-DE in $Na_2MoO_4@SZIF-8-DE$ are 12.49% and 87.51% respectively. Therefore, the conclusion is that the loading amount of the corrosion inhibitor Na_2MoO_4 in $Na_2MoO_4@SZIF-8-DE$ is 12.49%.

3.4 Analysis of the sustained-release performance of active fillers

The loading of Na_2MoO_4 into the $Na_2MoO_4@SZIF-8-DE$ carrier and its release behavior under different pH conditions were systematically investigated using ultraviolet–visible (UV–Vis) spectroscopy. As shown in Fig. 7, the absorption spectra of Na_2MoO_4 varies with pH. Under neutral conditions (pH = 7), the maximum absorption peak appears at 224 nm, indicating that the system maintains good stability [48]. Under alkaline conditions (pH

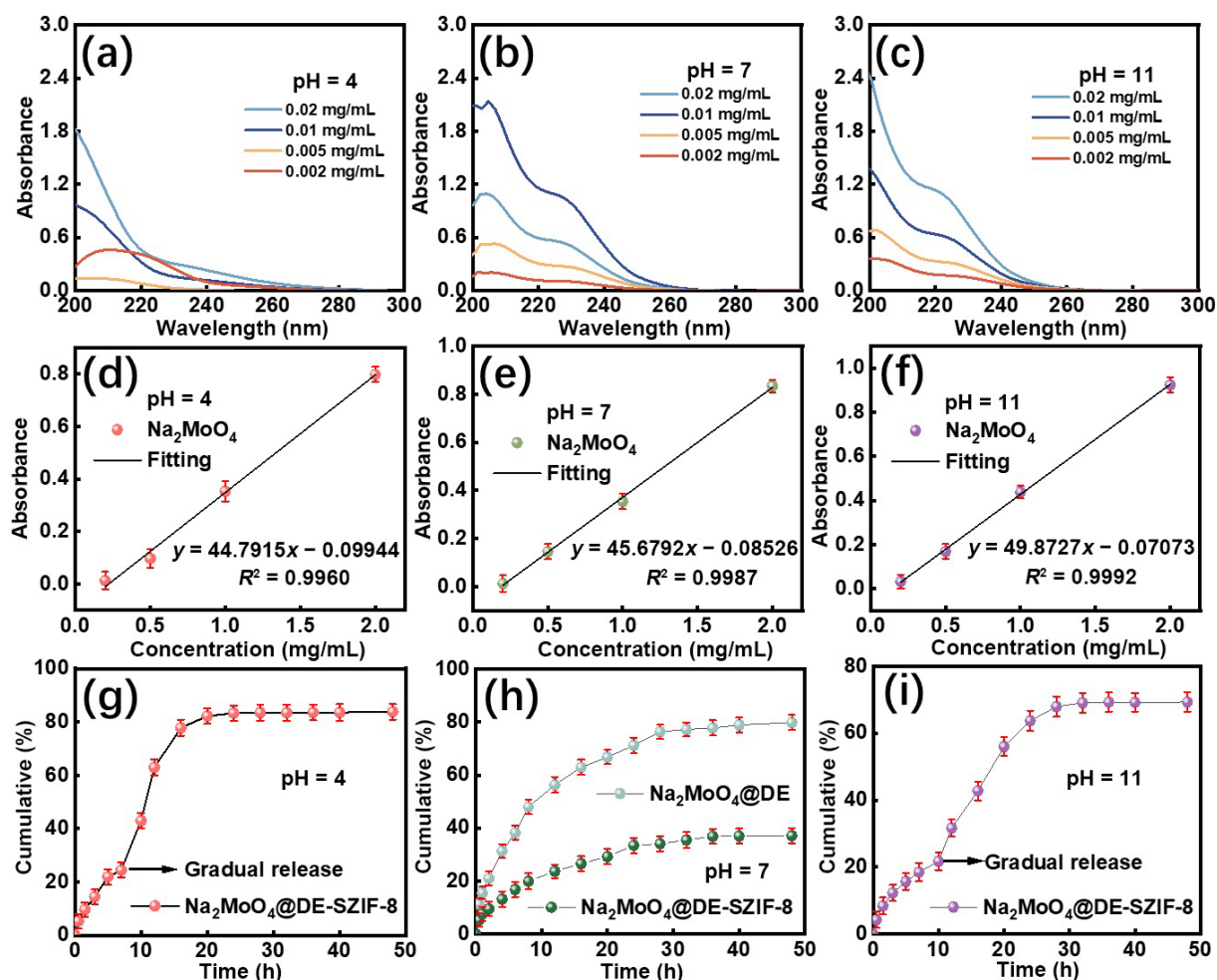


Figure 7 (a)–(c) Ultraviolet absorption rate under different pH conditions. (d)–(f) Calibration curves of the Na_2MoO_4 in 3.5 wt.% NaCl solution (pH values are 4, 7, and 11). (g)–(i) Release situation of the Na_2MoO_4 in Na_2MoO_4 @DE and Na_2MoO_4 @SZIF-8DE fillers under different pH values.

= 11), the position of the absorption peak shows no obvious change. In contrast, under acidic conditions (pH = 4), a noticeable shift of the absorption peak is observed, suggesting that the corrosion inhibitor system undergoes significant changes. Based on these results, standard calibration curves at different pH values were established to accurately determine the release concentration of the corrosion inhibitor. TG analysis indicates that the loading amount of Na_2MoO_4 in the composite is approximately 12.49%. The release kinetics curves of the Na_2MoO_4 @SZIF-8-DE filler at pH values of 4, 7, and 11 are shown in Figs. 7(g)–7(i). The results demonstrate that within the first 10 h, the release profile exhibits an initial rapid-release stage followed by a relatively slow-release stage. Subsequently, the release rate increases again, presenting another accelerated release stage before gradually approaching a slower release trend. This staged release behavior can be attributed to the hierarchical pore structure and the synergistic effect of SZIF-8 and DE, which together enable a controlled and stepwise release of the corrosion inhibitor.

The release behavior of Na_2MoO_4 can be clearly divided into two stages: an initial rapid release stage followed by a slower and sustained release stage. At pH = 4, the release of Na_2MoO_4 is maximal, with a cumulative release amount of 83%, whereas at pH = 11, the release is moderate, reaching 69%. In contrast, at pH = 7, both the release amount and rate are minimal, with a cumulative release of only 37%, demonstrating the pronounced pH

responsiveness of the material. This behavior can be attributed to the growth of SZIF-8 on the surface of DE. The pH-responsive mechanism of SZIF-8 is primarily associated with changes in the coordination environment of Zn^{2+} within its framework. Under acidic conditions, elevated H^+ concentrations can induce partial hydrolysis or coordination changes in the Zn^{2+} of ZIF-8, thereby disrupting the framework structure and reducing its stability and porosity. Although SZIF-8 exhibits greater stability in alkaline environments than in acidic ones, its framework can still be affected at higher pH values. OH^- interact with Zn^{2+} in SZIF-8, weakening the bonds between the metal ions and the framework. Excessively high pH values may promote Zn^{2+} detachment, leading to partial framework degradation or changes in prolongation. In summary, SZIF-8 shows superior structural stability under alkaline conditions compared with acidic conditions. Variations in pH significantly influence the stability and performance of SZIF-8 by modifying the coordination environment of Zn^{2+} and the extent of framework dissolution, thereby imparting the prepared composites with excellent pH-responsive properties.

3.5 Corrosion resistance

EIS is a highly sensitive and efficient electrochemical technique widely employed to evaluate the corrosion resistance and corrosion behavior of coatings. Analysis of the impedance response over a

range of frequencies provides detailed insights into the barrier properties, charge transfer processes, and interfacial reaction mechanisms of coatings [49, 50]. In electrochemical impedance spectroscopy testing, Bode, phase angle and Nyquist plots are commonly used for characterization.

The impedance magnitude at 0.01 Hz, denoted as $|Z|_{0.01\text{Hz}}$, is typically presented on the Bode plot and serves as a quantitative metric for assessing coating barrier performance. In the low-frequency region, defined as frequencies below 0.01 Hz, this magnitude effectively reflects the coating's ability to resist penetration by corrosive media. Higher $|Z|_{0.01\text{Hz}}$ values correspond to greater coating compactness and enhanced protective performance. Similarly, the radius of the impedance arc in the Nyquist plot is a key indicator of the coating's barrier properties. A larger arc radius corresponds to higher charge transfer impedance, indicating more effective inhibition of corrosion reactions. Extensive studies have shown that both the $|Z|_{0.01\text{Hz}}$ value and the Nyquist arc radius are positively correlated with corrosion resistance. Therefore, elevated values of these parameters serve as clear indicators of improved protective performance of the coating [51, 52].

3.5.1 Corrosion resistance of active fillers

To evaluate the corrosion protection performance of the prepared composite fillers, electrochemical measurements were conducted on different filler systems. In all electrochemical spectra, the discrete

symbols represent the experimental data, while the solid black lines correspond to the fitted curves obtained using ZSimpWin software. The samples were denoted as Blank, DE, $\text{Na}_2\text{MoO}_4\text{@DE}$, and $\text{Na}_2\text{MoO}_4\text{@SZIF-8-DE}$, and the corresponding Bode, phase angle and Nyquist plots are presented in Fig. 8.

As shown in Fig. 8(a), after 1 day of immersion, the low-frequency impedance modulus ($|Z|_{0.01\text{Hz}}$) values of the magnesium substrate for the Blank, DE, $\text{Na}_2\text{MoO}_4\text{@DE}$, and $\text{Na}_2\text{MoO}_4\text{@SZIF-8-DE}$ systems were 67.26, 108.72, 142.03, and 205.94 $\Omega\cdot\text{cm}^2$, respectively. With increasing immersion time, the impedance values of the Blank and DE samples decreased to 34.59 and 48.55 $\Omega\cdot\text{cm}^2$, respectively, indicating severe corrosion of the substrate in both systems. The DE sample exhibited slightly improved corrosion resistance compared with the Blank sample, which can be mainly attributed to the physical barrier effect of DE. However, this effect alone is insufficient to provide long-term corrosion protection. In contrast, the incorporation of $\text{Na}_2\text{MoO}_4\text{@DE}$ and $\text{Na}_2\text{MoO}_4\text{@SZIF-8-DE}$ fillers significantly increased the $|Z|_{0.01\text{Hz}}$ values, reaching 179.46 and 244.81 $\Omega\cdot\text{cm}^2$ after 7 days of immersion, respectively, demonstrating effective suppression of substrate corrosion. This improvement is primarily attributed to the gradual release of Na_2MoO_4 into the surrounding medium during immersion, which promotes the formation of a dense passivation film on the magnesium substrate surface and thereby retards the corrosion process. Furthermore, the *in-situ* growth of SZIF-8 on the $\text{Na}_2\text{MoO}_4\text{@DE}$ surface further

