REVIEW

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Strategic microstructure manipulation of porous materials for advanced corrosion protection in metallic alloys

Yajie Yang, [a] Yonghao Zhu, [a] Zhuojun Yan, [*b] Doudou Cao, [c] Yingbo Song, [c] Yue Zheng, [c] Ya Wu, [a] Jiakun Yue, [a] Jiarui Cao, [c] Sirui Li, [c] Lu Luo [c] and Ye Yuan [*c]

Corrosion of alloys poses a significant threat to infrastructure sustainability, economic stability, and environmental safety, necessitating innovative anticorrosion strategies. Porous solids, characterized by large surface area, tunable porosity, and versatile functionalization, have emerged as promising candidates for developing advanced anticorrosion coatings. This review encompasses diverse porous solids, including inorganic non-metallic solids, gels, metal–organic frameworks (MOFs), and porous organic frameworks (POFs), highlighting their roles in synthesis, structural regulation, corrosion inhibitor storage/release, and current challenges. Key topics include fabrication methods (*e.g.*, sol–gel, electrochemical deposition, templating), anticorrosion mechanisms (barrier effects, active inhibition, self-healing), and strategies to improve performance (surface modification, composite design, smart responsiveness). The review concludes with insights into future directions, emphasizing sustainable synthesis, multifunctional integration, and industrial scalability.

1. Introduction

Corrosion, a natural electrochemical process that leads to the degradation of materials, has been a persistent and formidable challenge across numerous industries for centuries.[1,2] It is estimated that globally, the annual cost of corrosion amounts to trillions of dollars, encompassing direct expenses such as material replacement, maintenance, and repair, as well as indirect costs like production losses, safety hazards, and environmental impacts.[3] Such problems are particularly noteworthy in many areas. In the marine industries, ships' hulls and offshore platforms are constantly exposed to seawater, which contains a high concentration of salts, dissolved oxygen, and various microorganisms.[4,5] The chloride ions in seawater can easily penetrate the passive film on alloy surfaces, initiating pitting corrosion and ultimately leading to structural failure. The hulls of oil tankers are vulnerable to corrosion, and if left unaddressed, can result in oil spills that cause severe ecological damage. In the chemical industry, equipment and pipelines are frequently in contact with highly corrosive chemicals, including acids, salt spray, and solvents. Even materials with inherent corrosion resistance, such as stainless steel, can experience localized corrosion under certain operating conditions. A chemical plant might use reactors and pipelines made of stainless steel to handle sulfuric acid, but over time, the acid can attack the metal at grain boundaries, leading to intergranular corrosion and potential leakage of hazardous substances. This not only disrupts the production process but also poses a significant threat to the safety of workers and the surrounding environment.[6]

Metal corrosion is the gradual depletion of metal atoms through spontaneous electrochemical reactions within a corrosive medium. When chemical potential differences exist on the metal surface, regions with higher energy become anodes, where metal atoms lose electrons and dissolve into the surrounding medium as ions. The released electrons migrate through the metal matrix to cathode regions with lower energy. They combine dissolved oxygen or water molecules to complete reduction reactions and form a closed charge circuit. This process leads to the gradual depletion of the metal substrate and the formation of a loose, porous layer of oxidation products on the surface. If there are stress differences, impurities or oxygen concentration gradients on the metal surface, localized galvanic cells may also form, accelerating corrosion. The application of corrosion-resistant coatings is one of the common anti-corrosion measures in industry.[7] Applying coatings to metal substrates isolates the metal from corrosive substances, effectively breaking the corrosion circuit. Currently, the coatings industry has reached a total value of US $196 billion, with widespread applications across sectors including

ᵃKey Laboratory of Automobile Materials, Ministry of Education & School of Materials Science and Engineering, Jilin University, Changchun 130025, PR China

ᵇCollege of Chemistry, Liaoning University, Shenyang 110036, PR China. E-mail: zhuojun_yan@126.com

ᶜKey Laboratory of Polyoxometalate and Reticular Material Chemistry of Ministry of Education, Northeast Normal University, Changchun 130024, PR China. E-mail: yuany101@nenu.edu.cn

energy, chemicals, marine, infrastructure, transportation, and machinery.

Traditional anticorrosion coatings on alloys, such as polymer-based coatings, have been widely used to protect substrates from corrosion. These coatings typically form a continuous film on the surface, acting as a physical barrier to prevent the ingress of corrosive substances. However, traditional coatings often face limitations, for instance: (1) organic coatings are very machinable and designable, but they may degrade over time due to exposure to ultraviolet (UV) radiation, temperature fluctuations, and mechanical stress; (2) inorganic coatings may have good long-term application stability, but they usually reveal some limitations in terms of structural components, and it is not possible to design components to actively respond to the corrosion process. Once the coating is damaged, even slightly, the underlying alloy substrate becomes vulnerable to corrosion, and the degradation can spread rapidly.[8-11]

Porous solids have emerged as a revolutionary class of materials for anticorrosion coatings, leveraging their distinctive structural features and inherent properties. One of the most notable characteristics of porous solids is their high porosity, which endows them with a large specific surface area, often measured in square meters per gram ($m^2\ g^{-1}$).[12] For instance, some porous aromatic frameworks (PAFs) exhibit specific surface areas exceeding 5000 $m^2\ g^{-1}$, providing an extensive surface for various interactions.[13] The pore size of porous solids is another crucial property, which can range from micropores (<2 nm), mesopores (2–50 nm), to macropores (>50 nm), as classified by the International Union of Pure and Applied Chemistry (IUPAC).[14-16] Microporous solids are excellent platforms for adsorbing molecules, such as water vapor, volatile organic compounds, and even individual ions. This property can be harnessed to selectively remove corrosive species from the surrounding environment before they reach the substrate. Mesoporous solids offer a balance between adsorption capacity and mass transfer rate, making them suitable for applications that require the accommodation of larger molecules, like the encapsulation of bulky corrosion inhibitors. Macroporous solids facilitate the flow of fluids and the diffusion of substances, which is beneficial for the rapid access to the internal surface of the coating, such as in self-healing mechanisms where repair agents need to quickly reach damaged areas. Through precise control of synthesis conditions, the pore size, shape, connectivity, and overall architecture of the porous solids can be tailored to meet specific requirements. For example, covalent organic frameworks (COFs) can be designed by choosing appropriate organic monomers and reaction pathways, allowing for the creation of pores with specific geometries that can interact with targeted corrosive species in a highly specific manner.[17-19] The COF was functionalized with binding groups that have a strong affinity for chloride ions, which are a major cause of corrosion in aircraft due to exposure to de-icing fluids and salt-laden air. Inorganic non-metallic porous solids, such as silica-based porous ceramics, can withstand exposure to harsh chemicals, high temperatures, and abrasive environments. These unique properties of porous solids enable them to perform multiple functions

simultaneously, and numerous practical examples demonstrate their effectiveness as anticorrosion coatings.

This review aims to provide a overview of the current state-of-the-art in this field, covering the classification, preparation methods, anticorrosion mechanisms, application fields, existing problems, and future development directions of porous solids as anticorrosion coatings (Fig. 1). By exploring the potential and challenges of these materials, this review hopes to inspire further research and innovation, ultimately leading to the development of more advanced and sustainable anticorrosion strategies.

2. Anticorrosion mechanisms

Traditional coatings on alloys, such as dense paints or enamel, rely primarily on a passive barrier effect. They form a continuous, non-porous film that physically blocks corrosive agents (water, oxygen, ions) from reaching the substrate. This dense structure acts as a shield, but its effectiveness diminishes with mechanical damage (e.g., scratches) or chemical degradation, as defects create pathways for corrosion initiation. Porous coatings offer key advantages over traditional ones. They leverage a combination of passive and active mechanisms. Their interconnected pores enable multifunctional protection: they can act as reservoirs for corrosion inhibitors, which are released upon coating damage or environmental triggers (pH, temperature, or light), actively suppressing corrosion at the defect site. Additionally, the porous structure promotes the formation of a stable passive film on the alloy surface by regulating ion diffusion, enhancing long-term resistance. Some porous coatings (those with nanostructured pores) also exploit capillary effects to repel water or trap corrosive species, reducing their mobility. The specific mechanisms are as follows (Fig. 2).

