Abstract: Although hexavalent chromium-based protection systems are effective and their long-term performance is well understood, they can no longer be used due to their proven Cr(VI) toxicity and carcinogenic effect. The search for alternative protection technologies for Mg alloys has been going on for at least a couple of decades. However, surface treatment systems with equivalent efficacies to that of Cr(VI)-based ones have only begun to emerge much more recently. It is still proving challenging to find sufficiently protective replacements for Cr(VI) that do not give rise to safety concerns related to corrosion, especially in terms of fulfilling the requirements of the transportation industry. Additionally, in overcoming these obstacles, the advantages of newly introduced technologies have to include not only health safety but also need to be balanced against their added cost, as well as being environmentally friendly and simple to implement and maintain. Anodizing, especially when carried out above the breakdown potential (technology known as Plasma Electrolytic Oxidation (PEO)) is an electrochemical oxidation process which has been recognized as one of the most effective methods to significantly improve the corrosion resistance of Mg and its alloys by forming a protective ceramic-like layer on their surface that isolates the base material from aggressive environmental agents. Part II of this review summarizes developments in and future outlooks for Mg anodizing, including traditional chromium-based processes and newly developed chromium-free alternatives, such as PEO technology and the use of organic electrolytes. This work provides an overview of processing parameters such as electrolyte composition and additives, voltage/current regimes, and post-treatment sealing strategies that influence the corrosion performance of the coatings. This large variability of the fabrication conditions makes it possible to obtain Cr-free products that meet the industrial requirements for performance, as expected from traditional Cr-based technologies.

Keywords: magnesium; coating; micro-arc oxidation (MAO); Cr(VI)-based coatings
Anodizing, an electrochemical oxidation process, is an effective method to improve the corrosion resistance of Mg and its alloys by forming a protective ceramic-like layer on their surface. Anodizing is commonly used for Al and Ti alloys, but less so for Mg alloys. Cheaper and technologically easier conversion treatment processes are typically preferred for Mg in engineering applications [3]. For details on advances in chromate-free conversion coatings for Mg alloys in engineering applications, the reader is referred to of the present review [4].

Technically, anodic films are also a conversion type of coating, as their composition comprises elements of the substrate and the electrolyte [5]. The anodic films on Mg alloys, formed in alkaline or acidic (less common) electrolytes, are usually crystalline and porous, with a typical thickness of 5–50 µm. The films typically comprise a barrier layer that isolates the base material from aggressive environmental agents and is characterized by good adhesion to the substrate and considerably greater corrosion protection than that of conversion films. The latter is also because the properties of anodic films can be tailored by altering a variety of factors, such as the voltage/current regime, electrolyte composition, sealing, anodizing cell geometry, etc. This variability of the fabrication conditions makes it possible to obtain products which may be easily adapted to industrial requirements. Large-scale production tends to search for efficient, safe, easy, and fast anti-corrosion treatment procedures with minimal production and operation costs.

The present work forms Part II of our review and summarizes the present and future outlooks for corrosion protection strategies for Mg-based anodizing, including traditional chromium-based processes and newly developed chromium-free alternatives, such as plasma electrolytic oxidation (PEO) technology and anodizing in organic electrolytes. It should be mentioned that although a vast body of work exists on PEO technology as applied to Mg alloys for biomedical applications (which, by necessity, are free of toxic elements), this is outside of the scope of this review; the reader can consult the following references for more information [6–9]. Rather, the present review pinpoints recent developments in anodic treatment systems for Mg alloys that have been shown to be capable of meeting industrial requirements based on the performance associated with traditional Cr-based technologies.

2. Evolution of Anodic Treatments for Mg Alloys

2.1. Fundamentals of Anodizing Below and Above the Breakdown Potential

Anodizing can be carried out under Direct Current (DC), Alternating Current (AC), unipolar pulsed, and bipolar pulsed conditions with current, voltage, or power input control. In a simple DC mode, potentiostatic or galvanostatic regimes are used, which lead to different morphologies of the resulting anodic films [10]. A constant voltage regime causes a systematic current drop with processing time due to the growth of the dielectric oxide layer and the increase of its resistance. Under current limitations, the increasing resistance of the growing barrier layer causes the voltage to rise with processing time. Figure 1 shows an example of the voltage and current variations during PEO, an advanced form of anodizing. In the initial stage, the process is under constant current control, but once the maximum set voltage is reached, the current decays.

Voltage is a crucial factor that determines the final characteristics of the anodic film. There is a certain potential threshold, i.e., a so-called dielectric breakdown potential, above which the mechanism of the electrochemical oxidation process changes (Figure 2).

Below the breakdown potential, the growth of the oxide coating is relatively slow, and the obtained structure is mostly amorphous. In the case of Mg and its alloys, it is typically composed of hydrated magnesium oxide with a thin barrier layer adjacent to the substrate and an outer finely porous layer, as confirmed by AFM [12] and TEM [13] of the coating cross-sections.
Figure 1. Voltage and current vs. time plots and evolution of discharge sparks. Reprinted from [11] with permission from Elsevier.

Figure 2. Schematic of current–voltage diagram with the corresponding metal oxide film formation steps during plasma electrolytic oxidation treatment (a) in the near-electrode area and (b) in the dielectric film on the electrode surface. Reprinted from [10] with permission from Elsevier.

The effect of the electrolyte on the final coating composition in the case of pre-breakdown anodizing is relatively small (the incorporated electrolyte species migrate inward at a constant rate in the electric field). This type of anodic film is not as mechanically and thermodynamically stable, like the aluminum oxide formed during the anodizing of aluminum alloys. The value of the Pilling-Bedworth ratio (molar $V_{ox}/V_m$) for a MgO/Mg system is only 0.81, and therefore, such oxide films develop cracks [14]. According to the
Pourbaix diagram, MgO is stable above pH 10.5, which is out of the typical pH range found in service conditions. This is also the reason why strong acids such as sulfuric and phosphoric acids, typically used in the anodization of Al alloys, cannot be used for anodic treatments of Mg alloys.

The first attempts to anodize Mg were most likely carried out around 1920, with the first patents being filed in 1923 [15,16]. However, the majority of work was done between 1930 and 1950, with the appearance of processes such as AMC K, DOW 9, DOW 13, Framalit (all chromate based), Seomag-W, Seomag G, Elomag, AMC R, DOW 12, DOW 14, DOW 17, CVAC (all alkaline based), Flussal (fluoride based), and Manodyz (silicate based) [17], some of which will be further discussed in Section 2.2.

Anodizing above the breakdown potential is much more common for Mg alloys, although it has only recently been used on a larger scale. The process is known as plasma electrolytic oxidation (PEO) or micro-arc oxidation (MAO). The beginning of the modern age of fundamental and applied studies of PEO was marked by the works of Brown et al. in the US [18] and Markov et al. in Russia [19] in the 1970s. Our understanding of the process was further developed in the 1980s and 1990s through the work of Fyedorov et al. [20], Kurze et al. [21,22], Snezhko et al. [23,24], and Gordienko et al. [25,26], and the first commercial PEO processes were developed for Al and Mg (Tagnite [27], Magoxide [28], Keronite [29]). An influential review of PEO processes and technology for surface engineering was published by Yerokhin et al. in 1999 [10]. The achievements of the last decade are mainly associated with developments in PEO process diagnostic methods [30–36], coating multifunctionalization [37–41], and energy consumption reduction [42,43] (Figure 3). Third generation processes aim at the development of electrolytes which are universally suitable for different types of light alloys (Al, Ti, and Mg) and which offer multifunctional performance (e.g., corrosion resistance, abrasion resistance, thermal resistance, final finish). This can be achieved through the use of additives (e.g., particles) and process control.

The formation mechanism of ceramic-like PEO coatings is very complex due to the simultaneous occurrence of several electrochemical, plasma-chemical, and thermal-chemical reactions [10]. Various models have been proposed to describe it [44,45], but the most feasible seems to be the model of oxide film dielectric breakdown [46] (Figure 4).

Under these circumstances, in the initial stage of the process, a thin (100–200 nm) insulating barrier layer is formed, as in conventional anodizing carried out below breakdown potential. In the high voltage region, the electric field across the metal-oxide-gas system is sufficient to generate a dielectric breakdown of the pre-formed oxide that manifests as visible microdischarges (Figure 2). Extremely high localized temperature and plasma pressure, formed from vaporized electrolyte and gas in the discharge channel (~2 × 10^4 K, 100 MPa) [10,48], cause the ejection of the molten oxide material from the discharge channel onto the coating surface. Then, contact between the liquid phase and a cool electrolyte leads to the very fast solidification of the ejected oxide. This stage occurs with simultaneous pore formation in the middle and outer parts of the coating as a result of the gas passing through the softened oxide material; the coating often contains microcracks caused by thermal stresses and volume changes related to phase transformations (Figure 5a) [49]. The discrete micro-discharges, often occurring in cascades, with the duration of each being in the order of ~10 µs [50–52], appear in places where the oxide layer is weakest (e.g., thinnest and/or heterogeneous), causing local thickening of the oxide layer. This sequence of events leads to the synthesis of a three- (sometimes two-) layer coating of uniform thickness. The coating morphology comprises an outer porous section, a compact middle layer, and a thin barrier layer which is well adhered to the magnesium substrate (Figure 5b,c).
The formation mechanism of ceramic-like PEO coatings is very complex due to the simultaneous occurrence of several electrochemical, plasma-chemical, and thermal-chemical reactions [10]. Various models have been proposed to describe it [44,45], but the most feasible seems to be the model of oxide film dielectric breakdown [46] (Figure 4).

Figure 3. Simplified timeline for the development of PEO coatings on Mg alloys.
The anti-corrosion properties of PEO coatings are mainly attributed to their submicrometric barrier layer (Figure 5e) [54,55]. Nevertheless, the middle layer, which often develops under AC regimes, also contributes to the corrosion resistance to a certain extent, since its pores are not penetrating and mostly not interconnected, limiting species diffusion.

Anodic films formed above breakdown potential are quite different in terms of their microstructure and morphology compared to those formed below breakdown. The former usually exhibits a crystalline structure, a thicker barrier layer, and a composition that is strongly dependent on the electrolyte constituents, while the latter is easily incorporated during the treatment through short-circuit paths [56]. In alkaline environments, PEO-formed MgO undergoes partial conversion to Mg(OH)$_2$, which has a Pilling-Bedworth ratio of 1.77 [57], resulting in greatly improved surface coverage. The ability of PEO processes to incorporate the electrolytes species opens new possibilities for coating design and obtaining the desired properties of surface-treated Mg alloys (Figure 6).

For instance, in the presence of aluminum compounds, a very stable MgAl$_2$O$_4$ spinel can be formed in the coating in addition to magnesium oxide [58]. This spinel is characterized by excellent chemical, thermal, dielectric, and mechanical features and also has a higher Pilling-Bedworth ratio than MgO (1.3 [59]), which is crucial for providing good corrosion protection. Additionally, PEO coatings on Mg alloys offer advantages like high thickness, fast growth rate, and good paintability, enabled by the relatively rough and porous top part of the coating. Mechanical properties like hardness and wear resistance can also be improved by PEO treatment [6,60]. It is worth noting that, unlike in pre-breakdown
anodizing, PEO processing does not require special surface pre-treatment, thus reducing the complexity of the procedure, saving time, and reducing the processing costs, which is especially desirable in industrial applications [61].

Figure 5. Scanning electron micrographs of two-layer (a,b) [49] and three-layer (c–e) [53] PEO coatings on Mg alloys. Schematic diagrams of two-layer and three-layer PEO coatings (f). (a,b) Reprinted from [49], (c–e) reprinted from [53] with permission from Elsevier.
Anodic films formed above breakdown potential are quite different in terms of their microstructure and morphology compared to those formed below breakdown. The former usually exhibits a crystalline structure, a thicker barrier layer, and a composition that is strongly dependent on the electrolyte constituents, while the latter is easily incorporated during the treatment through short-circuit paths [56]. In alkaline environments, PEO-formed MgO undergoes partial conversion to Mg(OH)₂, which has a Pilling-Bedworth ratio of 1.77 [57], resulting in greatly improved surface coverage. The ability of PEO processes to incorporate the electrolytes species opens new possibilities for coating design and obtaining the desired properties of surface-treated Mg alloys (Figure 6).

Figure 6. General overview of the most frequently used electrolytes components and phases formed in the PEO process on Mg. * Phase formed in a presence of K₂TiF₆.

Due to the much more desirable properties of the PEO coatings compared with pre-breakdown anodic films on Mg, the last two decades have witnessed a surge of publications on PEO research in China, UK, Russia, Germany, France, Spain, and Turkey [39,49,56,58,62–67], associated with the strategic interest of lightweight materials and the need of their protection and functionalization.

2.2. Cr-Based Anodic Treatments

As mentioned above, chromium-based protective coatings have been used for a long time. The first satisfactory method of Mg anodic treatment was developed in 1937, and it was Cr-based. The electrolyte was composed of 10% sodium dichromate (Na₂Cr₂O₇) and 2–5% monosodium phosphate (NaH₂PO₄). The process was carried out at a constant current of 0.5–1 A m⁻², 50 °C, for 30–60 min. After painting, the anodic coating exhibited better anti-corrosion properties than a traditional CC obtained by pickling in highly concentrated Cr-based solution (180 g/L of Na₂Cr₂O₇·2H₂O with 190 mL/L of HNO₃) and painting [68]. One of the oldest commercial anodizing processes for Mg, DOW17 (1942), which is still commonly used in industrial treatments, also owes its anti-corrosion properties to the presence of Na₂Cr₂O₇ in the electrolyte, with the other components of the concentrated electrolyte being NH₄HF₂ and H₃PO₄ (pH~5) [69,70]. The DOW17 procedure
produces 5–75 μm-thick crystalline coatings containing MgF₂, NaMgF₃, MgₓCrₙOₓ(OH)ₓ, with some small amounts of Cr₂O₃ (Figure 7a), by applying AC or DC at a voltage below 100 V and at a temperature above 70 °C [60,69,71].

Figure 7. (a) X-ray diffraction pattern [71] and (b) backscattered electron cross-sectional micrograph of DOW17 coating on AZ91 alloy [72], the latter produced by applying constant current with the voltage rising to 200 V.

An example of the DOW17 coating structure is presented in Figure 7b. Note that its morphology is strikingly similar to that of PEO coatings. As can be seen, the obtained coating is quite porous and irregular and has significant cracks; nevertheless, the process has been widely used because, for a very long time, there was no better alternative.

Surprisingly, despite the search for environmentally friendly alternatives, Cr (VI)-containing processes are still being developed. For instance, recently, DC anodizing of a Mg-Li alloy was reported in a mixture of K₂Cr₂O₇ and (NH₄)₂SO₄ (pH 5.5, 24 °C, 60 min) [70]. The corrosion-resistant coating was obtained due to reactions (1)–(2):

\[
\text{Mg}^0 \rightarrow \text{Mg}^{2+} + 2e^- \quad (1)
\]

\[
2\text{Mg}^{2+} + 2\text{Cr}_2\text{O}_7^{2-} + 6\text{OH}^- / 3\text{SO}_4^{2-} \rightarrow 2\text{MgCrO}_4 + 2\text{Cr(OH)}_3/\text{Cr}_2(\text{SO}_4)_3 + 3\text{O}_2 + 6e^- \quad (2)
\]

In the presence of chromate, the protective coating is formed by a chemical reaction between the electrochemically oxidized Mg and hexavalent chromium, with the latter being partially reduced to the trivalent state. The excellent corrosion performance of anodic and conversion chromium-based coatings is related to several factors. Studies on CCC have shown that after drying samples treated in Cr(VI) solution, dehydration of chromium hydroxide occurs, leading to the formation of amphoteric Cr₂O₃ [73]. Cr₂O₃ is almost insoluble in water, slightly soluble in acids and alkalis [74], and is characterized by a corundum structure and high hardness (almost 9 on the Mohs scale). Moreover, the presence of trapped hexavalent chromium in the form of either salts or oxides is responsible for the self-healing ability of the coating during corrosion [75]. Additionally, some studies have suggested that the presence of polar oxo-Cr(VI) anions prevents the adsorption of de-passivating anions like chlorides [76].
2.3. Cr-Free Anodic Treatments: State-of-the-Art Technologies and Patents

Since Cr(VI) is highly toxic and carcinogenic, Cr-based industrial processes must be replaced by new, environmentally-friendly technologies. Further, there is an unceasing need to improve the functional properties of coatings and to reduce fabrication costs, which both affect the economic sustainability of Mg-based components. The majority of the alternative anodizing technologies adopt safe, alkaline-based and chromate-free electrolytes. The optimal electrolyte compositions and process parameters that provide the best coating properties are being intensively researched.

One of the first commercial treatments which departed from the use of chromates was HAE (1955) [77]. The highly alkaline electrolyte (pH~14), composed of KOH, Al(OH)$_3$, K$_2$F$_2$, Na$_3$PO$_4$, and K$_2$MnO$_4$, operates at 20–30 °C. The treatment is carried out under an AC regime at 1.5–2.5 A dm$^{-2}$ and, in most cases, the final voltage does not exceed 125 V. The coating thickness ranges between 5–75 µm and is determined by the cut-off voltage limit (60 V for thinnest coatings). The processing time varies between 7 and 60 min for thin and thick coatings, respectively [60]. The quality of the obtained coatings is reported to surpass that of DOW17 [78].

Modern commercial developments in Mg anodizing technology offer anti-corrosion properties that are at least comparable to or better than older, acidic chromate-based processes like DOW17 or fluoride-based HAE (Figure 8).

The commercial anodization Anomag (Magnesium Technology) process, as well as PEO processes like Keronite (Keronite), and Magoxid-Coat (Aalberts Surface Technologies), use Cr-free dilute alkaline solutions. The treatment conditions and anti-corrosion characteristics of popular commercial procedures, as well as selected recent related studies, are presented in Table 1.

![Figure 8. Magnesium test plates after TAGNITE-8200, HAE, and Dow 17 treatments and exposure to salt spray (ASTM B117) for 168 (Types I) and 336 (Types II) hours. Adapted from [79].](image-url)
Table 1. Summary of the conditions and corrosion properties of commercial anodic coating treatments and selected research results.

| Name of Process | Electrolyte | Procedure Parameters | Composition of Coating | Thickness of Coating | Salt Spray Test | Ref. |
|-----------------|-------------|----------------------|------------------------|----------------------|----------------|------|
| Dow-17          | NH₄HF₂, Na₃Cr₂O₇, H₃PO₄ | pH - 5 70–80 °C AC 0.5-5 A/dm² Thin coating; Vₐₚₐₖ 60–75 V, 4–5 min Thick coating; Vₐₚₐₖ 90–100 V, 25 min | MgF₂, NaMgF₂, Mg₃(PO₄)₂(OH)₄ small amounts of Cr₂O₃ | 2.5–7.5 µm (thin coatings) 23–38 µm (thick coatings) | AZ91D Rating 5–14 days | [22,60,69] |
|                 |             |                       |                        |                      | ZE41A Rating 0–2 days | (ASTM D1654-Method B) |
| HAE             | KOH, Al(OH)₃, K₂F₂, Na₃PO₄, K₂MnO₄ | pH - 14 27 °C AC 1.5-2.5 A/dm² Thin coating; Vₐₚₐₖ 65–70 V, 7–10 min Thick coating; Vₐₚₐₖ 80–90 V, 60–90 min | - | 5–10 µm (thin coatings) 25–80 µm (thick coatings) | AZ91 HP 25 µm (3–41 corrosion points/dm²) after 24 and 100 h 40 µm (0-18 corrosion points/dm²) after 24 and 100 h | [22,60,77] |
| Tagrite         | Alkali hydroxide, metal fluorides, alkali metal fluorosilicates, hydrogen fluorides, | 10–20 °C DC polarization 1–5 A/dm² Vₐₚₐₖ 200–400 V | MgO with minor surface deposition of hard fused silicates | 5–10 µm (thin coatings) 20–25 µm (thick coatings) | ZE41 Rating 9: 24–200 h (ASTM D1654-Method B) Far superior compared to HAE and Dow 17 | [22,27,60] |
| Anomag          | NH₄, NaNH₄HPO₄ | RT DC 10 mA/cm² 170–350 V | MgO-Mg(OH)₂, some additives like Mg₁₋ₓFeₓ(OH)₃ depending on bath composition | 3–8 µm 10–15 µm 20–25 µm | AZ91 3–8 µm Rating 9: 150 h 10–15 µm Rating 9: 400 h 20–25 µm Rating 9: 1300 h | [60,80,81] |
| Keronite        | different alkaline solutions | 20–50 °C Bipolar signal | Mostly Mg₃Al₂O₇, minor content of SiO₂ and SiP₂ | 35 µm | AZ91 Die cast Rating 9: 1000 h with a polymer top-coat (ASTM D1654-92 Method B) | [60,82] |
| MagOxid         | - | RT DC 1–2 A/dm² 400 V Thin coating; Vₐₚₐₖ 90–100 V, 25 min | MgO, MgO(Mg(OH)₂, Mg₃O₂F, MgAl₂O₇) | 5 µm (thin coatings) 30 µm (thick coatings) | AZ91HP 80–100 h (DIN EN ISO 10 289) | [28,81] |
| SweetMag        | alkaline solution, free from chromates, borates and fluorides | DC 2 A/dm² Vₐₚₐₖ < 180 V (average); < 300 V (max) 18 min | - | 20 µm | FSI (dichromate pickle) ASTM B-117-44T 48, 120, 312 h | [84] |
|                 | KOH, Al₃(OH)₄Cl, KF, Na₃PO₄ varied additives: chromate, tungstate, vanadate, stannate, manganate (HAE bath) | DC 15 A/m² 7–90 min, 24 °C optional post-treatment 45 s immersion NH₄HF₂ + Na₃Cr₂O₇ aging procedure 4 h at 100% relative humidity 175–180 °C | - | - | chrome | [84] |
|                 | KOH, Na₂CO₃, Na₂SiO₃, Na₂B₄O₇ | DC 5–85 °C, current density 5–500 mA/cm², 150 Vₐₚₐₖ 10–80 min | - | 10–53 µm | AZ91D 336 h 14 µm: Rating 7–8 30 µm Rating 9 53 µm: Rating 9 336 h (ASTM B893-98) Far superior compared to HAE (Rating 2–3) and Dow 17 (Rating 5–6 (15 µm) 8–9 (122 µm)) | [85] |
It can be seen that commercial processes are based on silicate, phosphate, and sometimes, fluoride compounds. The coating corrosion resistance properties are often evaluated in terms of their performance in neutral salt spray tests (NSST); unfortunately, different coating thicknesses make the comparison of different commercial processes difficult. However, it is evident that newer commercial treatments, which abandon the use of toxic compounds, show much greater corrosion resistance than older methods like the DOW17 or HAE. A cross-section view of a Keronite coating [86] is shown in Figure 9.