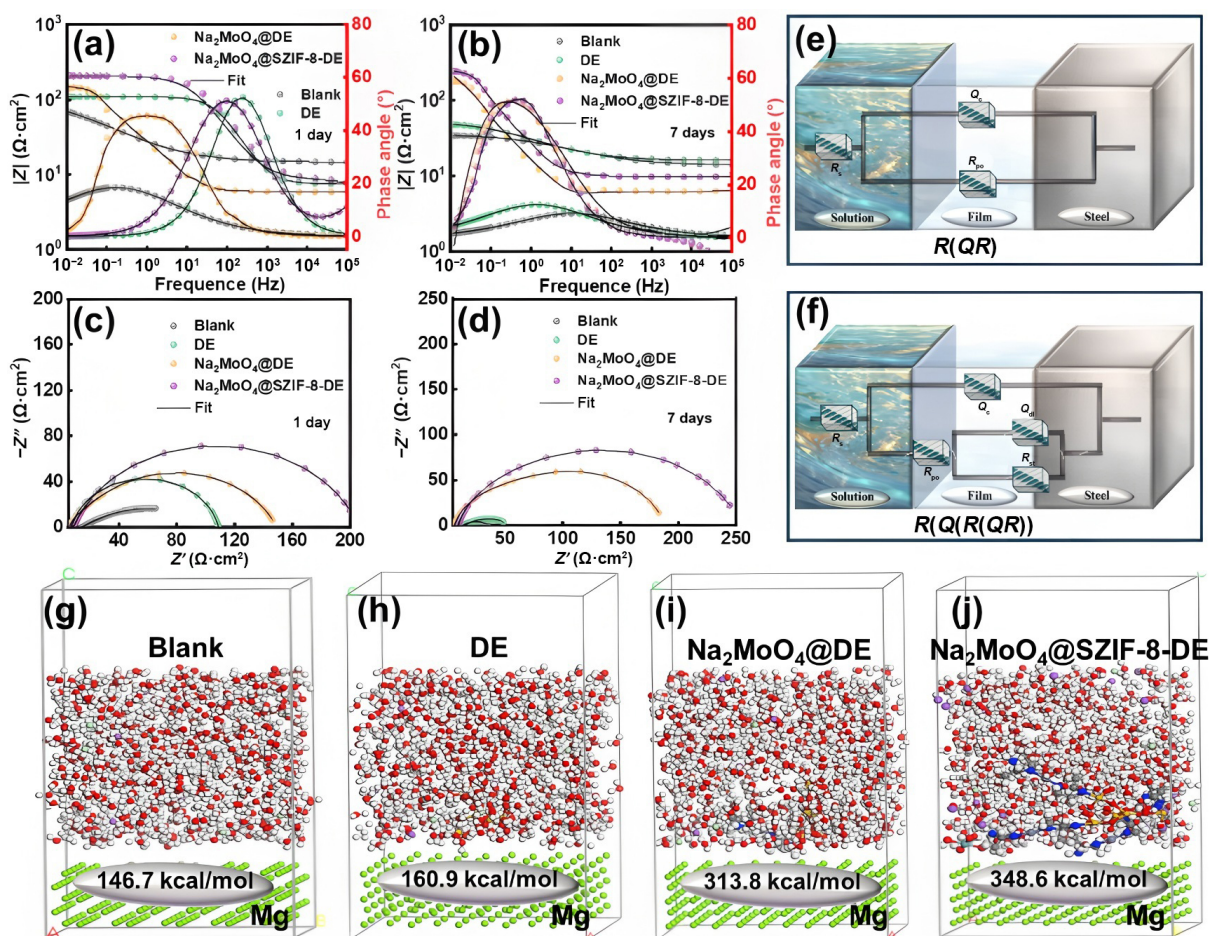


Figure 8 Bode plots, Nyquist plots, and fitted circuits of DE, $\text{Na}_2\text{MoO}_4\text{@DE}$ and $\text{Na}_2\text{MoO}_4\text{@SZIF-8-DE}$ at different times on the surface of AZ31B magnesium alloy: (a) and (b) bode plots obtained after 1 and 7 days of testing; (c) and (d) Nyquist plots obtained after 1 and 7 days of testing; (e) and (f) Fitted circuits at different measurement stages. Equilibrium configurations for the adsorption of studied materials on the steel surface: (g) Blank, (h) DE, (i) $\text{Na}_2\text{MoO}_4\text{@DE}$, and (j) $\text{Na}_2\text{MoO}_4\text{@SZIF-8-DE}$.

enhances the corrosion resistance of the system. The intrinsic barrier properties and structural stability of SZIF-8, together with the synergistic staged release of Na_2MoO_4 from the SZIF-8-DE carrier, endows the system with superior and long-lasting corrosion protection.

To quantitatively evaluate the corrosion inhibition capability of the fillers, the obtained EIS data were fitted using equivalent circuit models. Relevant fitting parameters are summarized in Table S3 in the ESM, and the corresponding equivalent circuit models are presented in Figs. 8(e) and 8(f). During the fitting process, three main impedance components were considered: the electrolyte solution resistance, the pore or defect resistance associated with coating surface imperfections or trapped air, and the resistance related to electron transport within the material. In the equivalent circuit, these components are represented by R_s , R_{po} , and R_{st} , respectively. Among these parameters, R_{st} is closely associated with the corrosion protection performance of the filler system, and a higher R_{st} value generally indicates stronger protective capability of the coating toward the substrate [53, 54]. Results from this study reveal that both the $\text{Na}_2\text{MoO}_4/\text{DE}$ and $\text{Na}_2\text{MoO}_4/\text{SZIF-8-DE}$ filler systems exhibit significantly increased R_{st} values, confirming their excellent corrosion inhibition performance. Additionally, two capacitive elements were incorporated into the equivalent circuit model. One element represents the non-ideal double-layer capacitance at the solution-substrate interface and is described by a constant phase element (CPE).

The other capacitive element corresponds to the capacitance associated with the passivation film formed by the corrosion inhibitor on the substrate surface and is denoted as Q_{di} . For the Blank and DE samples, only a small amount of corrosion products formed on the substrate surface after 1 day of immersion, indicating relatively mild corrosion at this stage. These limited corrosion products, together with the presence of DE, partially hindered the diffusion of O_2 to the substrate surface, thereby delaying the anodic reaction process. Under these conditions, the electrochemical behavior of the system can be adequately described using an $R(QR)$ equivalent circuit model (Fig. 8(e)). With the immersion time extended to 7 days, a considerable amount of corrosion products accumulated at the interface between the test samples and the substrate. Although this corrosion layer exhibited a relatively loose structure, it could still be regarded as a degraded coating-like layer. Consequently, the corrosion behavior of the substrate required a more complex equivalent circuit model, namely $R(QR(QR))$, to accurately describe the electrochemical processes involved (Fig. 8(f)).

Following a 7-day period of immersion, no significant corrosion products were observed on the magnesium substrate surface for the $\text{Na}_2\text{MoO}_4/\text{DE}$ and $\text{Na}_2\text{MoO}_4/\text{SZIF-8-DE}$ filler systems. This phenomenon can be primarily attributed to the complex reaction between the metallic corrosion inhibitor Na_2MoO_4 and Mg^{2+} released from the solution into the substrate surface. This reaction leads to the formation and deposition of a dense and stable complex passivation layer, which effectively inhibits the corrosion process.

The formation of this complex layer markedly alters the physicochemical properties of the substrate surface, particularly affecting electron transport and interfacial electrochemical reaction behavior. As indicated by the fitted parameters listed in Table S3 in the ESM, the charge transfer resistance of the substrate increased significantly after 7 days of immersion in the presence of $\text{Na}_2\text{MoO}_4/\text{DE}$ and $\text{Na}_2\text{MoO}_4/\text{SZIF-8-DE}$ fillers. This observation suggests that the composite passivation layer effectively impedes the

diffusion of corrosive species to the substrate surface and hinders the interfacial charge transfer process. Furthermore, by incorporating the film capacitance parameter obtained from the equivalent circuit model and applying Eq. (3), the thickness (d_{film}) of the protective film formed under different potential conditions can be further estimated [32].

$$d_{\text{film}} = \frac{\varepsilon \varepsilon_0 A}{C_{\text{EP}}} \quad (3)$$

In this equation, ε_0 denotes the vacuum permittivity (8.85×10^{-12} F/m), ε is the relative permittivity, taken as 30, and A represents the effective surface area of the sample (m^2). C corresponds to the capacitance of the passivation film (F). In the present study, the working electrode area was $1.256 \times 10^{-3} \text{ m}^2$ and the measured capacitance was $1.047 \times 10^{-4} \text{ F}$, from which the thickness of the passivation film formed on the $\text{Na}_2\text{MoO}_4/\text{SZIF-8-DE}$ -filled magnesium substrate was calculated to be 3.18 nm.

To provide further elucidation on the corrosion-inhibiting mechanism of fillers, MD simulations were employed to theoretically analyze the corrosion-retardation behavior. This objective was realized through the prediction of the most stable adsorption configurations of varying fillers on the AZ31B magnesium substrate surface, in conjunction with their respective binding strengths [55]. As shown in Figs. 8(g)–8(j), the simulated system encompassed four scenarios: The samples are designated as Blank, DE, $\text{Na}_2\text{MoO}_4/\text{DE}$ and $\text{Na}_2\text{MoO}_4/\text{SZIF-8-DE}$. A comparative analysis was conducted, which revealed discrepancies in the interactions observed between the fillers and the AZ31B magnesium substrate. The stable adsorption configurations of each filler on the AZ31B magnesium plate surface are demonstrated. To facilitate quantitative evaluation, binding energies were subsequently calculated. The results indicate that the binding energies between AZ31B magnesium plate and $\text{Na}_2\text{MoO}_4/\text{DE}$ and $\text{Na}_2\text{MoO}_4/\text{SZIF-8-DE}$ fillers are 313.8 and 348.6 kcal/mol, respectively, which are significantly higher than those for DE (160.9 kcal/mol) and Blank (146.7 kcal/mol). It has been demonstrated that higher binding energies are indicative of the enhanced adsorption capabilities of the corrosion inhibitor components on the magnesium substrate surface. This, in turn, facilitates the formation of a stable protective interface. The experimental results obtained in this study provide a theoretical basis for the conclusion that $\text{Na}_2\text{MoO}_4/\text{DE}$ and $\text{Na}_2\text{MoO}_4/\text{SZIF-8-DE}$ fillers can effectively enhance the corrosion resistance of AZ31B magnesium plates in 3.5 wt.% NaCl solutions.

3.5.2 Analysis of anti-corrosion properties of composite coatings

EIS measurements of the coatings were carried out for 60 days in a 3.5 wt.% NaCl solution at 25 °C. The impedance modulus at a low frequency of 0.01 Hz is commonly regarded as an important parameter for evaluating the corrosion resistance of coatings, where higher values generally indicate better protective performance [56]. Figure 9 presents the Bode impedance plots and the corresponding evolution of $|Z|_{0.01\text{Hz}}$ during the immersion process. At the initial stage, all coatings exhibited relatively high impedance values, indicating strong barrier properties. However, with increasing immersion time, the impedance magnitude gradually decreased for all samples, suggesting a progressive deterioration of the protective performance of the coatings. This phenomenon can be attributed to the gradual degradation of the cross-linked network of the coating and the progressive penetration of corrosive species, which together