2.1 Barrier effect

The barrier effect is a fundamental anti-corrosion mechanism for coatings. When a porous material is applied as a coating on a metal substrate, it forms a physical barrier between the substrate and the corrosive environment. In addition, the pores in the porous solids act as a tortuous path for corrosive media such as water, oxygen, and corrosive ions. These media need to diffuse through the complex pore structure to reach the metal substrate. The longer the diffusion path, the more difficult it is for the corrosive substances to penetrate, thus significantly reducing the rate of corrosion reactions on the substrate. For example, in a marine environment where seawater contains high concentrations of chloride ions, a porous solid-based coating on a metal ship hull can slow down the diffusion of chloride ions towards the metal, effectively protecting the hull from chloride-induced corrosion.[20-22]

2.2 Inhibitor release

Porous solids can be used as carriers for corrosion inhibitors, and the inhibitor-release mechanism is an important anti-corrosion strategy. The high porosity of porous solids provides
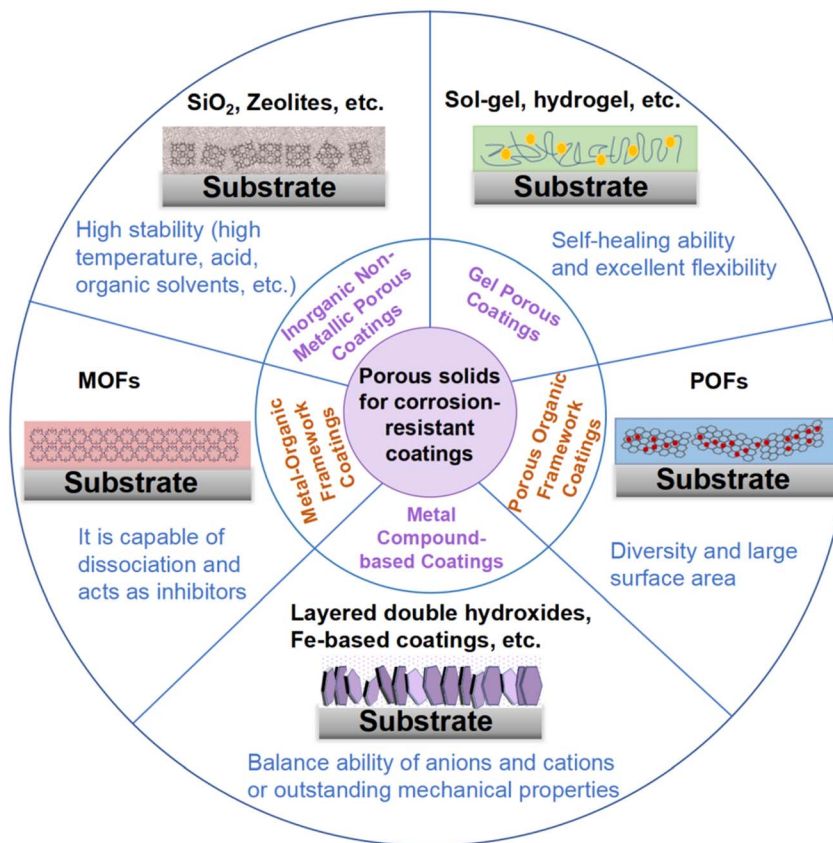
Fig. 1 Schematic representation of porous solids as corrosion-resistant coatings: structure–component engineering and advanced applications.

a large number of spaces to load corrosion inhibitors through physical or chemical adsorption. When the coating is exposed to a corrosive environment, the corrosion inhibitors are gradually released from the porous architectures. The release rate can be controlled by factors such as pore sizes, binding interactions (between the inhibitor and the pore wall), and concentration gradients of the corrosive media in the environment. When the equipment is exposed to acidic solutions, a porous solid-based coating loaded with corrosion inhibitors can release the inhibitors to react with the metal surface,
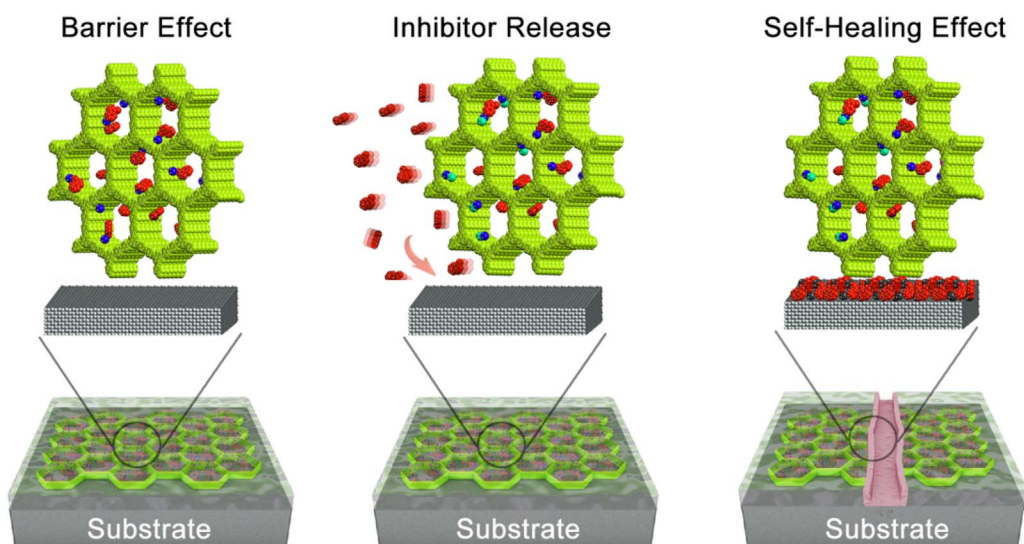

Fig. 2 Schematic representation of corrosion-resistant mechanisms of porous solids. Adapted with permission from ref. 25. Copyright 2024 Wiley-VCH.

forming a protective film that inhibits the corrosion reaction. POFs and MOFs are particularly suitable for loading corrosion inhibitors due to their large pore volumes and customizable structures. One is able to synthesize the porous framework with specific functional groups that have a tunable affinity for corrosion inhibitors, allowing for the controlled release of the inhibitors.[23,24]

2.3 Self-healing effect

Some porous solids possess self-healing properties, which can repair themselves when damaged and maintain their anti-corrosion performance. When these porous coatings are scratched or cracked, the flexible and viscoelastic nature of porous solids (gel and MOFs are the typical examples) allows them to flow and rearrange, filling the small cracks and defects through a process similar to viscous flow. In addition, some porous solids can undergo chemical reactions to repair the damaged areas. For example, a hydrogel-based coating containing metal ions and ligands will undergo spontaneous changes when the coating is damaged. The metal ions and ligands in the gel can diffuse to the damaged site and form new coordination bonds, bringing about a new cross-linked structure that fills the crack and restores the integrity of the coating.[25–27]

3. Characteristics and preparation of porous coatings

All porous coatings have some generic advantage – porosity, which provides a large specific surface area. This large surface area can be used to load corrosion inhibitors or to enhance the adhesion of the coating to the substrate. The porosity also allows for better adhesion between the coating and the substrate, as the pores can interlock with the surface of the substrate, forming a more stable bond. In addition, their pore structure can be diverse, which is beneficial for the storage of corrosion inhibitors, allowing the gradual release into the corrosive environment for a long-term anti-corrosion protection. In addition to these, the different components of the coating have their advantages and characteristics, which are listed below.

3.1 Inorganic non-metallic porous coatings

Inorganic non-metallic porous solids, with porous SiO_2 being a typical example, possess a series of unique characteristics that make them suitable for anti-corrosion coatings. These coatings can endure the high-temperature gas flow during engine operation, which reaches temperatures of up to 1500 °C or even higher in some cases. In addition, they are highly resistant to a wide range of chemical substances, including acids, alkalis, and various organic solvents.[28–31]

Several common preparation methods exist for the fabrication of inorganic non-metallic porous coatings. (a) Particle stacking and sintering method. In this method, inorganic powder particles are first stacked together to form a certain shape, either by simple loose packing or by applying pressure to make the powder particles closely arranged. Then, the powder particles are sintered, in which the powder particles bond together through atomic diffusion and strengthen the coating structure. (b) Pore-former addition method. A pore-former, like starch, urea, or a salt such as sodium chloride, can be added to the inorganic mixture (such as silica powder). The inorganic mixture and the pore-former are thoroughly mixed in a certain proportion, and then the mixture is shaped and sintered. Organic pore-formers decompose into gases such as carbon dioxide, water vapor, *etc.*, leaving behind voids, while salts can be removed by washing with an appropriate solvent. The amount and size of the pore-former added can be adjusted to control the porosity and pore size of the coating.[32]

3.2 Gel porous coatings

Gel porous solids used as anti-corrosion coatings are well-known for their high water absorption. Some hydrogel coatings can absorb water up to several hundred times their weight. In the anti-corrosion mechanism, the gel porous coating can absorb the water molecules in a humid environment, reducing the relative humidity near the metal substrate. This helps to prevent the formation of an electrolyte layer on the metal surface, reducing the corrosion rate of electrochemical corrosion. Good biocompatibility makes gel coatings suitable for applications in the biomedical and food industries. The biocompatible gel coating can reduce the immune response of the human body to the metal implant and prevent the corrosion of the metal in the physiological environment. The most remarkable feature of gel coatings is the high flexibility, which can deform under stress without cracking or losing its integrity. They can maintain their anti-corrosion function in applications where the coated substrate may experience mechanical deformation, such as in flexible electronic devices or in the automotive industry, where components may be subject to vibrations and shocks. Gel porous solids also have strong designability. Their properties can be easily adjusted by changing the composition of the gel precursor, the cross-linking degree, and the addition of various additives. For example, by adding nanoparticles to the gel matrix, the mechanical strength and anti-corrosion performance of the gel porous coating can be enhanced.[33–36]

