*Int. J. Electrochem. Sci.*, 15 **(2020)** 3040 – 3053, doi: 10.20964/2020.04.36

International Journal of
ELECTROCHEMICAL
SCIENCE
www.electrochemsci.org

*Mini Review*

# A Review on Self-Healing Coatings Applied to Mg Alloys and Their Electrochemical Evaluation Techniques

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*Received:* 10 September 2019 / *Accepted:* 5 February 2020 / *Published:* 10 March 2020

Magnesium (Mg) and its alloys are being used as substitutes for conventional structural materials due to their helpful characteristics, such as low density and exceptional mechanical properties. However, the electrochemical stability of Mg and its alloys inhibits their utilization in various applications. Therefore, the development of active self-healing coatings that can not only protect Mg alloys at the experimental scale but also be utilized at the commercial scale is imperative. The study of self-healing coatings for Mg alloys is increasing at an unexpected rate. However, the mechanisms of self-healing and their electrochemical evaluations for inorganic coatings are scarcely summarized for Mg alloys. In the present appraisal, a comprehensive overview is provided for both self-healing mechanisms and evaluation techniques that have been utilized for Mg alloys. Finally, a future perspective of self-healing coatings and evaluation techniques is provided that illuminates the lack of information that is available and confirms that a substantial amount of work is needed to fill those research area gaps for Mg alloys.

**Keywords:** Magnesium alloys, self-healing, evaluation techniques, coatings, electrochemistry

## 1. INTRODUCTION

Corrosion is an inevitable issue for industries all over the world, and it causes safety and environmental risks[1]. It also poses a significant burden on the gross domestic product (GDP) of any country. It has recently been reported that corrosion alone costs 3.34% of China's GDP, which amounts to over 310 billion US dollars. If a similar trend is assumed for the global economy, the total cost reaches ~2.5 trillion US dollars annually [2]. Several reasons are responsible for this loss, such as occasional maintenance of working equipment or components because of corrosion. Mg alloys also suffer due to poor corrosion resistance in corrosive environments, and that makes them vulnerable in most applications [3, 4]. However, Mg and its alloys are emerging as light and strong structural materials that are being used to replace conventional materials [5-7] in many applications, such as automobile, aerospace and biomedical products [8]. Therefore, researchers are consistently working on developing techniques that can enhance the corrosion resistance of Mg alloys. There are many treatments available for the protection of Mg alloys i.e., conversion coatings [9, 10], organic coatings [11], and electroless plating [12]. Although these coatings provide better corrosion protection, it is not convenient to repair or replace components such as aerospace products and medical implants [13]. Therefore, a system of active coatings is imperative to elongate the service life.

Active coatings, also called self-healing coatings, have an ability to fill defects generated in the coatings without external assistance [13]. Coatings with built-in self-healing functionality can be fabricated either by incorporating healing agents into the coating or changing the coating composition to include elements that can produce healing compounds as they interact with aggressive electrolyte. There are several reviews available discussing the self-healing behavior of polymer or organic coatings. Therefore, organic coatings are not conferred in this review [14, 15].

Self-healing involves both electrochemical and chemical processes. Consequently, electrochemical and nonelectrochemical evaluation techniques are useful for describing the self-healing behaviors of coatings. Thus, electrochemical and nonelectrochemical techniques that have been used for self-healing coatings on Mg alloys are described in this review. This review also identifies the plausible scarcity in the usage of several evaluation techniques while attempting to endorse the usage of techniques that are not being considered for self-healing coatings on Mg alloys.

## 2. SELF-HEALING MECHANISM OF COATINGS

Metals are always trying to revert to their native state, and this process is named corrosion [16]. It mostly occurs when the metals are in contact with aggressive media such as seawater or acid [16]. Therefore, active protective coatings, also termed smart coatings, are developed on the surface of metals to form barriers between corrosive electrolytes and metal substrates and provide healing effects to the defects produced due to corrosive electrolyte action.

To achieve active protection, compounds or particles are incorporated into the coatings that rush towards the defective sites and heal them. Therefore, the cracks or defects will not be able to propagate further. However, there must be a stimulus available to trigger the release of healing agents to begin the self-healing process. The stimulus could be a variety of things, such as changes in pH, temperature, redox activity, electric field, and mechanical and chemical stimuli[13]. Figure 1 shows the general mechanism of the self-healing process in the presence of a stimulus.

