

Anticorrosion with green ionic liquids additives

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17.1 Introduction

Ionic liquids, which have good corrosion resistance, have become a research hotspot in the field of corrosion in recent years. However, there are still some problems in the research and application of ionic liquids, especially in dynamic environment such as corrosion resistance, thermal oxidation, lubricity, and so on. To solve these problems, researchers used the designability of ionic liquid structure to prepare functional ionic liquids with anticorrosion and wear resistance in dynamic environment. To reduce the crawling and leakage of ionic liquids under dynamic friction and decrease serious mechanical wear, ionic liquids are prepared in gel state, which can respond to dynamic shear and temperature. For the surface anticorrosion and lubrication of light metals, ionic liquids are combined with surface treatment technology to form an ionic liquid-based composite coating, which further improves its performance and industrial application.

17.2 Ionic liquids as corrosion inhibitors

Due to the increasing ecological awareness and strict environmental regulations, it is very desirable to develop a green and sustainable anticorrosion technology. In recent years, ionic liquids, as a new type of metal corrosion inhibitor, have attracted much attention because of their low volatility, non-flammability, nontoxicity, high thermal and chemical stability, and adsorption capacity on metal surfaces [1–10]. As “green corrosion inhibitor” of different metals and alloys, ionic liquids have been widely used in several media, such as steel, aluminum, copper, zinc, and magnesium [11–16]. Ionic liquid is a promising, green, and sustainable candidate material to replace the traditional volatile corrosion inhibitor, which can be effectively adsorbed on the metal surface [17–24].

Ionic liquids refer to liquids composed entirely of ions, such as NaCl and NaOH at high temperature. Here, ionic liquids generally refer to ionic compounds that are liquid at or below 100°C. Compounds composed of ions that are liquid at or near room temperature are called room-temperature ionic liquids or room-temperature molten salts. They are generally composed of specific cations with asymmetric structure and relatively large volume and inorganic or organic anions with relatively small volume. In ionic compounds, the force between cation and anion is related to the

charge quantity and radius of cation and anion. The larger the ion radius, the smaller is the force between them and the lower is the melting point of this ionic compound. The anion and cation of some ionic compounds are very large and asymmetric. The large steric hindrance makes it impossible for the anion and cation ions to be densely stacked and arranged in space. In this way, the anion and cation ions cannot only vibrate on the lattice, but also rotate and translate, which destroys the whole ordered crystal structure, reduces the force between ions, reduces the lattice energy, and reduces the melting point. When the melting point decreases to a certain extent, it becomes room-temperature ionic liquid. There are many kinds of ionic liquids [11,25–35]. Theoretically, liquids can be designed and synthesized by changing the combination of anions and cations. According to different anions, ionic liquids can be divided into two categories: one is AlCl_3 ionic liquids with adjustable composition. This kind of ionic liquids has been studied earlier and reported more, but AlCl_3 ionic liquids are very sensitive to water and air and must be treated and applied under vacuum and inert gas; the other is ionic liquid without AlCl_3 developed after 1992. Unlike AlCl_3 ionic liquid, this kind of ionic liquid not only has fixed composition, but also is not sensitive to water and air. Its use has increased rapidly in recent years, such as including the groups SnCl_3^- , NO_3^- , PO_4^- , BF_4^- , PF_6^- , SbF_6^- , AsF_6^- , CF_3SO_2^- , CF_3SO_3^- , $\text{C}_4\text{F}_9\text{SO}_3^-$, $(\text{CF}_3\text{SO}_2)_3\text{C}^-$, CF_3COO^- , $\text{C}_3\text{F}_7\text{COO}^-$, $(\text{CF}_3\text{SO}_2)_2\text{N}^-$, $(\text{C}_2\text{F}_5\text{SO}_2)_2\text{N}^-$, etc. In addition, more and more researchers introduce functional groups into the cations or anions of ionic liquids to obtain “task specific ILS” and make it obtain greater application [24,27,36–46]. Therefore, with the deepening of research work, many new ionic liquids will continue to emerge.