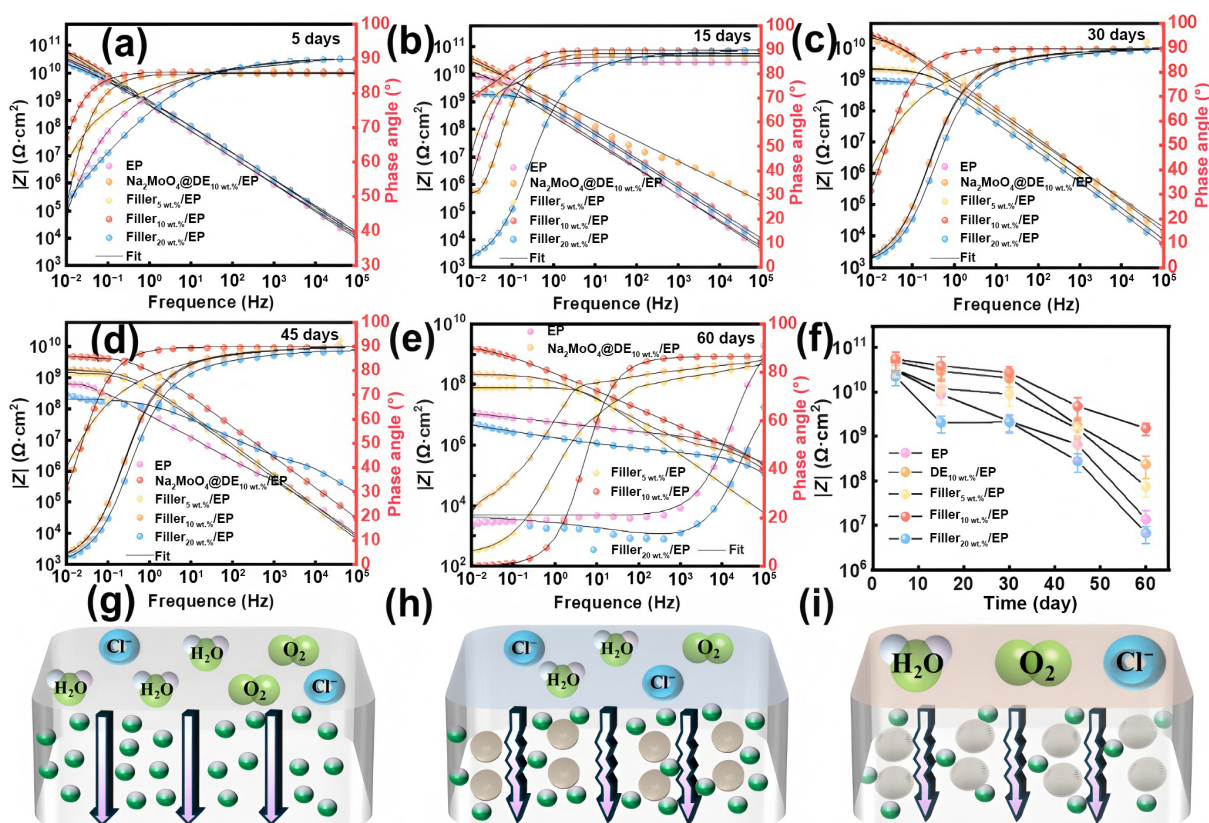


Figure 9 Bode diagrams of EP, DE/EP, $\text{Na}_2\text{MoO}_4\text{@DE}_{10\text{ wt.\%}}/\text{EP}$, 5 wt.%, 10 wt.% and 20 wt.% $\text{Na}_2\text{MoO}_4\text{@SZIF-8-DE}/\text{EP}$ at 3.5 wt.% NaCl at different times: (a) 5, (b) 15, (c) 30, (d) 45, and (e) 60 days. (f) Variation curve of impedance modulus of sample coating during testing. (g)–(i) the invasion diagrams of corrosive media of EP, $\text{Na}_2\text{MoO}_4\text{@DE}_{10\text{ wt.\%}}/\text{EP}$ and $\text{Filler}_{10\text{ wt.\%}}/\text{EP}$, respectively.

reduce the coating resistance. Consequently, the low-frequency impedance in the Bode plots continuously decreased as the immersion time increased.

As demonstrated in the accompanying Fig. 9, throughout the immersion process, the impedance modulus of both the pure EP coating and $\text{Na}_2\text{MoO}_4\text{@DE}_{10\text{ wt.\%}}/\text{EP}$ composite coating devoid of SZIF-8 growth diminished by approximately three orders of magnitude, thereby signifying a substantial deterioration in their anti-corrosion performance. Conversely, composite coatings incorporating $\text{Na}_2\text{MoO}_4\text{@DE}$ and $\text{Na}_2\text{MoO}_4\text{@SZIF-8-DE}$ (Fillers) at varying concentrations exhibited significantly enhanced corrosion resistance. Among these, the composite coating with 10 wt.% filler exhibited optimal protective performance even after 60 days of immersion. At this juncture, the $|Z|_{0.01\text{ Hz}}$ values for the EP, $\text{Na}_2\text{MoO}_4\text{@DE}_{10\text{ wt.\%}}/\text{EP}$, $\text{Filler}_{5\text{ wt.\%}}/\text{EP}$, $\text{Filler}_{10\text{ wt.\%}}/\text{EP}$, and $\text{Filler}_{20\text{ wt.\%}}/\text{EP}$ coatings were 1.38×10^7 , 2.37×10^8 , 7.48×10^7 , 1.53×10^9 , and $1.53 \times 10^9 \Omega\cdot\text{cm}^2$, respectively. This finding suggests that the protective performance of EP, $\text{Filler}_{5\text{ wt.\%}}/\text{EP}$, and $\text{Filler}_{20\text{ wt.\%}}/\text{EP}$ coatings is approaching a state of complete loss. It is noteworthy that the corrosion rate of the composite coating with a filler content as high as 20 wt.% exceeds that of pure EP and other samples. This is primarily attributed to excessive filler affecting the effective crosslinking of the resin, increasing coating defects, and thereby accelerating the penetration of corrosive media. This phenomenon will be further validated in subsequent atomic force microscopy (AFM) images of the wear surface. Furthermore, the composite coating containing 10 wt.% filler demonstrated higher impedance than other samples throughout the testing period, thus exhibiting optimal protective performance. This finding suggests that the

optimal filler-to-matrix ratio of approximately 10 wt.% is achieved when utilizing Filler and EP resin in a composite system.

The $\text{Filler}_{10\text{ wt.\%}}/\text{EP}$ composite coating exhibits excellent protective performance, which can be mainly attributed to the incorporation of 10 wt.% filler that significantly enhances the corrosion resistance of the coating. The introduction of an appropriate number of fillers leads to the formation of a dense and uniform barrier network within the EP matrix. On one hand, the porous structure of the filler effectively prolongs the penetration pathway of corrosive media, thereby suppressing the diffusion of water and aggressive ions. On the other hand, the filler can fill micropores within the resin matrix, improving the structural integrity of the coating without interfering with the cross-linking reaction of the epoxy resin. As a result, an optimal balance between barrier properties and mechanical stability is achieved, leading to enhanced corrosion resistance. Moreover, DE itself functions as a physical barrier that further extends the diffusion pathway of corrosive species. The porous layered structure of the filler also enables the adsorption and gradual release of corrosion inhibitors (e.g., MoO_4^{2-}), thereby generating a sustained controlled-release protection effect within the coating system. When the filler content reaches 10 wt.%, the pore network becomes uniformly distributed, effectively blocking the permeation of water and Cl^- while maintaining efficient release of the active inhibitor to retard substrate corrosion. In contrast, insufficient filler content results in limited barrier and inhibitor-release effects, whereas excessive filler loading may induce particle agglomeration and coating defects, ultimately deteriorating the protective performance. Therefore, the incorporation of 10 wt.% filler achieves an optimal balance among barrier performance,

inhibitor release, and coating structural integrity.

The use of equivalent circuit models enables a deeper understanding of the corrosion processes occurring in the coatings. Figure 10 shows the Nyquist plots together with the corresponding equivalent circuit models fitted using ZSimpWin software. The results indicate that the protective performance of the coating is closely related to the diameter of the capacitive arc in the Nyquist plot, where a larger arc corresponds to better corrosion resistance. During the initial immersion period (5 days), all samples exhibited a single large capacitive semicircle, which can be attributed to the effective barrier property of the EP coating, indicating that the coatings maintained excellent corrosion resistance at this stage. As immersion time increased, the diameter of the capacitive arc gradually decreased, as shown in Fig. 10(f), suggesting a progressive deterioration of the corrosion resistance. To further analyze the corrosion behavior, elements associated with Q_c (coating capacitance) and Q_{dl} (double-layer capacitance) were introduced in the equivalent circuit. These elements indicate that corrosive media partially penetrated the coating and caused local delamination, allowing a small number of corrosive species to reach the coating-substrate interface. The corrosion processes of both EP and $\text{Na}_2\text{MoO}_4/\text{DE}_{10\text{ wt.\%}}/\text{EP}$ coatings can be described by the equivalent circuit shown in Fig. 10(g). With further extension of the immersion time, a Warburg (W) element was incorporated into the fitted circuit [57], indicating the diffusion-controlled process of corrosive species within the coating system. This behavior may be

related to the partial adsorption of Cl^- by the coating, which can form complexes that hinder the diffusion of corrosive media. After 60 days of immersion, the corrosive medium eventually reached the metal substrate surface. Nevertheless, the composite coating containing 10 wt.% filler still exhibited a larger capacitive arc than the other coatings, demonstrating its superior protective performance. The corresponding corrosion behavior can be described by the equivalent circuit shown in Fig. 10(h). These results are consistent with the previously discussed analysis.

The variation in coating resistance (R_c) obtained from the fitting results is summarized in Table S4 in the ESM. The R_c value generally reflects the compactness and barrier performance of the coating; a higher R_c indicates stronger impermeability, whereas a lower R_c suggests that corrosive media can more easily penetrate the coating. During the immersion process, the R_c values of all samples gradually decreased due to the progressive erosion of the coatings by the corrosive medium. After 60 days of immersion, the R_c of the pure EP coating decreased to $1.03 \times 10^6 \Omega\cdot\text{cm}^2$, indicating a significant deterioration in protective performance. In contrast, the R_c value of the $\text{Na}_2\text{MoO}_4/\text{SZIF-8-DE}_{10\text{ wt.\%}}/\text{EP}$ composite coating remained approximately three orders of magnitude higher than that of pure EP. This result demonstrates that the incorporation of 10 wt.% $\text{Na}_2\text{MoO}_4/\text{SZIF-8-DE}$ significantly improves the compactness and barrier capability of the coating, thereby effectively suppressing the penetration of corrosive media. In addition, the corrosion inhibitor encapsulated within the DE-based

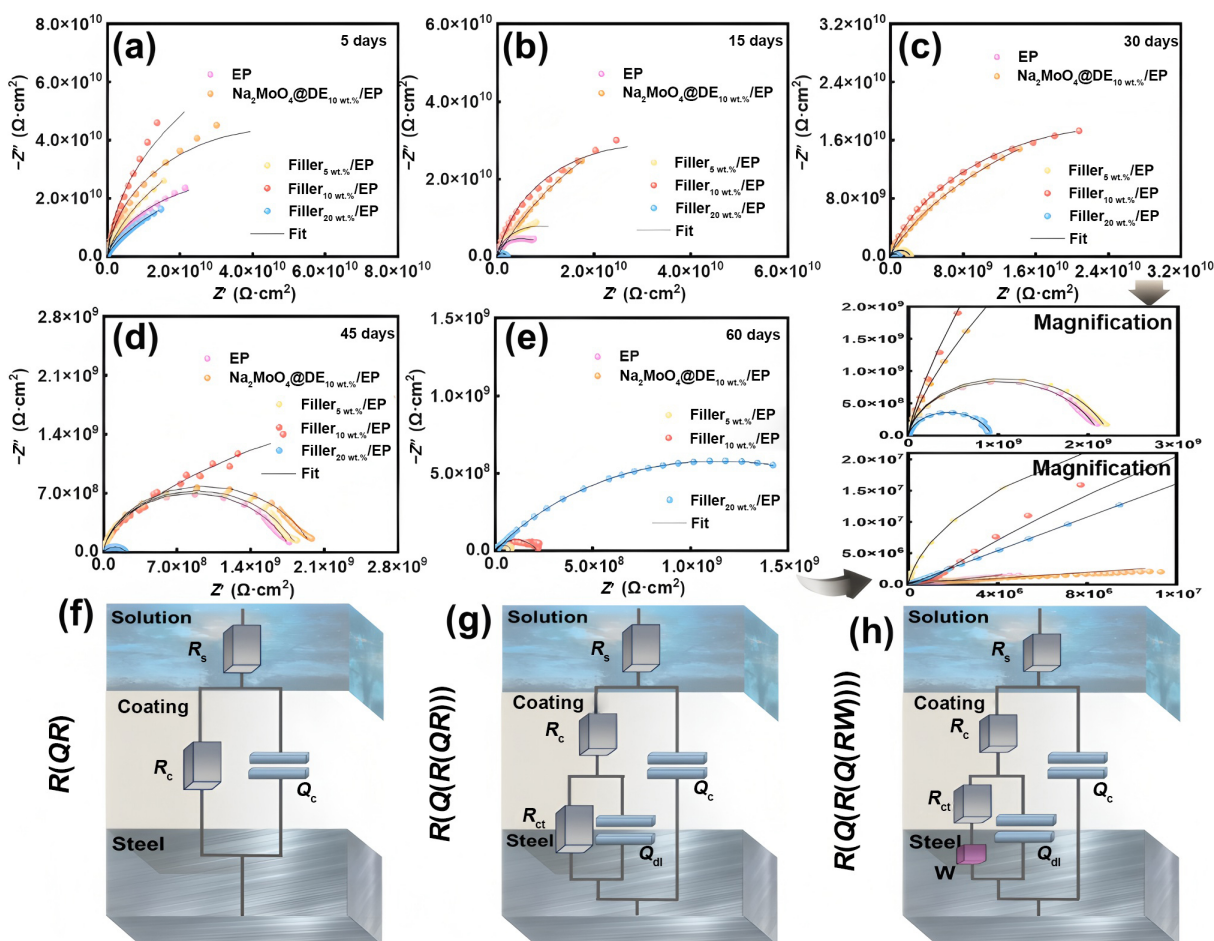


Figure 10 Nyquist plot and fitting circuit of coatings immersed in 3.5 wt.% NaCl solution for different time: (a) 5, (b) 15, (c) 30, (d) 45, and (e) 60 days. (f) $R(QR)$ fitting circuit, (g) $R(Q(R(QR)))$ fitting circuit, and (h) $R(Q(R(Q(RW))))$ fitting circuit.