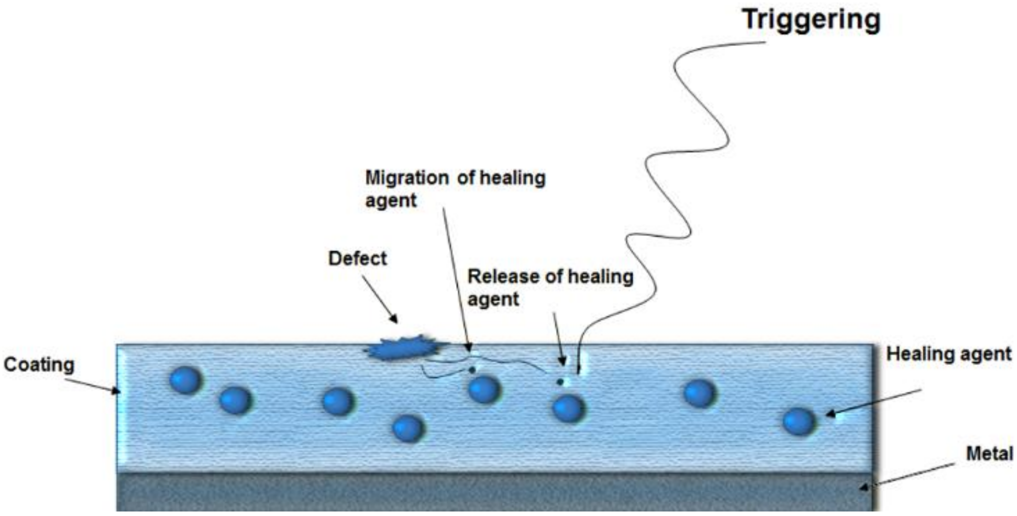


**Figure 1.** Schematic of the self-healing coating mechanism on metallic substrates.

## 3. SELF-HEALING SYSTEMS FOR Mg ALLOYS

There are several active systems available for Mg alloys that provide self-repair. The healing agents could be organic or inorganic in nature. However, the basic principle is to heal the defect, stopping it from further propagation and stabilizing the coating performance against corrosion. Many coating systems offer self-healing, such as conversion coatings, silane coatings and organic coatings. However, the organic coating is not a part of this review; therefore, the self-healing mechanism of coatings other than organic coatings is summarized in the following sections.

In general, there are three types of self-healing mechanisms available for Mg alloys. First, the healing agent can be incorporated into the coating formed layer (mostly oxide) by some chemical reaction. Second, the healing agents may form complexes or a chelate with produced metal ions because of corrosive action and then deposit on the defective area. Third, the coating itself has the capability to heal by either forming an oxide layer (in the case of conversion coatings) or healing bonds (in the case of silane coatings).

### *3.1 Healing by forming a passive layer*

Various coating systems provide protection to Mg alloys by forming protective films on defects, especially conversion coatings comprising of metal ions such as Ce [17], V [18], Sn [19] or Cr [20]. They may also contain some nanoparticles that are already an oxide or inhibitors that can form a protective layer after some reactions due to the interactions between the electrolyte and substrate [21].

The self-healing mechanism of this coating may be explained with the help of some examples, such as chromium-based conversion coatings. These coatings work well inhibiting corrosion, and the healing properties of chromate coatings are also good. For instance, when a scratch is produced on the coating, a passive film of $Cr_2O_3$ is formed as the coating comes in contact with the electrolyte, subsequently healing the scratch [20, 22]. However, hexavalent chromate ions are toxic and not environmentally friendly. Therefore, studies are focused on finding active systems that can economically replace chromate-based coatings [23]. Vanadia-based coatings may have the capability to replace chromate coatings [18]. Self-healing is frequently observed in vanadia conversion coatings. The optimum amount of vanadia present in the coating can form a protective layer on Mg alloys, which heals the defect and stops further degradation of the substrate. However, the self-healing ability of vanadia-based coatings disappear as the pH of the electrolyte increased. No healing effects are observed in an alkaline pH range [18].

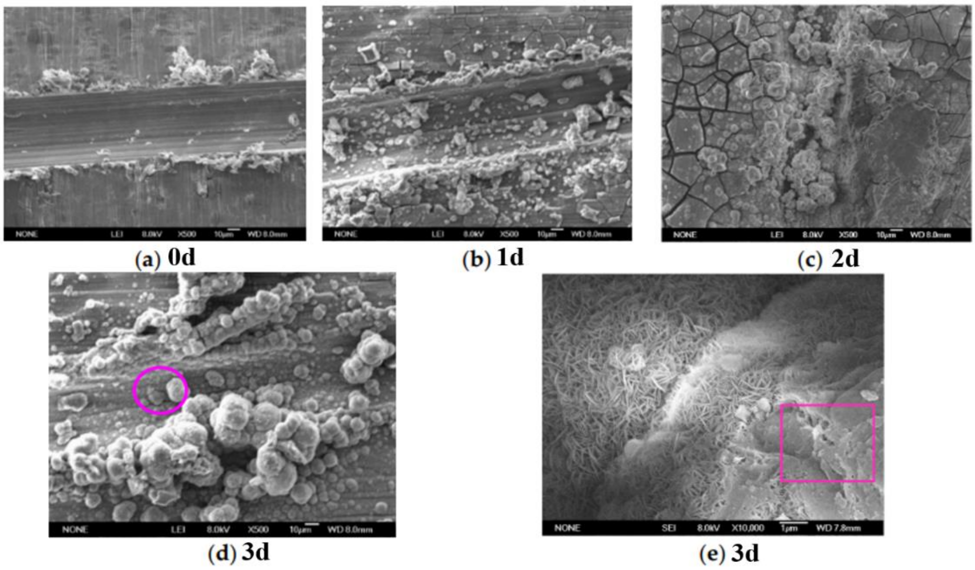


**Figure 2.** Self-healing of vanadia-containing coatings after different immersion times [24] (Creative Commons Attribution License).