Since the first application of ionic liquids in the field of tribology, the research on ionic liquids as new lubricants in moving parts is still growing. Ionic liquid lubricant not only has high thermal stability and wide temperature application range, but also has excellent antifriction and wear resistance. However, in the research process of ionic liquid lubricant, there are still several problems, such as complex synthesis steps, expensive raw materials, corrosiveness to metal substrate, and poor solubility in base oil, which limits its application. To solve the above problems, the concept of “in-situ” synthesis of ionic liquid lubricant in base oil and grease was introduced, which has made a major breakthrough in reducing the cost of ionic liquid lubricants, improving its solubility in base oil, and solving its corrosive problem. On this basis, low-cost green ionic liquid lubricants were synthesized, such as ionic liquid lubricating oil and grease additives synthesized in situ in base oil and grease by one-step method [47]. Lithium ionic liquids with homotriazine and cyclotriphosphazene groups reduce the corrosion and improve the wear resistance, lithium ionic liquids containing benzotriazole groups synthesized “in situ” in Macs have good solubility and corrosion resistance in Mac for excellent antifriction and antiwear properties for steel/steel friction pairs, and so on.

Ionic liquid lubricants with antioxidation and anticorrosion properties are also designed and prepared [48–52]. As additives of lubricating oil and grease, they not only have good antioxidation and anticorrosion properties, but also have excellent antifriction and antiwear properties. Several sterically hindered phenolic substituted ionic liquids were synthesized for the first time, and these antioxidant ionic liquids have good solubility in polyethylene glycol (PEG). Thermal analysis shows that they have good antioxidant properties. The tribological properties of ionic liquids as PEG additives at room temperature were investigated by Small Recreation Vehicle (SRV) and four-ball friction and wear tests. It showed that these ionic liquids have excellent antifriction and antiwear performance, which is about 100 times higher than that of the base oil under the same conditions. A series of ionic liquids containing benzotriazole were also synthesized, which have

good solubility in PEG and polyurea grease. Copper strip corrosion test and accelerated corrosion test show that ionic liquid has good corrosion resistance due to the presence of benzotriazole group. These ionic liquids are also novel low molecular-weight gel factors, which can be used for self-assembly of supramolecular and gelation of ordinary ionic liquids. In addition to its excellent corrosion resistance and oxidation resistance, supramolecular gels also exhibit excellent electrical conductivity and excellent tribological properties at high and low temperatures. Therefore the gels are expected to be used as semisolid lubricants for electrical contact lubrication. In addition, an antioxidation and anticorrosion ionic liquid containing both steric phenol and benzotriazole bifunctional groups was synthesized, which has good solubility in PEG. Because steric-hindered phenol and benzotriazole groups exist together, the ionic liquid has good oxidation resistance and corrosion resistance at the same time. Bifunctional ionic liquids show very good antifriction and antiwear properties as lubricants for steel/steel and steel/copper friction pairs. The experimental results show that the three antioxidation and anticorrosion ionic liquid additives have better tribological properties than ordinary ionic liquid.

Room-temperature imidazole ionic liquids with different chain lengths were synthesized [50]. As polyurea grease additives, their thermal stability, copper corrosion, and temperature tribological properties at different temperatures were investigated. The results of copper strip corrosion test show that ionic liquid as polyurea grease additive has no corrosion to copper strip, which fully meets the requirements of grease additive. SRV and four-ball friction and wear tests show that the antifriction and wear resistance of ionic liquid additives at high temperature is more significant than that at room temperature; As an additive of polyurea grease, it has better antifriction and antiwear properties both at 20°C and 150°C. It was found that the ionic liquid additives have good antifriction and antiwear ability at appropriate concentration.

17.3 Ionic liquids as anticorrosion gels

Ionic liquids are a kind of important corrosion inhibitors and lubricants. The urea functional groups capable of forming intermolecular hydrogen bonds can be introduced into ionic liquid molecules, which can cooperate with long-chain alkyl groups. When alkyl chain length is longer than 16, it can rapidly form stable gel in ordinary ionic liquids. The gel-forming ability of the gel factor increased with the increase of the alkyl chain in the imidazole ring. The ionic liquid gel lubricants exhibit better tribological properties than pure ionic liquids in vacuum at different temperature. It is also found that the ionic liquid gel lubricant has good corrosion resistance because the ionic liquid gel factor can be coordinated with the metal substrate to form an effective anti-corrosive protective film.