There are several preparation methods for the fabrication of gel porous coatings. (a) Sol–gel method. This is a widely used method for preparing gel porous solids. It starts with metal–organic or inorganic precursors by dissolving them in a suitable solvent. Then, water and a catalyst, such as hydrochloric acid or ammonia, are added to initiate hydrolysis and condensation reactions. As the reactions proceed, the initially homogeneous solution transforms into a sol and then into a gel, where the solid particles form a continuous network. (b) Two-step cross-linking and particle dissolution kinetics regulation method. In this method, first, a polymer or a gel-forming substance is synthesized and cross-linked in a controlled manner to form a primary network structure. Then, particles, such as certain salts or polymers, with specific dissolution kinetics are introduced into the system to strengthen the network while the sacrificial particles are gradually dissolved during a subsequent treatment process. By precisely controlling the cross-linking

reactions and the dissolution kinetics of the particles, a gel porous material with a well-defined pore structure can be obtained for use as an anti-corrosion coating.[37,38]

3.3 Metal compound-based coatings

High strength is one of the key features of metal compound-based coatings. Metals such as stainless steel, titanium, and aluminum, when made into porous solids, still retain a relatively high level of mechanical strength. These coatings can ensure the structural integrity of the aircraft while also providing anti-corrosion protection. Good electrical and thermal conductivity are also important properties. In electronic devices, metal compound-based coatings can be used to protect the metal components from corrosion while also facilitating the dissipation of heat generated during device operation. Moreover, the electrical conductivity of metal compound-based coatings can be utilized to prevent the accumulation of static electricity related to corrosion. Metal compounds are highly malleable and can be easily processed into various shapes and sizes. This property makes them suitable for coating substrates with complex geometries. In the automotive industry, metal compound-based coatings can be applied to engine parts with irregular shapes, such as cylinder heads and pistons. The ease of processing allows for precise control over the thickness and porosity of the coating, ensuring optimal anti-corrosion performance.[39,40]

Several common preparation methods exist for the fabrication of metal compound-based coatings. (a) Powder metallurgy method. As starting materials, metal powders can be of a single metal or a mixture of different metal powders, which are first mixed with a suitable binder or lubricant to improve their formability. Then, they are compacted into a desired shape, such as a sheet or a pre-form that can be applied to a substrate as a coating precursor. After sintering at a temperature below the melting point of the metal, the atoms at the contact points of adjacent metal particles move across the boundaries, forming strong metallic bonds. The porosity of the final product can be controlled by factors such as the particle size of the metal powder (smaller particles tend to result in higher porosity), the amount of binder added, and the sintering temperature and time. (b) Fiber sintering method. Metal fibers are used instead of metal powders, made from various metals, such as stainless-steel fibers for high-temperature and corrosion-resistant applications. The fibers are first arranged or randomly distributed to form a fiber mat or a pre-form by methods like electrospinning. During sintering, the metal fibers bond at their contact points, forming a porous structure. The porosity of the resulting metal compound-based coatings can be adjusted by controlling the density of the fiber mat before sintering. The interconnected pores formed by the sintered metal fibers provide good permeability and mechanical strength, making this type of metal compound-based porous solid suitable for applications such as filters and heat-exchange components in corrosive environments. (c) Metal melting and foaming method. A metal or an alloy is first melted, and then a foaming agent, such as titanium hydride, is added to the molten metal. As heated, the

metal hydride decomposes and releases gas, such as hydrogen gas in the case of titanium hydride, which bubbles generated in the molten metal cause the metal to expand and foam. After foaming, the molten metal foam is cooled and solidified, either in a mold to form a specific shape or directly on a substrate to form a porous metal coating. The porosity can be adjusted by changing the amount of foaming agent added, the temperature during foaming, and the cooling rate.[41]

3.4 Metal–organic framework coatings

One of the most prominent features of metal–organic framework (MOF) solids is extremely high specific surface areas, often reaching several thousand square meters per gram.[42] This high surface area provides a large number of active sites for the adsorption of corrosive media. For example, in a chemical storage tank where acidic gases are present, a MOF-based coating can adsorb a large amount of the acidic gas molecules on its surface, reducing the concentration of the corrosive gases near the metal substrate. By choosing different metal ions and organic ligands during the synthesis process, MOFs with different pore sizes, shapes, and connectivity can be obtained. This tunability allows for the optimization of the MOF's properties for specific anti-corrosion applications. If the corrosive environment contains large-molecule corrosive substances, MOFs with larger pores can be designed to allow the diffusion of corrosion inhibitors while blocking the penetration of the large-molecule corrosive agents. On the other hand, for environments with small-molecule corrosive ions, MOFs with smaller and more precisely sized pores can be synthesized to prevent the diffusion of these ions towards the metal substrate. Exceptionally, MOF-based coatings can be engineered to incorporate a high density of open metal sites. These sites are capable of strong binding to many corrosive media (acids, ions, *etc.*), resulting in high-performance protection of the metal substrate.[43,44]

Several preparation methods have been developed for the fabrication of MOF coatings.[45] (a) Solvothermal method. Metal salts and organic molecules are dissolved in a mixture of solvents, often an organic solvent like *N,N*-dimethylformamide (DMF). The solution is then transferred to a sealed autoclave. The system is heated to a specific temperature, usually in the range of 100–200 °C, and maintained at this temperature for a certain period, typically several hours to days. Under solvothermal conditions, the metal ions from the metal salt and the organic ligands react to form a metal–organic framework structure. (b) Vapor deposition method. In the case of MOF synthesis, chemical vapor deposition (CVD) can be used. Metal–organic precursors are vaporized and carried into the chamber by an inert gas flow, and then decomposition and reaction occur on the substrate surface as contact with the heated substrate. The metal atoms from the precursor react with organic species or ligands present in the system (either pre-adsorbed on the substrate or introduced simultaneously) to form a metal–organic framework coating on the substrate. The deposition process can be precisely controlled by adjusting parameters such as the temperature of the substrate, the flow rate of the precursor vapor, and the reaction time.[46,47]

3.5 Porous organic framework coatings

Porous organic framework (POF) solids are composed of well-defined covalent-bonded networks, which result in relatively ordered local structures.[48] The covalent bonds in POFs are strong and can withstand a certain degree of chemical attack. In a moderately acidic or alkaline environment, the POF structure can remain intact, continuing to provide anti-corrosion protection. Similar to MOFs, the pore structure of POFs can be precisely designed by choosing monomers and the reaction conditions during the synthesis, which allows for the control of the pore size, shape, and distribution. Moreover, their covalent-bonded frameworks can be modified with various functional groups to achieve specific anti-corrosion functions. For example, hydrophobic functional groups can be introduced into the POF structure to enhance its water-repellent properties, preventing water from contacting the metal substrate. Chelating groups can also be incorporated into the POFs, which bind to metal ions in the corrosive environment, forming stable complexes and inhibiting the corrosion process.[49]

The preparation methods for the fabrication of POF coatings were summarized as follows. (a) Monomer polymerization method. POF solids are synthesized by the polymerization of monomers. For example, monomers with reactive groups such as boronic acid groups and amine groups can be used to form covalent bonds and gradually build up a one, two, or three-dimensional porous network. The resulting POF can be directly used as a coating on a substrate by methods like spin-coating or drop-casting, or it can be incorporated into a polymer matrix to form a composite coating. (b) Pore modification method. On the basis of POF architectures, one can introduce functional groups into the pore walls, e.g., long-chain alkyl groups or coordination groups. Long-chain alkyl groups provide hydrophobicity, reducing the contact of water and corrosive substances with the substrate, while coordination groups bind to metal ions in the corrosive environment, inhibiting the corrosion process.[50]