It is also a common practice to add nanoparticles to coatings as inhibitors. The most commonly used inhibitor that provides a barrier against corrosive ions and has self-healing capacity is $CeO_2$ nanoparticles. The self-healing ability of $CeO_2$ is described with a layer-by-layer coating system. As the coating is destroyed by the corrosive media, $Mg(OH)_2$ is produced. However, $CeO_2$ is readily changed to $Ce_2O_3$, which dissolves in corrosive medium and produces $Ce^{3+}$. The $Ce^{3+}$ migrates to the substrate surface and is converted to $Ce^{4+}$, consequently forming a Ce-rich passive coating on the surface of the substrate [17].

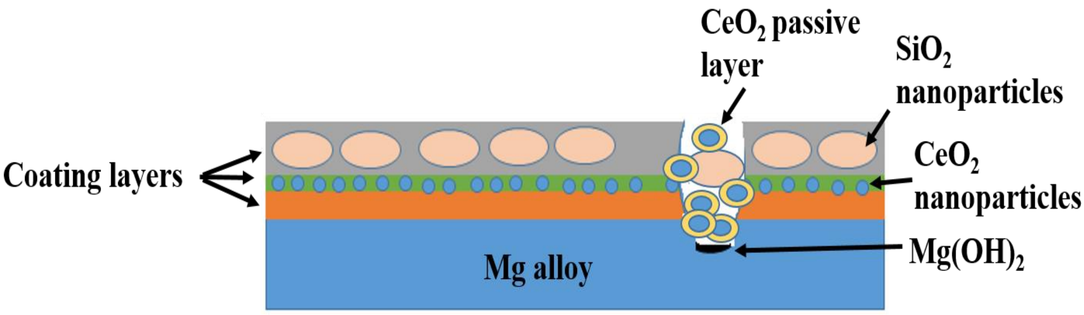


**Figure 3.** Self-healing offered by $CeO_2$ nanoparticles.

A self-healing capability is reported for Sn compounds, in particular, stannate-based coatings when a potassium stannate bath is used. The self-healing offered by Sn is due to the formation of a $Mg(OH)_2$-rich layer in Sn oxide that provides a barrier against aggressive ions attempting to reach the substrate. This barrier shifts the pitting potential to more-noble values [19]. Yang et al. [25] also reported a superhydrophobic and self-healing stannate coating and explained it with a “solving-reprecipitation theory”. They simulated an acid rain environment to investigate the performance of the coating, and the stannate coating showed an appropriate corrosion resistance. Although the layer formed due to stannate is not thick, it has a noteworthy positive influence on augmenting the self-healing capability and enhancing the corrosion resistance of stannate coating [19].

### *3.2 Healing by curing hydrolysis*

A coating that heals bonds is frequently observed in organic or organo-silane coatings. However, organic coatings are not part of this review. Therefore, only one example of silane coating is included to give an idea about the mechanism. The healing agents are loaded inside the microcapsules or porous nanoparticles. Huang et al. implanted poly(urea-formaldehyde) microcapsules filled with 1H,1H,2H,2H-perfluorooctyl triethoxysilane (POTS) in a silane coating. The corrosion-resistant behavior of the prepared POTS-based coating can be explained as follows. As the coating is scratched, the implanted microcapsules burst open, and the POTS liquid is released. Upon the interaction of POTS with water in the electrolyte or moisture in air, POTS starts to hydrolyze and polycondensation occurs, yielding a silane-based solid that is introduced in the engraved areas[26].

### *3.4 Healing with chelates or precipitates*

Healing agents could also be loaded in nanocontainers such as those made of layered double hydroxide (LDH) or embedded into coatings, which release them as an electrolyte interacts with the nanocontainers or coatings. LDH has an ion exchange capability that allows the intercalation of inhibitor anions between its interlayer galleries. For instance, 8-hydroxyquinoline (8HQ) [27] has the capability to form chelates with $Mg^{2+}$ ions. Therefore, 8HQ molecules are utilized in an LDH coating as anions that can be exchanged with $Cl^-$ ions that are present in the electrolyte, subsequently releasing $HQ^-$ ions. When the $HQ^-$ ions are released, they can make chelates with $Mg^{2+}$ ions that are responsible for healing defects. However, 8HQ is not water-soluble; first, it must be converted to $HQ^-$ ions with the help of NaOH [28]. A similar trend can be observed with sodium benzoate. However, sodium benzoate has not yet been studied for Mg alloys [29]. Similarly, a molybdate-intercalated LDH coating also provides good corrosion protection along with a self-healing ability [30].