![Cross-section SEM image of a 25 µm-thick Keronite coating on die cast AZ91D. Reprinted from [86] with permission from Elsevier.]

The last two rows in Table 2 present selected research results. They demonstrate that the electrolytes containing compounds like vanadates [84] or borates [76] can provide better anti-corrosion properties compared with HAE and DOW17 treatments, which are the most commonly used commercial techniques. Nevertheless, it must be considered that both chemicals are hazardous, toxic, and suspected of damaging fertility, similarly to chromates [87,88].

It is worth noting that PEO processes typically work in a high voltage range and therefore are characterized by relatively high energy consumption. Expensive power supplies with high energy output and specially designed output waveforms are often required. These drawbacks limit the application of PEO technology for the production of large parts in the aircraft or automotive industries; this will be discussed further below.

The number of patents of anodizing techniques for Mg alloys has been steadily increasing over the last 20 years (Table 2). As can be seen in the observations, many of these patents focus on the chemistry of the electrolyte and the effect of additives such as particles and organic/inorganic compounds. It is also common to find patents where two-step processes are used to confer additional functionality to the coating.
## Table 2. PEO patent overview.

| Patent or Application No./Title | Observations | Ref. |
|-------------------------------|--------------|------|
| WO/2017/064185                | **Method** | Salicylic acid derivatives encapsulated in micro-/nanoparticles as corrosion inhibiting molecules for Mg coatings. |
|                              | **Outcome** | Corrosion protection and improved corrosion inhibiting efficiencies compared to 1,2,4-triazole and benzotriazole as known from US 6,569,264 B1. |
| Ru0002614917                  | **Method** | Three steps treatment: PEO coating in silicate-based electrolyte followed by dipping in a tetrafluoroethylene telomer solution in acetone and then heat treatment. |
|                              | **Outcome** | Increased service life and improved corrosion resistance, anti-friction, and hydrophobic properties of the coated material. |
| Ru0002543580                  | **Method** | Four steps treatment: PEO coating in silicate-based electrolyte, dipping in 8-oxyquinoline C$_9$H$_7$NO solution, followed by boiling in NaOH and posterior heat treatment. |
|                              | **Outcome** | Reduction of corrosion rate, self-healing properties, increased service life in high humidity environment containing Cl. |
| US20140318974                 | **Method** | Oxide layer formed by PEO with the presence of oxides of secondary elements (not present in the alloy) coming from different sources: (i) a soluble salt of the secondary element(s) in the electrolyte; (ii) an enrichment of the surface of the substrate metal with the secondary element(s) prior to PEO processing; (iii) a suspension of the secondary element(s) or oxide(s) of the secondary element(s) applied to the oxide of the metal after this has been formed by the PEO process. |
|                              | **Outcome** | Corrosion and erosion-resistant mixed oxide coatings. |
| DE102011007424 A1             | **Method** | PEO in a clay-containing phosphate/silicate electrolyte. |
|                              | **Outcome** | Fabrication of amorphous and glassy oxide surface layer. |
| EP1820882                    | **Method** | Formation of an oxide or metallic layer comprising at least the POMs (e.g., Mo, V, W) and/or a crack-healing agent (e.g., CaO-Al$_2$O$_3$ or CaO·2Al$_2$O$_3$). These layers can be deposited/grown on the substrate via conventional anodizing, hard anodizing, PEO, and electroless deposition. |
|                              | **Outcome** | Protective multifunctional layers with self-healing properties. |
| WO/2006/007972               | **Method** | PEO & anodization process in a neutral/alkaline, phosphate-derivatives containing solution. Additional additives: Silicates, H$_2$O$_2$, alcohol, and either Zr, Ti, or Al-particles. |
|                              | **Outcome** | High hardness and high corrosion resistance coatings. |
### Table 2. Cont.

| Patent or Application No./Title | Observations | Ref. |
|-------------------------------|--------------|------|
| **US20040238368**<br>Magnesium anodization methods | Method<br>Anodization process in a phosphate alkaline electrolyte containing a sequestering agent to suppress plasma during anodization and a tertiary amine.<br>Outcome<br>-Controlled coating thickness and porosity by choosing various combinations of both current density and time (e.g., high current density for a short time produce a less porous layer).<br>-The addition of a small amount of a phosphonate such as “Dequest” 2066 or 2041 to the anodizing bath allows the anodizing process to proceed with both pulsed waveforms and also DC. | [96] |
| **WO/2003/083181**<br>Process and device for forming ceramic coatings on metals and alloys, and coatings produced by this process | Method<br>PEO (at high frequency pulses) supported by sonic acoustic vibrations for the use of stable hydrosols as electrolytes (for the introduction of fine-disperse particles).<br>Outcome<br>-Controlled micro-discharges during PEO process.<br>-Improved energy efficiency.<br>-Low-porous, 150 µm thick, hard microcrystalline ceramic coatings. | [97] |
| **WO/2003/016596**<br>Magnesium anodization system and methods | Method<br>Anodization process in a phosphate alkaline electrolyte containing a sequestering agent and a tertiary amine.<br>Outcome<br>Process to create oxide layers with sequestering agents in the form of ethylene diamine tetramethylene phosphonic acid and DEQUEST. | [98] |
| **CN106119846 a**<br>Method for preparing corrosion resistant and abrasion-resistant coating on surface of magnesium alloy | Method<br>Two-step treatment process: micro-arc oxidation treatment followed by microwave plasma vapor deposition.<br>Outcome<br>Improved corrosion and wear properties. | [99] |
| **WO/2016/010541**<br>Electroceramic coating for magnesium alloys | Method<br>Two steps process: Plasma oxidative deposition in a fluoride-containing solution followed by different organic/inorganic surface finishing.<br>Outcome<br>Improved corrosion resistance. | [100] |
| **WO/2015/008064**<br>High thermal conductivity insulated metal substrates produced by plasma electrolytic oxidation | Method<br>PEO in alkaline solution, specified voltage/current parameters, and pulses.<br>Outcome<br>Improved corrosion protection along with high thermal conductivity achieved on surfaces with high dielectric strength. | [101] |
| **US20090223829**<br>Micro-arc assisted electroless plating methods | Method<br>PEO followed by electroless Ni plating (EN).<br>Outcome<br>Duplex coatings revealed superior corrosion resistance to salt spray testing as compared to the traditional EN coatings. | [102] |
| **US20080248214**<br>Method of forming an oxide coating with dimples on its surface | Method<br>AC, DC, or DC pulse treatments in an alkaline electrolyte.<br>Outcome<br>Wear and corrosion prevention. | [103] |
| Patent or Application No./Title | Observations | Ref. |
|-------------------------------|-------------|------|
| US20070270235<br>Golf club head and method for making the same | Sample degreased by weak alkaline, cleaned, and dried followed by PEO in silicate-phosphate electrolyte at 10–45 °C. Outcome PEO layers developed on golf components. | [104] |
| EP 1793019 A2<br>Multivalent electrolytic process for the surface treatment of nonferrous metallic material | Anodization process in an alkaline electrolyte (pH 7–10) based on phosphate/ammonia, NaOH/KOH/LiOH. Followed by the coloring stage (dye). Outcome Colored oxide layers. | [105] |
| II152307<br>Oxidising electrolytic method for obtaining a ceramic coating at the surface of a metal | Standard PEO process in an alkaline solution (alkali hydroxide + oxyacid salt of an alkali metal). Outcome Specimens with semiconductive properties. | [106] |
| 131996<br>Method of anodizing magnesium metal and magnesium alloys | Anodization of Mg using alkaline electrolytes containing ammonia or an amine and phosphoric acid or a water-soluble phosphate salt. Outcome Details of different processes methodology. | [107] |
| WO/2003/002776<br>Method of anodizing of magnesium and magnesium alloys and producing conductive layers on an anodized surface | Anodization electrolyte: hydroxylamine, phosphate, nonionic surfactant, alkali hydroxide. Process followed by rendering anodized Mg with an electrolyte containing Ni, pyrophosphate, hypophosphite, and thiocyanate/lead nitrate. Outcome Conductive layers on anodized Mg surface. | [108] |
| WO/2002/031230<br>Method for anodizing magnesium and magnesium alloy components or elements | Anodization process using alkaline electrolytes containing phosphates/aluminates. | [109] |
| WO/1998/042892<br>Anodizing magnesium and magnesium alloys | Anodization of magnesium or magnesium alloys using an electrolytic solution (preferably derived from phosphoric acid) containing ammonia, amines, or both. | [110] |
| US5385662 A<br>Method of producing oxide ceramic layers on barrier layer forming metals and articles produced by method | Plasma chemical oxidation of Mg and other metals. Electrolyte: Phosphate, borate, fluoride, stabilizer urea, hexamethylenedi( or tetra)amine, glycol/glycerin. | [111] |
| DE4104847 A1<br>Production of uniform ceramic layers on metals surfaces by spark discharge- used for metal parts of aluminium, titanium, tantalum, niobium, zirconium, magnesium, and their alloys with large surface areas | Metal parts are immersed in an electrolytic bath (without cathode) and connected to a controllable power source supplying time-dependent, multiphase, periodic current. | [112] |
| US4976830 A<br>Method of preparing the surfaces of magnesium and magnesium alloys | Mg anodization in electrolyte containing alkali hydroxide, borate/sulfonate, phosphate/fluoride. | [113] |
| US 3956080<br>Coated valve metal article formed by spark anodizing | PEO conducted in alkaline electrolyte based on silicates and containing oxyacid of Te or Se. | [114] |
3. Corrosion of Anodized Mg Alloys

Understanding the influence of the anodic coatings on the mechanisms of corrosion of Mg alloys is crucial for the identification and design of coating characteristics that ensure good protection. The stages leading to corrosion initiation in the presence of anodic coatings are discussed below.

A protective anodic layer separates the alloy from the environment; its main role is to delay the ingress of aggressive species to the substrate [1]. As a consequence, features like big cracks and pores in the coating that enable easy access of the electrolyte to the metal and quick initiation of the corrosion process are undesirable. This is the case for the top porous layer of the coating, which is non-protective. The thick, intermediate layer with discontinuous porosity can considerably delay the corrosion process because the solution cannot easily infiltrate the coating [54,115]. The compact pore-free barrier layer, adjacent to the substrate, is the most protective part of the coating. Defects and partial dissolution of the outer layers, especially when they are amorphous, eventually lead to the penetration of corrosive species down to the barrier layer. The stability of this layer is greatly influenced by the local pH. Low values lead to the fast dissolution of the barrier layer and the corrosion of the substrate, whereas high pH values promote the formation of Mg(OH)₂, which is voluminous and causes a blocking effect that limits the corrosion rate. This alkalization is particularly facilitated in the limited volume of the pore band that is sometimes present between the barrier layer and the intermediate porous layer [116]. A schematic of the corrosion process is shown in Figure 10.

Figure 10. Schematic diagrams of (a) PEO coating, (b) simplified model of pores, and (c) corrosion initiation.

Typical corrosion morphologies of PEO-coated Mg alloys include general undercoating corrosion [49,117], localized corrosion [118], and coating dissolution [116,119] (Figure 11).

Another aspect to bear in mind is that the influence of the type of Mg alloy only becomes relevant when the PEO coating has failed [54]. Grain boundaries or impurities in the Mg alloy, despite being active corrosion points in the bare substrate, are not so active when covered by a dielectric passive film. Indeed, the probability that continuous pores will be located directly above the active point is small; therefore, the corrosion process is slowed [55]. However, recent research has shown that the second phase segregates in the substrate may also contribute to more extensive discharges and increase the probability of through-going pores there [120]. The impurity level determines how long the coating survives under the same test conditions; this is particularly true for flash-PEO of alloys with strong micro-galvanic coupling [121].
Figure 11. SEM microphotographs showing the types of corrosion morphologies of PEO-coated Mg alloys: (a) general undercoating corrosion [49,117], (b) localized corrosion [118], and (c) coating dissolution [116]. Reprinted (a) from [49], (b) from [118], (c) from [116] with permission from Elsevier.

Considering the described mechanism, the corrosion of PEO-coated Mg alloys can be minimized by enhancing the chemical stability of the coatings and reducing the pore number and size (especially open porosity), which can be realized in several ways during and/or after anodizing. Fine-tuning the electrical input characteristics, the in situ incorporation of corrosion inhibiting species into the coating from the electrolyte, and sealing the pores during post-treatment are examples of current, successful strategies. Further, PEO coatings exhibit very good paintability due to their high roughness; therefore, the application of polymer top-coats significantly improves the corrosion resistance.

4. Effect of Energy Input and Electrolyte Composition on Coating Protection Properties

4.1. Energy Input

Anodic treatments can be performed using either constant voltage or constant current (DC/AC) regimes or in more advanced unipolar and bipolar pulsed modes. The energy driven into the system feeds several processes: the electrochemical oxidation and Joule heat in the case of conventional anodizing and plasma chemical reactions, thermal oxidation, and electrolyte vaporization in the case of the PEO [122–125]. As a result, the way the energy is supplied and distributed has a significant impact on the final structure of the coating [126–129]. For instance, DC constant current conditions sustain intensive, long-lasting, and less mobile micro-discharges which promote the formation of large channels and coating material destruction [130,131], greater pore size, and lower pore population...
Materials 2022, 15, 8515

18 of 56

density. Eventually, DC micro-discharges transform into microarcs, accompanied by more intensive gas evolution, the formation of very large size pores, and the thermal cracking of the coating [10].

Typically, anodic treatments of Mg and its alloys use current densities between 0.01–0.1 A cm$^{-2}$. The ranges of final voltages are quite varied. The lowest values can be found below 50 V [132], whereas the highest can be up to 500–600 V [66,133]. In most cases, applied voltages are within the 150–350 V range [60]. Compared to aluminium, the durations of anodic treatments of Mg-based alloys are relatively short. Typically, within 3–15 min, the coating thickness can reach about 4–40 µm, with a growth rate of 0.5–13 µm min$^{-1}$. These thicknesses are not maximal for Mg-based PEO coatings but are optimal for practical applications, especially from an economical and industrial point of view. Optimizing the PEO parameters makes it possible to achieve relatively low energy consumption, for instance, 0.632 kWh m$^{-2}$ µm$^{-1}$ [134]. It was recently shown that so-called flash-plasma electrolytic oxidation coatings (FPEO), with a process duration <90 s and corrosion performance better than that of a commercial Cr(VI)-based coating, consume a very low amount of energy (~1 kWh m$^{-2}$ µm$^{-1}$) [135,136]. In concentrated alkaline electrolytes (>150 g/L dissolved solids) under a DC regime, the energy consumption can be as low as ~0.07 kWh m$^{-2}$ µm$^{-1}$ [137]; however, there is a lack of information on the corrosion behavior of such coatings.

Nowadays, unipolar or bipolar current pulse modes are frequently used in PEO of Mg alloys, as they can decrease the coating porosity and improve homogeneity, and thus, improve the corrosion resistance. Combinations of anodic and cathodic pulses and modifications of the frequency and duty cycle provide a wide range of energy input options that can help to avoid destructive, long-lasting micro-discharges, increase their population density [138], and obtain denser coatings with better corrosion resistance. Some examples of different energy input-related processing parameters and their effect on coating properties are summarized in Table 3.

### Table 3. Summary of energy input parameters during PEO of Mg alloys.

| Variable | Process Parameter | Alloy Electrolyte | Effects | Corrosion Data | Ref. |
|----------|------------------|------------------|---------|----------------|------|
| 100, 120, 140, 160 V | AC square | AZ91D NaOH, H$_3$BO$_3$, Na$_2$B$_4$O$_7$, organic additive | 14.88–37.32 µm ↑, ↑, ↑, pores, and cracks | 140 V, 2000 Hz, 0.4 duty cycle (22.3 µm) → best EIS performance $R_{cor} = 1.54 	imes 10^5$ Ω cm$^2$ | [139] |
| 20, 30, 40 mA/cm$^2$ | 20 °C, 700 s | AZ91HP HF, H$_3$PO$_4$, H$_2$BO$_3$, NH$_3$ | 9–22 µm Factors influence on thickness: final voltage > current density > duty cycle > frequency. ↑, ↑ | Effect of factors on $R_{cor}$: voltage > frequency > duty cycle > current density 20 mA/cm$^2$, 440 V, 600 Hz, 15 or 35% duty cycle → best (336 h of salt spray test (ASTM B117-95 and ASTM B537-70) with no evidence of pitting corrosion) | [140] |
| Voltage mode | DC-bipolar(−20 V), 20% | ZK60 Na$_3$AlO$_2$, Na$_2$PO$_4$, NaOH, Na$_2$B$_4$O$_7$, C$_6$H$_3$Na$_2$O$_7$ | Two-step 20.2 µm (denser) Three-step 15.76 µm (smoother) | Two-step → best $R_{cor}$ Z$_{corr}$ = 1.414 × 10$^3$ Ω cm$^{-2}$-order of magnitude higher compared with the three-step voltage mode | [141] |
| 200, 400, 800, 1000, 1500 Hz | constant current density 5 A/dm$^2$, 30 °C, 10 min | AZ91D Na$_2$SiO$_3$, NaF, NaOH | ↑, ↑ | ↑ | [142] |
Table 3. Cont.