4. Development status of porous coatings

4.1 Inorganic non-metallic porous coatings

Inorganic non-metallic porous coatings, such as porous SiO_2, have been widely studied due to the outstanding thermal and chemical stability. These coatings withstand extremely high
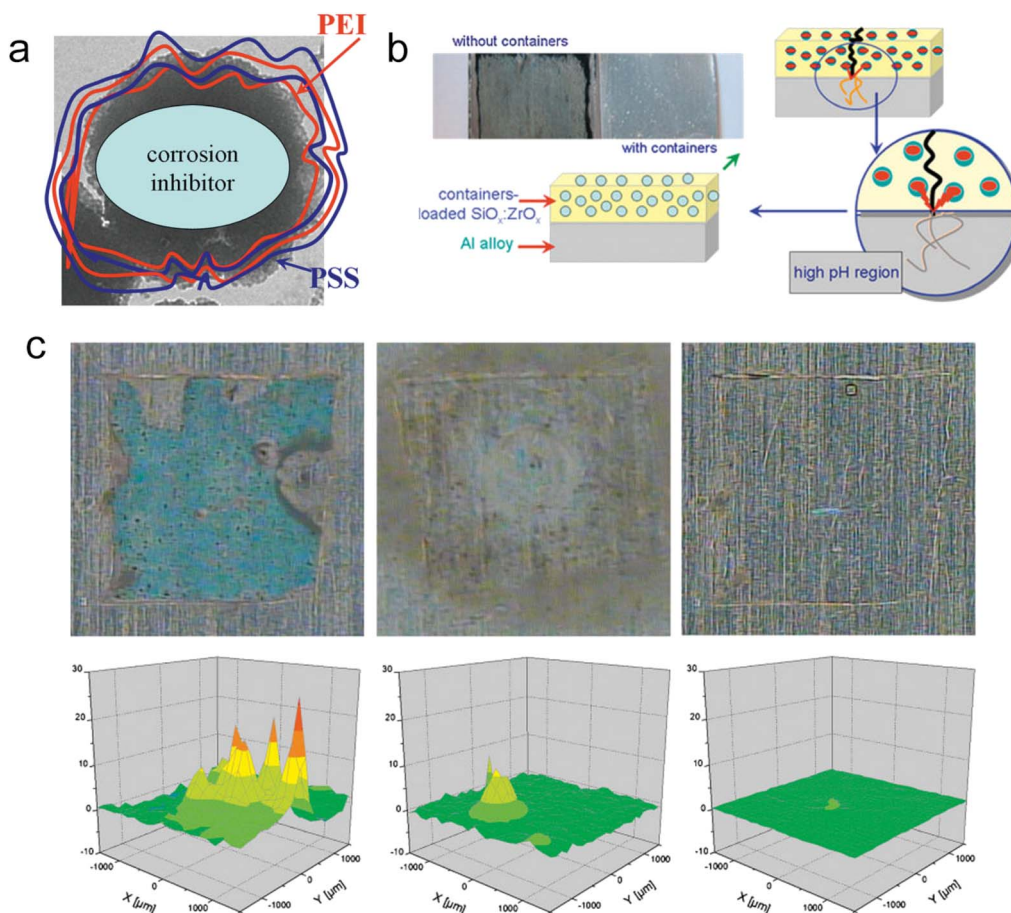

Fig. 3 (a) Porous container loaded with corrosion inhibitors. (b) Scheme of anticorrosion coatings. (c) Scanning vibrating electrode measurements (SVET) and the corresponding optical images of the unmodified aluminum alloy (left); aluminum alloy coated with $SiO_x : ZrO_x$ film (middle); aluminum alloy coated with container-loaded $SiO_x : ZrO_x$ film (right). Adapted with permission from ref. 51. Copyright 2009 Wiley-VCH.

temperatures and harsh chemical environments, ensuring the long-term stable operation of aerospace equipment. The high chemical stability makes them an ideal choice for protecting equipment in such harsh chemical environments to resist the corrosion of strong acids, strong alkalis, and other corrosive media. Skorb's team develops surface-modified mesoporous SiO_2 containers loaded with 2-(benzothiazol-2-ylsulfanyl)-succinic acid, coated with polyelectrolyte layers (via layer-by-layer assembly), and embedded in a silica–zirconia sol–gel coating for AA2024 aluminum alloy (Fig. 3). The polyelectrolyte shell prevents premature inhibitor leakage but opens at corrosion-induced pH extremes (e.g., pH 10.1, typical of cathodic zones), triggering inhibitor release. The coating provides long-term corrosion protection via a self-healing mechanism: released inhibitor forms a protective film at defects. Scanning vibrating electrode technique (SVET) shows negligible anodic activity after 54 h in 0.1 M NaCl, unlike coatings without containers. Compared to conventional sol–gel coatings (lacking self-healing), this system actively responds to corrosion initiation, and the polyelectrolyte shell offers better control over inhibitor release than unmodified porous carriers.[51,52]

As a typical porous material, SiO_2 can be encapsulated or doped with many functional nanoparticles, e.g., cerium oxide, graphene oxide, and so on.[53,54] Recently, a composite coating was prepared by combining horizontally aligned amino-functionalized h-BN nanosheets doped SiO_2 coating and MBT-loaded porous anodic alumina (PAA-MBT) film on Al alloy. The h-BN nanosheets extend the diffusion path of corrosive media, while MBT released from PAA forms a protective film at defects. The SiO_2 coating provides full-thickness hydrophobicity and reveals ultra-low self-corrosion current density, 4 orders of magnitude lower than bare Al. Unlike random 2D filler distributions, the oriented h-BN maximizes barrier effects, and the PAA layer enhances adhesion, distinguishing it from single-layer inorganic coatings.[55] In addition to the above methods,

some new hybrid coating strategies are being actively developed. For instance, a slippery liquid-infused porous surface (SLIPS) was fabricated on 6061 Al alloy via plasma electrolytic oxidation (PEO) and hydrothermal treatment, followed by fluorination (FAS) and silicone oil infusion (Fig. 4). The PEO creates micro-pores, and hydrothermal treatment grows nano-prickles, forming a hierarchical structure to retain oil. The SLIPS repels ethylene glycol–water droplets (sliding angle 1.1°) and acts as a physical barrier against corrosive media. Its corrosion current density is as low as 2.4×10^{-10} A cm^{-2}, 4 orders of magnitude lower than the bare alloy.[56]

4.2 Gel porous coatings

Gel porous solids can form a dense and uniform film on the metal surface, providing effective barrier protection. Researchers have focused on optimizing the sol–gel process to improve the quality of the coatings. They have studied the effects of various factors, such as the type of precursors, the hydrolysis and condensation conditions, and the addition of additives, on the structure and performance of the coatings. Tan et al. investigated multilayer coatings (anodized layer + sol–gel layers) for magnesium corrosion protection. The porous anodized layer enhanced adhesion, while sol–gel layers (MEMO-TPTMS-silica) sealed pores. Electrochemical tests (EIS, polarization) showed that double-layer coatings (two sol–gel layers) exhibited the highest impedance ($>10^8 \ \Omega$ cm^2) and no pitting up to 14 V, outperforming single-layer or anodized-only systems. Unlike single sol–gel coatings (prone to defects), multilayers eliminated continuous diffusion paths for corrosive species. This design avoids cracking from thick single layers, making it more effective for long-term protection of Mg alloys.[57]

By adding nanoparticles to the sol–gel system, the mechanical strength and anti-corrosion performance of the resulting gel porous coatings can be enhanced. The nanoparticles can fill the pores in the gel structure, reducing the permeability of
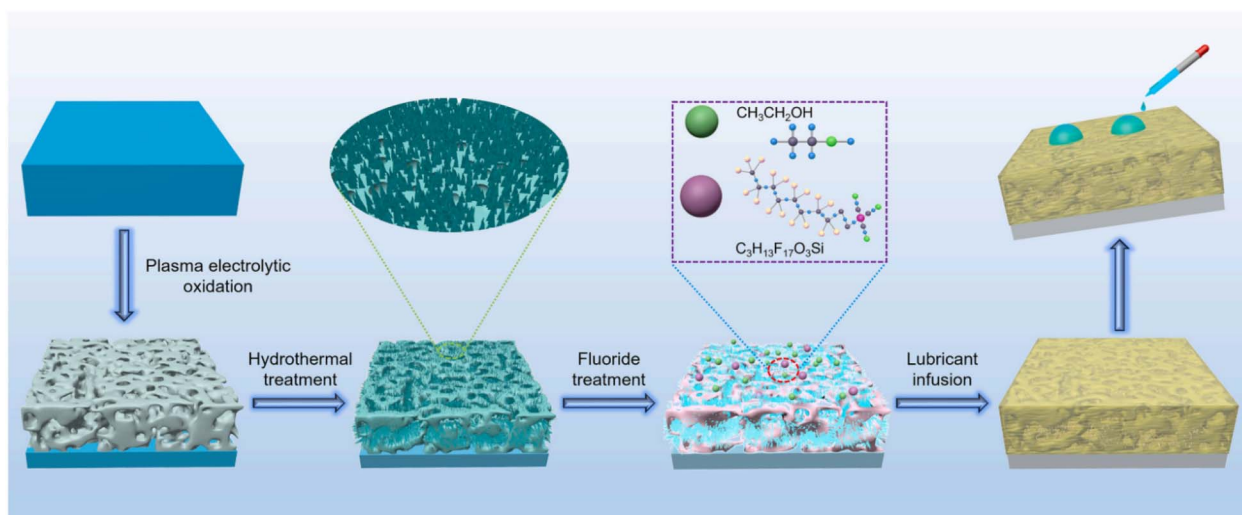