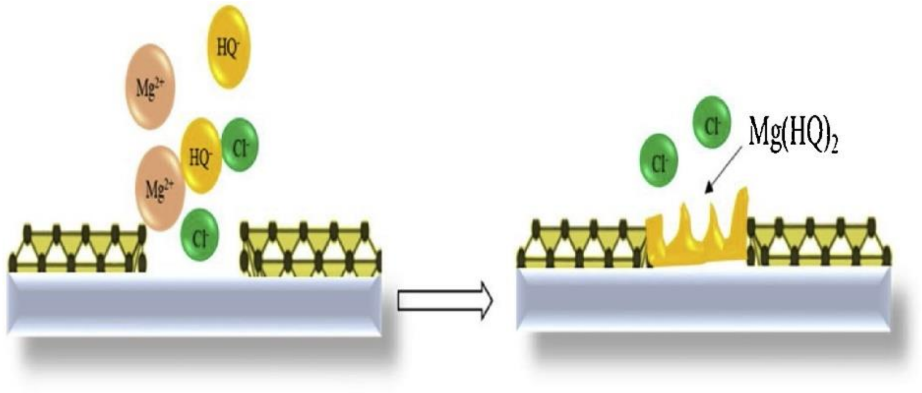


**Figure 4.** Self-healing mechanism offered by 8HQ [28] (Reproduced with permission from Elsevier).

Phosphate ($K_3PO_4$) [31], molybdate [30], tetraphenylporphyrin [32] and many other chemicals could be used as healing agents for Mg alloys and provide active protection for a long duration. These compounds could be used in different systems, such as silane coatings [33], L-b-L coatings [17], organic coatings [34], chemical conversion coatings, such as a layered double hydroxide coating, or vanadia coatings [18, 28]. The mechanisms involved for most of the healing agents are the same. They react with Mg ions produced by the attack of aggressive media. Then, they make complexes or compounds that are then redeposited on the defective sites, thus, healing them and stopping further corrosion.

## 4. EVALUATION METHODS OF THE SELF-HEALING CAPABILITY OF COATINGS

It is a rudimentary procedure to introduce an artificial defect and evaluate the self-healing capability of coatings. The standard practice is to scratch the coated sample and immerse it in the electrolyte. The immersion time may vary depending upon the chemistry and the healing agent utilized [24, 35, 36]. After immersion, the engraved portion of the coated sample may be studied with the help of nonelectrochemical and electrochemical techniques. Nonelectrochemical techniques include optical microscopy (OM) [37], scanning electron microscopy (SEM), energy dispersive spectroscopy (EDS), X-ray diffraction (XRD) and Fourier transform infrared spectroscopy (FTIR) [30]. Whereas electrochemical techniques are electrochemical impedance spectroscopy (EIS) [38], more-sensitive microelectrochemical techniques can also be utilized, such as a scanning vibrating electrode technique (SVET) [39], scanning electrochemical microscopy (SECM) [40, 41], localized electrochemical impedance spectroscopy (LEIS) [42], scanning Kelvin probe (SKP) methods and a scanning ion-selective electrode technique (SIET) [42]. However, EIS, SEM, EDS and SVET techniques are frequently employed compared to other techniques to evaluate the self-healing mechanism of a prepared coating on Mg alloys.