composite can be gradually released, leading to the formation of a protective complex film on the magnesium substrate surface, which further enhances corrosion resistance. Overall, the Na₂MoO₄@SZIF-8-DE_{10 wt.%}/EP composite coating exhibits the best corrosion protection performance among all the tested coatings.

3.6 The establishment of simulation model and mechanism analysis

The present study systematically investigated the diffusion kinetics of corrosive media in eight coating systems (pure EP, DE_{10 wt.%}/EP, various concentrations of Na₂MoO₄@DE/EP, and Filler/EP composite coatings) using molecular dynamics simulations. Although current models still have certain limitations in fully describing the diffusion behavior of particles, they remain valuable tools for qualitatively comparing the barrier properties of different coatings. According to Einstein's diffusion theory, the molecular diffusion coefficient (D) was employed as a key parameter to quantitatively evaluate the migration rate of corrosive species within the coatings. Analysis of MSD curves, together with the calculated diffusion coefficients derived from the diffusion equations, reveals a clear inverse relationship between D and coating barrier performance: lower D values correspond to more effective inhibition of corrosive media transport and improved corrosion resistance. Furthermore, the temporal evolution of the MSD functions (Eq. (4)) provides an intuitive description of the transport behavior of corrosive species within the coatings, offering valuable insight into the underlying protection mechanisms [58, 59].

$$\text{MSD} = |r_i(t) - r_i(0)| \quad (4)$$

Furthermore, the diffusion coefficient D can be determined using the following Eq. (5)

$$D = \frac{1}{6Na} \lim_{t \rightarrow \infty} \frac{d}{dt} \sum_{i=1}^{Na} [|r_i(t) - r_i(0)|] \quad (5)$$

In this study, the initial position of atom i is denoted as $r_i(0)$, while its position at time t is represented as $r_i(t)$. Na denotes the total number of molecules involved in the diffusion process. The MSD is a key parameter used to evaluate the diffusion behavior of molecules and is commonly employed to calculate the diffusion coefficient for particles undergoing 3D Brownian motion. According to Einstein's diffusion relationship, the diffusion coefficient can be obtained from the slope of the linear region of the MSD-time curves. Based on this approach, the diffusion behavior of corrosive species within the coating systems was analyzed. The MSD curves of Cl⁻, O₂, and H₂O in different coatings are shown in Figs. 11(a)–11(h), 12(a)–12(h), and 13(a)–13(h), respectively, while the corresponding linear fitting results used to calculate the diffusion coefficients are presented in Figs. 11(i), 12(i), and 13(i). The calculated diffusion coefficients are summarized in Table S5 in the ESM. A lower diffusion D indicates a stronger hindrance effect of the coating against the penetration of corrosive media. As shown in Table S5 in the ESM, the diffusion coefficients of Cl⁻, O₂, and H₂O molecules are significantly reduced in the Filler_{10 wt.%}/EP coating, indicating suppressed migration of corrosive species within the coating. This result demonstrates the improved barrier performance and enhanced corrosion resistance of the composite coating.

As the free volume fraction (FFV) increases, the diffusion rate of the corrosive medium accelerates. FFV can be expressed by the following Eq. (6)

$$\text{FFV} = \frac{V_{\text{free}}}{V_{\text{free}} + V_{\text{occupy}}} \quad (6)$$

In polymeric materials, the total volume is generally considered to consist of two components: the volume occupied by atoms and the free volume. Free volume refers to atomic-scale voids generated by the random packing of polymer chains. These voids are distributed throughout the polymer matrix and provide the necessary space for molecular or atomic motion [60]. In this study, two structural parameters, V_{occupy} and V_{free} , were employed to quantitatively characterize the occupied volume and free void volume within the coating system. The FFV was calculated as the ratio of free volume to the total volume of the model. It is well known that an increase in free volume generally leads to a higher diffusion rate of penetrant species. Cl⁻, O₂, and H₂O were selected as representative corrosive species in the simulation, and their corresponding free volume distributions are illustrated in Figs. 11(a)–11(h), 12(a)–12(h), and 13(a)–13(h), respectively. The calculated FFV values are summarized in Table S6 in the ESM. The results indicate that the coatings provide only limited accessible volume for the diffusion of corrosive particles. Therefore, a lower FFV typically corresponds to a slower diffusion rate. Among the studied systems, the Filler_{10 wt.%}/EP coating exhibits the lowest FFV, which effectively restricts the penetration of corrosive species toward the metal substrate, thereby significantly enhancing the corrosion resistance of the coating. This result is consistent with the conclusions obtained from the EIS analysis.

3.7 Wear resistance analysis

Long-term protection of coatings depends strongly on their wear resistance, which is recognized as a key factor influencing durability [61, 62]. To evaluate the wear behavior and investigate the internal structure of the coatings, comparative tests were performed using a Taber abrasion tester on pure EP coatings and composite coatings containing different amounts of Filler/EP. The macroscopic post-abrasion morphologies and corresponding AFM images are shown in Fig. 14. The results indicate that the wear resistance of the composite coatings improves with increasing filler content, with the Filler_{10 wt.%}/EP coating exhibiting optimal performance. As shown in Figs. 14(b) and 14(c), the composite coatings display substantially lower mass loss and thickness loss compared with the pure EP coating, confirming their enhanced wear resistance. Figures 14(h)–14(o) presents the macroscopic and AFM images of the pure EP, Filler_{5 wt.%}/EP, Filler_{10 wt.%}/EP, and Filler_{20 wt.%}/EP coatings, revealing distinct wear features and further supporting the observed trends.

AFM images provide a direct visualization of the surface roughness induced by wear. The measured roughness values for the pure EP, Filler_{5 wt.%}/EP, Filler_{10 wt.%}/EP, and Filler_{20 wt.%}/EP coatings are 139.44, 119.04, 103.13, and 143.09 μm, respectively. As shown in Figs. 14(d)–14(g), distinct scratches are observed on both the pure EP and Filler_{20 wt.%}/EP coatings after abrasion, whereas the surfaces of the Filler_{5 wt.%}/EP and Filler_{10 wt.%}/EP coatings remain relatively smooth and compact, indicating reduced wear damage. The improved wear resistance of the composite coatings is mainly attributed to the incorporation of an appropriate amount of filler. As a solid lubricant, Na₂MoO₄ can form a lubricating film during wear, which reduces direct contact between surfaces and lowers the wear coefficient. The high specific surface area and porous structure of SZIF-8-DE facilitate uniform dispersion of the Na₂MoO₄, enhancing the structural stability and density of the coating. Furthermore, SZIF-8-DE provides additional mechanical

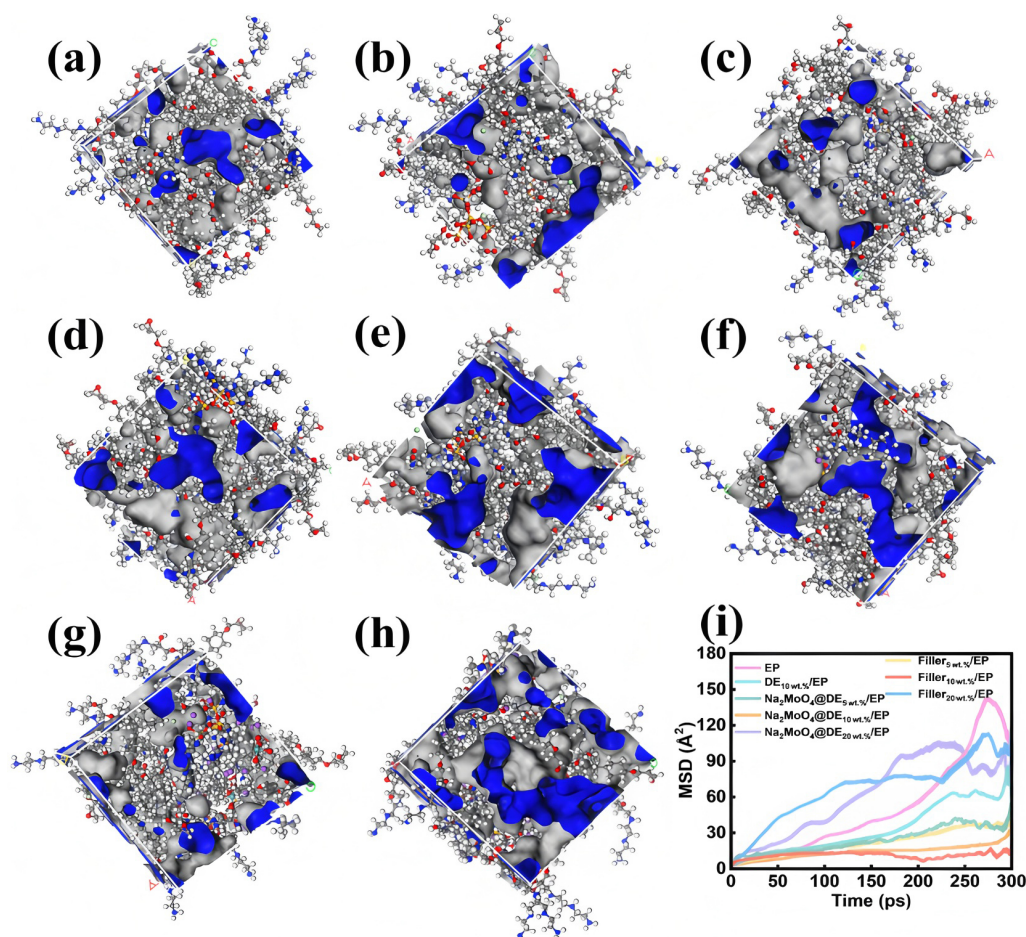


Figure 11 (a)–(h) Free volume distribution of EP, DE₁₀ wt%/EP, Na₂MoO₄@DE₅ wt%/EP, Na₂MoO₄@DE₁₀ wt%/EP, Na₂MoO₄@DE₂₀ wt%/EP, Filler₅ wt%/EP, Filler₁₀ wt%/EP, and Filler₂₀ wt%/EP coatings were detected using H₂O. (i) MSD curves of H₂O in the above coatings.

reinforcement and allows sustained release of Na₂MoO₄ through pore adsorption, delivering continuous lubrication during wear. The inherent hardness of DE also contributes to the coating's wear performance. In summary, the incorporation of an appropriate amount of filler improves the wear resistance of the composite coatings through multiple mechanisms, including lubrication, structural reinforcement, and enhanced surface stability.