Fig. 4 Preparation process for the slippery liquid-infused porous surface on 6061 Al alloy. Adapted with permission from ref. 56. Copyright 2024 Elsevier.

corrosive media and improving the overall barrier function of the coating. Schem *et al.* developed CeO_2 nanoparticle-doped sol–gel coatings for AA2024-T3 aluminum alloy. TEM showed 5 nm CeO_2 nanoparticles uniformly distributed in the hybrid matrix. Electrochemical tests revealed that coatings with 7 wt% CeO_2 reduced anodic current density by 7 orders of magnitude *vs.* uncoated alloy. Salt spray tests indicated that high Ce content (20 wt%) effectively blocked scratch corrosion, while low content (7 wt%) inhibited general corrosion. Apart from the barrier protection from the dense matrix, the Ce ion release from nanoparticles suppresses cathodic reactions. Unlike undoped sol–gel coatings (limited passive range), CeO_2-doped coatings showed extended passivity and self-healing. However, high Ce content slightly reduced barrier properties due to increased porosity. The coatings also improved scratch/abrasion resistance, distinguishing them from inhibitor-free systems.[58]

In addition, the self-healing ability of some gel porous coatings has been exploited. When the coating is damaged, the gel-like structure can rearrange and fill the cracks to a certain extent, maintaining the integrity of the anti-corrosion barrier. Pereira *et al.* evaluated the corrosion protection of WE43 Mg alloy using three coating systems: cerium conversion coating (CeP), hybrid sol–gel coating (Hyb), and a duplex coating (CeP-Hyb). Morphological characterization (SEM, AFM) showed that the duplex coating improved surface coverage compared to single coatings, with the CeP layer providing a rough base for

better adhesion of the Hyb layer (Fig. 5). Electrochemical tests (EIS, potentiodynamic polarization) revealed that the duplex coating exhibited the highest corrosion resistance, with a low corrosion current density (0.6 $\mu A\ cm^{-2}$ after 24 h) and high impedance modulus ($3.01 \times 10^4\ \Omega\ cm^2$ after 24 h). A self-healing *via* Ce ions from CeP migrating to defects, as confirmed by LEIM. The duplex system synergistically combines barrier protection and active inhibition, outperforming both in long-term corrosion resistance.[59]

4.3 Metal compound-based coatings

Metal compound-based solids are widely used in the aerospace and automotive industries to prevent corrosion. Their high strength-to-weight ratio and good corrosion resistance make them ideal for applications where weight reduction is crucial while maintaining structural integrity. Numerous researchers have investigated different preparation methods to control the pore structure and distribution of the metal compound-based materials. Wang *et al.* evaluated porosity sealing treatments (sodium orthosilicate, aluminum phosphate, cerium salt) on HVOF-sprayed Fe-based amorphous metallic coatings to enhance corrosion resistance. The coatings, with intrinsic porosity, were sealed to block pores and improve durability. Aluminum phosphate ($AlPO_4$) sealant penetrated ≥50 μm into the coating, increasing hardness (1000 HV *vs.* 800 HV for uncoated) and providing long-term corrosion resistance in 3 wt% NaCl, attributed to its ability to fill pores and form
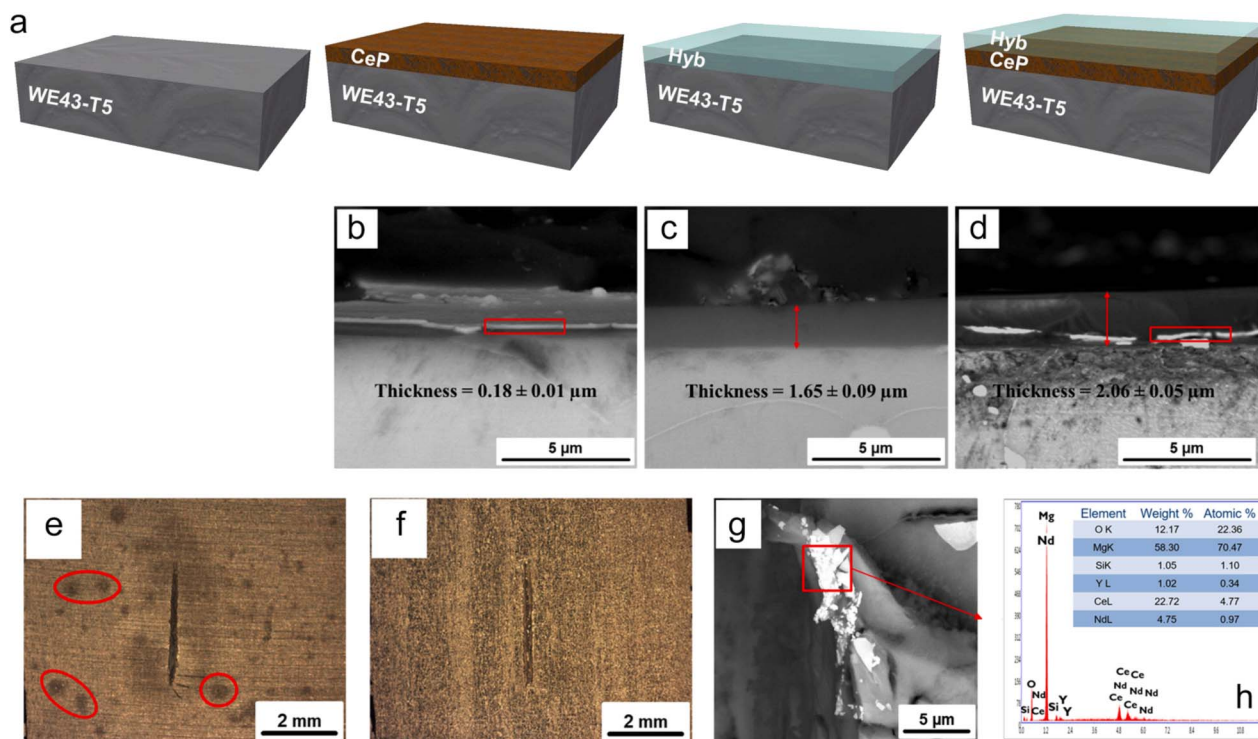

Fig. 5 (a) WE43-T5 samples: bare substrate, cerium conversion coating (CeP), hybrid sol–gel coating (Hyb), and duplex CeP-Hyb coating. Cross-sectional SEM micrographs: (b) CeP, (c) Hyb, and (d) CeP-Hyb. Optical micrographs of the artificial defects after the LEIM test: (e) hybrid sol–gel sample (Hyb) and (f) duplex CeP-Hyb sample. (g) SEM micrograph and (h) EDS analysis of the duplex CeP-Hyb sample after the LEIM test. Adapted with permission from ref. 59. Copyright 2022 Elsevier.

a protective barrier. Cerium salt coatings showed superior pitting resistance but poor performance in micro-crack regions, suitable for temporary protection. Sodium orthosilicate sealed only surface pores, offering short-term protection. Unlike organic sealants, these inorganic sealants withstand high temperatures and abrasion, with $AlPO_4$ being optimal for long-term corrosive/abrasive environments.[60]

Some studies have also focused on the surface modification of metal compound-based solids. By depositing a thin layer of corrosion-resistant materials on the surface of metal compound-based coatings, such as noble metals or corrosion-resistant alloys, the anti-corrosion performance can be significantly enhanced. Kultamaa *et al.* investigated the corrosion protection of porous 440C stainless steel, fabricated *via* metal injection molding (MIM) with sodium chloride as a space holder, using electroplated zinc coatings. The study prepared samples with 10, 20, and 30 wt% porosity and applied zinc coatings using three electrolytes: zinc acetate, zinc sulfate, and zinc chloride. The corrosion resistance was evaluated *via* a 240 hours neutral salt spray test. Results showed that all zinc coatings significantly improved corrosion resistance compared to uncoated samples. Zinc acetate electrolyte yielded the lowest corrosion rate, particularly at 30 wt% porosity, due to its ability to form a uniform, web-like zinc deposition within pores. In contrast, zinc chloride resulted in more crystalline deposits but poorer corrosion protection due to electrolyte acidity, causing initial substrate corrosion.[61]

Tong reported a robust, hydrophobic, and anti-corrosion slippery liquid-injected porous surface (SLIPS) coating with a unique bilayer structure fabricated on Mg alloys (Fig. 6). The coating consists of a bottom barrier layer of dense epoxy-coated ZnO nanoparticles and an upper layer of *in situ* grown ZnO nanorods forming a micro-nano rough porous structure, where perfluoropolyether (PFPE) lubricant is locked *via* capillary action after the perfluorooctyltriethoxysilane (PFOTES) pretreatment. The anti-corrosion mechanism of this SLIPS coating lies in replacing the fragile "air cushion" of super-hydrophobic surfaces (SHS) with a stable "oil film" formed by PFPE. The lubricant, trapped in ZnO nanorod gaps, resists long-term infiltration of corrosive media, while the bottom epoxy/ZnO layer provides an additional physical barrier. This synergistic effect effectively blocks corrosion pathways. After 70 days of immersion in 3.5 wt% NaCl, the charge transfer resistance (R_{ct}) remains 1.41×10^8 Ω cm^2, comparable to the initial value.[62]