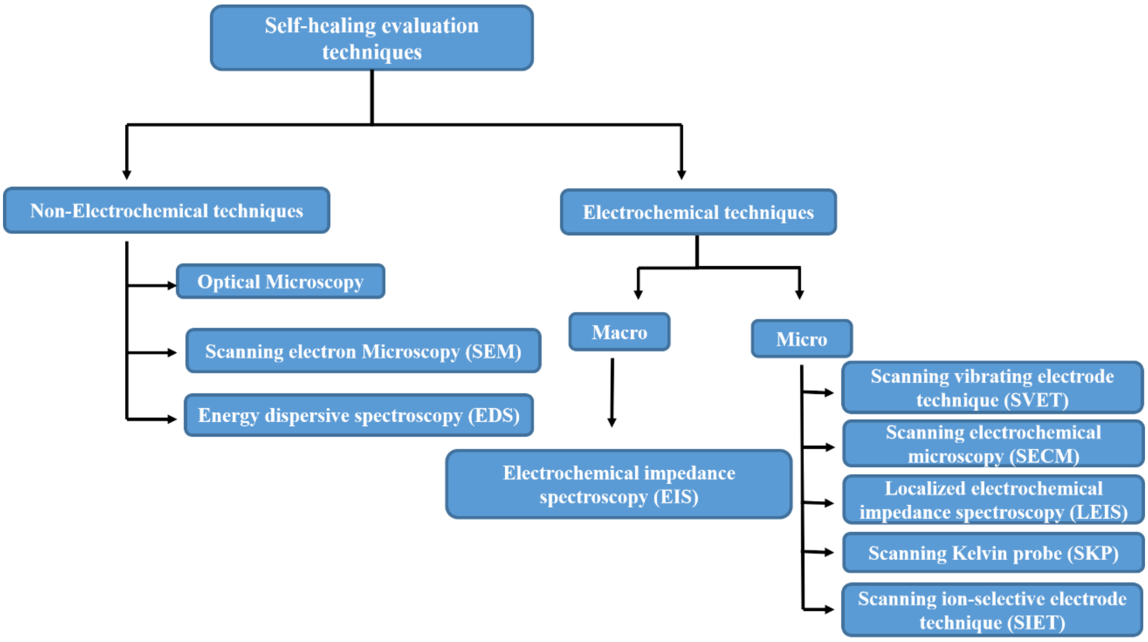


**Figure 5.** Self-healing evaluation techniques used for Mg alloy coatings.

### *4.1 Nonelectrochemical techniques*

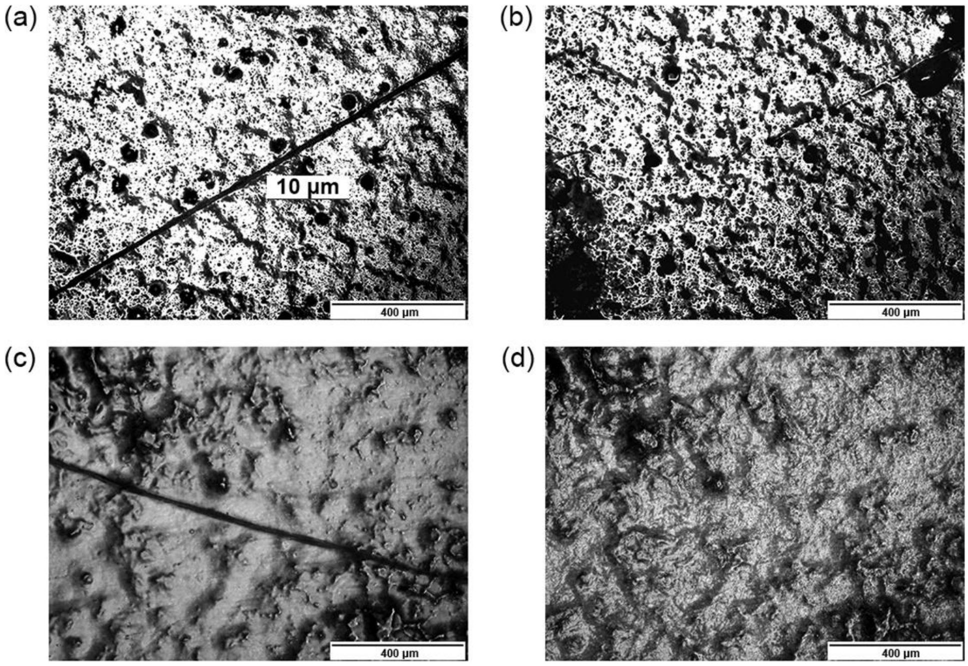
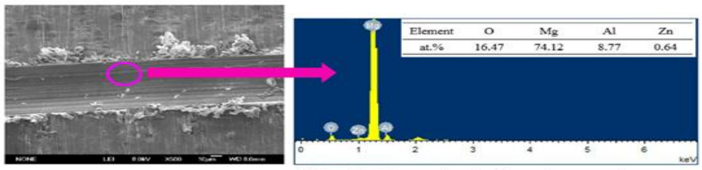


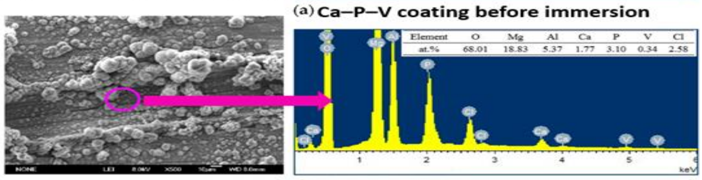
**Figure 6.** Self-healing offered by ceria in a layer-by-layer coating [43] (Reproduced with permission from American Chemical Society).

OM is used to investigate self-healing coatings on Mg alloys by few researchers [18, 37]. A vanadia self-healing coating was investigated with OM, and an untreated Mg alloy showed pitting after immersion in a 3.5% NaCl solution. The addition and gradual increase in vanadia concentration successfully healed the pits produced in the untreated Mg alloys, and a vanadia-rich thick film was formed on the surface [37]. The self-healing ability of the layer-by-layer coating containing graphene and ceria was also investigated by OM with different immersion times. Clear evidence of the scratch healing was observed. OM provides distinct evidence of healing products formed on the substrate [43]. However, this technique provides information only after the formation of precipitates or oxide layers. Moreover, the detection of healing products is possible only when they have grown to a specific thickness.

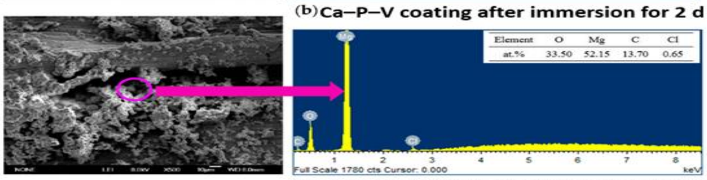
An in-depth understanding or further investigation of the healing process can be carried out with the help of more sensitive techniques, especially SEM and EDS [21, 24, 42, 44, 45], depending upon the focus points of the study. The scratch in the coating can be observed with SEM after different immersion times and can detect the early stages of self-healing. The products formed due to a self-healing process can be validated further with an elemental composition obtained from EDS. Therefore, these techniques can provide evidence about the self-healing process. However, they do not provide any information about prehealing of the coating. Moreover, a specimen utilized for these experiments cannot be used for any additional experiment due to the application of a conductive layer to obtain the SEM images [24].