3.8 Salt spray resistance test of coating

The corrosion resistance of Filler/EP composite coatings was evaluated by preparing pure EP coatings and composite coatings containing different mass fractions of filler. Artificial scratches of approximately 2 cm in length were made on the coating surfaces using a scalpel. The samples were then subjected to corrosion testing in a 5 wt.% NaCl salt spray environment at 50 °C for 7 days [63, 64]. The macroscopic morphologies of the samples before and after exposure are shown in Figs. 15(a)–15(d). After 7 days of salt spray exposure, the magnesium substrate protected by the pure EP coating exhibited severe corrosion at the scratch sites, with rapid degradation of the exposed areas. SEM and optical imaging of the scratched regions (Fig. 15(a)) revealed wide gaps along the scratches, allowing facile penetration of corrosive media and resulting in a rough, heavily corroded substrate surface. In contrast, the composite coating containing 5 wt.% filler exhibited only minor corrosion at the defect site (Fig. 15(b)). The filler partially filled and sealed the scratches, leading to a relatively smooth substrate surface

and a noticeable reduction in corrosion severity. Increasing the filler content to 10 wt.% further enhanced the filling effect at the scratch site, producing an even smoother substrate surface and optimal corrosion resistance (Fig. 15(c)). However, at 20 wt.% filler content (Fig. 15(d)), gaps reappeared at the scratches, accompanied by the formation of irregular corrosion products. The substrate surface became rougher, and the protective performance of the coating deteriorated, demonstrating the poorest corrosion resistance among the tested samples.

Figure 15(i) presents the elemental mapping of the scratched area in the Filler₁₀ wt%/EP composite coating after 7 days of salt spray corrosion, showing the distributions of C, O, N, Si, Zn, Mo, and Na. Carbon distribution is relatively uniform across the observation area, indicating that the EP resin matrix maintains good continuity near the scratch site without extensive delamination or failure. O is enriched in the scratched region, likely to originate from corrosion products (e.g., Mg(OH)₂) as well as oxygen-containing functional groups in the coating and oxides associated with the corrosion inhibitors. N and Zn exhibit relatively uniform and synchronous distributions within the scratch, confirming that the SZIF-8 structure remains stable under corrosive conditions and actively participates in local protection. This observation indicates that the SZIF-8-DE microcapsules do not undergo significant agglomeration or loss during salt spray exposure, allowing the formation of a stable barrier layer at the scratch site. Notably, Mo and Na signals are clearly detected in the scratched area and display

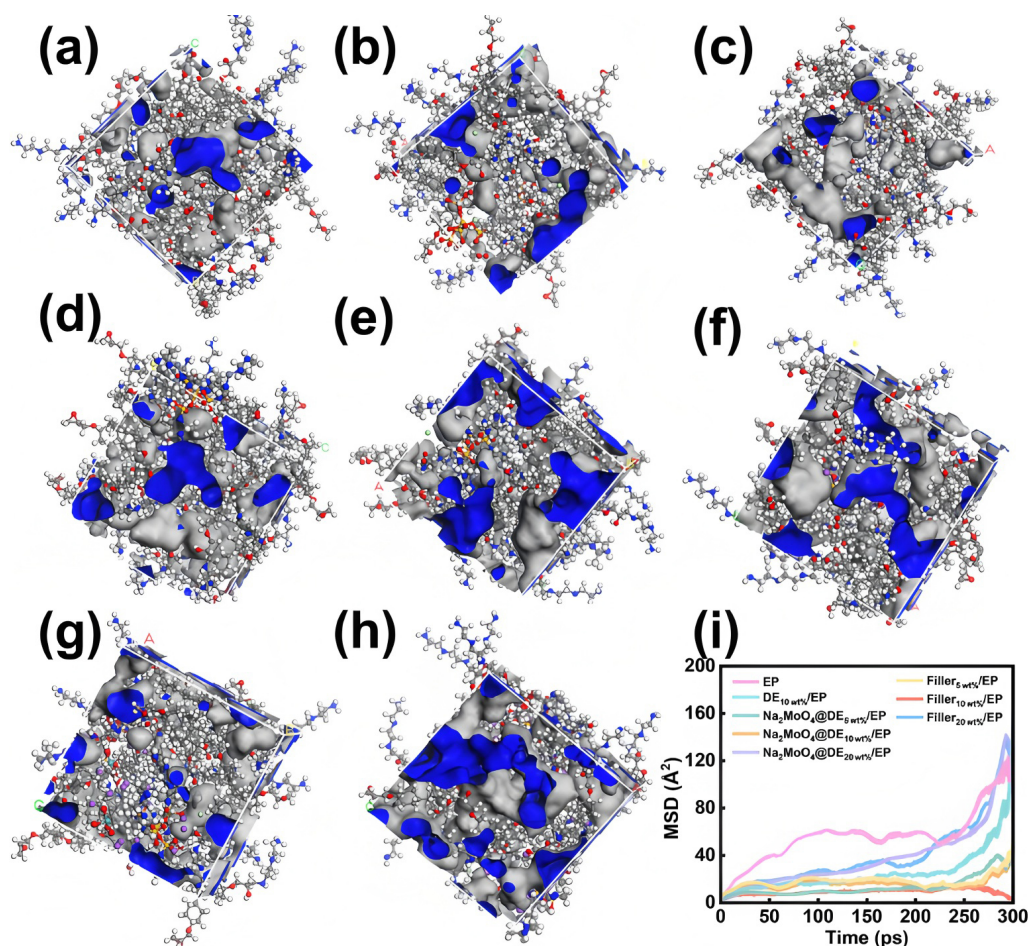


Figure 12 (a)–(h) Free volume distribution of EP, DE_{10 wt%}/EP, Na₂MoO₄@DE_{5 wt%}/EP, Na₂MoO₄@DE_{10 wt%}/EP, Na₂MoO₄@DE_{20 wt%}/EP, Filler_{5 wt%}/EP, Filler_{10 wt%}/EP, and Filler_{20 wt%}/EP coatings were detected using O₂. (i) MSD curves of O₂ in the above coatings.

a diffuse distribution rather than being confined to localized points. This suggests that Na₂MoO₄ is gradually released from the microcapsules in a controlled manner, diffusing into the scratch and surrounding regions to form a molybdate-rich corrosion-inhibiting layer on the metal substrate. MoO₄²⁻ effectively retards further substrate erosion by either inhibiting cathodic reactions or promoting the formation of a dense protective corrosion product layer. In summary, the EDS results demonstrate that, at a 10 wt.% filler loading, the composite coating achieves synergistic barrier protection and corrosion inhibition in scratched regions under salt spray conditions. The structural stability of the ZIF-8 framework, combined with the controlled release of Na₂MoO₄, facilitates the formation of a protective layer at the scratch site, which is a key factor underlying the exceptional corrosion resistance of this composite coating.

The results obtained from 3D optical profilometry were highly consistent with the macroscopic salt spray morphology as well as SEM and EDS analyses, collectively revealing the anti-corrosion mechanism of the Filler/EP composite coating in the scratched region. For the pure EP coating (Fig. 15(e)), significant corrosion expansion occurred along the scratch after salt spray exposure. Both macroscopic and SEM observations showed that the substrate surface was covered with loose, non-compact corrosion products. The surface roughness was measured at 4.702 μm, indicating rapid penetration of the corrosive medium along the defect and vigorous reaction at the substrate surface, with the coating exhibiting

virtually no effective defect repair capability. When the filler content reached 5 wt.% (Fig. 15(f)), the scratched region exhibited significantly reduced corrosion, and the substrate surface appeared relatively smooth. At this stage, the composite coating provided synergistic protection through both physical filling of the defect and chemical corrosion inhibition, reducing the surface roughness to 1.647 μm and achieving moderate anti-corrosion efficiency. Increasing the filler content to 10 wt.% resulted in the smoothest substrate surface beneath the scratch, with the lowest roughness of 1.227 μm as measured by 3D profilometry (Fig. 15(g)). Macroscopic and SEM observations revealed minimal corrosion products, while EDS analysis showed uniform distribution of Na and Mo within the scratched area. This indicates sustained release of Na₂MoO₄ under corrosive conditions, forming a molybdate-rich protective layer on the substrate surface. The protective layer effectively suppresses cathodic reactions and promotes formation of a dense corrosion product film, thereby preventing further penetration of the corrosive medium. At this filler content, the composite coating achieves an optimal synergy between barrier protection and chemical corrosion inhibition, resulting in maximum anti-corrosion efficiency.

However, as shown in Fig. 15(h), further increasing the filler content to 20 wt.% led to significant corrosion expansion and accumulation of irregular corrosion products in the scratched regions, as revealed by macroscopic and SEM observations. Pronounced local agglomeration was also observed. This

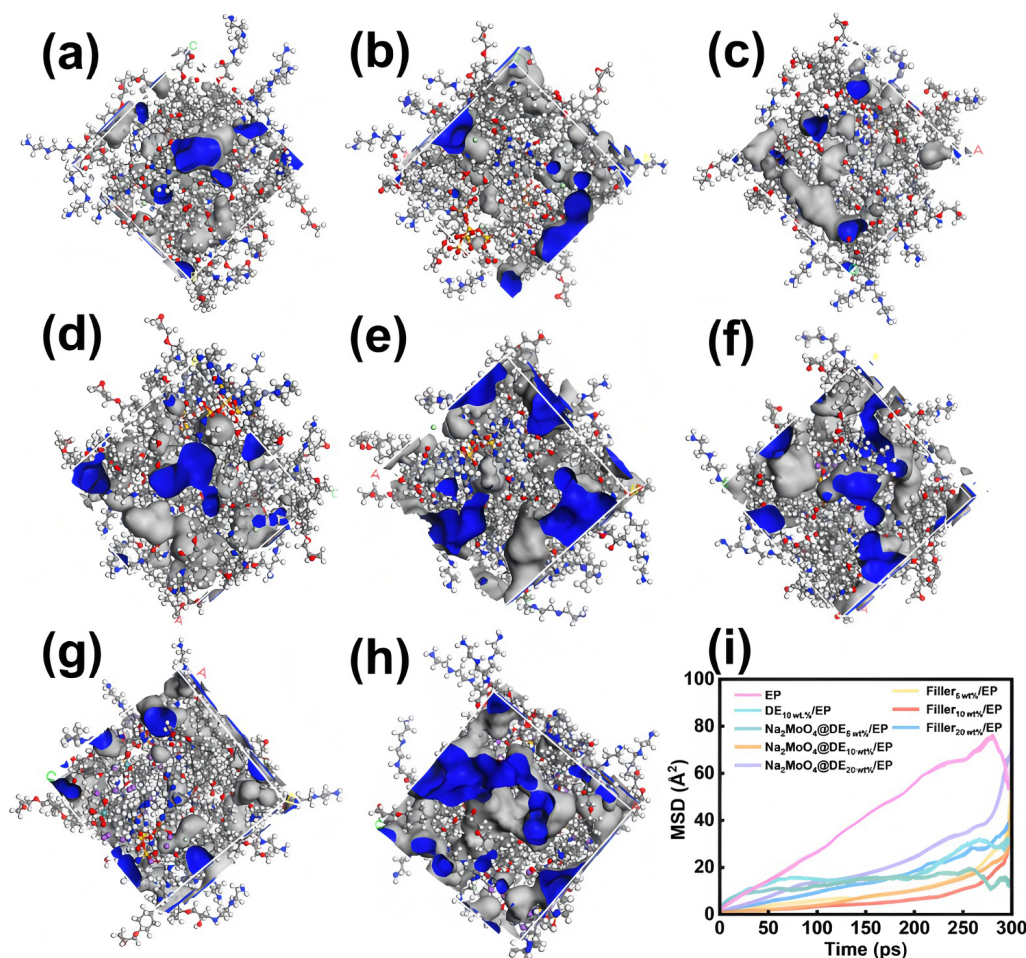


Figure 13 (a)–(h) Free volume distribution of EP, DE₁₀ wt%/EP, Na₂MoO₄@DE₅ wt%/EP, Na₂MoO₄@DE₁₀ wt%/EP, Na₂MoO₄@DE₂₀ wt%/EP, Filler₅ wt%/EP, Filler₁₀ wt%/EP and Filler₂₀ wt%/EP coatings were detected using CI. (i) MSD curves of CI in the above coatings.

corresponded to a markedly increased surface roughness of 5.084 μm measured by 3D profilometry, indicating that excessive filler can induce structural defects within the coating and weaken interfacial bonding. Consequently, the effective release of corrosion inhibitors and the self-healing capacity of the coating are impaired. In summary, surface roughness serves as a key quantitative indicator for assessing corrosion severity and self-healing efficiency. Incorporation of an appropriate amount of filler enables a synergistic protective mechanism that combines physical defect filling, corrosion inhibitor release, and formation of a protective layer at damaged sites. At a filler content of 10 wt.%, the composite coating achieves an optimal balance between coating compactness, inhibitor utilization, and self-healing capability, thereby exhibiting the highest corrosion resistance.