The rapid development of modern industry has accelerated the excessive consumption of energy. According to statistics, friction consumes 30% of the energy consumed by mechanical equipment, and 80% of the equipment loss is caused by abnormal wear caused by lubrication failure. Lubrication is the most effective means to reduce friction or avoid wear. With the improvement of energy conservation and environmental protection requirements, higher requirements are put forward for the properties of lubricants, such as green environmental protection, high efficiency, long service life, excellent lubrication performance, and so on. As a new type of high-efficiency lubricant and additive, ionic liquid

was investigated. Since then, researchers from relevant fields all over the world have carried out a lot of research work, which has made remarkable achievements in the research of ionic liquid lubricant both in academic field and in practical application. Although ionic liquids have high antifriction and antiwear properties when used as lubricants, it can be recognized that ionic liquids still have a large number of inevitable disadvantages when used as lubricants and corrosion inhibitors. First, the high preparation cost limits their wide production and application. Second, they cannot be effectively dissolved in common nonpolar oils, Therefore they cannot be used as high-efficiency additives. Moreover, ordinary ionic liquids produce corrosive acidic substances due to hydrolysis, which seriously corrodes metal materials, and indirectly limits its application. Finally, ionic liquids have serious consequences such as friction failure due to leakage and creep. In order to overcome the problems of corrosion, solubility, and cost of ionic liquids, researchers have effectively designed some oil-soluble and noncorrosive functional ionic liquids through reasonable molecular design, and greatly reduced the production cost. However, there is still the problem of overcoming the friction failure caused by the leakage and creep of ionic liquids. As a strategy towards avoid this failure, a functional ionic liquid gel factor based on oxidation and corrosion resistance has been designed, which can form an effective gel network in ordinary ionic liquids, and confining ionic liquids to the three-dimensional space network of ionic liquid gel factor. It prevents its creeping and effectively reduces the lubrication failure caused by the leakage and volatilization loss of ionic liquid. It is important that this type of lubricating and anticorrosion material has good thermal reversible and thixotropic properties. It can rapidly change from a gelatin state to a liquid at a certain temperature or shear effect. When the external force is disappearing or the temperature decreases, it will quickly become condensed. In this way, the defects such as creeping or leakage of anticorrosion and lubricating ionic liquid can be effectively solved. At the same time, it can also be used as a substitute for lubricating grease under some specific conditions. Urea-based ionic liquids containing functional groups which are easy to form supramolecular hydrogen bonds onto imidazole rings, were prepared as a new gel lubricant in the common ionic liquid by self-assembly. These ionic gel lubricants exhibit very good tribological properties. Corrosion tests also show that these ionic liquid gel lubricants can effectively reduce the corrosion of metal substrates. It is expected to be widely used as a new lubricating material.

Kazutoshi Takahashi et al. developed a kind of base oil gel lubricant, prepared by self-assembling of two amine derivatives in polyalphaolefin (PAO) which exhibited better tribological properties than ordinary lubricating grease and lubricating oil. This gel lubricant material can convert between gel state and liquid in addition or cooling [53–55].

Cai et al. designed and prepared a new ionic liquid type small molecule gel factor. It has been found that it can form stable gel through self-assembly of supramolecular in common ionic liquids. The ionic liquid supramolecular gel as lubricant has excellent corrosion resistance and good conductivity. The ionic gels obtained in high vacuum and high temperature environment show excellent lubricating properties (Fig. 17.1) [29,49,50,56–60].

The gelation behavior of M-4, M-8, M-12, and M-16 in several imidazole ionic liquids were evaluated. Except M-4a and M-4b, other gel factors can coagulate ionic liquids at gel concentration of 3–5 wt.%. The initial gel forming process of M-8 took about 15 days, and the ionic liquid formed was still partially transparent until a final complete opaque gel was formed for about 17 days. When the carbons atoms of the alkyl chain increases to 16, a complete opaque gel can be completely formed within 1 min. The gel was caused by supramolecular interaction between the gel factors. The gel factor first gathered in a small amount to form needle-like structure, and then further branched to form a three-dimensional network structure.