(a) Ca–P–V coating before immersion



(b) Ca–P–V coating after immersion for 2 d



(c) uncoated AZ91D after immersion for 2 d

**Figure 7.** Scratch test examined with SEM and EDS [24] (Creative Commons Attribution License).

XRD and FTIR can provide information about self-healing either by displaying shifts in peak positions or by changing peak intensities. Zeng et al. investigated the self-healing of molybdate-intercalated LDH coatings on Mg alloys. A shift in the (003) plane from the XRD patterns of samples with different immersion times verified the formation of self-healing products. In addition, the characteristic band of molybdate anions was also weakened, which was in agreement with the XRD results [30].

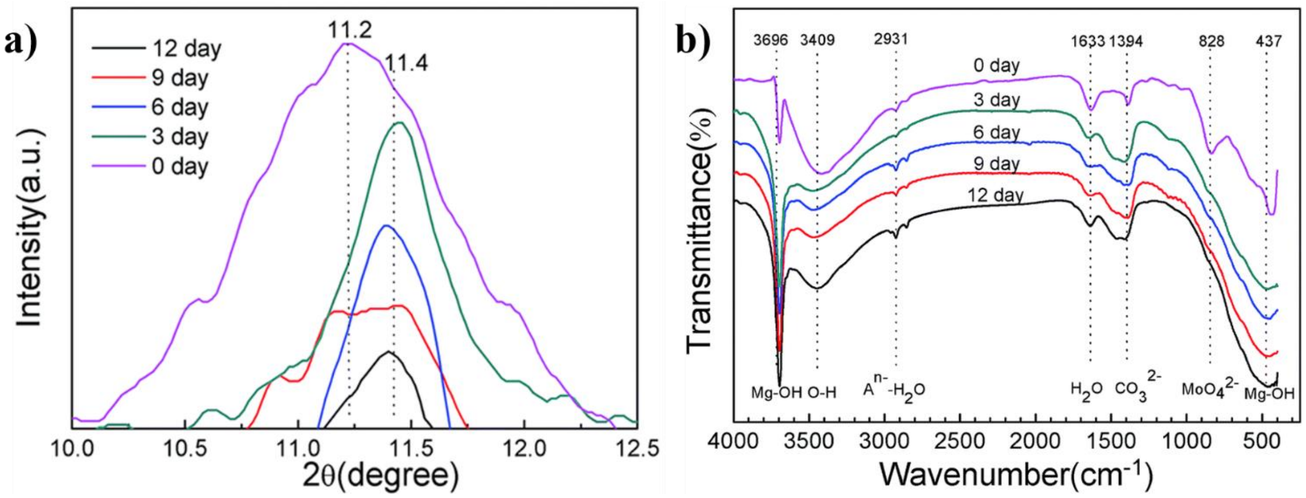


**Figure 8.** The shifting in XRD peaks (a) and band weakening in FTIR (b) of a molybdate-intercalated LDH [30] (Reproduced with permission from Royal Society of Chemistry).

### *4.2 Electrochemical techniques*

EIS along with a potentiodynamic polarization test (PPT) can be utilized to study the surface activity and self-healing performance of coatings. Additionally, the results can be compared with those from the SEM and EDS studies to verify the suggested mechanism of self-healing. Gnedenkov et al. [46] utilized the EIS test after PPT to study the self-healing mechanism of 8HQ in plasma electrolytic oxidation coatings. The modulus of impedance (|Z|) value after the PPT was decreased but still showed better corrosion resistance compared to that of a coating without 8HQ. Sun et al. [47] also employed an EIS test to investigate the self-healing mechanism of a benzotriazole inhibitor in a PEO coating. Similarly, PPT was also used to investigate the self-healing of a molybdate-intercalated LDH coating, where distinct steps appeared in an anodic curve of PPT that is characteristic for the self-healing of an LDH coating [30]. However, PPT is a destructive test that makes the sample unusable for further investigation and choosing the correct equivalent circuit (EC) to model the EIS results are the main drawbacks. If an unsuitable EC or some EC parameters are chosen incorrectly, the resultant coating resistance value will be erroneous. Furthermore, as the healing behavior of a coating changes, the model may need to be changed to interpret the new coating arrangements.