| Variable                          | Process Parameter | Alloy  | Electrolyte | Effects                                                                 | Corrosion Data                        | Ref.   |
|-----------------------------------|-------------------|--------|-------------|-------------------------------------------------------------------------|----------------------------------------|--------|
| 10, 100, 1000 Hz                  | DC$_{pulsed}$ 30 mA cm$^{-2}$ | AM50   | KOH, Na$_2$PO$_4$, | ~73 $\mu$m for 10 Hz, ~45 $\mu$m for 1000 Hz | 10 Hz $\rightarrow$ best EIS performance Z$_{corr}$ = 2.5 $\times$ 10$^7$ $\Omega$ cm$^2$ | [143]  |
|                                   | I$_{on}$/I$_{off}$ = 1:9 |        |             | $\uparrow$ frequency $\rightarrow$ $\uparrow$ growth rate, additional phases $\uparrow$ (frequency (1000 Hz) $\rightarrow$ V$_{corr}$ (551 V-1000 Hz), smooth surface with fine microstructure/surface morphological features |
| Bipolar pulse (S4):              |                   |        |             |                                                                         | Z$_{corr}$ = 50 h, 1.1 $\times$ 10$^5$ $\Omega$ cm$^2$ |        |
| Time, 1.5–10 min                  | DC$_{pulsed}$ 30–50 mA cm$^{-2}$ | AZ31B  | KOH, KF, | No duty cycle data provided. 4–5 $\mu$m-thick coating in 3 min, dense inner layer, fine surface porosity. | Non-sealed 3 min coating—no corrosion in 80 h NSST, pitting at 100 h. | [145]  |
| Positive pulse 250–400 V, negative pulse $\sim$ 20 V, 500 Hz, 15% duty cycle, 40 $^\circ$C, 15 min | ZK60 | Na$_2$SiO$_3$, NaOH, NaF | Bipolar mode (400 V/−20 V) $\rightarrow$ shorter and slower discharges $\rightarrow$ thicker and denser coating layer. | Bipolar 400 V $\rightarrow$ 20 V $\rightarrow$ best $t_{corr}$ in 3.5% NaCl, 6.7 $\times$ 10$^{-7}$ A cm$^{-2}$ | [145]  |
| 10% duty cycle, 10 min            | cp-Mg             |        |             |                                                                         | Unipolar $Z_{corr}$ $\times$ 2 h, 508 $\Omega$ cm$^2$ | [146]  |
| Unipolar vs. Bipolar              |                   |        |             |                                                                         | Bipolar $Z_{corr}$ $\times$ 2 h, 113 $\Omega$ cm$^2$ | [146]  |
| i$^+$ = 30 mA/cm$^2$ i$^-$ = 10–20 mA/cm$^2$ | 3000 Hz | Ca(OH)$_2$, Na$_2$PO$_4$ | Bipolar $\rightarrow$ finer porosity and denser inner region, albeit the coating thickness reduced with increasing negative current density, but apparent macroscopic defects | No qualitative difference in the chemical and phase compositions after the unipolar and bipolar pulses application |
| Unipolar pulse (S1):             |                   |        |             |                                                                         | Unipolar $Z_{corr}$ $\times$ 2 h, 508 $\Omega$ cm$^2$ | [146]  |
| Bipolar pulse (S2):              |                   |        |             |                                                                         |
| Bipolar pulse (S3):              |                   |        |             |                                                                         |
| Bipolar pulse (S4):              |                   |        |             |                                                                         |
| Bipolar vs. Bipolar              |                   |        |             |                                                                         |
| Positive pulses (PP) added during each positive AC interval | 5–12 A/dm$^2$, t$_{on/off}$, 0–8 ms, 20–25 $^\circ$C, 60 min | MA2-1 | NaOH, Na$_2$P$_2$O$_7$ | 50–75 $\mu$m Positive and negative peaks $\rightarrow$ $\uparrow$ efficiency of coating deposition. Optimal combination appeared to be 6-4 ms for positive pulses and 2–6 ms for negative ones. | Droplet test in HCl + CuCl$_2$ PP mode $\rightarrow$ longest time until potential change | [147]  |
| Negative pulses (NP) added during each negative AC interval |                   |        |             |                                                                         |
| Time, 1.5–10 min                  | DC$_{pulsed}$ 30–50 mA/cm$^2$ 380 V | AZ80   | Na$_2$SiO$_3$, KOH, KF | Non-sealed 3 min coating—no corrosion in 80 h NSST, pitting at 100 h. | | [145]  |

Parameter Cont. | C, 15 min 380 V | Na$_2$SiO$_3$, KOH, KF, | Non-sealed 3 min coating—no corrosion in 80 h NSST, pitting at 100 h. | | [145]  |

$\uparrow$ $t_{corr}$ = 35–45 $\mu$m, $t_{corr}$ = 35–45 $\mu$m, $t_{corr}$ = 35–45 $\mu$m | Bipolar (S2) $\rightarrow$ best EIS performance Z$_{corr}$ $\times$ 2 h, 2.8 $\times$ 10$^6$ $\Omega$ cm$^2$ | [144]  |

$\uparrow$ $t_{corr}$ = 35–45 $\mu$m, $t_{corr}$ = 35–45 $\mu$m, $t_{corr}$ = 35–45 $\mu$m | Bipolar (S2) $\rightarrow$ best EIS performance Z$_{corr}$ $\times$ 2 h, 2.8 $\times$ 10$^6$ $\Omega$ cm$^2$ | [144]  |

$\uparrow$ $t_{corr}$ = 35–45 $\mu$m, $t_{corr}$ = 35–45 $\mu$m, $t_{corr}$ = 35–45 $\mu$m | Bipolar (S2) $\rightarrow$ best EIS performance Z$_{corr}$ $\times$ 2 h, 2.8 $\times$ 10$^6$ $\Omega$ cm$^2$ | [144]  |

$\uparrow$ $t_{corr}$ = 35–45 $\mu$m, $t_{corr}$ = 35–45 $\mu$m, $t_{corr}$ = 35–45 $\mu$m | Bipolar (S2) $\rightarrow$ best EIS performance Z$_{corr}$ $\times$ 2 h, 2.8 $\times$ 10$^6$ $\Omega$ cm$^2$ | [144]  |

$\uparrow$ $t_{corr}$ = 35–45 $\mu$m, $t_{corr}$ = 35–45 $\mu$m, $t_{corr}$ = 35–45 $\mu$m | Bipolar (S2) $\rightarrow$ best EIS performance Z$_{corr}$ $\times$ 2 h, 2.8 $\times$ 10$^6$ $\Omega$ cm$^2$ | [144]  |

$\uparrow$ $t_{corr}$ = 35–45 $\mu$m, $t_{corr}$ = 35–45 $\mu$m, $t_{corr}$ = 35–45 $\mu$m | Bipolar (S2) $\rightarrow$ best EIS performance Z$_{corr}$ $\times$ 2 h, 2.8 $\times$ 10$^6$ $\Omega$ cm$^2$ | [144]  |

$\uparrow$ $t_{corr}$ = 35–45 $\mu$m, $t_{corr}$ = 35–45 $\mu$m, $t_{corr}$ = 35–45 $\mu$m | Bipolar (S2) $\rightarrow$ best EIS performance Z$_{corr}$ $\times$ 2 h, 2.8 $\times$ 10$^6$ $\Omega$ cm$^2$ | [144]  |

$\uparrow$ $t_{corr}$ = 35–45 $\mu$m, $t_{corr}$ = 35–45 $\mu$m, $t_{corr}$ = 35–45 $\mu$m | Bipolar (S2) $\rightarrow$ best EIS performance Z$_{corr}$ $\times$ 2 h, 2.8 $\times$ 10$^6$ $\Omega$ cm$^2$ | [144]  |

$\uparrow$ $t_{corr}$ = 35–45 $\mu$m, $t_{corr}$ = 35–45 $\mu$m, $t_{corr}$ = 35–45 $\mu$m | Bipolar (S2) $\rightarrow$ best EIS performance Z$_{corr}$ $\times$ 2 h, 2.8 $\times$ 10$^6$ $\Omega$ cm$^2$ | [144]  |

$\uparrow$ $t_{corr}$ = 35–45 $\mu$m, $t_{corr}$ = 35–45 $\mu$m, $t_{corr}$ = 35–45 $\mu$m | Bipolar (S2) $\rightarrow$ best EIS performance Z$_{corr}$ $\times$ 2 h, 2.8 $\times$ 10$^6$ $\Omega$ cm$^2$ | [144]  |
As can be seen in Table 3, there are many possibilities in terms of modifying the energy parameters, but the final effect on the anti-corrosion properties of the coatings is always a result of all system factors, such as voltage, current density, frequency, and duty cycle, and it is hard to determine the effect of an individual variable. For instance, the influence of the application of uni- or bipolar pulses modes on corrosion resistance is ambiguous, as shown in the contradictory results presented in [144–146,148]. Current frequencies tested in the range of 10–2000 Hz exhibit a tendency of corrosion resistance increase with higher frequency values [139,140,142,149]; however, in one case, the opposite trend was observed [143]. Based on the summarized results, it can be concluded that duty cycles should typically be below 40% for both unipolar [139,140,149] and bipolar treatments [141,146], and that higher values are not suitable for the improvement of the anti-corrosion properties of PEO coatings [139]. The coating growth rate in these conditions can be slower than under DC; nevertheless, in well-chosen conditions, it is comparatively fast, usually between 0.77–12.44 µm min⁻¹ (Table 3). The influence of system parameters on coating thickness can be arranged from the most to least relevant as follows: final voltage > current density > duty cycle > frequency. The significance of individual parameters on the anti-corrosion properties may be arranged in the following order: final voltage > frequency > duty cycle > current density [140]. Importantly, a literature analysis confirmed that high thickness is not always a guarantee of the best anti-corrosion properties of PEO coatings on Mg alloys.

4.2. Electrolyte Composition

The type and concentration of the electrolyte play a crucial role in the morphology, composition, and ultimately, in the corrosion resistance [8,60]. The first and most basic distinction is the pH of the solution. Acidic electrolytes are not preferred for PEO treatment because they completely suppress micro-discharges below pH 3 [150], enhancing the oxide dissolution rate and leading to the formation of porous-type structures with poor corrosion resistance [151,152]. Electrolytes with higher pH values promote the earlier onset of micro-discharges, and the oxide film develops typical PEO three-layered structures.

To ensure an alkaline environment, KOH or NaOH are often chosen as primary components. This also prevents excessive anodic dissolution. With regard to the specific role of K⁺ or Na⁺ ions, it has been shown that the former (as a hydroxide, phosphate, or both) promotes more compact coatings, whereas the latter reduces the pore size in the outer part of the coating [153]. The effects of KOH or NaOH concentrations on coating properties have been intensively investigated. For instance, a three-fold increase of KOH concentration (up to 0.27 M) increased the pH (by ~1 unit) and conductivity (by more than 2.5 times), decreased the breakdown and final voltage values, and increased the compact layer thickness and the MgO/Mg(OH)₂ ratio, resulting in higher corrosion resistance of coating in salt spray [154]. Similar results were found for a fluoride- and phosphate-based electrolyte containing 1.5 M and 3 M KOH, i.e., better corrosion performance was observed with a more concentrated solution due to the reduced coating porosity [155].

Comparing the results for 5 g/L and 100 g/L NaOH-based electrolytes, the breakdown voltages were 282 V and 82 V, respectively. Furthermore, the coating obtained from the concentrated electrolyte exhibited higher corrosion resistance (two orders of magnitude lower corrosion current and one order of magnitude higher total impedance, |Z|₁₀₀MHz) due to the increased coating thickness [156]. It is evident that due to the effect of decreasing breakdown voltage, the concentration of the electrolytes is a significant factor in minimizing the energy consumption. Sustainable recycling and circular economy routes need to be developed for such electrolytes in order to avoid the increase of the environmental footprint when they need to be disposed of.

Other additives, like phosphates, silicates, fluorides, aluminates, zirconates, permanganates, etc., are used to modify the coating composition and properties. Under the electric field, anions like PO₄³⁻, SiO₂⁵⁻, and F⁻ migrate inward and get incorporated into the
coating [157]. The following reactions (3)–(7) are examples describing the different phase formation in the presence of some of these additives:

\[
\begin{align*}
3\text{Mg}^{2+} + \text{PO}_4^{3-} & \rightarrow \text{Mg}_3(\text{PO}_4)_2 \\
2\text{Mg}^{2+} + \text{SiO}_3^{2-} + 2\text{OH}^- & \rightarrow \text{Mg}_2\text{SiO}_4 + \text{H}_2\text{O} \\
\text{Mg}^{2+} + \text{SiO}_3^{2-} & \rightarrow \text{MgSiO}_3 \\
\text{Mg}^{2+} + 2\text{F}^- & \rightarrow \text{MgF}_2 \\
\text{Mg}^{2+} + 2\text{AlO}_2^- & \rightarrow \text{MgAl}_2\text{O}_4
\end{align*}
\]

The X-ray diffraction patterns of PEO-treated Mg alloys confirmed the presence of the aforementioned compounds [143,158,159]. These phases can have a great effect on the physico-chemical properties of the coatings; for instance, the following order of corrosion resistance to Cl\(^-\) attack was identified: amorphous material < MgO < Mg\(_3\)(PO\(_4\))\(_2\) < Mg\(_2\)SiO\(_4\) [116].

The beneficial effect of fluoride-based electrolytes on the corrosion resistance of PEO coatings on Mg alloys is often related to the formation of passivating MgF\(_2\) phase [160,161], associated with more compact layers, nobler corrosion potential, and reduced susceptibility to pitting [133,160,162,163]. It was also reported that the addition of fluoride to various electrolytes (based on NaAlO\(_2\), Na\(_2\)SiO\(_3\), NaAlO\(_2\) with Na\(_3\)PO\(_4\), and Na\(_2\)SiO\(_3\) with Na\(_3\)PO\(_4\)) always caused much quicker growth of the PEO layer, which led to a significant reduction of specific energy consumption [135]. On the other hand, it was shown that similar corrosion resistance can be achieved in more benign, fluoride-free electrolytes, such as aluminate-phosphate [164].

The influence of phosphates, common additives in commercial electrolytes (Anomag CR1 and CR2, Henkel Japan Co., Ltd.), on corrosion properties has been shown [49] and seemed to depend on the various types of phosphates (orthophosphate, pyrophosphate, polyphosphate, hydrophosphates, etc.) and the treatment conditions [165–167]. Phosphorus-containing coatings typically favor the formation of amorphous phases, although Mg\(_3\)(PO\(_4\))\(_2\) can also be detected [165]. It has been suggested that amorphous phosphate participates in a self-repairing mechanism consisting of its dissolution and subsequent re-deposition as an insoluble crystalline hydrated magnesium phosphate at the locations where the PEO coating fails [168].

The presence of sodium orthophosphate in the electrolyte has been shown to promote the coating growth rate through a more uniform distribution of micro-discharges, avoiding local coating destruction [165]. However, the phosphate concentration must be carefully chosen. According to [164], too low concentrations (<0.21 M) result in non-uniform coatings, whereas concentrations higher than 0.25 M lead to recurrent micro-discharges at specific locations on the surface.

The addition of aluminates, like NaAlO\(_2\), to the electrolyte has been shown to decrease the number and size of discharge channels [58] and increase the coating thickness [159]. More importantly, the formation of MgAl\(_2\)O\(_4\) results in enhanced corrosion resistance, which is associated with its chemical stability and a higher Pilling-Bedworth ratio compared with MgO [48,169,170]. It has been proven that for a long immersion time (9 days), the corrosion resistance of the aluminate-containing coating was higher than that of silicate- and phosphate-based electrolytes [171]. Less frequently used aluminum nitrate, Al(NO\(_3\))\(_3\), also helps to form a thick and uniform passive layer when used in the 0.15–0.20 M range [164].

Perhaps the most common component of PEO electrolytes is sodium silicate, Na\(_2\)SiO\(_3\). Compared with equivalent amounts of phosphates and aluminates, it has a greater influence on the electrolyte conductivity, final voltage, and therefore, coating thickness. A corrosion study comparing the effect of phosphate, aluminate, molybdate, and silicate sodium salts revealed that the latter provided the biggest improvement. This was probably due to a higher coating thickness and less open porosity [159].
Frequently, mixtures of the aforementioned chemicals work much better than simple composition electrolytes. The study of the FPEO (>90 s treatment, ~5 µm coatings thickness) obtained from varied electrolytes based on mixtures of KOH with one, two, or three components from NaAlO₂, Na₂SiO₃, Na₃PO₄, KF showed the highest performance with the most complex (four elements) compositions (either aluminate or silicate mixtures with potassium hydroxide, phosphate, and fluoride). The best coating achieved superb corrosion protection, significantly outperforming commercial Cr(VI)-based reference samples [135,136].

Sodium borate, Na₂B₄O₇, is usually used in combination with silicate, phosphate, or aluminate salts. Borate ions promote coating growth, since the decomposing B₄O₇²⁻ is an additional source of oxygen. The presence of sodium tetraborate in a solution of Na₂SiO₃, KOH, NaH₂PO₄, and, optionally, KF, improved the coating resistivity by ten fold, although it tended to cause a “coral reef” surface morphology [172]. A Mott–Schottky examination of the electronic properties of the borate- and fluoride-based coatings indicated their lower donor concentration, much more negative flat band potential, and, therefore, higher corrosion resistance. Some other works have also shown the beneficial effect of Na₂B₄O₇ on corrosion resistance and even suggested that it assists in a self-repairing mechanism [158,173].

4.2.1. Organic and Inorganic Soluble Additives

The compounds discussed above are the most frequently used constituents of electrolytes in PEO of Mg alloys. However, a lot of attention is currently being paid to the further improvement of the coating properties, which can be achieved by using various types of organic and inorganic additives in the basic electrolyte mixtures (Figure 12).

It should be noted that while the introduction of some soluble inorganic compounds strongly modifies the chemical composition of the coating, it also changes the pH and conductivity of the electrolyte, which influence the breakdown and final voltages and discharge density, resulting in structural modifications to the coatings [173–175]. The main criterion behind the choice of an additive salt is its capacity to form highly stable compounds that improve the passivity of the coating [84,132]. For example, elements like Mo (VI) [176] or rare-earth Ce(III) and La(III) [174] have the potential to provide a self-healing capacity of the coating under corrosion.

Titanium [177–179] and zirconium compounds [150,180–184] are being actively researched as additives due to their very high stability and pore-sealing effect [177,178,184]. While titanium is typically used in a form of K₂TiF₆, various types of zirconium salts have been tested. The best results (denser internal film and a more uniform surface) were yielded by K₂ZrF₆ compared with ZrOCl₂ and Zr(NO₃)₄ [150]. The inconvenience of K₂ZrF₆ is the hydrolysis of Zr⁴⁺ ions at pH > 4.0, which leads to the precipitation of Zr(OH)₄ in the electrolyte and, consequently, non-uniform discharge distribution and low coating quality. This limits the choice of basic components of the electrolytes to those that support relatively low pH, such as NaH₂PO₄ [182,183], which, in turn, limits the range of coating phase compositions. Some authors have circumvented this by dual- or two-step anodizing (Figure 13), where PEO of magnesium alloy in the acidic electrolytes [180] is preceded by a short anodic pre-treatment in alkaline electrolyte; this prevents the excessive anodic dissolution of the magnesium alloy and ensures good corrosion protection [180,181].

Organic additives usually do not change the coating composition but can provide some unique effects compared with inorganic compounds. Firstly, they can either decrease or increase the breakdown potential [185,186], with the latter imposing an additional economic burden. Further, they adsorb on the electrode and significantly reduce the anode/electrolyte interface tension [66,187], modulating gas evolution and the discharge population density [185,187]. All these effects can affect the mechanism of the discharge and change the structure of PEO coatings, reduce the surface porosity, inhibit defect development and improve the corrosion resistance [188]. The detailed effects of organic and inorganic additives are presented in Table 4.
The analysis in Table 4 indicates that additives in a mixture of 2–3 basic components (e.g., silicates, fluorides, phosphates) can provide significantly improved corrosion protection; however, the final result is not a direct sum of the effects of the individual constituents. Initial studies of the effect of electrolyte additives carried out by McNeil in 1957 demonstrated a positive influence of tungstate, vanadate, and stannate on corrosion resistance (although it is worth noting that the substrates were pickled in dichromate solution before anodic treatment and, optionally, after treatment). The best results before and after the post-treatment were obtained in the presence of vanadate.

In most of the cases presented in Table 4, the additives led to enhanced corrosion protection compared to additive-free PEO coatings (higher corrosion potential, lower corrosion current, lower tribocorrosion rate) [84,174–176,184–187,191,192,196,197,201]; however, negative results were also reported [132,189]. Often, the additives demonstrated positive effects within a certain concentration limit, beyond which the properties deteriorated [126,176,179,185,192,201,202]. It is also evident that additives in the electrolyte often reduce the coating thickness, without reducing the coating protective properties, which is associated with improved morphological parameters of the coatings, such as compactness, roughness, or pores size [174,175,192,196,203,204].

The reduction of corrosion current by two orders of magnitude compared with the untreated substrate (e.g., down to $10^{-7}$ A/cm$^2$) is frequently achieved in the presence
of an additive. One of the most notable improvements was obtained by the addition of KMnO$_4$ ($10^{-9}$ A/cm$^2$) (Figure 14) [175] or EDTA ($10^{-8}$ A/cm$^2$) into the electrolyte [196].