4.4 Metal–organic framework coatings

Metal–organic frameworks have attracted significant attention in the development of anti-corrosion coatings. Their customizable structures can be designed to have specific chemical affinities with the stored chemicals, thus enhancing the anti-corrosion performance. For example, some studies have synthesized MOFs with built-in corrosion-resistant functional groups, which can actively participate in the anti-corrosion process by reacting with corrosive substances or forming stable complexes on the metal surface.[63] Chen *et al.* prepared various metal–organic framework (MOFs) coatings on micro-arc oxidation (MAO) layers of AZ31 Mg alloys to address the poor corrosion resistance of Mg alloys and the inferior film-forming ability and adhesion of MOFs. The MAO layer served as an intermediate carrier to facilitate *in situ* growth of MOFs (Ce-MOF, HKUST-1, Mg-MOF-74, MOF-5, Zn-MOF), improving their film-forming performance and adhesion (Fig. 7). In its mechanism, MAO provides a dense ceramic layer and enhances MOFs' adhesion; while MOFs crystals seal MAO pores, blocking corrosive media and capture corrosive ions (*e.g.*, Cl^-) and form insoluble chelates, inhibiting corrosion. Among all coatings, Ce-MOF exhibited the best corrosion resistance, with a corrosion current density of 8.68×10^{-8} A cm^{-2} after 30 min immersion.[64]
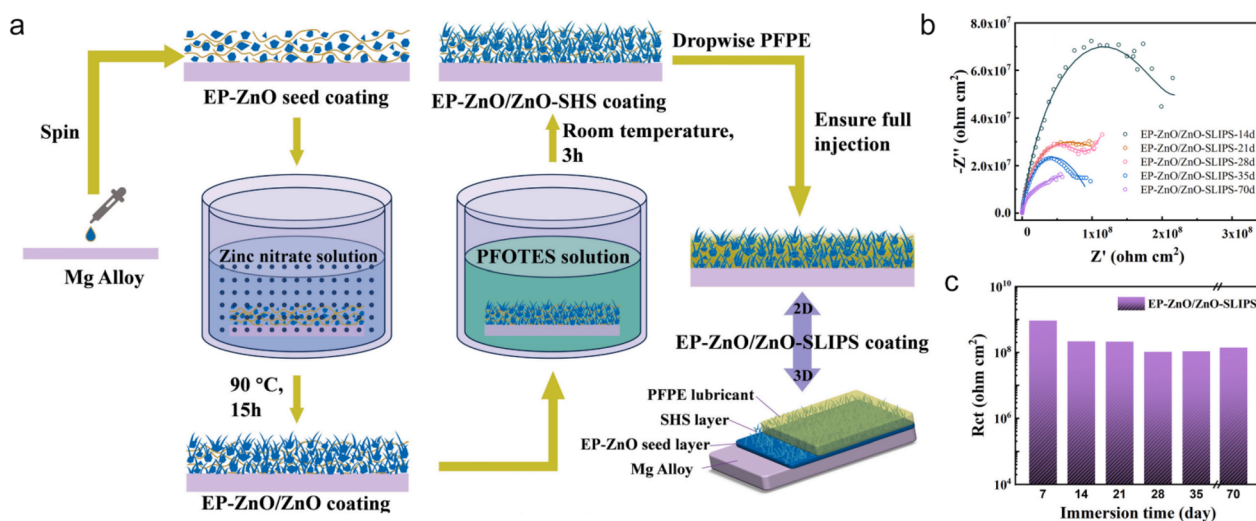

Fig. 6 (a) Preparation of EP-ZnO/ZnO-SHS and EP-ZnO/ZnO-SLIPS coatings. (b) EIS plots of EP-ZnO/ZnO-SLIPS coatings. (c) R_{ct} change of EP-ZnO/ZnO-SLIPS coatings. Adapted with permission from ref. 62. Copyright 2024 Elsevier.
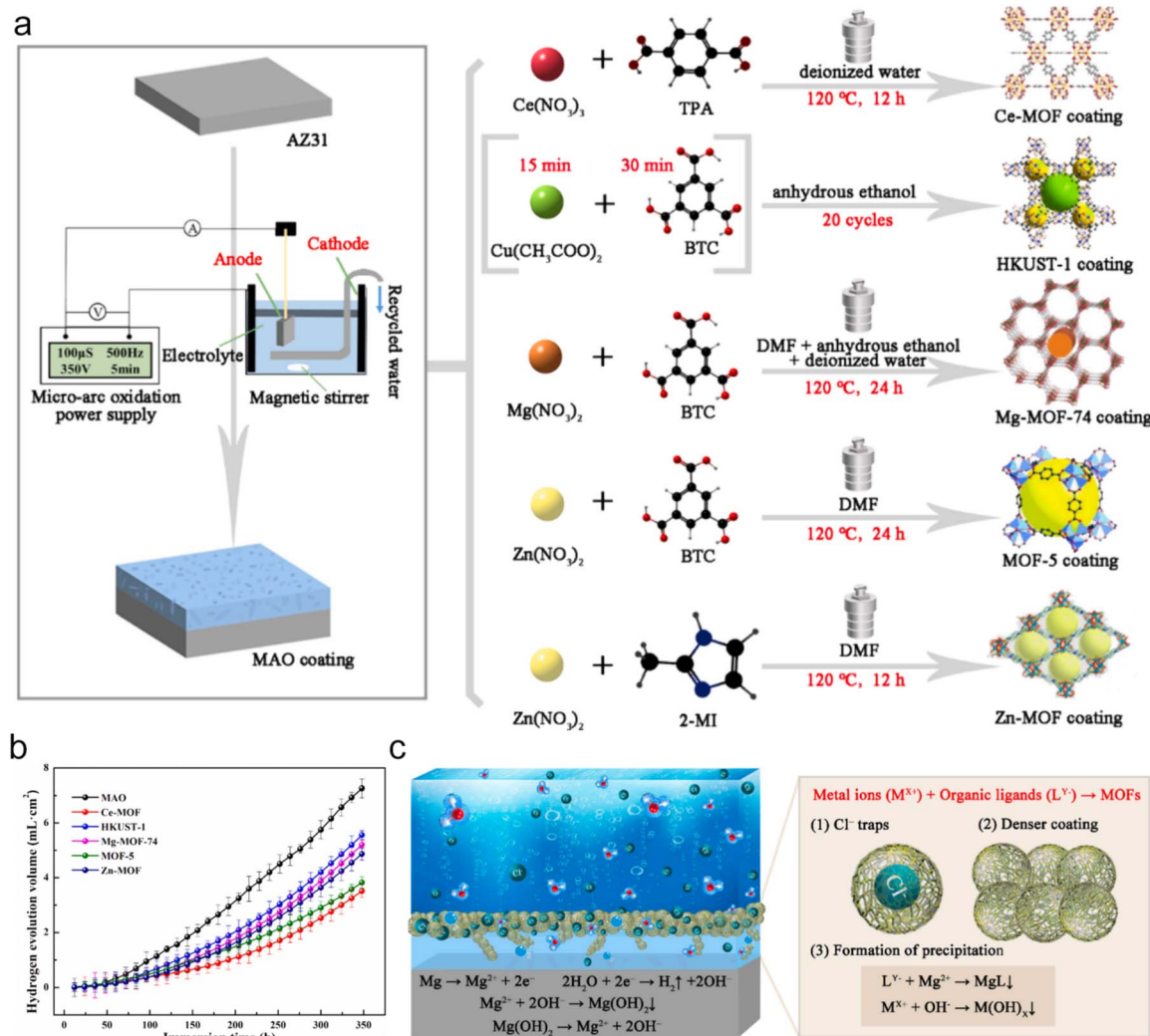
Fig. 7 (a) Preparation of MAO-based MOF coatings. (b) HEV for each coated specimen. (c) Corrosion resistance mechanism of MAO-based MOF coatings. Adapted with permission from ref. 64. Copyright 2024 Elsevier.