EIS and PPT provide helpful information to understand the self-healing mechanism of a coating. However, local information near a defect provides more understanding of the self-healing mechanism of a particular coating. Therefore, microelectrochemical techniques are utilized to obtain a deep understanding of the mechanisms involved in self-healing. SECM can also be used to describe the self-healing capability of coatings applied on Mg alloys. Primarily, it is an electrochemical imaging technique employed to study charge transfer near a metal exterior. SECM can also be used to understand the kinetics of reactions for a small area of the coating, which helps to recognize the probable mechanism of electrochemical progression [48]. Jamali et al. [41] studied the self-healing mechanism of a praseodymium conversion coating on an AZNd Mg alloy with this technique. The principle for the detection of self-healing was based on $H_2$ evolution such that the treated areas had less current and less $H_2$ evolution after being immersed for a few hours. The reduced current and $H_2$ evolution was attributed to the formation of praseodymium oxides and hydroxide due to changes in the pH of nearby untreated areas.

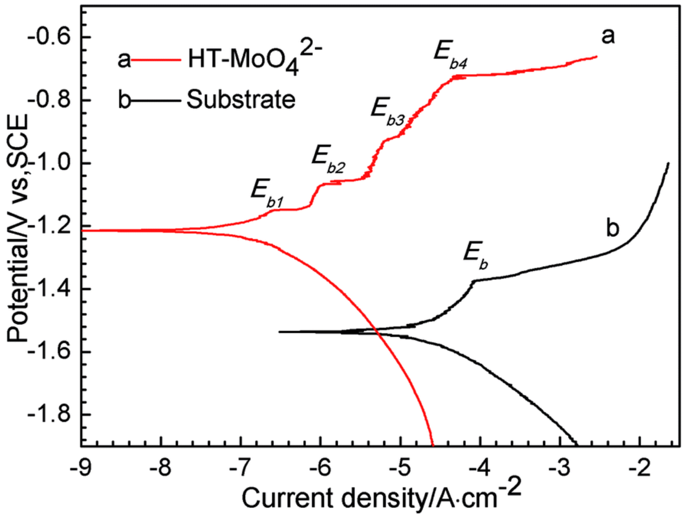


**Figure 9.** Self-healing of a molybdate-intercalated LDH coating investigated with PPT [30] (Reproduced with permission from Royal Society of Chemistry).

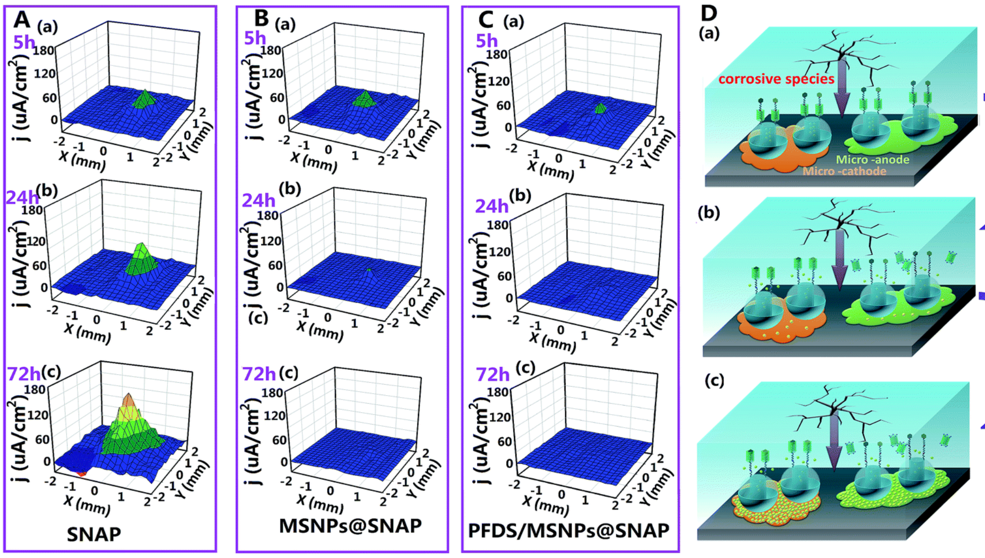


**Figure 10.** SVET studies to understand the healing mechanism of HMAP [39] (Reproduced with permission from Royal Society of Chemistry).

SVET is generally utilized for an insight evaluation of the self-healing mechanism of a coating. It provides evidence about the overall ionic fluxes caused by corrosion actions. It also allows studying anodic and cathodic zones formed around the defects in a coating [49, 50]. Some researchers have utilized SVET to analyze the self-healing mechanism of Mg alloys [39, 50, 51]. The healing mechanism of 2-hydroxy-4-methoxy-acetophenone (HMAP) inhibitor loaded on self-assembled nanophase particles (SNAP) and mechanized silica nanoparticles (MSNPs) was investigated with SVET. It is reported that current densities disappear as the immersion time is prolonged, representing the self-healing capability of HMAP on Mg alloys [39]. Although SVET is a powerful technique to investigate the local ionic flux, it does not provide any information about the local activity or the species responsible for generating the electric flux.