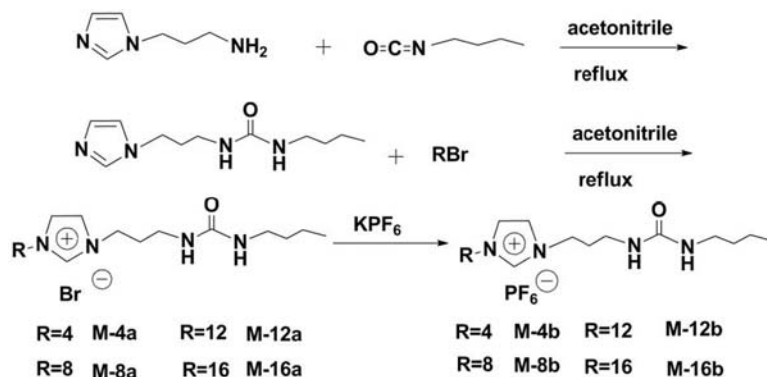


FIGURE 17.1

Chemical structure of imidazole ionic liquids.

Frequency scanning tests of ionic gels with different contents of M-12a and M-12b were carried out in order to analyze the rheological properties of the corresponding gels. It indicated that the storage modulus (G') and loss modulus (G'') do not vary with the shear frequency. It implies that the gel has strong resistance to external stimuli. The results of frequency scanning also showed that these ionic gels showed similar rheological properties, and storage modulus (G') increased with increasing alkyl chain length and concentration of gel factor.

The corrosion study showed that the surface of the iron sheet has undergone destructive corrosion and there is an obvious damage. However, the surface corrosion of iron after immersion in ionic liquid gel is relatively mild. These indicate that the gel can effectively inhibit the corrosion of metals. The excellent corrosion resistance of ionic liquid gel is largely attributed to the adsorption film formed by the coordinative interaction between the gel factor and metal, which effectively blocks the corrosion of metal.

These ionic liquid gel lubricants showed a lower friction coefficient than the blank ionic liquid, and the friction coefficient of the corresponding ionic liquid gel decreased gradually with the increase of the alkyl chain length from 8 to 16. So, the ionic liquid gel prepared by the ionic liquid gel factor has low corrosion resistance to copper and iron. The ionic liquid exhibits excellent mechanical stability, thixotropic and tribological properties than ordinary ionic liquids. The ionic liquid gel has also excellent electrical conductivity. It is expected to play a potential application in electrical contact lubrication and low-temperature conductive lubrication.

17.4 Ionic liquids anticorrosion composite coating

Metal corrosion is a common phenomenon, which may have a significant impact on the development of global economy and environment. Therefore the development of new anticorrosion strategies and the establishment of corrosion control system have become one of the most popular and important issues for many industrial applications to metal materials in recent years.

With the development of aerospace, biomedicine, and emerging electronic industries, the demand for the functionalization of light metal materials represented by aluminum, magnesium, titanium, and their alloys is particularly prominent. In addition to meeting the basic mechanical properties, they also need to have certain anticorrosion, antifriction, and antiwear properties in extremely harsh environments. However, the application of light metal materials is limited to a great extent because of their soft nature, easy wear, high chemical activity, and easy corrosion. Therefore it is particularly important to improve the antifriction, antiwear, and anticorrosion properties of light-metal materials.