Recent interest has centred on the studies of the MOF-based composite coatings in different corrosive environments. Majidi et al. developed a dual-functional self-healing nanocomposite by growing ZIF-8 nanoparticles on oxidized multi-walled carbon nanotubes (OCNT) via hydrothermal (OCNTZ-I) and coprecipitation (OCNTZ-II) methods, then incorporating them into epoxy coatings. The corrosion protection mechanism includes: (1) OCNT provides a physical barrier, increasing the diffusion path of corrosive ions; (2) ZIF-8 exhibits pH-responsive release of Zn^{2+} and 2-methylimidazole, forming protective films at defects. After 8 weeks in 3.5 wt% NaCl, intact OCNTZ-II/epoxy coatings maintained an impedance modulus over 10^9 Ω cm². For scratched coatings, the charge transfer resistance (R_{ct}) was 4 times higher than pure epoxy after 24 h. Adhesion loss was reduced to ~40%, far lower than pure epoxy (86.67%).[65] Choudhary et al. reviewed MOF/graphene oxide (GO) nanocomposites as potential anti-corrosive coatings. GO, with oxygen-containing groups (–OH, –COOH), enhances compatibility with MOFs, while MOFs' porous structure provides active

corrosion inhibition. The corrosion protection mechanism is synergistic: (1) GO acts as a physical barrier, slowing ion diffusion; (2) MOFs load and release inhibitors (e.g., benzotriazole); in response to corrosion stimuli (pH changes), forming protective films. Electrochemical impedance spectroscopy (EIS) showed MOF/GO coatings have higher impedance modulus and lower corrosion current density than standalone MOFs or GO, due to improved dispersion and dual barrier/active effects.[66]

4.5 Porous organic framework coatings

Porous organic frameworks (POFs) have emerged as a new class of materials for anti-corrosion coatings, and research on them is in an active stage globally.[67] The unique covalent-bonded frameworks of POFs provide high chemical stability, and the introduction of hydrophobic groups into the framework can endow the material with superhydrophobic properties. In addition, the large surface area of POFs can be used to load corrosion inhibitors, further enhancing the anti-corrosion performance. Yang et al. designed a self-repairing coating for

magnesium (Mg) alloys using two-dimensional covalent organic frameworks (COFs) with nanofluidic channels (1.5–2.9 nm) to achieve responsive protection against multicorrosive media. The COFs load Ag^+ ions and 2-mercaptobenzimidazole (2-MB) inhibitors *via* silver bridges (Fig. 8). When exposed to corrosive anions (*e.g.*, Cl^-, Br^-, SO_3^{2-}), Ag^+ reacts to form precipitates, while 2-MB is rapidly released through the channels, forming a passivation film with Mg^{2+} to block corrosion. Integrated with polyethersulfone (PES), the coating achieves 100% damage restoration within 7 h, outperforming existing Mg alloy coatings (*e.g.*, Ce-based, LDH-based). It maintains ~100% protection in harsh environments (473 K, pH 4.0/10.0). The nanofluidic channels enable ultrafast inhibitor release (141.2 mg g^{-1} min^{-1}), 200% faster than traditional carriers (*e.g.*, carbon nanotubes, ZIF-8). Unlike rigid or slow-releasing coatings, this system combines structural stability, multi-ionic responsiveness, and rapid self-healing.[25]

Furthermore, research has explored the combination of POFs with other materials to develop composite anti-corrosion coatings. For instance, POFs can be combined with polymers to form hybrid coatings. The polymers provide good adhesion and flexibility, while the POFs contribute to the anti-corrosion and self-healing properties. This combination results in coatings with excellent overall performance, including high corrosion resistance, good mechanical strength, and long-term durability. A novel nanocontainer was developed by growing a ultrastable porous covalent organic framework (COF) based on terephthalaldehyde and melamine on multi-walled carbon nanotubes (CNTs), denoted as CC. Zinc cations were loaded into CC to form CCZ, which was then incorporated into an epoxy coating (CCZ/EP) for corrosion protection. The anti-corrosion mechanism combines passive and active protection. Passively, the CNT/COF hybrid structure prolongs the diffusion path of

corrosive electrolytes, enhancing barrier properties. Zinc cations are smartly released under acidic conditions (418 ppm released in 24 h at acidic pH), forming insoluble zinc oxide/hydroxide complexes on the steel surface to inhibit corrosion. The coating exhibits 75% inhibition efficiency of CCZ in saline solution, excellent barrier properties of CCZ/EP after 9 weeks of immersion, and significantly enhanced mechanical properties (137% increase in elastic modulus compared to neat epoxy). The dry and wet pull-off adhesion strengths of CCZ/EP reached 8.53 MPa and 2.7 MPa, respectively, with the lowest adhesion loss (68.3%).[68]

A hybrid structure was also synthesized by *in situ* growing imine-based COFs on amino-functionalized Ti_3C_2 MXene nanosheets (SMX) to form SMXC, followed by loading zinc cations and glutamate as dual inhibitors (SMXCGZ). The composite was embedded into epoxy coatings for corrosion protection. The anti-corrosion mechanism synergizes barrier effects and active self-healing. MXene's 2D sheet-like structure blocks electrolyte diffusion, while COFs provide porous spaces for inhibitor storage. Under pH gradients (*e.g.*, acidic conditions from corrosion reactions), zinc and glutamate are released: zinc forms $Zn(OH)_2$ at cathodic sites, and glutamate chelates with Fe^{2+}/Fe^{3+} at anodic sites to form protective films. SMXCGZ achieved 88% corrosion inhibition efficiency in saline solution over 96 h. The epoxy coating with SMXCGZ maintained a $log|Z|_{10m}$ Hz value of 10.64 Ω cm^2 after 11 week of immersion, with minimal adhesion loss (22.5%).[49]

In summary, porous solids endow corrosion-resistant coatings with excellent protective capabilities. These coatings can effectively block the corrosion of metals from the external environment, providing invaluable support for industrial development (Table 1).
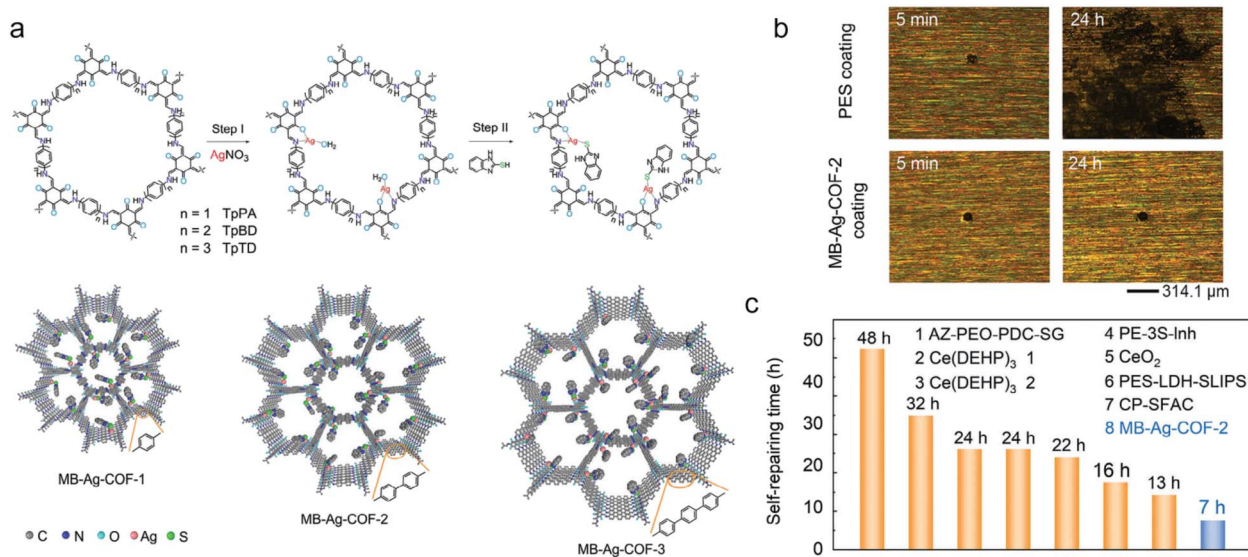

Fig. 8 (a) A series of COF carriers with 1D mass-transport channels ranging from 1.5 to 2.9 nm. (b) Optical micrographs of the artificial crack. (c) Comparison of the repairing time of the MB-Ag-COF-2 and other reported coatings. Adapted with permission from ref. 25. Copyright 2024 Wiley-VCH.