LEIS is a microelectrochemical technique used to study the localized behavior of coating defects. Calado et al. [42] verified the self-healing property of $CeO_2$ on Mg alloy. In the presence of defects, the coating would continually disintegrate due to a reaction with the corrosive electrolyte. However, LEIS studies showed that the presence of $CeO_2$ provided stable protection against aggressive ions even though the defect was present. The admittance curve showed less corrosion activity on the coating containing $CeO_2$. LEIS is proficient in studying local data about impedance changes in the vicinity of a defect site in a coating, but one restriction of this method is that the tip must be held at a fixed distance from the coating surface. Furthermore, an ordinary surface roughness generates issues with LEIS [52].

SIET is a very sensitive technique; it delivers significant data on confined pH gradients and the chemical nature of constituents taking part in a corrosion process [50]. The $CeO_2$-containing coating was also evaluated with the help of SIET, and a suppressed cathodic activity was observed after 7 h of immersion in an electrolyte. However, the cathodic activity was high at the early stages compared to after 7 h of immersion time, and the pH became stable over time, indicating the healing property of $CeO_2$ [42]. The main drawback of this technique is the use of a specific electrode to detect a specific ion, e.g., the use of Mg-selective microelectrodes to detect Mg ions.

SKP is a technique that investigates the healing capability of a coating on the principle of lateral change in a work function between the probe and the substrate. The work function is the energy needed to extract an electron from the surface of the substrate [44, 53]. It gives a two-dimensional map of potential distribution, and a decreased potential difference ($\Delta V$) suggests improved surface intactness. A self-healing evaluation with the use of SKP can provide increased understanding by considering an example of a slippery liquid-infused porous surface (SLIPS) utilized in plasma-electrolytic oxidation (PEO) and LDH systems. It was observed that the defect completely disappeared when scanned with SKP after 40 min of immersion in the electrolyte, confirming the healing effect of SLIPS [44]. In the beginning, the potential was more negative around the defect, and after the third scan, the potential difference was appreciably reduced, which indicates the defect was fully healed. However, the SKP technique cannot be used in full immersion; in such a case, it is likely to quantitatively measure the delamination rate of the coating at defects, and thus, the full immersion behavior can be simulated from the quantitative data.

## 5. FUTURE PERSPECTIVE

Chromate coatings can provide better corrosion protection and are economically feasible. However, environmental hazards arise from chromate coatings that make their use vulnerable to both marine and human societies. Therefore, chromate coatings have no future in industrial applications. Some coatings require pretreatments before coating a Mg-alloy surface because they do not provide good adhesion on their own and thus, undergo delamination when applied alone on Mg alloys. Therefore, the development of active systems, which not only heal the defect but also stabilize the coating in a wide range of pH environments, is needed. Research on the development of intelligent healing agents, which overcome these problems and provide cheap and long-term protection, is the focus of future research.

Vanadia conversion coatings, as well as vanadia pigments used in epoxy coatings, are emerging as a replacement for chromate coatings with a self-healing ability. In most cases, vanadia coatings provide protection with nearly the same results as chromate coatings with aluminum alloys [18, 54]. However, they is still being researched with a goal of developing a coating that is eco-friendly and can be used to replace chromate coatings [18, 37].

Self-healing evaluation techniques are useful for developing an understanding of self-healing mechanisms. However, several techniques are still not utilized to investigate the self-healing mechanism for coatings on Mg alloys. Nonelectrochemical techniques, such as confocal laser scanning microscopy (CLSM), X-ray photoelectron spectroscopy (XPS) and electron probe microanalysis (EPMA), are not employed to study self-healing mechanisms. Electrochemical techniques, including linear polarization resistance (LPR), electrochemical noise analysis (ENA), cyclic potentiodynamic polarization (CPDP), potentiostatic pulse testing (PPT) and hydrogen evolution reaction testing (HERT), could be used in future studies to investigate self-healing mechanisms of Mg-alloy coatings. Furthermore, many of these techniques are not used for other structural materials, i.e., steels and aluminum alloys.

## 6. CONCLUSIONS

Several active systems are available for the protection of Mg alloys. The common triggering mechanism of a healing agent is a redox activity change caused by the production of $Mg^{2+}$ ions. The produced $Mg^{2+}$ forms complexes with healing agents, which are not soluble in the electrolyte and hence deposit on the defective areas and heal them. There are also some coatings that have the capability to cure their bonds and heal their defects. However, there is still no system available, which provides long-term protection in a wide range of solution/electrolyte pH.

There are many techniques useful for studying the available self-healing mechanisms, as discussed in this review. However, the frequently used nonelectrochemical techniques for Mg alloys are SEM and EDS, and the most commonly used electrochemical techniques are EIS and SVET. Microelectrochemical techniques are very sensitive and helpful for a better understanding of the self-healing mechanism. However, these techniques are scarcely reported for the evaluation of self-healing behavior on Mg alloys. Moreover, in spite of having benefits, each technique has its own limitation, such as difficulty attaining a stable open-circuit potential, inability to determine the nonelectrochemical nature of the coating in question and requiring the development of an EC that matches the physical system in EIS.

ACKNOWLEDGEMENT
The authors thank the National Natural Science Foundation of China for financial support of this work (No. 51471021).

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