To further investigate the composition of corrosion products, XRD analysis was performed on AZ31B magnesium plates coated with either pure EP or Na₂MoO₄@SZIF-8-DE/EP composite coatings. For the pure coating, diffraction peaks corresponding to the α -Mg matrix and alloy phases were observed, with a prominent peak at $2\theta = 36^\circ$ characteristic of α -Mg, along with peaks associated with magnesium alloy corrosion products (Fig. 15(j)). These results indicate that, in the absence of composite materials, NaCl solution can penetrate the coating and induce corrosion on the magnesium substrate. In contrast, the composite coating containing filler exhibited no distinct crystalline diffraction peaks after immersion,

with only a faint background signal detected. This behavior is attributed to the formation of an amorphous molybdate conversion layer (e.g., MgMoO_4) on the magnesium surface, resulting from the corrosion inhibitor Na₂MoO₄ within the composite. The amorphous film effectively covers the AZ31B substrate, masking its crystallographic peaks and acting as a barrier between the corrosive medium and the metal surface. This “film-forming masking” effect provides a protective mechanism by which Na₂MoO₄ enhances the corrosion resistance of the magnesium substrate.

The XPS comparison of magnesium substrates coated with pure EP and Filler/EP composite coatings is shown in Figs. 15(k)–15(r). For the pure EP-coated substrate, the full spectrum primarily detected Mg 1s and Al 2p signals, with no elements indicative of corrosion inhibition observed. The high-resolution Mg 1s peak at 1304.7 eV corresponds to corrosion products such as MgO or $\text{Mg}(\text{OH})_2$, while the Al 2p peak at 74 eV is attributed to Al_2O_3 or $\text{Al}(\text{OH})_3$. These results indicate that, under salt spray conditions, corrosive media rapidly penetrate coating defects, inducing oxidative corrosion of the magnesium substrate. In contrast, the XPS full spectrum of the substrate under the Filler/EP composite coating clearly shows characteristic Na 1s and Mo 3d peaks in addition to Mg and Al signals, demonstrating successful release and interfacial participation of Na₂MoO₄ during corrosion. The high-resolution Mo 3d spectrum (Fig. 15(q)) is resolved into two peaks at 232.5 (Mo 3d_{5/2}) and 235.7 eV (Mo 3d_{3/2}), indicating that Mo

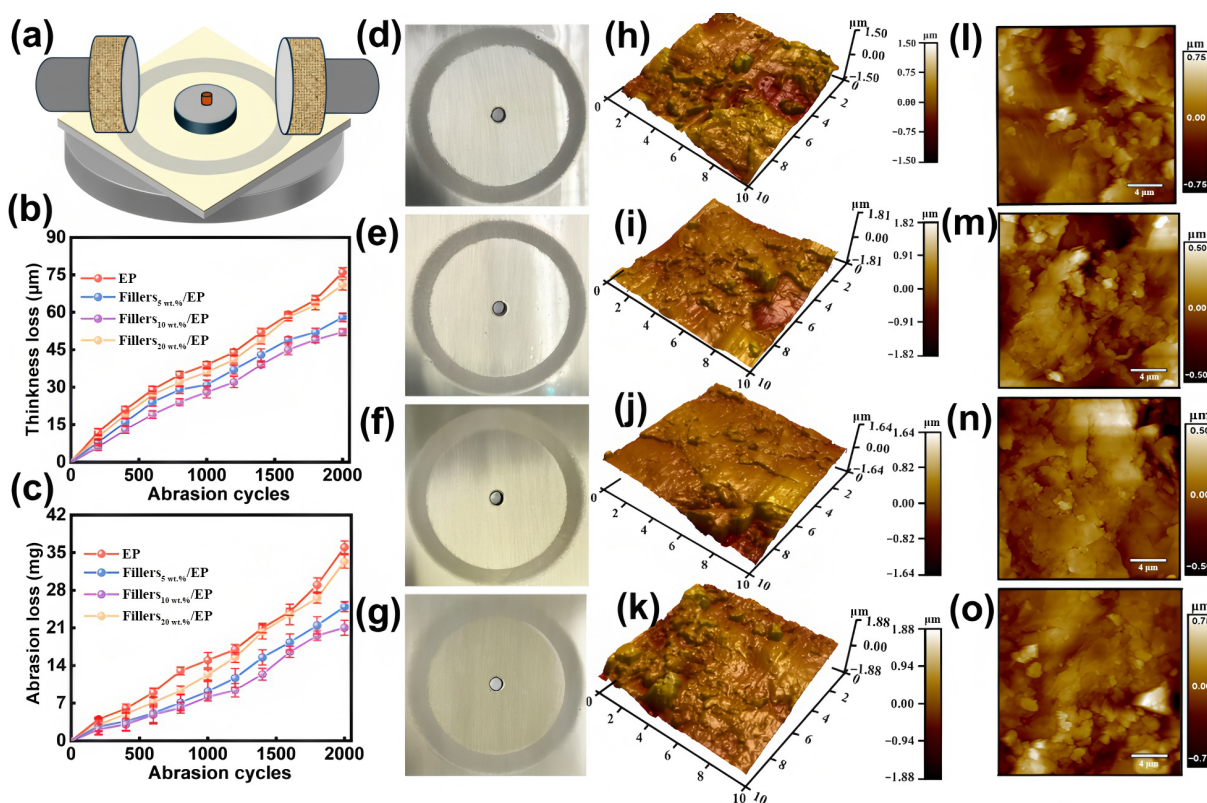


Figure 14 (a) Schematic diagram of sample wear. (b) Thickness loss and (c) mass loss of EP, Filler₅ wt%/EP, Filler₁₀ wt%/EP, and Filler₂₀ wt%/EP. (d), (h), and (l) Macroscopic images and atomic particle micrograph image of EP coating after rubbing for 2000 revolutions respectively; (e), (i), and (m) macroscopic images and atomic particle micrograph image of Filler₅ wt%/EP coating after rubbing for 2000 revolutions respectively; (f), (j), and (n) macroscopic images and atomic particle micrograph image of Filler₁₀ wt%/EP coating after rubbing for 2000 revolutions respectively; (g), (k), and (o) macroscopic images and atomic particle micrograph image of Filler₂₀ wt%/EP coating after rubbing for 2000 revolutions respectively.

predominantly exists in the Mo(VI) oxidation state. The Na 1s peak at 1071 eV further confirms the enrichment of molybdate species on the substrate surface. Additionally, the Mg 1s peak in the composite coating exhibits diminished intensity and a more concentrated shape, indicating the formation of a denser and more stable corrosion product layer. These results suggest that the Na₂MoO₄@SZIF-8-DE/EP coating provides dual protection: (1) It physically blocks the penetration of corrosive media and (2) the released molybdate inhibitors form a protective layer on the metal surface, markedly enhancing corrosion resistance, particularly in defect-prone regions.

Figure 16 shows the Raman mapping profiles of corrosion products formed on scratched coating surfaces. Artificial scratches were introduced until the magnesium substrate was fully exposed, followed by a 7-day indoor neutral salt spray test. After exposure, the samples were rinsed with deionized water and dried under ambient conditions. Raman spectroscopy revealed the spatial distribution of corrosion products on the four samples. Based on the corrosion behavior of magnesium alloys and Raman spectral characteristics, four major corrosion products were identified: Mg(OH)₂, MgCO₃·3H₂O, MgO, and Mg(OH)Cl. Significant differences in both the distribution and relative content of these products were observed among the samples. For the bare magnesium alloy, Mg(OH)₂ was the dominant corrosion product, although its overall content was relatively low. MgCO₃·3H₂O and MgO were more uniformly distributed but were present at lower total contents than Mg(OH)₂. Notably, Mg(OH)Cl was detected in considerable amounts, primarily concentrated around the scratch

edges. The formation and accumulation of Mg(OH)Cl indicate continuous penetration of Cl⁻ from the salt spray into the substrate, suggesting that the corrosion process has entered an accelerated stage [65, 66].

Raman surface mapping of corrosion products under different coatings provides insight into the anti-corrosion performance. For the blank coating, Mg(OH)₂ exhibited a scattered and discontinuous distribution, while the deleterious product Mg(OH)Cl showed extensive, continuous strip-like aggregation. MgO and MgCO₃·3H₂O were distributed irregularly and in a disordered manner, indicating that the blank coating failed to effectively block Cl⁻ penetration, resulting in severe damage to the protective passivation film. In the DE composite coating, Mg(OH)₂ coverage was significantly increased and more uniformly distributed. Mg(OH)Cl appeared only in small, isolated regions, and the signals of MgO and MgCO₃·3H₂O were markedly reduced. This confirms the physical barrier effect of the DE filler, which promotes the predominance of the protective Mg(OH)₂ phase. For the ZIF-8-DE composite coating, Mg(OH)₂ distribution was further enlarged and homogenized, accompanied by a notable reduction in Mg(OH)Cl content and decreased signals of MgO and MgCO₃·3H₂O. This trend reflects the effective pore-filling capability of ZIF-8 within the coating matrix, as well as its intrinsic corrosion-inhibiting properties. In the Na₂MoO₄@SZIF-8-DE composite coating, Mg(OH)₂ formed a continuous, high-coverage, and uniformly distributed passivation layer. Mg(OH)Cl was nearly undetectable, and the remaining corrosion products exhibited only weak Raman signals. These results demonstrate that the controlled