Figure 13. (a) Surface morphology; (b) cross sectional morphology; (c) EDS spectrum, along with the chemical composition. (d–i) X-ray elemental mapping of the MAO coating deposited on Mg in two stages, sequentially using the alkaline silicate electrolyte in the first stage, followed by the acidic zirconate electrolyte in the second stage, both at 300 V and for 3 min each stage [180]. Reprinted from [180] with permission from Elsevier.
Table 4. Organic and inorganic electrolyte additives.

| Additive | Alloy/ Electrolyte/ Process Parameter | Effects | Corrosion Data | Ref. |
|----------|--------------------------------------|---------|----------------|------|
| inorganic | HAF bath (KOH, Al₂(OH)₃), KOH, Na₂PO₄, AC 15 A ft⁻², 90 min, 24 °C | varied colors | ASTM B117-44T312 h | [84] |
|                | Optional post-treatment | similar hardness | corrosion: vanadate < stannate < chromate < tungstate < | |
|                | (1) 45 s immersion | | manganate < no-additive < manganese | |
|                | NH₄H₂PO₄ + Na₂Cr₂O₇ | | | |
|                | (2) 4 h at 100% relative humidity 175–180 °C | | | |
| KMnO₄ 0.07 M | | 80–90 V | PDP in 3.5 wt.% NaCl (Ecorr; corr) | [175] |
| AZ91 KOH, KF, Na₂SiO₃ | | Vcorr < 250 V | Untreated: 1.55 V, 1.5 × 10⁻⁵ A/cm² | |
| DC 100 mA cm⁻², 1–5 min | | | 0 g/L: −1.39 V, 3.5 × 10⁻⁶ A/cm² | |
| | | | 0.3 g/L: −1.37 V, 1 × 10⁻⁶ A/cm² | |
| | | | 3 g/L: −1.41 V, 7 × 10⁻⁶ A/cm² | |
| NaN₂MoO₄ 0.3, 0.6, 1, 3 g/L | | 1 μm (0.3 g/L), 40 μm (3 g/L) | PDP in 0.1 M Na₂SiO₃ + 0.05 M NaCl (Ecorr; corr) | [176] |
| AZ91 Na₂SiO₃, NaOH, diethyldiamine | | Vcorr < 100 μV | Untreated: −1.55 V, 1.5 × 10⁻⁵ A/cm² | |
| DC 0.05 A cm⁻², 15 min | | | 0 g/L: −1.39 V, 3.5 × 10⁻⁶ A/cm² | |
| | | | 0.3 g/L: −1.37 V, 1 × 10⁻⁶ A/cm² | |
| | | | 3 g/L: −1.41 V, 7 × 10⁻⁶ A/cm² | |
| Inorganic | K₂SnO₃ 0.1, 0.2, 0.5 M | | PDP/dib in DI384-87 ASTM water | [132] |
| AZ91D KOH, KF, Na₂PO₄ | | Vcorr < 65 V | 148 ppm Na₂SiO₃, 138 ppm NaHCO₃, 165 ppm NaCl (Ecorr) | |
| DC 10 mA cm⁻², 10 min | | 0.8–2.9 at.% Sn, MgSi(OH)₄ | Untreated: −1.4 V | |
| | | | 0–0.5 M: −1.55 to −1.6 V | |
| NaN₂WO₄ 2, 4, 6, 8 g/L | | 1 μm (0.3 g/L), 40 μm (3 g/L) | Immersion in 3.5 wt.% NaCl for 24 h | [189] |
| AZ91HP NaOH, phytic acid | | Vcorr < 4.6–5.5 μm | untreated: −1.45 V | |
| Constant current density | | | 0 g/L: one small corrosion pit | |
| 40 mA/cm², frequency | | | 8 g/L: four corrosion pits, largest pit | |
| 2000 Hz, duty cycle 20% | | | 8 mm × 6 mm | |
| 30 °C, 3 min | | | | |
| CoSO₄ 0.2, 0.4, 0.6, 0.8 g/L | | 8 μm | PDP in 3.5 wt.% NaCl (Ecorr; corr) | [190] |
| AZ91B Na₂SiO₃, NaOH, NaF, KNa₃Cu₄Cl₄·H₂O, C₆H₅O₂ | | MgO, MgSiO₃, SiO₂, -1 at.% Co | 0.4 g/L: one small corrosion pit | |
| DC pulsed: 100 Hz, duty cycle 20%, | | | 8 g/L: four corrosion pits, largest pit | |
| 5 A dm⁻², 30 °C, 30 min | | | 8 mm × 6 mm | |
| | | | (2000 cycles) | |
| Ce(NO₃)₃ 0.1 g/L | | 13.2 μm (0 g/L), 11.9 μm (Ce) | PDP in 3.5 wt.% NaCl (Ecorr; corr) | [174] |
| La(NO₃)₃ 0.1 g/L | | Vcorr < 325 V (La > Ce > | Untreated: −1.45 V | |
| | | 0 g/L) | 3.69 × 10⁻³ A/cm² | |
| | | | 0.4 g/L: 6.82 × 10⁻³ A/cm² | |
| | | | 0.6 g/L: 7.09 × 10⁻³ A/cm² | |
| | | | 0.9 g/L: 7.17 × 10⁻³ A/cm² | |
| K₂ZrF₆ 5,10,15 g/L | | 5–8 μm | PDP in 3.5 wt.% NaCl (Ecorr; corr) | [184] |
| AZ91D Na₂SiO₃, NaF, NH₄H₂PO₄, C₆H₅O₂Na, AC 300 V, 480 Hz, duty cycle | | MgO, MgF₂, t-ZrO₂, MgSiO₃ | 0 g/L: −1.503 V, 6.37 × 10⁻³ A/cm² | |
| 30% 45 °C, 10 min | | and amorphous phosphate | 5 g/L: −1.407 V, 9.79 × 10⁻³ A/cm² | |
| | | self-sealing effect | 10 g/L: −1.483 V, 6.71 × 10⁻² A/cm² | |
| | | | 15 g/L: −1.421 V, 4.04 × 10⁻² A/cm² | |
### Table 4. Cont.

| Additive | Alloy/Electrolyte/Process Parameter | Effects | Corrosion Data | Ref. |
|----------|-------------------------------------|---------|----------------|------|
| K$_2$TiF$_5$ 0.2, 4, 8, 10, 12 g/L | AZ91D (NaPO$_4$)$_2$, NaOH, (HCO$_2$HCH$_2$)$_2$N, positive pulse voltages, different current densities (RMS) 3–10 A/dm$^2$, 200 Hz, duty cycle of 15%, 40 °C, 15 min | 20 μm (0 g/L), 52 μm (2.0 g/L), 39.8 μm (12.0 g/L) | ASTMB117, 240 h | [179] |
| Mixture of K$_2$ZrF$_6$, 0.035 M Y(NO$_3$)$_3$, 0.002 M | AZ91D NaAlO$_2$, KOH AC, anodic voltage 300 V, cathodic voltage −60 V, frequency 700 Hz, duty ratio 30%, 30 °C, 5 min | −11 μm Al$_2$O$_3$ – c-ZrO$_2$, t-ZrO$_2$, Y$_2$O$_3$, MgO, MgF$_2$, MgAl$_2$O$_4$ | PDP in 3.5 wt.% NaCl (E$_{corr}$, com) | [191] |
| borate potassium phthalate (KAP) 0–6.0 g/L | AZ91D NaOH Na$_2$B$_2$O$_4$ AC, 120 V, 50 Hz | MgO | PDP in 3.5 wt.% NaCl (E$_{corr}$, com) | [192] |
| calcium glycerophosphate (CaGly) | AZ31B Na$_2$SiO$_3$, KOH, Al$_2$O$_3$, Ni, Na$_2$EDTA, DC: 100 mA cm$^{-2}$, 200 V, 20 °C, 45 min | 1 μm, MgO measured with and without 25 μm-thick inhibitor-free epoxy primer | EIS in 0.5 wt.% NaCl (E$_{corr}$, com) | [193] |
| Nd(NO$_3$)$_3$ 20, 40, 60, 80, 100 mM as a pre-treatment | KBM10 Na$_2$SiO$_3$, KOH, Al$_2$O$_3$, NaF, AC, 350 V, 400 Hz, 15 min | 60 mM: −23 μm Nd(NO$_3$)$_3$ precipitates in the alkaline electrolyte used as an electrode | PDP in 3.5 wt.% NaCl (E$_{corr}$, com) | [194] |
| nickel acetate (NiAc) 0.5 g L$^{-1}$ | AZ63B Na$_2$SiO$_3$, Na$_2$B$_2$O$_4$, NaOH, TEA DC pulsed: 3 A dm$^{-2}$, 400 Hz, duty cycle 50%, 10–30 °C, 570 s | −35 μm MgO, Mg$_5$SiO$_3$, Mg$_2$SiO$_4$, Al$_2$O$_3$, SiO$_2$, Na$_2$SiO$_3$ | NSST 50 h, corroded area PEO: 26.3% | [195] |
| ethylene glycol oligomers EG10 g/L PEG400 10 g/L PEG2000 10 g/L | AZ11B NaOH Na$_2$SiO$_3$, Na$_2$B$_2$O$_4$, C$_2$H$_4$O$_2$Na$_2$ DC 10 mA cm$^{-2}$ | Thickness undisclosed V$_{end}$ < 130 V | PDP in 3.5 wt.% NaCl (E$_{corr}$, com) | [186] |
| Mg–5 mass % Li | Mg–5 mass % Li Na$_2$SiO$_3$, Na$_3$PO$_4$, NaF, NaOH constant current density 2 A dm$^{-2}$, pulse frequency of 300 Hz, duty cycle 45%, 5 min | V$_{end}$ < 9.5 μm (0.5 g/L) | PDP in 3.5 wt.% NaCl (E$_{corr}$, com) | [196] |
| EDTA 0.5 g/L | AZ31B Na$_2$SiO$_3$, KOH, glycerol DC 100 mA cm$^{-2}$, 10 min | Thickness undisclosed V$_{end}$ < 500 V | - | [66] |
Recently, a number of works have applied orthogonal experiment designs in order to evaluate the interaction of several electrolyte components, such as K$_2$ZrF$_6$ and EDTA-Na, with the electrical parameters. Both of these additives are being increasingly used in new PEO coating developments [205–208]; K$_2$ZrF$_6$ as a source of Zr, with the aim of forming ZrO$_2$ in the coating from particle-free electrolytes, and EDTA-Na as a complexing agent to stabilize cations of interest in the electrolyte [193]. K$_2$ZrF$_6$ is problematic on its own in terms of the surface passivation and coating growth that occur due to its acidity; however, it can successfully form self-sealing coatings when combined with other additives, such as phytic acid and ammonium fluoride [206].
One of the most notable improvements was obtained by the addition of \(\text{KMnO}_4\) (10^{-9} \text{A/cm}^2) (Figure 14) \cite{175} or EDTA (10^{-8} \text{A/cm}^2) into the electrolyte \cite{196}. 

Figure 14. Potentiodynamic polarization curves of coatings formed in electrolyte without (Bath 1) and with \(\text{KMnO}_4\) (Bath 2); (a) samples coated for 60 s; (b) samples coated for 120 s; (c) samples coated for 300 s \cite{175}. Reprinted from \cite{175} with permission from Elsevier.

Recently, a number of works have applied orthogonal experiment designs in order to evaluate the interaction of several electrolyte components, such as \(\text{K}_2\text{ZrF}_6\) and EDTA-Na, with the electrical parameters. Both of these additives are being increasingly used in new PEO coating developments \cite{205–208}; \(\text{K}_2\text{ZrF}_6\) as a source of Zr, with the aim of forming \(\text{ZrO}_2\) in the coating from particle-free electrolytes, and EDTA-Na as a complexing agent. 

Organic additives in the electrolyte typically decompose during PEO micro-discharge, leading to excessive gas generation and, as a result, a looser coating microstructure with compromised corrosion resistance. However, additives such as silanes, e.g., 3-aminopropyltrimethoxysilane (APTMMS), have been shown to increase the coating thickness and corrosion resistance due to the densification of the coating and the reduction of pore size associated with the formation of Mg-O-Si chemical bonds \cite{199}.
The introduction of N and C into the coating via plasma electrolytic nitrocarburizing (PENC) from formamide/NaOH aqueous electrolytes, where Mg acts as a cathode, followed by PEO in an alkaline silicate electrolyte is a new strategy that offers sustainable, high corrosion resistance of a Mg alloy due to the formation of a thick and extremely compact coating [200].

4.2.2. Particle Addition

New PEO coatings with added functionality are being investigated through the in situ incorporation of insoluble particles in the electrolyte (Figure 15). This approach modifies both the electrochemistry of the PEO process (e.g., conductivity, pH, breakdown voltage, etc.) and the coating characteristics (e.g., porosity, thickness, phase composition, compactness of the layer, etc.). The added particles bring new functionalities to the coating and can be introduced into the coating in an inert manner, without reaction or the formation of new phases, or by reactive or partially reactive incorporation, when a reaction between the particles and the coating matrix takes place [209].

![Figure 15. Overview of the insoluble particle types added in situ into the PEO electrolyte and their effect on the formed phases.](image)

Reactive incorporation includes one of the following: melting, phase transformation, and reaction with electrolyte constituents, substrate, or other phases in the coating. Crucially, the extent of these processes is dependent on many factors, such as the size, melting point, concentration, and the zeta potential of the added particles, the composition of the electrolyte, type of substrate, and energy input from the micro-discharges. Examples of particles that reactively incorporate into PEO coatings on Mg are Al₂O₃, ZrO₂, SiO₂, and clay particles [209].

The size of the suspended particles should be small enough, i.e., less than 500 nm, to prevent their sedimentation and to enable their easy transport into discharge channels. The zeta potential is an important parameter that characterizes the degree of electrostatic repulsion between the particles in the electrolyte; the more negative its value, the more uniform the dispersion of particles and the more homogeneous their distribution in the coating. Typically, in alkaline solutions, particles are negatively charged, which facilitates their electric field-assisted incorporation into the coating matrix. More information on the stabilization of particles in the electrolytes using organic additives (e.g., urea, sodium dodecyl sulfate) and the mechanisms of particle incorporation into PEO coatings on Mg alloys can be found in [210,211].
Many types of particles can be used to improve the corrosion resistance of PEO coatings on Mg alloys. One of the largest groups includes ceramic oxides such as ZrO$_2$ [53,212–217], CeO$_2$ [53,218–222], Y$_2$O$_3$ [223], Sb$_2$O$_3$ [224], TiO$_2$ [225,226], Al$_2$O$_3$ [227–229], SiO$_2$ [230–233], and clay [116,234]. Depending on the PEO parameters and thermodynamic stability of these ceramic oxides, they experience either inert [213,222,227,231] or reactive/partly reactive incorporation, resulting in the formation of new stable phases like Mg$_2$Zr$_2$O$_{12}$, Mg$_2$TiO$_4$, Mg$_2$SiO$_4$, or MgAl$_2$O$_4$ [212,219,220,225,228,230,231]. Improved corrosion performance can also be achieved by the addition of non-oxide particles such as SiC [234,235], TiC, NbC [236], WS$_2$ [237], MoS$_2$ [238], Si$_3$N$_4$ [234], and TiN [239–241].

Recently, a new range of particles came into focus. For instance, graphene oxide (GO) was successfully introduced into a PEO coating [242–244], reducing the number of micropores and improving the corrosion resistance due to the increased tortuosity of the electrolyte species diffusion pathway. Similarly, the addition of graphite [237,245,246], multi-walled carbon nanotubes (CNT) [247,248], or carbon spheres (CS) [249] into the electrolyte produced a coating densifying effect, thereby increasing the corrosion resistance while the CNT oxidized during PEO (new). However, the primary benefits of the incorporation of carbon-based particles are enhanced hardness, wear resistance, and heat dissipation [247–249]. Another innovative idea is the in situ incorporation of nanocantainers loaded with corrosion inhibitors (e.g., halloysite or aluminosilicate nanotubes loaded with benzotriazole, molybdate, or vanadate salts or 8-hydroxyquinoline) [250–252]. The inhibitor is released when the pH changes during the corrosion process, which confers self-healing properties upon the PEO coating. The effects of particle addition on the coating properties and corrosion resistance are summarized in Table 5.

### Table 5. Effect of in situ particle additives in PEO electrolytes on the structural and corrosive properties of the obtained coating.

| Particles          | Alloy Electrolyte Treatment Conditions | Thickness Phases Incorporation | Corrosion Data | Ref. |
|--------------------|----------------------------------------|--------------------------------|----------------|------|
| 9 g/L m- and t-ZrO$_2$, 200–400 nm | AZ91 KOH, KE, K$_2$CO$_3$, AC 50 mA/cm$^2$, 7 min | 10 µm MgO, t-ZrO$_2$, Mg$_2$(PO$_4$)$_2$ Inert | PDP in 3.5 wt.% NaCl ($E_{corr}$, $i_{corr}$) | [213] |
| 5 vol.% ZrO$_2$ sol | AZ91D Na$_2$SiO$_3$, KOH DCP$_{polo}$10 A/dm$^2$, 20 min, 200 Hz, 15% duty cycle | 36 to 40 µm (5 vol% ZrO$_2$) MgO, Mg$_2$SiO$_4$, Mg$_2$Zr$_2$O$_4$ Reactive | PDP$_{min}$ in 3.5 wt.% NaCl ($E_{corr}$, $i_{corr}$) | [212] |
| 5 g/L n-SiO$_2$:12 nm, µ-SiO$_2$:1–5 µm | AM50 Na$_2$CO$_3$, KOH DCP$_{polo}$450 V, 10 min, 250 Hz, 15% duty cycle | 145 ± 3, 33 ± 3 µm (µ-SiO$_2$), 25 ± 4 (n-SiO$_2$) Amorphous coating (n-SiO$_2$), Amorphous, MgO, SiO$_2$ (µ-SiO$_2$) Reactive (n-SiO$_2$) Inert (µ-SiO$_2$) | PDP$_{min}$ in 0.5 wt.% NaCl ($E_{corr}$, $i_{corr}$) | [231] |
| 1 vol.% silica sol | Mg-Li alloy Na$_2$SiO$_3$, NaOH DCP$_{polo}$5 A/dm$^2$, 10 min, 2000 Hz, 15% duty cycle | 35 µm MgO, SiO$_2$, Mg$_2$SiO$_4$ Partly reactive | PDP$_{min}$ in 0.5 wt.% NaCl ($E_{corr}$, $i_{corr}$) | [230] |
| 5 g/L clay 12 µm | AM50 KOH, Na$_2$PO$_4$ DCP$_{polo}$450 V, 10 min $i_{cor}$=0.3 A/cm$^2$, $t_{polo}$=2 ms, 10 µs, 10°C (1) $h$ = high, $m$ = medium, $s$ = standard concentration (2) $h$ = hydroxide, $p$ = phosphate | 43 ± 7 µm MgO, Mg$_2$(PO$_4$)$_2$, Mg$_2$SiO$_4$ mb-50 ± 8 µm MgO, Mg$_2$(PO$_4$)$_2$ (np-mp), Mg$_2$SiO$_4$ amorphous phase mp-43 ± 7 µm amorphous phase $s$-15 ± 5 µm MgO Reactive | PDP$_{min}$ in 0.5 wt.% NaCl ($E_{corr}$, $i_{corr}$) | [116] |
| Materials | Treatment Conditions | Corrosion Data | Ref. |
|-----------|---------------------|---------------|------|
| 2 vol.% alumina sol | NaAlO₂, KOH DC pulsed 15 mA/cm², 25 min | PDP < 0.02 μm in 3.5 wt.% NaCl (Ecorr: 0.02 V); 5 g/L: −1.575 V; 3.5 × 10⁻⁶ A/cm² 1–5 μm: −1.575 V; 3.5 × 10⁻⁶ A/cm² | [241] |
| 10 g/L Al₂O₃ 500 nm | NaSiO₃, NaOH, ethylene diamine tetra acetic acid, polymeric surfactant DC 15 mA/cm², 20 min | PDP < 0.02 μm in 3.5 wt.% NaCl (Ecorr: 0.02 V); 5 g/L: −1.575 V; 3.5 × 10⁻⁶ A/cm² 1–5 μm: −1.575 V; 3.5 × 10⁻⁶ A/cm² | [227] |
| 4 vol.% TiO₂ | AM60B NaAlO₂, KOH DC pulsed A/dm², 26–30 min, 150 Hz, 37.5% duty cycle | PDP < 0.02 μm in 3.5 wt.% NaCl (Ecorr: 0.02 V); 5 g/L: −1.575 V; 3.5 × 10⁻⁶ A/cm² 4 vol.%: −1.51 V; 4.3 × 10⁻⁶ A/cm² | [226] |
| 2, 4, 6 g/L TiO₂ nanoparticles | AZ91D (NaPO₄)₃, NaOH DC pulsed 3 A/dm², 15 min, 200 Hz, 15% duty ratio | PDP < 0.02 μm in 3.5 wt.% NaCl (Ecorr: 0.02 V); 5 g/L: −1.575 V; 3.5 × 10⁻⁶ A/cm² | [220] |
| 10, 20, 30 g/L CeO₂ | AZ31 NaSiO₃, KF DC pulsed 5 A/dm², 10 min, 100 Hz, 6% duty cycle | PDP < 0.02 μm in 3.5 wt.% NaCl (Ecorr: 0.02 V); 5 g/L: −1.575 V; 3.5 × 10⁻⁶ A/cm² | [223] |
| 1 g/L CeO₂ | AZ31 NaOH DC pulsed 4 A dm⁻², 100 Hz, duty cycle 30% 20°C, 30 min. | PDP < 0.02 μm in 3.5 wt.% NaCl (Ecorr: 0.02 V); 5 g/L: −1.575 V; 3.5 × 10⁻⁶ A/cm² | [224] |
| 0, 1, 3, 5 g/L | NaSiO₃, KOH, NaPO₄, glycerol, Y₂O₃ Bipolar pulsed: +500–−30 V, 800 Hz, duty cycle 10%, duty ratio 1:1, 20 min | PDP < 0.02 μm in 3.5 wt.% NaCl (Ecorr: 0.02 V); 5 g/L: −1.575 V; 3.5 × 10⁻⁶ A/cm² | [225] |
| 0, 2, 4, 6, 8 g/L Sb₂O₃ | DC pulsed 4 A dm⁻², 100 Hz, duty cycle 30% 20°C, 30 min. | PDP < 0.02 μm in 3.5 wt.% NaCl (Ecorr: 0.02 V); 5 g/L: −1.575 V; 3.5 × 10⁻⁶ A/cm² | [226] |
| 2 g/L SIC | NaSiO₃ (NaPO₄)₃ DC pulsed 1000 Hz, 20 min, 10% duty cycle, 40°C Higher positive/negative current densities (HC) −0.22/0.09 A cm⁻² Lower positive/negative current densities (LC) −0.13/0.03 A cm⁻² | HC-SiC 126 μm, HC 121 μm, LC-SiC 88 μm, LC 76 μm Mg₂SiO₄, MgO, SiC | [235] |
| 5 g/L Sn₃N₄ | AM50 NaAlO₂, KOH DC pulsed 450 V, 10 min, 50 Hz, 10% duty cycle | (0.02 μm) 40 μm (0.1–0.8 μm) 25 μm (1–5 μm) 10 μm MgO, Si₃N₄, Mg₃(PO₄)₂ | PDP < 0.02 μm in 3.5 wt.% NaCl (Ecorr: 0.02 V); 5 g/L: −1.60 V; 2.96 × 10⁻⁶ A/cm² | [241] |
| 1, 2, 3, 4 g/L Sn₃N₄ | K₂PO₄, NaAlO₂ dispersant alcohol and surfactant SDS DC pulsed 83.3 mA/cm², 475 Vmax, 10 min, 1000 Hz, 50% duty cycle | 13.1 μm (0 g/L), 17.8 μm (3 g/L), 16.8 μm (4 g/L) MgAl₂O₄, MgO, Mg₃SiO₄ | PDP < 0.02 μm in 3.5 wt.% NaCl (Ecorr: 0.02 V); 5 g/L: −1.575 V; 3.5 × 10⁻⁶ A/cm² | [239] |
Based on the results in Table 5, it can be concluded that the incorporation of in situ particles is a very promising way to improve the anti-corrosion properties of PEO coatings. In almost all studies, the corrosion current density decreased compared with the particle-free PEO coatings fabricated under the same conditions. The lowest values were obtained for treatments with the addition of zirconia sol \((1.4 \times 10^{-8} \text{ A/cm}^2)\) \([212]\), clay \((2.3 \times 10^{-8} \text{ A/cm}^2)\) \([116]\), and alumina sol \((2.6 \times 10^{-8} \text{ A/cm}^2)\) \([228]\). Comparing these values with those shown in Table 4, it is evident that the addition of particles can be more effective than the use of soluble electrolyte additives.