In marine environment, their anticorrosion performance is also very important under the condition of meeting certain antiwear performance. The addition of corrosion inhibitor can realize the corrosion protection of metal substrate to a certain extent; it cannot meet the needs of use in some specific environments. At the same time, surface treatment technology is also an effective strategy to improve the corrosion resistance of metals. Among them, micro-arc oxidation (MAO) technology, as the most commonly used means, has been recognized and applied in various fields. Light metals and their alloy materials will produce a certain porous structure through the MAO process. If the porous structure is used as a micro/nano container for the storage of corrosion inhibitor, it will delay the release of corrosion inhibitor to a certain extent and avoid the direct contact between corrosion inhibitor and base material. In addition, coating protection is also a popular anticorrosion method, mainly including epoxy anticorrosion coating and some functional coatings, such as superhydrophobic or hydrophobic coating. If the porous structure of MAO is organically combined with corrosion inhibitor and functional coating, and the synergistic structure–activity relationship of the above three components is fully utilized, it is expected to achieve an effective anticorrosion effect on light-metal materials. Therefore the coordination of structures and methods will improve the overall performance of materials.

17.4.1 Preparation scheme of composite anticorrosion coatings

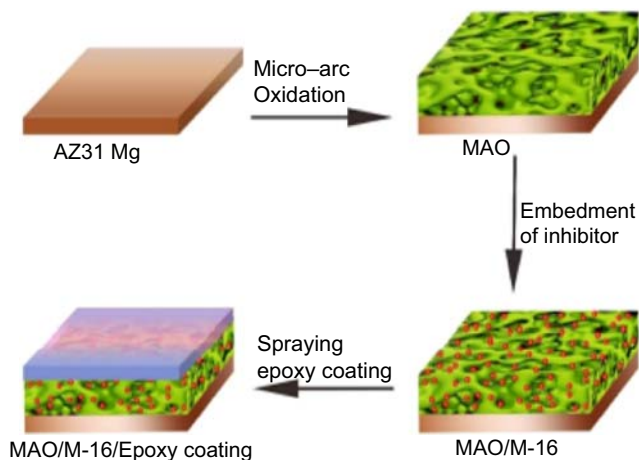
As a typical light metal structural engineering material, magnesium and its alloys have great potential applications in aerospace, biomedical engineering, and automotive industries because of their excellent specific strength, low density, and good castability. However, the chemical properties of magnesium and its alloys are active, and they are easy to be corroded when exposed to humid environment or chlorine-containing medium. Therefore it is very necessary to inhibit the occurrence of the above corrosion processes. At present, many surface treatment technologies have been proposed, mainly based on the surface passivation and isolation effect to improve the corrosion resistance of AZ31 magnesium alloy, such as MAO, corrosion inhibition, chemical conversion coating, and surface modification. For the protected metal, the important way to inhibit corrosion is to isolate the contact between it and the outside air, mainly by forming a passivation layer on the surface of the protected metal, such as the formation of inorganic layer. In recent years, many researchers have turned their attention to the MAO technology, forming a layer of oxide film with high hardness, good wear resistance, and corrosion resistance on the metal surface by using high pressure. The performance of the MAO coating mainly depends on their microstructure and phase composition, and can be regulated by adjusting the MAO parameters and composition. Although in the process of MAO, it is easy to form some micropores and microcracks on the MAO film, which become the transmission channel of corrosive medium or increase the opportunity of corrosive