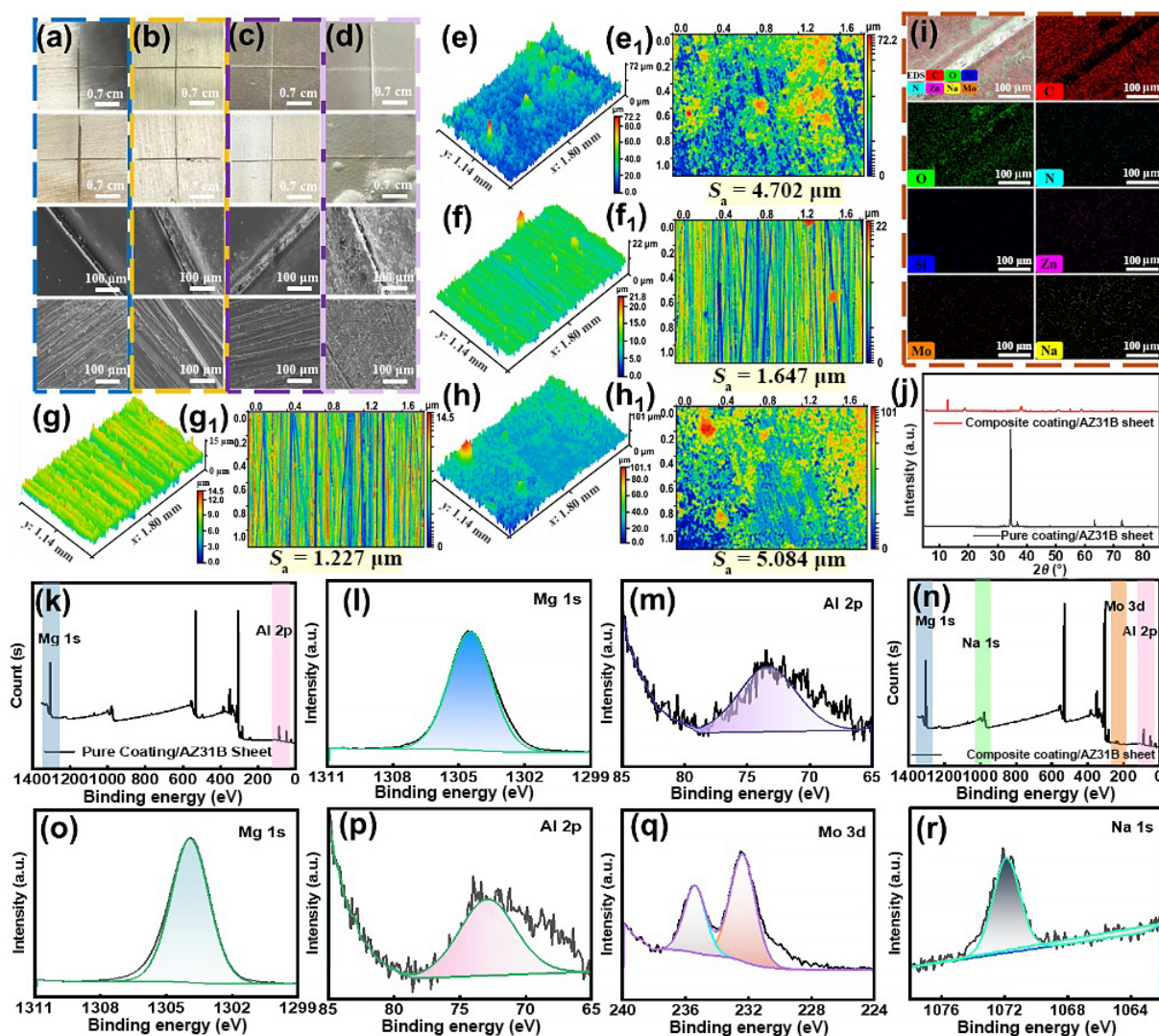


Figure 15 (a)–(d) The macroscopic images of the EP scratch coating and the macroscopic images of the different contents of the Na₂MoO₄@SZIF-8-DE/EP composite coating at the scratch site before the salt spray test, the SEM image of the EP scratch coating and the different contents of the Na₂MoO₄@SZIF-8-DE/EP composite coating scratch area after 7 days of salt spray test, macroscopic images and SEM images of the AZ31B magnesium alloy plate before and after salt spray testing under the EP coating and the different contents of the Na₂MoO₄@SZIF-8-DE/EP composite coating. (e)–(h) 3D and 2D AFM images of AZ31B magnesium alloy plates under EP coating and the different contents of the Na₂MoO₄@SZIF-8-DE/EP composite coating. (i) EDS images of the scratch area of the Na₂MoO₄@SZIF-8-DE/EP composite coating. (j) XRD patterns of Pure coating/AZ31B sheet and Na₂MoO₄@SZIF-8-DE coating/AZ31B sheet. (k)–(r) XPS of EP/AZ31B sheet and Na₂MoO₄@SZIF-8-DE/EP/AZ31B sheet.

release of MoO₄^{2−}, combined with the synergistic passivation effect of SZIF-8 and DE, effectively stabilizes the Mg(OH)₂ passivation film. This stabilization is a key factor underlying the optimal corrosion protection performance of the composite coating.

The corrosion process initiates with the anodic dissolution of the magnesium substrate ($\text{Mg} \rightarrow \text{Mg}^{2+} + 2\text{e}^-$), accompanied by a cathodic water reduction reaction ($2\text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{H}_2\uparrow + 2\text{OH}^-$). The released Mg²⁺ ions subsequently react with OH[−] to form the primary corrosion product, Mg(OH)₂, which initially acts as a protective passivation layer. In the presence of atmospheric CO₂, Mg(OH)₂ can further react to generate magnesium carbonate trihydrate (MgCO₃·3H₂O). However, under salt spray conditions, aggressive Cl[−] readily penetrates and disrupts the Mg(OH)₂ passivation film, resulting in the formation of soluble basic magnesium chloride, Mg(OH)Cl. This process significantly compromises the integrity of the protective layer and accelerates the corrosion reaction. In addition, a small amount of MgO may form through the partial

dehydration of Mg(OH)₂ during the corrosion process.

The Na₂MoO₄@ZIF-8-DE composite coating provides effective protection for magnesium alloys through a synergistic mechanism involving a physical barrier, chemical corrosion inhibition, and passivation stabilization. Structurally, the porous DE combined with the dense SZIF-8 growth forms a dual physical barrier, effectively reducing electrolyte penetration and retarding the migration of corrosive ions. Chemically, Na₂MoO₄@ZIF-8-DE reacts with Mg²⁺ to form a stable chelated layer, thereby suppressing anodic dissolution. Meanwhile, 2-Mim released from SZIF-8 initiates EP ring-opening polymerization, enhancing filler-matrix compatibility, increasing cross-linking density, and improving the mechanical integrity of the coating. From a corrosion protection perspective, the blank sample exhibits abundant Mg(OH)Cl, indicative of accelerated corrosion, whereas the Na₂MoO₄@SZIF-8-DE coating shows a high proportion of protective Mg(OH)₂ with almost no Mg(OH)Cl. These results confirm the effective inhibition

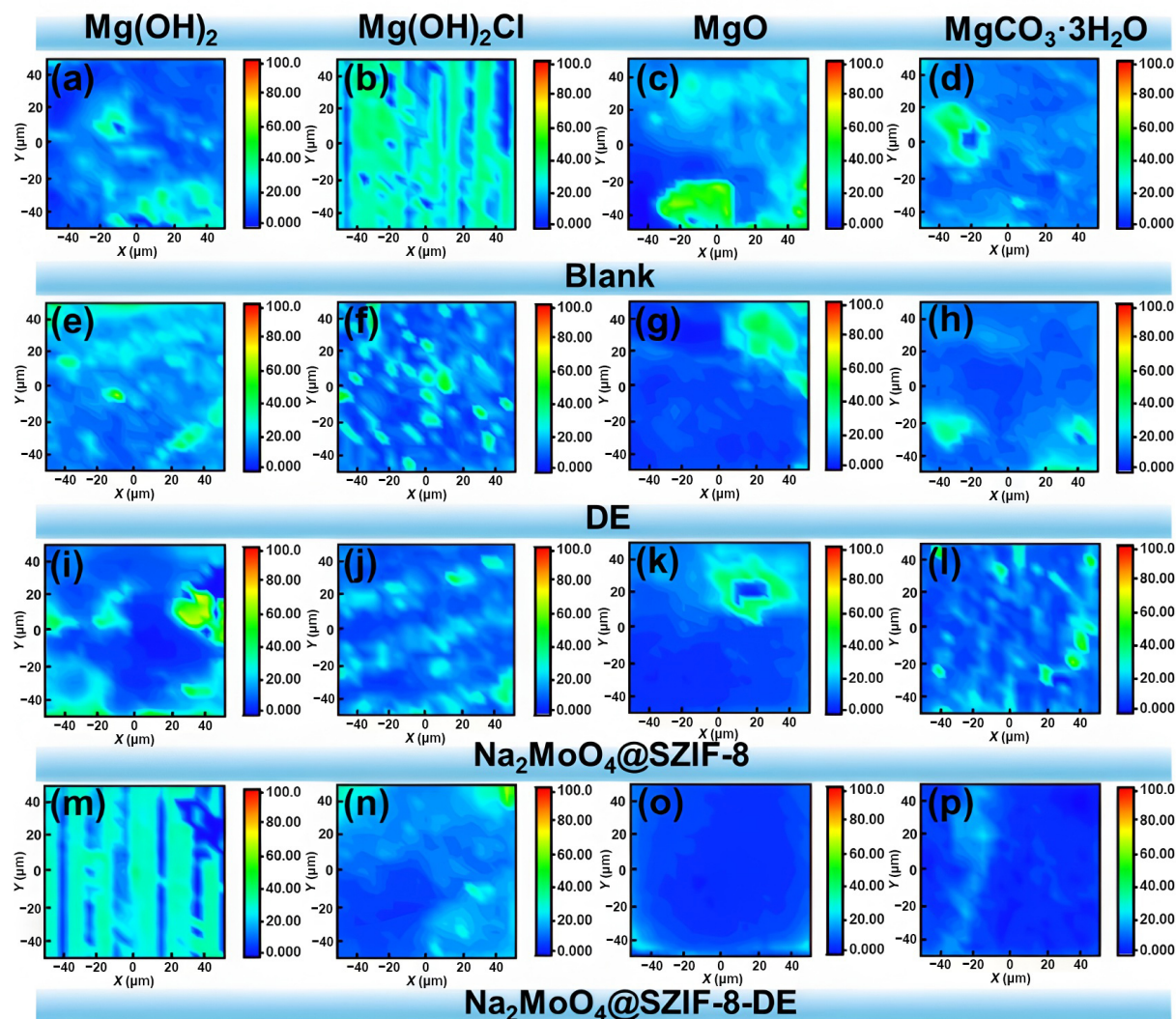


Figure 16 The Raman mappings of the corrosion product.

of Cl^- induced corrosion and demonstrate the superior protective performance of the composite coating on magnesium alloys.

3.9 Adhesion test

Figure 17 systematically presents the pull-off adhesion strength and corresponding fracture morphologies of the pristine EP coating and the composite coatings containing 5 wt.%, 10 wt.%, and 20 wt.% $\text{Na}_2\text{MoO}_4@\text{SZIF-8-DE}$ fillers. The pristine coating exhibits an adhesion strength of 5.12 MPa. With the incorporation of 5 wt.% and 10 wt.% fillers, the adhesion strength increases to 6.06 and 6.08 MPa, respectively, corresponding to an enhancement of approximately 18% compared with the pristine coating. This improvement cannot be solely attributed to the defect-filling effect of low-to-moderate filler contents but is primarily associated with the interfacial regulation induced by SZIF-8 grown on the DE surface. The 2D morphology of SZIF-8 significantly enlarges the contact area between the filler and the EP matrix, while its porous architecture enables effective resin infiltration and anchoring, thereby enhancing the filler-matrix interfacial bonding energy. Under tensile loading, this reinforced interface facilitates efficient stress transfer and suppresses crack initiation and propagation, ultimately strengthening the mechanical adhesion between the

coating and the substrate.

In contrast, when the filler content is increased to 20 wt.%, the adhesion strength decreases to 5.05 MPa, slightly lower than that of the pristine coating. This degradation is mainly attributed to the secondary agglomeration of $\text{Na}_2\text{MoO}_4@\text{SZIF-8-DE}$ at high loadings, which disrupts the structural continuity of the coating and introduces heterogeneous stress concentration sites at the interface. Consequently, the critical stress required to trigger cohesive fracture or interfacial debonding is reduced under pull-off loading. Overall, these results clearly demonstrate the filler content-dependent interfacial reinforcement behavior of the $\text{Na}_2\text{MoO}_4@\text{SZIF-8-DE}$ system: moderate incorporation maximizes the interfacial strengthening effect and adhesion performance, whereas excessive loading leads to agglomeration-induced deterioration, providing critical guidance for optimizing the filler formulation of the composite coating.