However, the testing period appears to be important. Recently, it was reported that some particle-incorporated coatings provide only a short-term increase in corrosion resistance; longer testing times often reveal the opposite effect, with faster relative degradation \([209,234,253]\). Additionally, as observed with other electrolyte constituents, particles are only effective up to a certain concentration, usually below 20 g/L, beyond which their positive effect on corrosion resistance declines \([239,242]\). Their effect on coating thickness is variable and not correlated with corrosion resistance. This notwithstanding, particle-modified coatings are good for additional functionalities, such as, for instance, wear resistance \([254]\).

### 4.2.3. Organic Electrolytes

Anodizing Mg alloys in non-aqueous electrolytes is an alternative route that has been actively explored in the last ten years \([255–261]\). Compared to aqueous anodizing, it avoids water decomposition, decreases Mg dissolution during anodizing, and opens a window for the development of defect-free anodic films. Ethylene glycol, triethanolamine, and glycerol are often used as base electrolytes which may also contain fluoride anions and a small percentage of water. Depending on the source of fluoride ions (HF, NH₄F, etc.) and

| Particles | Alloy Electrolyte Treatment Conditions | Thickness Phases Incorporation | Corrosion Data | Ref. |
|-----------|--------------------------------------|-------------------------------|---------------|-----|
| MA8       | NaF, Na₂SiO₃, sodium dodecylsulphate 1 step: DC, 0.5 A/cm², 300 Hz, 50% duty cycle, constant potential cathodic pulse (−30 V), 200 s, reached voltage 300 V 2 step: voltage dynamically reduced to 200 V, cathodic pulse reduced to (−10 V), 600 s | ~20 µm MgO, Mg₂SiO₄, TiN Inert | PDP in 3 wt.% NaCl \(E_{corr} \pm \Delta E_{corr}\) 0 g/L: −1.37 V; 1.2 × 10⁻⁷ A/cm² 1 g/L: −1.44 V; 1.4 × 10⁻⁷ A/cm² 2 g/L: −1.45 V; 1.6 × 10⁻⁷ A/cm² 3 g/L: −1.47 V; 1.8 × 10⁻⁷ A/cm² 4 g/L: −1.50 V; 7.9 × 10⁻⁷ A/cm² | [240] |
| 1, 2, 3 g/L TiN 20 nm | Na₂HPO₄, NaF, sodium citrate, glycerol, sodium dodecyl sulphate 1 step: Eₖ, 100 mA/cm², 20–30 °C, 1 min, 2 step graphene addition, constant voltage (400 V), 9 min | PEO 40.7 µm 1 g/L 3.5 µm 2 g/L 3.4 µm 3 g/L 3.67 µm MgO | PDP in 3 wt.% NaCl \(E_{corr} \pm \Delta E_{corr}\) Untreated: −1.48 V; 1.08 × 10⁻⁷ A/cm² 0 g/L: −1.49 V; 1.24 × 10⁻⁷ A/cm² 1 g/L: −1.47 V; 9.8 × 10⁻⁸ A/cm² 2 g/L: −1.44 V; 3.3 × 10⁻⁸ A/cm² 3 g/L: −1.41 V; 7.1 × 10⁻⁸ A/cm² | [242] |
| 1, 2, 3 g/L graphene oxide | Na₂HPO₄, NaF, sodium citrate, glycerol, sodium dodecyl sulphate 1 step: Eₖ, 100 mA/cm², 500 Hz, 10% duty cycle, 20–30 °C, 1 min, 2 step graphene addition, constant voltage (400 V), 9 min | PEO 40.7 µm 1 g/L 3.5 µm 2 g/L 3.4 µm 3 g/L 3.67 µm MgO | PDP in 3 wt.% NaCl \(E_{corr} \pm \Delta E_{corr}\) Untreated: −1.48 V; 1.08 × 10⁻⁷ A/cm² 0 g/L: −1.49 V; 1.24 × 10⁻⁷ A/cm² 1 g/L: −1.47 V; 9.8 × 10⁻⁸ A/cm² 2 g/L: −1.44 V; 3.3 × 10⁻⁸ A/cm² 3 g/L: −1.41 V; 7.1 × 10⁻⁸ A/cm² | [242] |
| 10 g/L halloysite nanotubes (HNT) or benzotriazole loaded HNT (BTA-HNT) 1–15 µm length 10–100 nm inner diameter | AM50 Na₂SiO₃, KOH, NaF DC, 40 mA/cm², 10 min, 100 Hz, 10% duty cycle | 0 g/L 30.1 µm HNT 29.5 µm BTA-HNT 36.2 µm Amorphous, Mg₂SiO₄, halloysite Inert | Potentiodynamic polarization is unsuitable because of dynamic processes on the polarized surface and in the electrolyte. BTA-HNT-PEO coating showed the smallest variation in |Z| during the 12 h of immersion, indicating the most stable corrosion resistance and protection to the substrate. | [250] |
| 2.5, 5, 10 g/L | Na₂SiO₃, KOH, KF DC 100 mA/cm², 10 min | 0 g/L 19.3 µm 2.5 g/L 14.2 µm 5 g/L 12.5 µm 10 g/L 8.0 µm MgO, Mg₂SiO₄ CNT oxidizes during PEO | PDP and EIS in 3 wt.% NaCl \(E_{corr} \pm \Delta E_{corr}\) \(|Z|_{impedance}\) 0 g/L: −1.49 V; 7.14 × 10⁻⁷ A/cm², 10⁷ Ωcm² 2.5 g/L: −1.45 V; 3.67 × 10⁻⁸ A/cm² 5 g/L: −1.47 V; 1.43 × 10⁻⁸ A/cm² 10 g/L: −1.38 V; 4.80 × 10⁻⁷ A/cm², 10⁷ Ωcm² | [247] |
the presence of water, barrier type [261] or self-organized nanoporous/nanotubular [260] films can be formed. For instance, ordered oxy-fluoride nanostructures (nanopores and nanotubes) with 70–100 nm pore diameter were formed in a WE43 Mg alloy by anodizing in ethyleneglycol and 0.2 M HF in the potential window between 70 and 120 V [260]. In another study, the effect of water content was explored regarding the transformation from a porous to a compact film morphology. In a solution of ethylene glycol and trimethylamine with 1% water, a porous structure (100 nm pore diameter) was formed, whereas a water content between 10% and 40% led to the formation of a barrier-type film. The latter showed better anticorrosion properties than the nanoporous films in a salt-spray test [259]. FTIR and GDOES results showed the incorporation of C, N, and O in the films and that the amount of incorporated species increased with decreasing water content.

It is worth mentioning that anodizing in organic electrolytes in the presence of fluoride ions helps to increase the efficiency of the process and increases the Pilling-Bedworth ratio up to ~1.7 [261] due to F-enrichment (~0.2 O/F ratio [258]), which is expected to be beneficial for corrosion protection. Efficiencies close to 100% are commonly reported for anodizing using these types of electrolytes (the lower the water content, the higher the current efficiency) [255].

Anodizing voltages can be as high as 440 V without dielectric breakdown [257], and the thickness of the coatings ranges from several hundreds of nanometers, in the case of barrier-type films (Figure 16), to several tens of micrometers in nanoporous/nanotubular films (Figure 16b) [256].

Qi et al. recently obtained a ~15 µm-thick PEO coating on AZ31B alloy in ethylene glycol-based electrolyte with 8 wt.% NH4F under pulsed bipolar conditions (Figure 17). The coating comprised pure MgF2 and had a gradient porosity reducing inward from 24.93% to 2.87%. The coating reduced the corrosion current density of the alloy in neutral and acidic (pH3.0) 3.5%NaCl by approximately two and one orders of magnitude, to ~5 × 10−7 A/cm² and to ~3 × 10−6 A/cm², respectively [262].

So far, studies on anodizing in organic electrolytes have been carried out using a range of commercial magnesium alloys (e.g., ZE41, WE43, AZ91D, Mg-Zn-RE, etc.). It has been observed that the second phases can be anodized and incorporated into the anodic films, locally affecting the film thickness and composition. However, there is a severe lack of applied and systematic studies of the film properties, energy efficiency, and corrosion behavior.
Sealing the pores provides long-term corrosion protection and can be achieved via different surface post-treatments, including immersion in solutions with inorganic and/or organic compounds [263–265], the application of sol-gels [266–269], electrophoretic deposition [270,271], electrodeposition [272], thermostetting polymers [273,274], and other top-coats [275–277]. These post-treatments can also be used with the aim of adding functionality to the surface, e.g., hydrophobicity, aesthetics, etc. [61].

Early approaches to seal the pores included immersion in hot KH$_2$PO$_4$ or Na$_2$SiO$_3$ solutions, with higher temperatures and longer treatment times resulting in enhanced corrosion performance [86,278]. The deposition of rare earth and molybdenum compounds is another effective and low-cost approach to block the pores and other defects in the anodic films. Chemical conversion treatments by immersion in aqueous solutions containing salts such as Na$_3$PO$_4$ [264], Ca(NO$_3$)$_2$ [279], (Ce(NO$_3$)$_3$ [280,281], La(NO$_3$)$_3$ [278], Na$_2$SnO$_3$ [282], NaNd(SO$_4$)$_2$ [283], or Na$_2$MoO$_4$ [284] rely on the redox reactions that take place on the surface, producing compounds such as Ca$_{10}$(PO$_4$)$_6$(OH)$_2$ [279], La(OH)$_3$ [278], CeO$_2$/Ce$_2$O$_3$ [280], MgSnO$_3$ [282], Nd$_2$O$_3$ [283], and MoO$_3$ [284]. An advantage of the process is that high temperature curing is not needed after sealing.

Another successful approach is the incorporation of corrosion inhibitors into the PEO pores by sample immersion in the inhibitor solution under low-pressure conditions. It has been proven that PEO pores, as a high capacity reservoir for corrosion inhibitors, can
provide long-term, active protection for Mg substrates [136]. For a deeper analysis of the corrosion inhibition mechanism using organic inhibitors added as a post-treatment, the reader is referred to Part III of this review [3]. The application of stable compounds such as SiO₂ [86], TiO₂ [285], and SiO₂-ZrO₂ [286] via sol-gel has also proved to be successful. The idea is to form a top barrier layer by covering the PEO surface and filling the micropores. Sol-gel coatings are not incorporated into the inner parts of the coating and rarely interact with the PEO coating material in an active way. Morphologically, sol-gel coatings are more uniform than conversion coatings produced by simple immersion, although cracking is likely to occur on their surface when thick multi-layers are produced. A typical practice in sol-gel treatments is to repeat the immersion/heat-treatment/drying sequence several times in order to obtain a coating that is thick enough to sufficiently cover the pores of the PEO layer [86,285–287].

Another novel approach consists of hydrothermal post-treatment, resulting in the formation of layered double hydroxides (LDH) [288]. LDHs, with a chemical formula $[\text{M}^{2+}_{1-x}\text{M}^{3+}_x(\text{OH})_2][\text{A}^{n-}_{1/n}\cdot z\text{H}_2\text{O}]$, are composed of positively charged brucite-like layers, containing both Mg²⁺ and Al³⁺, separated by regions containing anions and solvation molecules. LDH flakes can easily seal the pores of PEO coatings, but their greatest advantage is the possibility of loading their interlayer spaces with inhibitors which are released when triggered by chemical changes in the environment. This was first demonstrated on PEO-treated aluminum alloy, bringing about a remarkable increase in the corrosion resistance achieved through vanadate-intercalated LDH post-treatment [289].

The first directly grown LDH on PEO of Mg alloys without autoclave was achieved by Petrova et al. [290]. Currently, LDH post-treatment is being successfully exploited for the fabrication of composite PEO/inhibitor-loaded LDH coatings on Mg alloys in an increasing number of works [291–297]. Chen et al. investigated PEO/LDH systems with a variety of cations in the LDH layer, such as Ni-LDH, Zn-LDH, Al-LDH, and MgFe-LDH [294,295], of which Ni-LDH was found to form a continuous LDH layer over the PEO surface and produce an order of magnitude increase in total impedance (up to $5 \times 10^5$ $\Omega \text{cm}^2$) compared with a stand-alone PEO coating. It was also shown that PEO coatings modified with composite Zn-Al LDH with reduced graphene oxide (rGO) nanosheets could effectively enhance corrosion resistance and reduce $i_{\text{corr}}$ to 5 nA/cm² [298]. Alternatively, in contrast to the direct synthesis method, LDH nanocontainers can be in situ incorporated into PEO coatings [299] or can be formed as a secondary reaction product of the primary deposited MnOOH film, spontaneously reacting with the corrosion-produced Mg²⁺ and OH⁻ [300]. Apart from the sealing effect of the LDH layer that improves the barrier properties of the PEO coating, the abilities to exchange the anionic inhibitors between its hydroxide layers and release them “on demand” offer active corrosion protection. More details on the active inhibition properties of LDH are provided in Part III of this review [3].

Superhydrophobic composite coatings have been fabricated on magnesium alloys by combining micro-arc oxidation (MAO) with post-treatments such as cyclic assembly in phytic acid and Ce(NO₃)₃ solution [301], stearic acid ethanol solution [302], alkynol inhibitor loading followed by hydrophobic wax application [303], hydrothermal treatment in boiling water followed by self-assembled monolayer formation in perfluorodecylchlorosilane (FDTS) [304], LDH treatment followed by perfluorodecytriethoxysilane (PFDS) and perfluoropolyether (PFPE) lubricant infusion to form so-called slippery liquid-infused porous surface (SLIPS) [305], with some of these approaches maintaining remarkably high corrosion resistance for up to 21 days (Table 6). The application of fluorocarbons, such as polytetrafluoroethylene and fluoroparaffines [306–309], produced changes in impedance modulus and corrosion current density of up to two orders of magnitude (increase and decrease, respectively) and contact angles of 130°–152°.

The application of polymeric compounds, which infiltrate the coating pores, is a common practice for anodized Mg components [310]. Research on this topic has gone in several directions, including silanes [274,311] and E-coatings [312–314]. For instance, silane treatment KH550 has been shown to enhance the corrosion resistance of a magnesium alloy
with a silicate-based PEO coating [315]. E-coatings are widely applied in the automotive industry; they consist of the deposition of epoxy, epoxy polyester, or polyester resins by electrostatic powder spraying. For instance, AM60B alloy anodized at 70 V for 15 min in a strongly alkaline bath (KOH, Na\(_3\)PO\(_4\), KF, Al(NO\(_3\))\(_3\)), subjected to electrostatic powder spraying and curing (190 °C, 20 min), displayed no evidence of corrosion after salt spray testing for up to 595 h for a polyester paint [316]. Wierzbicka et al. reported that varied FPEO coatings covered with a three-component epoxy primer after a week of NSST were rated at up to 7 or 8 (out of a maximum of 10, according to the ASTM D 1654 standard) (Figure 18). These results are comparable with the rating of Cr(VI)-based commercial conversion coatings used in the aircraft industry [135]. The same authors demonstrated that FPEO coating loaded with 4-MSA inhibitor and coated with epoxy-based chromate-free primer with an active inhibition system based on lithium leaching technology outperformed a commercial Cr(VI)-based conversion coating with chromate-based primer after 1000 h of exposure in NSST (Figure 19) [136].

E-coating baths have also been shown to be suitable for the sealing of PEO coatings by a simple immersion process in an E-coating bath consisting of an epoxy resin and titanium dioxide [317].

![Figure 18. Salt spray testing results of Cr(VI)-based commercial coating and varied PEO covered with three-component epoxy primer, evaluated according to ASTM D 1654 standard [135].](image-url)
In [63], the mechanical and corrosion performance of a polymer-coated AZ31 magnesium alloy pre-treated by plasma electrolytic oxidation (PEO) was compared with that of a polymer coated fluorotitanate–zirconate conversion coating (Gardobond X4707) on the same alloy. The electrostatically sprayed polymer was composed of polyester resin (50 wt.%), triglycidyl isocyanurate, polypropylene wax (≤1 wt.%), inorganic pigments, and fillers (barium carbonate and barium sulfate). Tests showed that both coatings (PEO and conversion coating) passed the adhesion test (rating 0); however, the results of impact and impact + adhesion tests revealed better performance of the coating with Ti/Zr treatment (Figure 20).

Atmospheric corrosion tests, as per ASTM B117, and cyclic exposure to salt fog, as per VDA 621-415, revealed no damage either in the PEO or Ti/Zr treatments (Figure 21c,d). Greater differences were observed on scribed (ASTM D1654, procedure A) specimens, with the PEO + polymer coating showing a higher rating number, i.e., superior performance, than the Ti/Zr + polymer coating (Figure 21e,f). The superior anticorrosion properties of the PEO coating can be easily observed in Figure 22, which presents cross-sectional views of the studied samples after scribing and corrosion tests.
Other examples of polymer top coats enhancing the corrosion resistance of PEO coatings are multiple immersion in a titanium-based organic polymer [318] and sealing with hybrid epoxysilane [319], low-molecular weight polymers (e.g., MALPB, maleic anhydride-g-liquid polybutadiene) [320], and epoxy resins [321], which can be filled with inhibitor loaded nano- or micro-carriers, such as Ce\(^{3+}\) loaded zeolite microparticles [314] to ensure self-healing.

Post-treatment procedures and their effect on the PEO coating corrosion performance are presented in Table 6.