medium penetration, resulting in serious corrosion of magnesium alloy. On the other hand, some micropores and microcracks on the MAO film can also provide some mechanical bite sites to a certain extent, so as to improve the adhesion between the organic coating and the substrate. Therefore a good strategy is to weigh the advantages and disadvantages of porous structure in MAO membrane. Adding corrosion inhibitor is another way to improve the corrosion resistance of metal. It can form passivation or complex layer on the metal surface to protect it from corrosion. Generally, the inhibitor is directly added to the top organic protective coating, but the amount of inhibitor may affect the physical and chemical properties and anticorrosion performance of the organic coating. In recent years, many researchers have added some porous materials as containers for coating corrosion inhibitors to organic coatings to improve their corrosion resistance, such as mesoporous silica, halloysite, and capsule. At the same time, this method also has some disadvantages, such as high cost, short service life, easy peeling of coating, and so on. Therefore it is very important to design a new container coated with corrosion inhibitor, so as to improve the coating amount of corrosion inhibitor and reduce its impact on the physical and chemical properties, mechanical properties, and anticorrosion properties of organic coatings. A new anticorrosion strategy was reported, in which micropores and nanopores in MAO film were used as containers of corrosion inhibitors to prolong the corrosion resistance of AZ31 magnesium alloy substrate and enhance the interfacial adhesion between metal substrate and top paint [8,59–61]. A corrosion inhibitor with long alkyl chain containing urea group and imidazole heterocyclic structure was filled in the porous MAO film to form a protective film on the metal surface, so as to prevent corrosive substances and water molecules from contacting the substrate. In addition, in order to prevent the corrosion inhibitor from leaking out of the porous structure, a thin wax or epoxy anticorrosion coating is sprayed on its top surface to form the final organic/inorganic composite anticorrosion coating. The micro-nanoporous structure obtained by MAO surface treatment is used as the storage container of quaternary ammonium salt inhibitor, and the composite anticorrosion coating is obtained by coating with epoxy resin top coat. Compared with bare AZ31 magnesium alloy, the composite coating immersed in 3.5 wt.% NaCl solution has excellent corrosion resistance, which is mainly reflected in its low corrosion current density and high protection efficiency, and has strong salt spray resistance within 30 days. Based on the synergistic effect of porous micro arc oxide layer structure, corrosion inhibitor, and top organic coating, the composite coating shows excellent corrosion resistance.

Fig. 17.2 shows the preparation process of composite protective coating, which mainly comprises three steps, including preparing inorganic film with micropores and nanopores by MAO process, embedding anticorrosion inhibitor into the pores of MAO film, and encapsulating the surface of MAO film with embedded inhibitor by epoxy anticorrosion coating.

17.4.2 Property of the composite anticorrosion coating

MAO coating contains many irregular micro and nanopores, which are not connected with each other. The corrosion inhibitor particles are deeply embedded into the MAO porous structure. After the corrosion inhibitor is embedded, the surface of the sample with MAO film becomes more compact and uniform. The anticorrosion composite coating is composed of MAO layer filled with corrosion inhibitor and epoxy anticorrosion layer. The compact epoxy resin coating as the sealing layer of corrosion inhibitor will help to further protect the base material (Fig. 17.3).

**FIGURE 17.2**

Preparation scheme of the MAO/M-16/epoxy composite anticorrosion coating.

From Z. Li, W. Yang, Q. Yu, Y. Wu, D. Wang, J. Liang, F. Zhou, New method for the corrosion resistance of AZ31 Mg alloy with a porous micro-arc oxidation membrane as an ionic corrosion inhibitor container, *Langmuir* 35 (5) (2019) 1134–1145. <https://doi.org/10.1021/acs.langmuir.8b01637>.

Compared with the bare AZ31 Mg alloy, the samples with MAO coating showed a corrosion potential of -1.479 V, while the samples with composite coating showed a corrosion potential of -1.548 V, indicating that the corrosion potential of the prepared samples shifted positively. However, there are many factors affecting the anticorrosion performance of MAO, such as pore size, porosity, and the number of isolated pores. Compared with other coatings, MAO/M-16/epoxy coating shows a more negative potential. This is mainly due to many factors affecting the corrosion potential, such as coating crosslink, polarization, negative ion accumulation, and hydrogen and oxygen production reaction. In conclusion, the composite coating composed of MAO film, corrosion inhibitor, and epoxy topcoat improves the protection of AZ31 magnesium alloy substrate to a certain extent,

The salt spray test also showed that compared with the AZ31 Mg/M-16/epoxy coating, the MAO/M-16/epoxy coating had lower corrosivity, while the boundary corrosion occurred on the latter sample. Therefore the formation of composite anticorrosion coating significantly improves the salt spray resistance of the substrate to a certain extent (Fig. 17.4).