3.10 Analysis of the anti-corrosion capability of Na_2MoO_4

Figure 18 presents the molecular electrostatic potential (MEP) distribution of the $\text{Na}_2\text{MoO}_4\text{-Mg}^{2+}$ complex obtained from DFT calculations. In the MEP map, the color scale ranges from blue (high potential) to red (low potential), indicating variations in

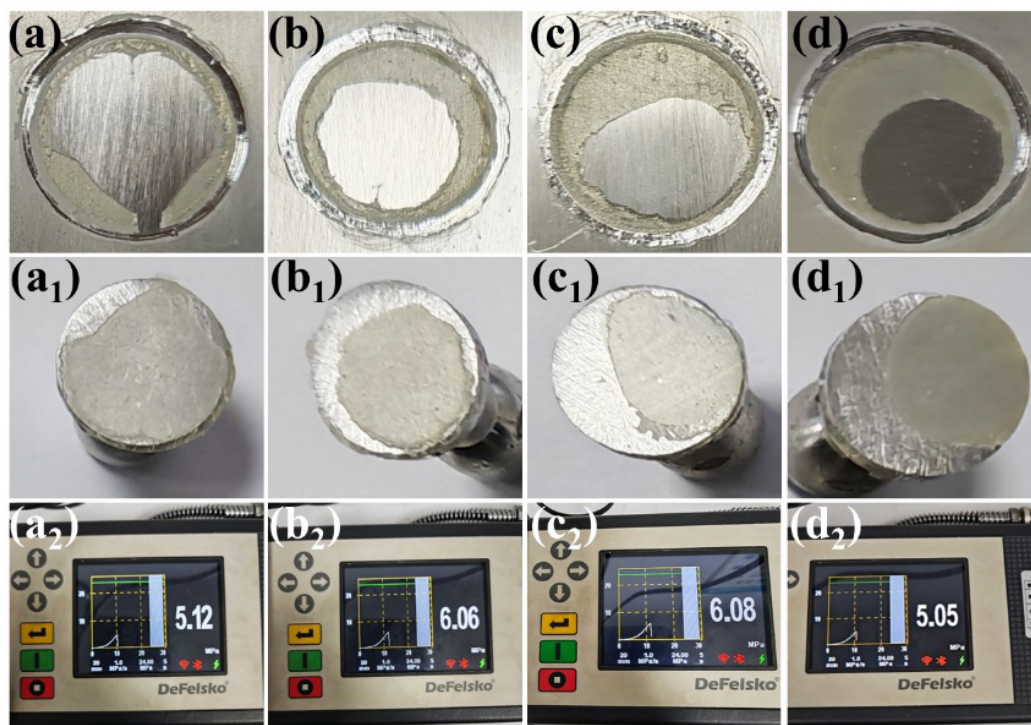


Figure 17 Pull-off adhesion test results and fracture morphology comparison of pure coating and different content of Na_2MoO_4 @SZIF-8-DE composite coating: (a) pure EP, (b) Filler_{5 wt.%}/EP, (c) Filler_{10 wt.%}/EP, and (d) Filler_{20 wt.%}/EP.

surface electrostatic potential. The red regions correspond to electron-rich active sites with a strong affinity for electrophilic species. The results show that the low-potential regions of the Na_2MoO_4 molecule are mainly localized around the Mo-centered coordination units, exhibiting pronounced negative charge characteristics that are favorable for the coordination and adsorption of Mg^{2+} . Further calculations of the binding energy (E_{ad}) for the Na_2MoO_4 - Mg^{2+} complex system reveal values indicating strong interactions between the two species, enabling the formation of a stable coordination complex structure. This result theoretically validates the feasibility of Na_2MoO_4 participating in passivation film formation on magnesium alloy surfaces by complexing Mg^{2+} . This provides compelling electronic structural evidence for its corrosion inhibition mechanism.

$$E_{\text{ad}} = E_{\text{ab}} - E_{\text{Na}_2\text{MoO}_4} - E_{\text{Mg}^{2+}} \quad (7)$$

In this equation, E_{ad} denotes the total energy of the adsorption system, while $E_{\text{Na}_2\text{MoO}_4}$ and $E_{\text{Mg}^{2+}}$ represent the monomer energies of the Na_2MoO_4 molecule and Mg^{2+} , respectively. The results presented in Table S7 in the ESM demonstrate that E_{ad} of the Na_2MoO_4 - Mg^{2+} complex system is -2.02752 eV, thereby substantiating the elevated thermodynamic stability of this chelate system. The negative binding energy indicates that the complexation process is a spontaneous reaction, with a significant reduction in the total energy of the system, reflecting strong chemical adsorption between the two components. From an electronic structure perspective, the MoO_4^{2-} group in Na_2MoO_4 functions as an electron donor, coordinating effectively with the vacant orbitals of Mg^{2+} to form stable coordination bonds. This has been demonstrated to enhance structural stability and electronic interactions within the composite system. These findings provide a theoretical basis for validating the ability of Na_2MoO_4 to form stable chelate protective layers on

magnesium alloy surfaces, thereby providing crucial evidence for its exceptional corrosion inhibition performance.

3.11 Mechanism of corrosion resistance of composite coating

As shown in Fig. 18, the corrosion protection mechanism of the Na_2MoO_4 @SZIF-8-DE_{10 wt.%}/EP composite coating on AZ31B magnesium alloy is governed by the synergistic coupling of a pH-responsive hierarchical release behavior and multi-functional protective effects enabled by the SZIF-8-DE hybrid carrier. Initially, the dense EP matrix, together with the multi-scale porous architecture of the SZIF-8-DE system, effectively prolongs the diffusion pathways of corrosive species such as H_2O , O_2 , and Cl^- , thereby providing a strong physical barrier against environmental ingress. Upon limited penetration of corrosive media and the onset of localized micro-corrosion, oxidation of the magnesium substrate generates Mg^{2+} , leading to local pH fluctuations. These changes activate the pH-responsive behavior of SZIF-8, inducing partial framework degradation and the preferential release of encapsulated sodium molybdate. The released molybdate ions rapidly interact with Mg^{2+} to form protective corrosion-inhibiting complexes, which adsorb onto active corrosion sites and effectively suppress both cathodic oxygen reduction and anodic magnesium dissolution reactions.

As corrosion progresses and SZIF-8 undergoes complete decomposition, sodium molybdate stored within the DE matrix is subsequently released in larger quantities, continuously replenishing the inhibitor supply to cover the expanding damaged regions. Simultaneously, corrosion by-products are stabilized, further mitigating corrosion propagation. Ultimately, the coordinated action of physical barrier protection, pH-triggered hierarchical inhibitor release, and chemical inhibition enable long-term and efficient corrosion protection of the magnesium alloy substrate.

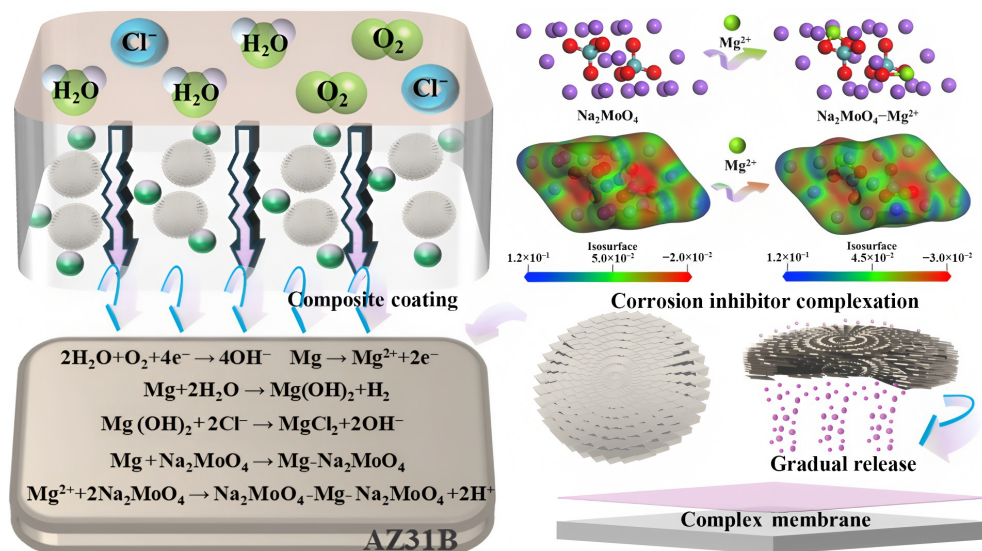


Figure 18 Schematic diagram of anti-corrosion mechanism of Filler_{10wt%}/EP composite coating.

4 Conclusion

A multi-level porous corrosion inhibitor carrier, Na₂MoO₄@SZIF-8-DE, was successfully constructed and incorporated into an EP coating to enhance the long-term corrosion resistance of AZ31B magnesium alloy in Cl⁻ environments. Uniform *in-situ* growth of lamellar ZIF-8 on DE formed a stable hierarchical porous structure, enabling efficient Na₂MoO₄ loading (12.49%) without structural degradation. The composite filler exhibited pH-responsive, controlled-release behavior, ensuring sustained inhibitor delivery under corrosive conditions.

Electrochemical results demonstrated that the Na₂MoO₄@SZIF-8-DE/EP coating significantly improved corrosion resistance, with the 10 wt.% filler coating showing the highest $|Z|_{0.01\text{Hz}}$ value and coating resistance after 60 days of immersion in 3.5 wt.% NaCl solution. Molecular dynamics simulations revealed strong interfacial adsorption between the composite filler and the magnesium substrate, consistent with experimental observations. Superior protective performance is attributed to a synergistic mechanism involving physical barrier enhancement, controlled inhibitor release, and interfacial stabilization. This study provides an effective strategy for designing intelligent and durable corrosion-resistant coatings for magnesium alloys.

Electronic Supplementary Material: Supplementary material (the research of self-adaptive pH-responsive ZIF-8 modified epoxy anti-corrosion coatings for Mg alloys, integrating multi-scale characterizations, long-term electrochemistry, permeation simulation and DFT computation: cross-section SEM (Fig. S1): fracture morphology comparison between blank epoxy and composite coating to clarify filler toughening & crack-blocking mechanisms; Tables S1 and S2: BET pore structure and TGA component ratio quantification of hierarchical SZIF-8-based inhibitors; Tables S3 and S4: short/long-duration EIS fitting parameters to quantify coating barrier and interfacial anti-corrosion performance over 60 days; Tables S5 and S6: diffusion coefficient and fractional free volume data of corrosive species to reveal coating mass transfer resistance; Table S7: DFT binding energy calculation validating the chelation passivation effect of molybdate inhibitors on Mg²⁺) is available in the online version of this article at <https://doi.org/10.26599/NR.2026.94908635>.

Data availability

All data needed to support the conclusions in the paper are presented in the manuscript and the Electronic Supplementary Material. Additional data related to this paper may be requested from the corresponding author upon request.

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Declaration of competing interest

All the contributing authors report no conflict of interests in this work.

Author contribution statement

F. G.: Investigation, visualization, writing – original draft, writing – review & analysis. X. Y. L.: Investigation. S. P. L.: Investigation. H. H. S.: Investigation. J. S. R.: Investigation. Y. X. Z.: Project administration, funding acquisition, investigation, visualization, writing – original draft, writing – review & editing, formal analysis. All the authors have approved the final manuscript.

Use of AI statement

None.

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