Based on the corrosion data, post-treatments are the most effective way to improve the corrosion resistance of anodic films on Mg alloys. Corrosion current density values in the order of \(10^{-9}\sim10^{-10}\) A cm\(^{-2}\) can be achieved [286,318]. The top coat not only seals the pores but also forms an additional layer that isolates the substrate from external aggressive factors. The thickness of top coats can be up to 130 µm [321]. Methods providing a self-healing effect, such as inhibitor loaded LDH nanocontainers, deserve special attention and should be explored in more detail, since they can actively protect Mg substrates during service by repairing small defects. Some disadvantages of post-treatments are the longer time...
required to obtain the final product and added cost of the high temperature drying/curing steps which are common in these processes.

**Figure 22.** BSE cross-sections of AZ31 specimens after exposure to ASTM B117 and VDA tests [63]. Reprinted from [63] with permission from Elsevier.
| Post-Treatment/Introduced Species | Alloy Electrolyte PEO Treatment Conditions | Post-Treatment | Thickness/Phases | Corrosion Data | Ref. |
|-----------------------------------|--------------------------------------------|----------------|-----------------|---------------|-----|
| Ce(NO$_3$)$_3$ (CeO$_2$, Ce$_2$O$_3$) | AM50 Na$_2$SiO$_3$, KOH AC square waveform 420 – 60 V, 500 Hz, 10 min, 10 °C Immersion Ce(NO$_3$)$_3$, 3 g/L, 20 min, 10 g/L, 20 min, 3 h H$_2$O$_2$, H$_3$BO$_3$, 30 °C | PEO 30–40 μm Post-treatment dissolution – 10–15 μm Mg$_2$SiO$_4$, MgO Ce$_2$O$_3$, Ce$_2$O$_3$ | ↑ Ce(NO$_3$)$_3$, ↑ $i_{	ext{corr}}$→ ↑ $R_{	ext{corr}}$ (EIS) | [280] |
| La(NO$_3$)$_3$ (La(ODP)) | AZ91 La$_2$O$_3$, NaOH, Na$_3$P$_2$O$_7$ DC 0.5 A/cm$^2$, 2 min Immersion 12 g/L La(NO$_3$)$_3$, 30, 40, 50 °C 10 or 30 min | PEO 30 μm | MgO, Mg$_2$PO$_4$, Mg$_2$SiO$_4$, La(ODP) | PDP in 0.1 M Na$_2$SO$_4$ 0.05 M NaCl (E$_{	ext{corr, bare}}$) Untreated: –1.88 V; $2 \times 10^{-5}$ A/cm$^2$ PEO: –1.87 V; 1.5 × 10$^{-5}$ A/cm$^2$ La 30 °C 10 min: –1.73 V; 8 × 10$^{-7}$ A/cm$^2$ La 30 °C 30 min: –1.83 V; 4 × 10$^{-7}$ A/cm$^2$ La 40 °C 10 min: –1.82 V, 5 × 10$^{-7}$ A/cm$^2$ La 40 °C 30 min: –1.69 V; 2.8 × 10$^{-7}$ A/cm$^2$ La 50 °C 10 min: –1.73 V, 9 × 10$^{-7}$ A/cm$^2$ La 50 °C 30 min: –1.65 V; 2.8 × 10$^{-7}$ A/cm$^2$ | [278] |
| Na$_2$MoO$_4$ (MoO$_3$) | Mg-Li Na$_2$SiO$_3$, NaOH, trehalose DC$_{sust}$5 A/dm$^2$, 2000 Hz, 15% duty cycle,10 min Immersion 20 g/L Na$_2$MoO$_4$, 4 g/L NaF, 30 wt.% H$_2$O$_2$, 50 °C, 2 h | PEO and PEO-Mo 25 μm Na$_2$MoF$_4$, Mg$_2$SiO$_4$, MgO, MoO$_3$ | PDP$_{sust}$ in 3.5 wt.% NaCl (E$_{	ext{corr, bare}}$) Untreated: –1.685 V; $7.45 \times 10^{-4}$ A/cm$^2$ PEO: –1.446 V; $6.4 \times 10^{-7}$ A/cm$^2$ PEO-Mo: –1.354 V; $2.5 \times 10^{-7}$ A/cm$^2$ | [284] |
| Ce(NO$_3$)$_3$, Na$_2$SnO$_3$, Octadecylphosphonic acid (ODP) | AZ91D Na$_2$SiO$_3$, KOH, NaF AC 240 V/60 V, 500 Hz 200 mA cm$^{-2}$, 200 s Immersion Ce(NO$_3$)$_3$, 180 min 30 °C, Na$_2$SnO$_3$, 30 min 80 °C, 0.1672 g L$^{-1}$ ODP in ethanol 24 h 23 °C | 13 μm | | | [264] |
| Self-healing 8-hydroxyquinoline (8 HQ) | MA8 Na$_3$SiO$_3$, NaF bipolar pulses, anodic voltage 30 to 300 V, rate 0.45 V/s, cathodic pulse potentiostatic 30 V, 50% duty cycle, 300 Hz, 10 min, 25 °C Immersion 3 g/L 8HQ (8-hydroxyquinoline $C_8H_7(NO_2)$) 120 min dried 140 °C, 20 min | 16 μm | | | [265] |
| Self-healing NH$_4$NO$_3$ (LDH) | AZ31 Na$_3$SiO$_3$, KOH, KF DC$_{sust}$0.3 A/cm$^2$, 800 Hz, 10% duty cycle, $V_{\text{corr}}$ and 360 V. Immersion 0.02 M NH$_4$NO$_3$ (pH 12.8) 120 °C for 12 h | PEO 6.5 μm PEO-LDH 7 μm Mg$_2$SiO$_4$, Mg(OH)$_2$, LDH (Mg-Al LDH) | PDP$_{40}$, in phosphate buffer saline PBS 37 °C (E$_{	ext{corr, bare}}$) Untreated: –1.45 V; 1.66 × 10$^{-5}$ A/cm$^2$ LDH: –1.12 V; 3.34 × 10$^{-5}$ A/cm$^2$ PEO: –1.22 V; 9.45 × 10$^{-6}$ A/cm$^2$ PEO-LDH: –1.2 V; 3.92 × 10$^{-6}$ A/cm$^2$ | [288] |
| Inhibitors Ce(NO$_3$)$_3$, Ce$^{3+}$ ions or 8-hydroxyquinoline (8HQ) Sol-gel TiO$_2$ + silane-based alkoxil | ZK30 NaOH, Al(OH)$_3$, Na$_3$PO$_4$, KF DC 125 mA/cm$^2$, 70 V, 10 min | 0.005 M Ce(NO$_3$)$_3$ or 0.005 M (8-hydroxyquinoline $C_8H_7(NO_2)$) 30 min Sol-gel dip-coating TiO$_2$, (3-glycidoxypropyl)trimethoxysilane (GPTMS) 1:2 vol., 100 s, cured 120 °C, 80 min | anodized film 0.7–3.0 μm sol-gel 3–4 μm | | [323] |
| Inhibitor 1,2,4-triazole, Sol-gel TiO$_2$ + silane-based sols (GPTMS)+ (PTMS) | ZE41 Na$_2$SO$_4$, KF, NaOH poly(ethylene oxide), DC 3 mA cm$^{-2}$, 12 min, 20 ± 2 °C Immersion 0.01 M 1,2,4-triazole, 15 s Sol-gel dip-coating TiO$_2$, (3-glycidoxypropyl)trimethoxysilane (GPTMS), phenyltrimethoxysilane (PTMS), 40 s suspended at room temperature, relative humidity 60% in open air, 1 h cured 120 °C,1.5 h | anodized film 1.8 ± 0.1 μm sol-gel 6.3 ± 0.2 μm | | | [324] |

**Table 6.** PEO process parameters with post-treatment procedures and their effect on corrosion performance.
Table 6. Cont.

| Post-Treatment/Introduced Species | Alloy Electrolyte PEO Treatment Conditions | Post-Treatment | Thickness/Phases | Corrosion Data | Ref. |
|-----------------------------------|------------------------------------------|---------------|------------------|----------------|-----|
| KMH PO₄ (P) Na₂SiO₃ (Si) sol-gel SiO₂ | AM 50B KOH, NaAlO₂, K₃PO₄ DC 20–30 A/cm² 7 or 14 min | Immersion 12% KH₂PO₄ (P) 60 °C, 5 min Immersion 5% Na₂SiO₃ (Si) 95 °C, 15 min Sol-gel sealing 14 mL tetra-ethylortho-silicate (TEOS), 2 wt.% Methyl-tetra-hydro-silane (MTES), 1.2 mL ethanol, 2.5 mL H₂O, 0.35 mL HCl, 1 min, annealing 160 °C, 3 h | 10 or 25 μm MgO, MgAl₂O₄ | PEO in 3.5 wt.% NaCl (Ecorr; icorr) AM 50B Untreated: −1.55 V; 1.2 × 10⁻⁹ A/cm² 10 μm PEO: −1.52 V; 1.45 × 10⁻⁷ A/cm² 25 μm PEO: −1.47 V; 1.65 × 10⁻⁷ A/cm² PEO-P: −1.62 V; 2.6 × 10⁻⁹ A/cm² PEO-Si: −1.45 V; 2.4 × 10⁻⁹ A/cm² PEO-SiO₂: −1.39 V; 6.57 × 10⁻⁹ A/cm² AM 60B Untreated: −1.55 V; 8.2 × 10⁻⁹ A/cm² 10 μm PEO: −1.51 V; 1.40 × 10⁻⁷ A/cm² 25 μm PEO: −1.56 V; 1.51 × 10⁻⁷ A/cm² PEO-P: −1.67 V; 3.2 × 10⁻⁹ A/cm² PEO-Si: −1.49 V; 2.2 × 10⁻⁹ A/cm² PEO-SiO₂: −1.44 V; 1.2 × 10⁻⁹ A/cm² | [86] |
| sol-gel TiO₂ | AZ 91D NaAlO₂ KOH DC 25 mA/cm² 25 min, 25–30 °C | Sol-gel sealing tetra-n-butyl orthotitanate (TBT), ethanol, ethyl acetate, 1 min, x 3 repeated heated 150 and 350 °C, 1 h | PEO 4 μm TiO₂ | PEO in 3.5 wt.% NaCl (Ecorr; icorr) Untreated: −1.509 V; 2.352 × 10⁻⁹ A/cm² PEO: −1.479 V; 1.607 × 10⁻⁹ A/cm² PEO-TiO₂ (150 °C): −1.316 V; 7.96 × 10⁻⁹ A/cm² PEO-TiO₂ (350 °C): −1.261 V; 4.383 × 10⁻⁹ A/cm² | [285] |
| sol-gel SiO₂-ZrO₂ | AZ 91D NaAlO₂, NaOH, small quantity of Montmorillonite and acacia gum pulsed voltage, increased to 180–200 V, then 0.5 h | Sol-gel sealing stoichiometric amounts of ethyl silicate, zirconyl chloride octahydrate, 1 min drying 150 °C, 1 h | Sol-gel layer 5 μm | PEO in 3.5 wt.% NaCl (Ecorr; icorr) Untreated: −1.428 V; 3.95 × 10⁻⁹ A/cm² PEO: −1.326 V; 9.39 × 10⁻¹ A/cm² PEO-SiO₂-ZrO₂: −0.406 V; 1.577 × 10⁻⁹ A/cm² | [286] |
| Inhibitor loaded and sol-gel sealed | AZ 91 | Na₃PO₄ KOH DC pulsed: tcorr = 19, 250 Hz, 40 mA cm⁻², 60 s | Inhibitors: Na glycoclate (Gly), Na 4-amino-salicylate (4AmSal), Na 2-pyridinedicarboxylate (PDC), Sol-gel: (3-glycidoxypropyl)-trimethoxysilane (GPTMS) and Ti(N) propoxide (TPTO) | 2.5 μm PEO + 2.5 μm sol-gel | EIS in 0.5 wt.% NaCl (1Z |corr|), 2 h/336 h PEO-Gly-SG: 10⁶ Ωcm²/10³ Ωcm² PEO-4AmSal-SG: 10⁵ Ωcm²/10⁴ Ωcm² PEO-4AmSal-SG: 10⁴ Ωcm²/2 × 10³ Ωcm² PEO-PDC-SG: 10³ Ωcm²/3 × 10² Ωcm² | [325] |
| Inhibitor loaded halloysite nanotubes (HNT) | AZ 91 | Na₃PO₄ KOH, NaF Pulsed DC: 500 Hz, 10% duty cycles, 40 mA cm⁻², 10 min | Immersion: 10 min in an aqueous solution 20 g L⁻¹ of inhibitor loaded HNTs, 22 °C. Inhibitors: 8-hydroxyquinoline (8HQ), ammonium molybdate (MoO₃), ammonium hexametavanadate (V). | 30 μm PEO MgO, MgSiO₄ | LEIS in 0.05 M NaCl up to 34.1 h over 300 × 2000 μm and 250 × 500 μm artificial defects All PEO-HNT-inhibitor coatings provided self-healing of small defects, only PEO-HNT-V partially restored large defect. | [252] |
| Self-healing | AZ 31 | Na₃PO₄ KOH, NaF AC: 100 Hz, +250 V / −50 V, 26% duty cycle, 600 s | Ce-conversion coating: 50 °C, 2 h, LDH: NaNO₃ 125 °C, 12 h, Phytic acid immersion: pH11, 80 °C, 1 h | PEO-Ce 1.2 μm PEO-Ce-LDH 2.7 μm PEO-Ce-LDH-P 2.5 μm | EIS in 3.5 wt.% NaCl (1Z |corr|), 30 min: 10³ Ωcm² 7 days: 2 × 10⁸ Ωcm² 21 days: 10⁵ Ωcm² | [292] |
| Superhydrophobic | AZ 31 | Na₃PO₄ KOH, NaF DC: 100 mA cm⁻² 10 min | Hydrophobization with FDT and oil impregnation by solvent exchange with Krytox GPL 103 | ~20 μm Wettability | EIS in 3.5 wt.% NaCl (1Z |corr|), 0/15 days PEO-HDT-FDTS: 5 × 10⁸ Ωcm²/2 × 10⁷ Ωcm² PEO-HDT-FDTS-oil: const. × 10⁶ Ωcm² | [304] |
Table 6. Cont.

| Post-Treatment/Introduced Species | Alloy Electrolyte PEO Treatment Conditions | Post-Treatment | Thickness/Phases | Corrosion Data | Ref. |
|-----------------------------------|--------------------------------------------|----------------|-----------------|----------------|-----|
| Superhydrophobic PEO-LDH-SLIPS    | AZ91D Na2SiO3, NaOH Pulsed DC 30 mA cm⁻², 100 Hz, duty cycle 10%, 300 s | +Mo-intercalated Mg-Al-LDH, 120 °C, 8–48 h + PFDS + PFPE | ~9 µm 121° wettability | EIS in 3.5 wt.% NaCl (1 Zi métal) 0 days: 2 × 10⁶ Ω cm² 18 days: 2 × 10⁵ Ω cm² Water repellence, active protection by CT and MoCl₅²⁻ exchange, regeneration of barrier layer | [305] |
| Silane coupling agent (SCA)       | [36x779] 99.9% Mg silicate electrolyte 300 V, 500 Hz, 2.5% duty cycle, 10 min, ultrasonic frequency 60 kHz | Immersion NaOH (1, 2, 3 mol/L), 60 °C, 1 h Immersion silane coupling agent (SCA) KH550 C₃H₆O₃, H₂O 1:1 vol. heated | PEO-NaOH(1M)-SCA: −1.488 V; 2.73 × 10⁻³ A/cm² PEO-NaOH(2M)-SCA: −1.464 V; 8.927 × 10⁻⁴ A/cm² PEO-NaOH(3M)-SCA: −1.442 V; 2.383 × 10⁻⁴ A/cm² | | [315] |
| E-coating electrolux             | [36x779] E-coating bath solution (water 71–82 wt.%, epoxy resin 16–26 wt.%, TiO₂ 1.3 wt.%), 10 s, baked 171 °C, 35 min | PEO 20 µm | PEO 20 µm | PEO in 5 wt.% NaCl (Ecorr; icorr) | [317] |
| Titanium organic polymer (TOP)  | AZ91D Na2SiO3, KOH DCpulsed, 360–400 V, 1–2 h | Immersion organic polymer (TOP), solvent 1:20, applied vacuum, 1 min, 50 °C, 30 min × 2, 3 repeated | PEO 20 µm sealing layer 3–5 µm | PEO in 3.5 wt.% NaCl (Ecorr; icorr) Untreated: −1.574 V; 3.176 × 10⁻³ A/cm² PEO: −1.555 V; 2.962 × 10⁻³ A/cm² PEO-TOP: −1.119 V; 4.107 × 10⁻⁴ A/cm² | [318] |
| Epoxy-silane (ES)               | AZ91D Na2SiO3, KOH, 7.5 g/L poly(ethylene oxide) DC 3 mA/cm², 9 min, 20 °C | Immersion silane (0.14 M), epoxy (0.98 M), DETA amine (0.37 M), ethanol, and acetone × 4 repeated, baked 150 °C, 1.5 h | PEO 1.8 µm PEO-ES 10 µm | PEO in 0.5 M NaCl (Ecorr; icorr) Untreated vs. PEO: Ecorr by 2–4 orders of magnitude Immersion in 0.6 M NaCl for 31 days Untreated: filiform corrosion, multiple pits, most commonly located at the edge PEO-ES: no signs of corrosion onset nor any indication of coating delamination | [319] |
| Polymer (MALPB)                  | AZ31B KOH, Na3PO4·8H₂O, Al(NO3)₃ DC 5 mA/cm² up to 80 V 30 min, 30 °C | Immersion Maleic anhydride-g-poly(1,2-butadiene) polymer (MALPB) Mn = 1020 1 min cured 30 to 180 °C (10 °C/min) 15 min | PEO 3.5 µm, MALPB 10 µm | PEO in 3.5 wt.% NaCl (Ecorr; icorr) MALPB: −1.35 V PEO: −1.48 V | [320] |
| Epoxy resin Ni-P                 | AZ31 Na2SiO3, KOH, 600 V, 600 Hz, 10% duty cycle, 20 °C, 10 min | Immersion commercial epoxy resin (24 h drying) Pretreatment: NaOH, 75 °C, 40 min -silane solution, 20 °C, 3 min, -cured 100 °C, 30 min, -PdCl₂, HCl, 20 °C, 1 min -NaH₂PO₄, 20 °C, 10 min Electroless Ni-P plating (25 g/L Na₂SiO₃, 6H₂O, 25 g/L NaH₂PO₄·H₂O), 20 g/L, Na₂C₂H₃O₂·2H₂O, 24 g/L NH₄F, 3 mg/L Cs(NH₄)₂, 75 °C 20 min | Ni-P 5 µm polymer 130 µm PEO 8 µm | PEO in 3.5 wt.% NaCl (Ecorr; icorr) PEO-MALPB: −1.19 V NSEF-scratch test 50 g/L NaCl, 1–2 mL/h, 200, 400 h corrosion PEO-MALPB < MALPB PEO-MALPB almost unchanged after 200 h, smaller spoiled dots after 400 h | [321] |
chromate-based conversion layer coated with an organic chromate-based primer. The fault
tolerance of the composite coating is the result of the cumulative performance of all its
components, i.e.,: i) the anodic film, which provides barrier protection and serves as the
repository for ii) corrosion inhibitors that ensure active corrosion suppression; and iii) an
organic coating that enhances the protective properties of the barrier, seals the porous
anodic layer with inhibitors, and enhances the active corrosion inhibition due to its ability
to inhibit the action of corrosive agents [136,326].

Further development can be expected of each element of such combined protection
systems, which may also focus on coating multifunctionalization, such as abrasion, wear,
thermal resistance, biocidal effect, superhydrophobicity, self-cleaning, etc. For anodic layers
in particular, there is a large scope of future work to further minimize energy consumption.
In these regards, organic electrolytes, as well as more concentrated alkaline electrolytes,
should be explored to bring the coating formation voltage to below 150–200 V and limit the
treatment times to under 60 s. Appropriate recycling strategies will have to be considered
for such electrolytes in order to achieve sustainability and successful integration into
the circular economy. For sealing strategies, trends such as PEO/LDH and PEO/sol-gel
combinations are showing great potential. LDH scaffolds can be easily loaded with smart
inhibitors, but two major challenges of this strategy remain: (i) optimization of the PEO
layer thickness and composition to facilitate the growth of LDH; and (ii) the search for
suitable, environmentally friendly inhibitors that can be loaded into LDH. Sol-gel layers,
on the other hand, can be loaded with smart nanocontainers, such as clay particles, multi-
walled CNT, and mesoporous silica [327]. With regard to the latter in particular, there is a
wealth of knowledge in the field of smart drug release for biomedical applications [9,328],
but this appears to be almost completely overlooked when it comes to corrosion-resistant
engineering applications. The adaptation of mesoporous silica to smart inhibitor release
and making it part of a hybrid coating system, e.g., within the LDH layer [329] or organic
top-coat [330], seem to be the next logical next steps. The paintability of such hybrid
coatings is largely unknown and may present challenges of its own, for instance, due to the
hydrophobic nature of some of the loaded inhibitors.