Table 1 Summary of substrates, types, and properties of different corrosion-resistant coatings

Substrate	Porous solid	Coating	$|Z|_{0.01Hz}$ (Ω cm^2)	i_{corr} (A cm^{-2})	Ref.
Mild steel 1214	COF	Epoxy	1.6×10^4	—	9
ST12 steel	ZIF	Epoxy	3.8×10^{10}	—	10
Mild steel	LDH	Alkyd resin	5.0×10^3	—	22
Magnesium	COF	Polyethersulfone	6.3×10^6	2.7×10^{-5}	25
AA2024 aluminum	HMS	Alkyd resins	—	8.0×10^{-6}	26
Q235	HNT	Epoxy	2.8×10^{10}	—	27
Q235	TiO$_2$	PU	5.5×10^7	—	29
AA2024 aluminum	MSN	Sol–gel films	—	2.0×10^{-3}	51
2024-T6 Al	PAA	Sol–gel films	10^8	7.1×10^{-8}	55
Al alloy (6061)	Polymer	SLIPS	3.1×10^6	2.4×10^{-10}	56
AZ91D magnesium	Gel	Sol–gel films	10^8	—	57
AA2024-T3 aluminium	Gel	Sol–gel coatings	10^8	—	58
WE43 Mg alloy	Gel	Sol–gel coatings	3.0×10^4	6×10^{-7}	59
304 stainless steels	Porous iron	Metallic coatings	10^4	9×10^{-7}	60
Magnesium	Porous ZnO	SLIP coatings	3.3×10^9	8.97×10^{-12}	62
AZ31 Mg alloys	MOF	MAO coatings	10^6	8.68×10^{-8}	64
Mild steel	ZIF	Epoxy	5.4×10^{10}	—	65
Mild steel	COF	Epoxy	5.4×10^3	3.603×10^{-6}	68

5. Main existing problems

5.1 Inorganic non-metallic porous coatings

One of the main problems with inorganic non-metallic porous solids used as anti-corrosion coatings is the difficulty in balancing porosity and strength. High porosity is beneficial for functions like corrosion inhibitor loading and self-healing through the release of inhibitors. However, an excessive increase in porosity often leads to a significant reduction in the mechanical strength of the coating. For example, in some high-temperature applications, the coating may experience cracking or even collapse under thermal stress due to insufficient strength caused by high porosity, which not only reduces the anti-corrosion performance but also shortens the service life of the coating. In addition, the adhesion between inorganic non-metallic porous coatings and the substrate is sometimes insufficient. The difference in the physical and chemical properties between the porous ceramic coating and the metal substrate can result in poor bonding. Once the coating detaches, the metal substrate is directly exposed to the corrosive environment, accelerating the corrosion process.

5.2 Gel porous coatings

The preparation process of gel porous solids for anti-corrosion coatings is relatively complex. The sol–gel method, which is commonly used to prepare gel porous coatings, requires strict control of multiple factors such as the type and ratio of precursors, hydrolysis and condensation conditions (including temperature, pH value, and reaction time). Small changes in these factors can significantly affect the structure and properties of the resulting gel porous coatings. For example, an improper hydrolysis ratio may lead to an uneven gel structure, reducing the barrier function of the coating. The stability of gel porous coatings also needs to be improved. These coatings may be affected by environmental factors such as temperature, humidity, and chemical substances in the long-term service.

5.3 Metal compound-based coatings

Metal compounds used as anti-corrosion coatings are prone to corrosion themselves. Although they can provide certain protection to the substrate, the porous structure exposes a large amount of metal surface to the corrosive environment. In an acidic environment, metal ions in the porous material can react with acidic substances, leading to the dissolution of the metal and the generation of corrosion products. These corrosion products may accelerate the corrosion process due to the formation of local galvanic cells. The cost of metal compounds is relatively high. The preparation of metal compound-based solids often requires complex processes such as powder metallurgy, electroforming, and 3D printing. These processes not only require high-cost equipment but also consume a large amount of energy and raw materials.

5.4 Metal–organic framework coatings

The synthesis of metal–organic frameworks (MOFs) usually requires specific metal salts and organic ligands, some of which are expensive and difficult to obtain. The complex synthesis process, such as solvent–thermal methods, often requires high-temperature and high-pressure conditions, which consume a large amount of energy and increase the production cost. The stability of metal–organic framework coatings also has some problems. In some harsh environments, such as high-temperature and high-humidity conditions, the coordination bonds in MOFs may break, leading to the decomposition of the material structure and a reduction in anti-corrosion performance.

5.5 Porous organic framework coatings

The preparation of porous organic frameworks (POFs) has high requirements, which requires strict control of reaction conditions, such as the purity of raw materials, temperature, and reaction time. The reaction mechanism is complex, and side

reactions are likely to occur, resulting in the formation of materials with imperfect structures or low yields. For example, in the synthesis of some COFs, it is necessary to use special catalysts and reaction solvents, and the reaction system needs to be in an inert gas environment, which increases the difficulty and cost of preparation.[69] The large-scale application of COFs is restricted by many factors. Their relatively high preparation cost and complex preparation process make it difficult to produce them in large quantities at present.

6. Future development directions

6.1 Multifunctional integration

In the future, porous solid-based anti-corrosion coatings are expected to develop towards multifunctional integration. For example, combining self-healing, antibacterial, and heat-insulation functions into one coating. Self-healing ability can repair small cracks and defects in the coating in a timely manner, maintaining its integrity and anti-corrosion performance. Antibacterial properties are crucial in applications where the coated surface may be exposed to bacteria-containing environments, such as in the food and biomedical industries. Heat-insulation function can be achieved by optimizing the pore structure of the porous material. In high-temperature environments, such as in marine industries, industrial furnaces, and aerospace engines, a porous coating with multifunctional integration can reduce the environmentally induced corrosion and improve the energy efficiency of the equipment.

6.2 Green and sustainable development

Green and sustainable development will be an important direction for porous solid-based anti-corrosion coatings. This includes the use of environmentally friendly raw materials and the optimization of preparation processes. In terms of raw materials, researchers will explore more renewable and non-toxic substances. The preparation process should also be optimized to reduce energy consumption and waste generation. In addition, the recycling and reuse of waste materials generated during the preparation process should be emphasized.

6.3 Nanotechnology application

Nanotechnology will play an increasingly important role in improving the performance of porous solid-based anti-corrosion coatings. By using nanotechnology, the pore size and structure of porous solids can be precisely controlled at the nanoscale, which can improve the coating's densification and stability. Nanocomposites can also be formed by combining porous solids with nanomaterials.

7. Conclusions

In this work, the research on porous solids as anti-corrosion coatings for alloys has made significant progress in recent years. Different types of porous solids, including inorganic non-metallic porous coatings, gel porous coatings, metal compound-based coatings, MOF coatings, and POF coatings,

have been extensively studied for their unique properties and potential applications in anti-corrosion coatings. Although remarkable advancements have been achieved in the field of porous material-based corrosion protection for alloys, the research on their intrinsic working mechanisms and practical application strategies remains fragmented, calling for more systematic and in-depth exploration. Specifically, several core obstacles currently hinder the breakthrough development of this field, which can be summarized as follows:

First, the dynamic transport behavior of corrosive media (e.g., Cl^-, H^+, O_2) within complex porous structures is still not fully elucidated. Unlike the simple pore environments in model materials, real porous corrosion-protective materials feature intricate pore network topologies (including pore size distribution, pore connectivity, and tortuosity) and diverse surface chemical properties (such as hydrophobicity/hydrophilicity, surface charge, and functional group composition). These factors exhibit highly complex and non-linear regulatory effects on the initiation, propagation, and termination of the corrosion process—for instance, the transport of corrosive media is no longer a single diffusion-dominated process, but is instead jointly governed by interface adsorption–desorption effects, capillary forces, and steric hindrance from pore walls, coupled with the modulation of pore size, connectivity, and surface reactivity. The lack of a clear understanding of this multi-factor-coupled transport mechanism directly limits the precise regulation of protective performance and the accurate prediction of material failure risks.

Second, the current preparation of high-performance porous anti-corrosion materials still faces significant challenges in process feasibility and sustainability. Most advanced porous materials rely on complex multi-step synthesis routes (e.g., template-assisted synthesis, sol–gel method, or vapor deposition), which not only demand high-purity, high-cost precursors (such as specialized functional monomers, rare-earth-modified nanoparticles, or bio-based templates) but also often require harsh reaction conditions (e.g., high temperature (>800 °C), high pressure, or strong corrosive reagents like concentrated acids/bases). These factors directly drive up the preparation cost, making it difficult to meet the industrial demand for low-cost, large-scale supply, and severely hindering the transformation of porous anti-corrosion materials from laboratory research to commercial application. Based on this, developing green, low-cost, and scalable preparation technologies (e.g., solvent-free polymerization, hydrothermal green synthesis using industrial by-products as precursors, or continuous flow-based large-scale forming) has become a key breakthrough direction to promote the industrialization of porous anti-corrosion materials.

In summary, to realize the industrial and commercial large-scale application of porous materials in alloy corrosion protection, it is necessary to not only deepen the basic research on the transport behavior of corrosive media and interfacial protection mechanisms to provide theoretical support for material structure optimization but also break through the technical bottlenecks of green and large-scale preparation to reduce industrialization costs. At the same time, it is essential

to combine the actual needs of specific application scenarios (*e.g.*, marine corrosion, chemical industry, oil and gas exploitation) to achieve precise matching between material performance and practical application requirements.

Author contributions

Y. Yang designed the structure of the review and wrote the original draft. Y. Wu, J. Cao, and S. Li collected the papers for this review topic. Z. Yan and Y. Yuan supervised the review and revised the manuscript. Finally, the manuscript was revised by all authors.

Conflicts of interest

There are no conflicts to declare.

Data availability

Data available on request from the authors. The data that support the findings of this study are available from the corresponding author upon reasonable request.

Acknowledgements

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