In order to explain the corrosion resistance process of the composite coating, the mechanism is proposed. Compared with bare AZ31 Mg, MAO/M-16/epoxy composite coating is composed of inorganic ceramic MAO film, organic corrosion inhibitor, and epoxy top coating. The reason why the composite coating has good corrosion resistance can be attributed to the following aspects: (1) the corrosion resistance of inorganic ceramic membrane can block the penetration of chloride ions and make the corrosion potential move forward. (2) The inhibition effect of corrosion inhibitor is that it can form an adsorption film on the protected metal surface, which can prevent the invasion of corrosive ions such as Cl^- to some extent, so as to protect the material from erosion. (3) The anti-corrosion top coating with high binding energy with the substrate can prolong the transmission path

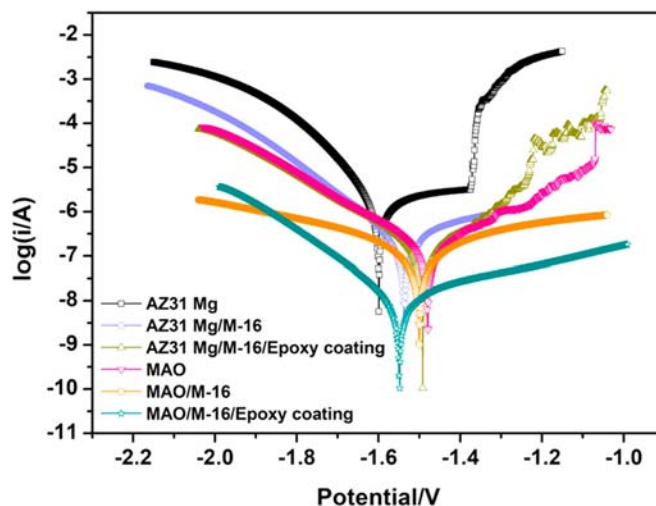


FIGURE 17.3

Polarization curves of AZ31 Mg, AZ31 Mg/M-16, AZ31/M-16/epoxy coating, MAO, MAO/M-16, and MAO/M-16/epoxy coatings immersed in 3.5 wt.% NaCl solution for 24 h.

From Z. Li, W. Yang, Q. Yu, Y. Wu, D. Wang, J. Liang, F. Zhou, New method for the corrosion resistance of AZ31 Mg alloy with a porous micro-arc oxidation membrane as an ionic corrosion inhibitor container, *Langmuir* 35 (5) (2019) 1134–1145. <https://doi.org/10.1021/acs.langmuir.8b01637>.

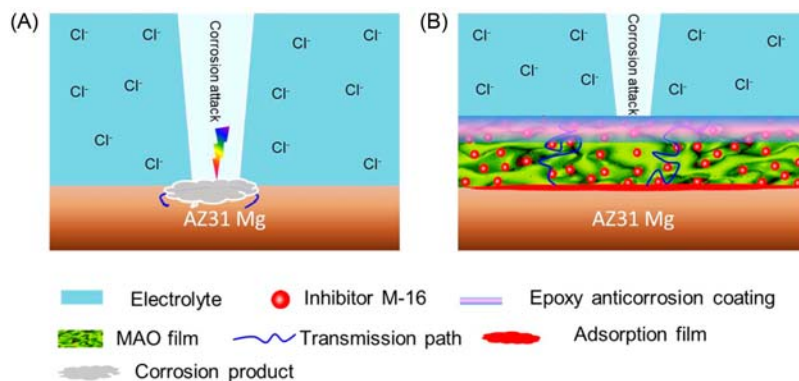


FIGURE 17.4

Schematic illustration of corrosion process of bare (A) AZ31 Mg and (B) composite coating in 3.5 wt.% NaCl electrolyte solution.

From Z. Li, W. Yang, Q. Yu, Y. Wu, D. Wang, J. Liang, F. Zhou, New method for the corrosion resistance of AZ31 Mg alloy with a porous micro-arc oxidation membrane as an ionic corrosion inhibitor container, *Langmuir* 35 (5) (2019) 1134–1145. <https://doi.org/10.1021/acs.langmuir.8b01637>.

of corrosive substances in contact with the substrate material, so as to play a long-term protective role. Therefore the above composite coating with synergistic effect is helpful to realize long-term protection of AZ31 Mg. In addition, the whole coating preparation process is simple and can realize mass production. Therefore the composite way can be used in corrosion protection of light alloy materials.

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