Last but not least, the rapid development of additive manufacturing technologies
for magnesium alloys [331–333] (which, until recently, has been lagging behind those for
other light alloy systems, such as aluminum and titanium, although this is a topic for a
separate discussion) will inevitably spur research in the field of corrosion protection by
anodic coatings, among other approaches. Such research is still in an embryonic state and
so far has been limited exclusively to biomedical applications [334,335].

**Author Contributions:** Conceptualization, E.W., E.M., R.A.; resources, M.Z., S.L., E.M., R.A.; data
curation, E.W., B.V., M.M., S.L., E.M., R.A.; writing—original draft preparation, E.W., B.V., M.M., PV,
R.P., C.B., M.Z., S.L., E.M., R.A.; writing—review and editing, E.W., B.V., M.M., PV, R.P., C.B., M.Z.,
S.L., E.M., R.A.; visualization, E.W., B.V., M.M., S.L., E.M., R.A.; supervision, E.W., S.L., E.M., R.A.;
project administration, S.L., E.M.; funding acquisition, S.L., E.M., R.A. All authors have read and
agreed to the published version of the manuscript.

**Funding:** The authors acknowledge the funding of Clean Sky 2 H2020 project ALMAGIC (Grant
Agreement Number 755515) and the support of the ADITIMAT-CM (S2018/NMT-4411, Regional Gov-
ernment of Madrid and EU Structural and Social Funds) and PID2021-124341OB-C22 (MICINN/AEI/
FEDER, UE) projects.

**Institutional Review Board Statement:** Not applicable.

**Informed Consent Statement:** Not applicable.

**Data Availability Statement:** Data sharing not applicable.

**Acknowledgments:** The authors would like to sincerely acknowledge Geralds Jordens for his con-
tribution to the preparation of this manuscript. Sadly, he passed away before the final version of this
review was completed.

**Conflicts of Interest:** The authors declare no conflict of interest.
57. Chen, J.; Wang, J.; Han, E.; Dong, J.; Ke, W. AC impedance spectroscopy study of the corrosion behavior of an AZ91 magnesium alloy in 0.1M sodium sulfate solution. Electrochim. Acta 2007, 52, 3299–3309. [CrossRef]

58. Liang, J.; Guo, B.; Tian, J.; Liu, H.; Zhou, J.; Liu, W.; Xu, T. Effects of NaAlO\textsubscript{2} on structure and corrosion resistance of microarc oxidation coatings formed on AM60B magnesium alloy in phosphate-KOH electrolyte. Surf. Coat. Technol. 2005, 199, 121–126. [CrossRef]

59. Kim, K. Formation of endogenous MgO and MgAl\textsubscript{2}O\textsubscript{4} particles and their possibility of acting as substrate for heterogeneous nucleation of aluminum grains. Surf. Interface Anal. 2015, 47, 429–438. [CrossRef]

60. Blawert, C.; Dietzel, W.; Ghali, E.; Song, G. Anodizing Treatments for Magnesium Alloys and Their Effect on Corrosion Resistance in Various Environments. Adv. Eng. Mater. 2006, 8, 511–533. [CrossRef]

61. Kaseem, M.; Fatimah, S.; Nashrah, N.; Ko, Y.G. Recent progress in surface modification of metals coated by plasma electrolytic oxidation: Principle, structure, and performance. Prog. Mater. Sci. 2021, 117, 107353. [CrossRef]

62. AlAbbasi, A.; Kannan, M.B.; Walter, R.; Stormer, M.; Blawert, C. Performance of pulsed constant current silicate-based PEO coating on pure magnesium in simulated body fluid. Mater. Lett. 2013, 106, 18–21. [CrossRef]

63. Arrabal, R.; Mota, J.M.; Criado, A.; Pardo, A.; Mohedano, M.; Matykina, E. Assessment of duplex coating combining plasma electrolytic oxidation and polymer layer on AZ31 magnesium alloy. Surf. Coat. Technol. 2012, 206, 4692–4703. [CrossRef]

64. Cai, Q.; Wang, L.; Wei, B.; Liu, Q. Electrochemical performance of microarc oxidation films formed on AZ91D magnesium alloy in silicate and phosphate electrolytes. Surf. Coat. Technol. 2006, 200, 3727–3733. [CrossRef]

65. Curran, J.A.; Clyne, T.W. The thermal conductivity of plasma electrolytic oxide coatings on aluminium and magnesium. Surf. Coat. Technol. 2005, 199, 177–183. [CrossRef]

66. Guo, H.; An, M. Effect of surfactants on surface morphology of ceramic coatings fabricated on magnesium alloys by micro-arc oxidation. Thin Solid Films. 2006, 500, 186–189. [CrossRef]

67. Vladimirov, B.V.; Krit, B.L.; Lyudin, V.B.; Morozova, N.V.; Rossiiskaya, A.D.; Suminov, I.V.; Epelfeld, A.V. Microarc oxidation of magnesium alloy in 0.1M sodium sulfate solution. Electrochim. Acta 2007, 52, 3299–3309. [CrossRef]

68. Buzzard, R.W.; Wilson, J.H. Anodic Coating of Magnesium Alloys. In J. Jpn. Inst. Light Met. 1992, 43, 65–70. [CrossRef]

69. Murakami, K.; Hino, M.; Kanadani, T. Anodization of Magnesium Alloys Using Phosphate Solution. In Magnesium Alloys—Corrosion and Surface Treatments; Czerwinski, F., Ed.; InTechOpen: London, UK, 2011.

70. Pommiers-Belin, S.; Frayret, J.; Uhart, A.; Ledeuil, J.; Dupin, J.-C.; Castetbon, A.; Potin-Gautier, M. Determination of the chemical mechanism of chromate conversion coating on magnesium alloys EV31A. Appl. Surf. Sci. 2014, 298, 199–207. [CrossRef]

71. Williams, M. The Merck Index: An Encyclopedia of Chemicals, Drugs, and Biologicals, 15th ed.; O’Neil, M.J., Ed.; PB—Royal Society of Chemistry: Cambridge, UK, 2013; 2708p, ISBN 9781849736701.

72. Kulinich, S.A.; Akhtar, A.S.; Susac, D.; Wong, K.C.; Mitchell, K.A.R. On the growth of conversion chromate coatings on Mg-Li alloys. Appl. Surf. Sci. 2007, 253, 3144–3153. [CrossRef]

73. Zhang, X.; van den Bos, C.; Sloof, W.G.; Hovestad, A.; Terryn, H.; de Wit, J.H.W. Comparison of the morphology and corrosion performance of Cr(VI)- and Cr(III)-based conversion coatings on zinc. Surf. Coat. Technol. 2005, 199, 92–104. [CrossRef]

74. Evangelides, H.A. Method of Electrolytically Coating Magnesium and Electrolyte Therefor. U.S. Patent 2723952A, 15 November 1955.
97. Shatrov, A.S.; Samsonov, V.I. Process and Device for Forming Ceramic Coatings on Metals and Alloys, and Coatings Produced by this Process. U.S. Patent US 20070270235, 22 November 2007.

98. Mawston, I.G. Magnesium Anodisation System and Methods. U.S. Patent WO/2003/016596, 27 February 2003.

99. Chong, H.; Hongchao, X.; Tunying, D. Method for Producing Corrosion-Resistant and Abrasion-Resistant Coating on Surface of Magnesium Alloy. Chinese Patent CN106119846A, 16 November 2016.

100. Dolan, S.E.; Kramer, K.; Murphy, M.; Salet, L.K. Electroceramic Coating for Magnesium Alloys. U.S. Patent WO/2016/010541, 20 January 2016.

101. Curran, J.A.; Hutchins, S.; Dunkin, O. High Thermal Conductivity Insulated Metal Substrates Produced by Plasma Electrolytic Oxidation. U.S. Patent WO2015/008064, 2 June 2015.

102. Gao, W.; Liu, Z. Micro-Arc Assisted Electroless Plating Methods. U.S. Patent US20090228329, 19 September 2009.

103. Nie, X.; Zhang, J. Method of Forming an Oxide Coating with Dimples on Its Surface. U.S. Patent US20080248214, 9 October 2008.

104. Man, S.C.Y. Golf Club Head and Method for Making the Same. U.S. Patent US20070270235, 22 November 2007.

105. Pozzoli, A.S.; Strazzi, E. Multivalent Electrolytic Process for the Surface Treatment of Non Ferrous Metallic Material. U.S. Patent EP1793019A2, 4 May 2007.

106. Beauvir, J. Oxidizing Electrolytic Method for Obtaining a Ceramic Coating at the Surface of a Metal. U.S. Patent IL152307, 20 August 2007.

107. Macculloch, J.A.; Ross, P.N.; Henshaw, G.S. Method of Anodising Magnesium Metal and Magnesium Alloys. U.S. Patent 131996, 11 April 1998.

108. Ostrovsky, I. Method for Producing a Hard Coating with High Corrosion Resistance on Articles Made of Anodizable Metals or Alloys. U.S. Patent WO/2006/007972, 26 January 2006.

109. Henshaw, G.S. Method for Anodising Magnesium and Magnesium Alloy Components or Elements. U.S. Patent WO/2002/031230, 18 April 2002.

110. Macculloch, J.A.; Ross, P.N.; Henshaw, G.S. Method of Anodising Magnesium and Magnesium Alloys. U.S. Patent 4976308A, 2 January 2003.

111. Ostrovsky, I. Method of Anodizing of Magnesium and Magnesium Alloys and Producing Conductive Layers on an Anodized Surface. U.S. Patent WO/2003/002776, 5 April 2003.

112. Verzich, D.E.A.N. Production of Uniform Ceramic Layers on Metals Surfaces by Spark Discharge—Used for Metal Parts of Aircraft. U.S. Patent DE102011007424A1, 3 April 2012.

113. Apachitel, I.; Fratila-Apachitel, E.L.; Duszycczyk, J. Self-Healing Layer on Non-Ferrous Metals using Polyoxometalates. U.S. Patent EP1820882, 22 August 2007.

114. Hradcovsky, R.J.; Bayles, S.H. Coated Valve Metal Article Formed by Spark Anodizing. U.S. Patent WO/2016/010541, 20 January 2016.

115. Schmeling, E.L.; Roschenbleck, B.; Weidemann, M.H. Method of Preparing the Surfaces of Magnesium and Magnesium Alloys. U.S. Patent WO/2003/083181, 13 October 2003.

116. Lu, X.; Sah, S.P.; Scharnagl, N.; Störmer, M.; Starykevich, M.; Mohedano, M.; Blawert, C.; Zheludkevich, M.L.; Kainer, K.U. Degradation behavior of PEO coating on AM50 magnesium alloy produced from electrolytes with clay particle addition. Surf. Coat. Technol. 2015, 269, 155–169. [CrossRef]

117. Matykina, E.; Garcia, I.; Arrabal, R.; Moshedano, M.; Mingo, B.; Sancho, J.; Merino, M.C.; Pardo, A. Role of PEO coatings in long-term biodegradation of a Mg alloy. Appl. Surf. Sci. 2016, 389, 810–823. [CrossRef]

118. Arrabal, R.; Pardo, A.; Merino, M.C.; Moshedano, M.; Casajús, P.; Matykina, E.; Skeldon, P.; Thompson, G.E. Corrosion behaviour of a magnesium matrix composite with a silicate plasma electrolytic oxidation coating. Corros. Sci. 2010, 52, 3738–3749. [CrossRef]
119. Rapheal, G.; Kumar, S.; Scharnagl, N.; Blawert, C. Effect of current density on the microstructure and corrosion properties of plasma electrolytic oxidation (PEO) coatings on AM50 Mg alloy produced in an electrolyte containing clay additives. Surf. Coat. Technol. 2016, 289, 150–164. [CrossRef]

120. Martin, J.; Nomine', A.V.; Stef, J.; Nomine', A.; Zou, J.X.; Henrion, G.; Grosdidier, T. The influence of metallurgical state of substrate on the efficiency of plasma electrolytic oxidation (PEO) process on magnesium alloy. Mater. Des. 2019, 178, 108789. [CrossRef]

121. Moreno, L.; Mohedano, M.; Arrabal, R.; Matykina, E. Development and screening of (Ca-P-Si-F)-PEO coatings for biodegradability control of Mg-Zn-Zn-Ca alloys. J. Magnes. Alloys. 2022, 10, 2220–2237. [CrossRef]

122. Snizhko, L.O.; Yerokhin, A.L.; Gurevina, N.L.; Patalakha, V.A.; Matthews, A. Excessive oxygen evolution during plasma electrolytic oxidation of aluminium. Thin Solid Films 2007, 516, 460–464. [CrossRef]

123. Snizhko, L.O.; Yerokhin, A.L.; Pilkington, A.; Gurevina, N.L.; Misnyankin, D.O.; Leyland, A.; Matthews, A. Anodic processes in plasma electrolytic oxidation of aluminium in alkaline solutions. Electrochim. Acta 2004, 49, 2085–2095. [CrossRef]

124. Troughton, S.C.; Nomine', A.; Dean, J.; Clyne, T.W. Effect of individual discharge cascades on the microstructure of plasma electrolytic oxidation coatings. Appl. Surf. Sci. 2016, 389, 260–269. [CrossRef]

125. Troughton, S.C.; Nomine', A.; Nomine', A.V.; Henrion, G.; Clyne, T.W. Synchronised electrical monitoring and high speed video of bubble growth associated with discharges during plasma electrolytic oxidation. Appl. Surf. Sci. 2015, 359, 405–411. [CrossRef]

126. Yabuki, A.; Sakai, M. Anodic films formed on magnesium in organic, silicate-containing electrolytes. Corros. Sci. 2009, 51, 793–798. [CrossRef]

127. Bai, A.; Chen, Z.-J. Effect of electrolyte additives on anti-corrosion ability of micro-arc oxide coatings formed on magnesium alloy AZ91D. Surf. Coat. Technol. 2009, 203, 1956–1963. [CrossRef]

128. Zhang, R.F.; Zhang, S.F.; Shen, Y.L.; Zhang, L.H.; Liu, T.Z.; Zhang, Y.Q.; Guo, S.B. Influence of sodium borate concentration in plasma electrolytic oxidation of aluminium. Thin Solid Films 2007, 516, 460–464. [CrossRef]

129. Wang, Y.Q.; Wu, K.; Zheng, M.Y. Effects of reinforcement phases in magnesium matrix composites on microarc discharge behavior and characteristics of microarc oxidation coatings. Surf. Coat. Technol. 2006, 201, 353–360. [CrossRef]

130. Srinivasan, P.B.; Liang, J.; Blawert, C.; Störmer, M.; Dietzel, W. Effect of current density on the microstructure and corrosion behaviour of plasma electrolytic oxidation treated AM50 magnesium alloy. Appl. Surf. Sci. 2009, 255, 4212–4218. [CrossRef]

131. Srinivasan, P.B.; Blawert, C.; Störmer, M.; Dietzel, W. Characterisation of tribological and corrosion behaviour of plasma electrolytic oxide coated AZ50 magnesium alloy. Surf. Eng. 2010, 26, 340–346. [CrossRef]

132. Barchiche, C.E.; Rocca, E.; Hazan, J. Corrosion behaviour of Sn-containing oxide layer on AZ91D alloy formed by plasma electrolytic oxidation. Surf. Coat. Technol. 2008, 202, 4145–4152. [CrossRef]

133. Guo, H.F.; An, M.Z. Growth of ceramic coatings on AZ91D magnesium alloys by micro-arc oxidation in aluminate-fluoride solution and evaluation of corrosion resistance. Appl. Surf. Sci. 2005, 246, 229–238. [CrossRef]

134. Dou, Q.; Li, W.; Zhang, G.; Wan, X. Preparation and characterisation of black ceramic coating on AZ91D magnesium alloy by plasma electrolytic oxidation with reduced energy consumption. Mater. Res. Innov. 2015, 19, S2–S23; S22–S27. [CrossRef]

135. Wierzbicka, E.; Mohedano, M.; Matykina, E.; Arrabal, R. Design and Multidimensional Screening of Flash-PEO Coatings for Mg Alloys in Comparison to Commercial Chromium(VI) Conversion Coating. Mater. Res. Innov. 2011, 15, S2–S23; S22–S27. [CrossRef]

136. Wang, Q.; Cao, F.; Chen, Z.-J. Effect of individual discharge cascades on the microstructure of plasma electrolytic oxidation coatings. Surf. Coat. Technol. 2009, 203, 2207–2220. [CrossRef]

137. Chang, L.-R.; Cao, F.-H.; Cai, J.-S.; Liu, W.-J.; Zhang, Z.; Zhang, J.-Q. Influence of electric parameters on MAO of AZ91D magnesium alloy using alternative square-wave power source. Trans. Nonferrous Met. Soc. China 2011, 21, 307–316. [CrossRef]

138. Zhang, R.F.; Shan, D.Y.; Chen, R.S.; Han, E.H. Effects of electric parameters on properties of anodic coatings formed on magnesium alloys. Mater. Chem. Phys. 2008, 107, 356–363. [CrossRef]

139. Yang, J.; Wang, Z.X.; Lu, S.; Lv, W.G.; Jiang, X.Z.; Sun, L. Characteristics of MAO coating obtained on ZK60 Mg alloy under two and three steps voltage-increasing modes in dual electrolyte. IOP Conf. Ser. Mater. Sci. Eng. 2017, 182, 012050. [CrossRef]

140. Zou, B.; Lu, G.-H.; Zhang, G.-L.; Tian, Y.-Y. Effect of current frequency on properties of coating formed by microarc oxidation on AZ91D magnesium alloy. Trans. Nonferrous Met. Soc. China 2015, 25, 1500–1505. [CrossRef]

141. Srinivasan, P.B.; Liang, J.; Balajee, R.G.; Blawert, C.; Störmer, M.; Dietzel, W. Effect of pulse frequency on the microstructure, phase composition and corrosion performance of a phosphate-based plasma electrolytic oxidation coated AM50 magnesium alloy. Appl. Surf. Sci. 2010, 256, 3928–3935. [CrossRef]

142. Hussein, R.O.; Zhang, P.; Nie, X.; Xia, Y.; Northwood, D.O. The Effect of Current Mode and Discharge Type on the Corrosion Resistance of Plasma Electrolytic Oxidation (PEO) Coated Magnesium Alloy AZ62, Surface and Coatings Technology. In Proceedings of the 38th International Conference on Metallurgical Coatings and Thin Films (ICMCTF) ICMCTF 2011, San Diego, CA, USA, 2–6 May 2011; Volume 206, pp. 1990–1997.
145. Lee, J.L.; Jian, S.Y.; Kuo, K.N.; You, J.L.; Lai, Y.T. Effect of Surface Properties on Corrosion Resistance of ZK60 Mg Alloy Microarc Oxidation Coating. *IEEE Trans. Plasma Sci.* 2019, 47, 1172–1180. [CrossRef]

146. Gao, Y.H.; Yerokhin, A.; Matthews, A. Effect of current mode on PEO treatment of magnesium in Ca- and P-containing electrolyte and resulting coatings. *Appl. Surf. Sci.* 2014, 316, 558–567. [CrossRef]

147. Timoshenko, A.V.; Magurova, Y.V. Investigation of plasma electrolytic oxidation processes of magnesium alloy MA2-1 under pulse polarisation modes. *Surf. Coat. Technol.* 2005, 199, 135–140. [CrossRef]

148. Gnedenkov, S.V.; Khrisanfova, O.A.; Zavidnaya, A.G.; Sinebryukhov, S.L.; Egorkin, V.S.; Nistratova, M.V.; Yerokhin, A.; Matthews, A. PEO coatings obtained on an Mg–Mn type alloy under unipolar and bipolar modes in silicate-containing electrolytes. *Surf. Coat. Technol.* 2010, 204, 2316–2322. [CrossRef]

149. Kumar, V.R.; Muthupandi, V.; Sivaprasad, K.; Srinivasan, P.B. Effect of frequency and duty cycle on growth, structure and corrosion resistance of MgO films on AZ31B Mg alloy formed in phosphate—Silicate mixture electrolytes. *Corros. Sci.* 2010, 52, 558–567. [CrossRef]

150. Luo, H.; Cai, Q.; Wei, B.; Yu, B.; He, J.; Li, D. Study on the microstructure and corrosion resistance of ZrO2-containing ceramic coatings formed on magnesium alloy by plasma electrolytic oxidation. *J. Alloys Compd.* 2009, 474, 551–556. [CrossRef]

151. Ono, S.; Kijima, H.; Masuko, N. Microstructure and voltage-current characteristics of anodic films formed on magnesium in electrolytes containing fluoride. *Mater. Trans.* 2003, 44, 539–545. [CrossRef]

152. Liang, J.; Guo, B.; Tian, J.; Liu, H.; Zhou, J.; Xu, T. Effect of potassium fluoride in electrolytic solution on the structure and properties of microarc oxidation coatings on magnesium alloy. *Appl. Surf. Sci.* 2005, 252, 345–351. [CrossRef]

153. Ghasemi, A.; Raja, V.S.; Blawert, C.; Dietzel, W.; Kainer, K.U. Study of the structure and corrosion behavior of PEO coatings on AM50 magnesium alloy by electrochemical impedance spectroscopy. *Surf. Coat. Technol.* 2008, 202, 3513–3518. [CrossRef]

154. Ko, Y.G.; Namgung, S.; Shin, D.H. Correlation between KOH concentration and surface properties of AZ91 magnesium alloy coated by plasma electrolytic oxidation. *Surf. Coat. Technol.* 2010, 205, 2525–2531. [CrossRef]

155. Barchiche, C.E.; Rocca, E.; Juers, C.; Hazan, J.; Steinmetz, J. Corrosion resistance of plasma-anodized AZ91D magnesium alloy by electrochemical methods. *Electrochim. Acta* 2007, 53, 417–425. [CrossRef]

156. Cheng, Y.L.; Qin, T.W.; Li, L.L.; Wang, H.M.; Zhang, Z. Comparison of corrosion resistance of microarc oxidation coatings prepared with different electrolyte concentrations on AM60 magnesium alloy. *Corros. Eng. Sci. Technol.* 2011, 46, 17–23. [CrossRef]

157. Durdu, S.; Aytac, A.; Usta, M. Characterization and corrosion behavior of ceramic coating on magnesium by micro-arc oxidation. *J. Alloys Compd.* 2011, 509, 8601–8606. [CrossRef]

158. Seekeanth, D.; Rameshbabu, N.; Venkateswarlu, K. Effect of various additives on morphology and corrosion behavior of ceramic coatings developed on AZ31 magnesium alloy by plasma electrolytic oxidation. *Ceram. Int.* 2012, 38, 4607–4615. [CrossRef]

159. Ghasemi, A.; Raja, V.S.; Blawert, C.; Dietzel, W.; Kainer, K.U. The role of anions in the formation and corrosion resistance of the plasma electrolytic oxidation coatings. *Surf. Coat. Technol.* 2010, 204, 1469–1478. [CrossRef]

160. Wang, L.; Chen, L.; Yan, Z.; Wang, H.; Peng, J. Effect of potassium fluoride on structure and corrosion resistance of plasma electrolytic oxidation films formed on AZ91 magnesium alloy. *J. Alloys Compd.* 2009, 480, 469–474. [CrossRef]

161. Hwang, D.Y.; Kim, Y.M.; Shin, D.H. Corrosion Resistance of Plasma-Anodized AZ91 Mg Alloy in the Electrolyte with/without Potassium Fluoride. *Mater. Trans.* 2009, 50, 671–678. [CrossRef]

162. Kazanski, B.; Kosenko, A.; Zinigrad, M.; Lugovsky, A. Fluoride ions as modifiers of the oxide layer produced by plasma electrolytic oxidation on AZ91D magnesium alloy. *Appl. Surf. Sci.* 2013, 287, 461–466. [CrossRef]

163. Mu, W.; Han, Y. Characterization and properties of the MgF2/ZrO2 composite coatings on magnesium prepared by micro-arc oxidation. *Surf. Coat. Technol.* 2008, 202, 4278–4284. [CrossRef]

164. da Forno, A.; Bestetti, M. Effect of the electrolytic solution composition on the performance of micro-arc anodic oxidation films formed on AM60B magnesium alloy. *Surf. Coat. Technol.* 2010, 205, 1783–1788. [CrossRef]

165. Sah, S.P.; Aoki, Y.; Habazaki, H. Influence of Phosphate Concentration on Plasma Electrolytic Oxidation of AZ80 Magnesium Alloy in Alkaline Aluminate Solution. *Mater. Trans.* 2010, 51, 94–102. [CrossRef]

166. Ma, H.; Li, D.; Liu, C.; Huang, Z.; He, D.; Yan, Q.; Liu, P.; Nash, P.; Shen, D. An investigation of (NaPO3)6 effects and mechanisms during micro-arc oxidation of AZ31 magnesium alloy. *Surf. Coat. Technol.* 2015, 266, 151–159. [CrossRef]

167. Luo, H.; Cai, Q.; Wei, B.; Yu, B.; Li, D.; He, J.; Liu, Z. Effect of (NaPO3)6 concentrations on corrosion resistance of plasma electrolytic oxidation coatings formed on AZ91D magnesium alloy. *J. Alloys Compd.* 2008, 464, 537–543. [CrossRef]

168. Mori, Y.; Koshi, A.; Liao, J.; Asosh, H.; Ono, S. Characteristics and corrosion resistance of plasma electrolytic oxidation coatings on AZ31B Mg alloy formed in phosphate—Silicate mixture electrolytes. *Corros. Sci.* 2014, 88, 254–262. [CrossRef]

169. Lv, G.-H.; Chen, H.; Wang, X.-Q.; Pang, H.; Zhang, G.-L.; Zou, B.; Lee, H.-J.; Yang, S.-Z. Effect of additives on structure and corrosion resistance of plasma electrolytic oxidation coatings on AZ91D magnesium alloy in phosphate based electrolyte. *Surf. Coat. Technol.* 2010, 205, S36–S40. [CrossRef]

170. Ma, Y.; Nie, X.; Northwood, D.O.; Hu, H. Systematic study of the electrolytic plasma oxidation process on a Mg alloy for corrosion protection. *Thin Solid Films.* 2006, 494, 296–301. [CrossRef]

171. Toulabifard, A.; Rahmati, M.; Raeissi, K.; Hakimizad, A.; Santamaria, M. The Effect of Electrolytic Solution Composition on the Structure, Corrosion, and Wear Resistance of PEO Coatings on AZ31 Magnesium Alloy. *Coatings* 2020, 10, 937. [CrossRef]

172. Duan, H.; Yan, C.; Wang, F. Effect of electrolyte additives on performance of plasma electrolytic oxidation films formed on magnesium alloy AZ91D. *Electrochim. Acta* 2007, 52, 3785–3793. [CrossRef]
202. Li, Z.M.; Chen, Z.G.; Feng, S.S.; Zhao, T.Y.; Wang, W.Z. Effects of Na2WO4 on the MAO coatings on AZ80. Surf. Eng. 2020, 36, 817–826. [CrossRef]

203. Jangde, A.; Kumar, S.; Blawert, C. Influence of glycerol on plasma electrolytic oxidation coatings evolution and on corrosion behaviour of coated AM50 magnesium alloy. Corros. Sci. 2019, 157, 220–246. [CrossRef]

204. Li, Z.; Ren, Q.; Wang, X.; Kuang, Q.; Ji, D.; Yuan, R.; Jing, X. Effect of phosphate additive on the morphology and anti-corrosion performance of plasma electrolytic oxidation coatings on magnesium—Lithium alloy. Corros. Sci. 2019, 157, 295–304. [CrossRef]

205. Zhuang, J.; Song, R.; Li, H.; Xiang, N. Effect of Various Additives on Performance of Plasma Electrolytic Oxidation Coatings Formed on AZ31 Magnesium Alloy in the Phosphate Electrolytes. J. Wuhan Univ. Technol. Mater. Sci. Ed. 2018, 33, 703–709. [CrossRef]

206. Zhu, Y.; Chang, W.; Zhang, S.; Song, Y.; Huang, H.; Zhao, R.; Li, G.; Zhang, R.; Zhang, Y. Investigation on Corrosion Resistance and Formation Mechanism of a P–F–Zr Contained Micro-Arc Oxidation Coating on AZ31B Magnesium Alloy Using an Orthogonal Method. Coatings 2019, 9, 197. [CrossRef]

207. An, L.; Ma, Y.; Liu, Y.; Sun, L.; Wang, S.; Wang, Z. Effects of additives, voltage and their interactions on PEO coatings formed on magnesium alloys. Surf. Coat. Technol. 2018, 354, 226–235. [CrossRef]

208. Rehman, Z.U.; Koo, B.H.; Jung, Y.-G.; Lee, J.H.; Choi, D. Effect of K2ZrF6 Concentration on the Two-Step PEO Coating Prepared on AZ91 Mg Alloy in Alkaline Silicate Solution. Materials 2020, 13, 499. [CrossRef] [PubMed]

209. Lu, X.; Mohedano, M.; Blawert, C.; Matykina, E.; Arrabal, R.; Kainer, K.U.; Zheludkevich, M.L. Plasma electrolytic oxidation coatings with particle additions—A review. Surf. Coat. Technol. 2016, 307, 1165–1182. [CrossRef]

210. Fattah-Alhosseini, A.; Chaharmahali, R.; Babaei, K. Effect of particles addition to solution of plasma electrolytic oxidation (PEO) on the properties of PEO coatings formed on magnesium and its alloys: A review. J. Magnes. Alloys 2020, 8, 799–818. [CrossRef]

211. Asgari, M.; Aliofkhazraei, M.; Darband, G.B.; Rouhaghdam, A.S. How nanoparticles and submicron particles adsorb inside coating during plasma electrolytic oxidation of magnesium? Surf. Coat. Technol. 2020, 383, 125252. [CrossRef]

212. Gou, Y.; Zhang, D.; Liu, Y.; Guo, X. A composite anodizing coating containing superfine Al2O3 particles on AZ31 magnesium alloy processed by plasma electrolytic oxidation. Surf. Coat. Technol. 2018, 354, 561–580. [CrossRef]

213. Tu, X.; Miao, C.; Zhang, Y.; Xu, Y.; Li, J. Plasma Electrolytic Oxidation of Magnesium Alloy AZ31B in Electrolyte Containing Al2O3 Sol as Additives. Materials 2018, 11, 1618. [CrossRef]
246. Pei Tao, G.; Ming Yang, T.; Chaoyang, Z. Tribological and corrosion resistance properties of graphite composite coating on AZ31 magnesium alloy. Surf. Coat. Technol. 2018, 359, 9166–9182. [CrossRef]
247. Hwang, M.; Chung, W. Effects of a carbon nanotube additive on the corrosion-resistance and heat-dissipation properties of plasma electrolytic oxidation coating on AZ31 magnesium alloy. Surf. Coat. Technol. 2019, 359, 197–205. [CrossRef]
248. Huang, M.; Zhang, C. Effect of the graphene oxide additive on the corrosion resistance of the plasma electrolytic oxidation coating of the AZ31 magnesium alloy. Corros. Sci. 2013, 71, 177–184. [CrossRef]
249. Li, C.-Y.; Feng, X.-L.; Fan, X.-L.; Yu, X.-T.; Yin, Z.-Z.; Kannan, M.B.; Chen, X.B.; Guan, S.K.; Zhang, J.; Zeng, R.C. Corrosion and wear resistance of micro-arc oxidation composite coatings on magnesium alloy AZ31—the influence of inclusions of carbon spheres. Adv. Eng. Mater. 2019, 21, 1900446. [CrossRef]
250. Sun, M.; Yerokhin, A.; Bychkova, M.; Shtansky, D.; Levashov, E.; Matthews, A. Self-healing plasma electrolytic oxidation coatings doped with benzotriazole loaded halloysite nanotubes on AZ50 magnesium alloy. Corros. Sci. 2016, 111, 753–769. [CrossRef]
251. Mingo, B.; Guo, Y.; Nemicova, A.; Gholinia, A.; Mohedano, M.; Sun, M.; Matthews, A.; Yerokhin, A. Incorporation of halloysite nanotubes into forsterite surface layer during plasma electrolytic oxidation of AM50 Mg alloy. Electrochim. Acta 2019, 299, 772–788. [CrossRef]
252. Mingo, B.; Guo, Y.; Leiva-Garcia, R.; Connolly, B.J.; Matthews, A.; Yerokhin, A. Smart Functionalization of Ceramic-Coated AZ31 Magnesium Alloy. ACS Appl. Mater. Interfaces 2020, 12, 30833–30846. [CrossRef]
253. Lu, X.; Schieda, M.; Blawert, C.; Kainer, K.U.; Zeludkevich, M.L. Formation of photocatalytic plasma electrolytic oxidation coatings on magnesium alloy by incorporation of TiO2 particles. Surf. Coat. Technol. 2016, 307, 287–291. [CrossRef]
254. Daavari, M.; Atapour, M.; Mohedano, M.; Arrabal, R.; Matykina, E.; Taherizadeh, A. Biotribology and biocorrosion of MWCNTs-reinforced PEO coating on AZ31B Mg alloy. Surf. Interfaces 2020, 22, 100850. [CrossRef]
255. Habazaki, H.; Kataoka, F.; Shahzad, K.; Tsuji, E.; Aoki, Y.; Nagata, S.; Skeldon, P.; Thompson, G.E. Growth of barrier-type anodic films on magnesium in ethylene glycol electrolytes containing fluoride and water. *Electrochim. Acta* 2015, 179, 402–410. [CrossRef]

256. Brunner, J.; Hahn, R.; Kunze, J.; Virtanen, S. Porosity tailored growth of black anodic layers on magnesium in an organic electrolyte. *J. Electrochem. Soc.* 2009, 156, C62–C66. [CrossRef]

257. Hernández-López, J.M.; Némécová, A.; Zhong, X.L.; Liu, H.; Arenas, M.A.; Haigh, S.J.; Burke, M.G.; Skeldon, P.; Thompson, G.E. Formation of barrier-type anodic films on ZE41 magnesium alloy in a fluoride/glycerol electrolyte. *Electrochim. Acta* 2014, 138, 124–131. [CrossRef]

258. Némécová, A.; Kubena, I.; Smid, M.; Habazaki, H.; Skeldon, P.; Thompson, G.E. Effect of current density and behaviour of second phases in anodizing of a Mg-Zn-RE alloy in a fluoride/glycerol/water electrolyte. *J. Solid State Electrochem.* 2016, 20, 1155–1165. [CrossRef]

259. Asoh, H.; Ono, S. Anodizing of Magnesium in Amine-Ethylene Glycol Electrolyte. In *Materials Science Forum*; Trans Tech Publications Ltd.: Bach, Switzerland, 2003; pp. 957–962.

260. Turhan, M.C.; Lynch, R.P.; Jha, H.; Schmuki, P.; Virtanen, S. Anodic growth of self-ordered magnesium oxy-fluoride nanoporous/tubular layers on Mg alloy (WE43). *Electrochem. Commun.* 2010, 12, 796–799. [CrossRef]

261. Habazaki, H.; Kataoka, F.; Tsuji, E.; Aoki, Y.; Nagata, S.; Skeldon, P.; Thompson, G.E. Efficient growth of anodic films on magnesium in organic electrolytes containing fluoride and water. *Electrochem. Commun.* 2014, 46, 30–32. [CrossRef]

262. Qi, Y.; Peng, Z.; Wang, L.; Zhou, J.; Wang, P.; Liang, J. Fluoride-dominated coating on Mg alloys fabricated by plasma electrolytic process in ambient non-aqueous electrolyte. *Surf. Eng.* 2021, 37, 360–364. [CrossRef]

263. Mingo, B.; Arrabal, R.; Mohedano, M.; Llamazares, Y.; Matykina, E.; Yerokhin, A.; Paro, A. Influence of sealing post-treatments on the corrosion resistance of PEO coated AZ91 magnesium alloy. *Appl. Surf. Sci.* 2018, 433, 653–667. [CrossRef]

264. Liu, D.; Song, Y.W.; Shan, D.Y.; Han, E.H. Self-Healing Coatings Prepared by Loading Interphase Inhibitors into MAO Coating of AM60 Mg Alloy. *J. Electrochem. Soc.* 2018, 165, C412–C421. [CrossRef]

265. Vaghefinazari, B.; Lamaka, S.V.; Blawert, C.; Serdechna, M.; Scharnagl, N.; Karlova, P.; Wieland, D.C.F.; Zheludkevich, M.L. Exploring the corrosion inhibition mechanism of 8-hydroxyquinoline for a PEO-coated magnesium alloy. *Corros. Sci.* 2022, 205, 110344. [CrossRef]

266. Na, Z.; Shengxue, Y.; Qian, X.; Xiaolei, C.; Mingxian, Z.; Deju, S. Corrosion Performance of Composite MAO/TiO2 Sol–Gel Coatings on Magnesium Alloy AZ91D. *J. Mater. Eng. Perform.* 2018, 27, 6080–6086. [CrossRef]

267. Pezzato, L.; Rigon, M.; Martucci, A.; Brunelli, K.; Dabal, M. Plasma Electrolytic Oxidation (PEO) as pre-treatment for sol-gel coating on aluminum and magnesium alloys. *Surf. Coat. Technol.* 2019, 366, 114–123. [CrossRef]

268. Li, N.; Chen, Y.; Deng, B.; Yue, J.; Qu, W.; Yang, H.; He, Y.; Xia, W.; Li, L. Low temperature UV assisted sol-gel preparation of ZrO2 pore-sealing films on micro-arc oxidized magnesium alloy AZ91D and their electrochemical corrosion behaviors. *J. Alloy. Compd.* 2019, 792, 1036–1044. [CrossRef]

269. Liu, C.; Lu, X.; Li, Y.; Chen, Q.; Zhang, T.; Wang, F. Influence of post-treatment process on corrosion and wear properties of PEO coatings on AM50 Mg alloy. *J. Alloys Compd.* 2021, 870, 159462. [CrossRef]

270. Wu, M.; Guo, Y.; Xu, G.; Cui, Y. Effects of deposition thickness on electrochemical behaviors of AZ31B magnesium alloy with composite coatings prepared by micro-arc oxidation and electrophoretic deposition. *Int. J. Electrochem. Sci.* 2020, 15, 1378–1390. [CrossRef]

271. Li, C.-Y.; Fan, X.-L.; Cui, L.-Y.; Zeng, R.-C. Corrosion resistance and electrical conductivity of a nano ATO-doped MAO/methyltrimethoxysilane composite coating on magnesium alloy AZ31. *Corros. Sci.* 2020, 168, 108570. [CrossRef]

272. Han, J.; Blawert, C.; Tang, S.; Yang, J.; Hu, J.; Zheludkevich, M.L. Formation and corrosion behaviors of calcium phosphate coatings on plasma electrolytic oxidized Mg under changing chemical environment. *Surf. Coat. Technol.* 2021, 412, 127030. [CrossRef]

273. Li, Z.; Yang, W.; Yu, Q.; Wu, Y.; Wang, D.; Liang, J.; Zhou, F. New Method for the Corrosion Resistance of AZ31 Mg Alloy with a Porous Micro-Arc Oxidation Membrane as an Ionic Corrosion Inhibitor Container. *Langmuir* 2018, 35, 1134–1145. [CrossRef]

274. Toorani, M.; Alikofkhazraei, M.; Mahdavian, M.; Naderi, R. Effective PEO/Silane pretreatment of epoxy coating applied on AZ31B Mg alloy for corrosion protection. *Corros. Sci.* 2020, 169, 108608. [CrossRef]

275. Duyunova, V.A.; Kozlov, I.A.; Kuznetsova, V.A.; Kozlova, A.A. Effect of operational heat on the protective properties of coatings for ML10 magnesium alloy. *Tsvetn. Met.* 2019, 3, 51–57. [CrossRef]

276. Dou, J.; Yu, H.; Chen, C.; Ma, R.L.-K.; Yuen, M.M.-F. Preparation and microstructure of MAO/CS composite coatings on Mg alloy. *Mater. Lett.* 2020, 271, 127729. [CrossRef]

277. Guo, J.; Liu, X.; Du, K.; Guo, Q.; Wang, Y.; Liu, Y.; Feng, L. An anti-stripping and self-healing micro-arc oxidation/acylamide gel composite coating on magnesium alloy AZ31. *Mater. Lett.* 2020, 260, 126912. [CrossRef]

278. Pezzato, L.; Brunelli, K.; Babbolin, R.; Dolcet, P. Sealing of PEO Coated AZ91 Magnesium Alloy Using La-Based Solutions. *Int. J. Corros.* 2017, 2017, 13. [CrossRef]

279. Lu, X.; Ma, J.; Mohedano, M.; Pillado, B.; Arrabal, R.; Qian, K.; Li, Y.; Zhang, T.; Wang, F. Ca-based sealing of plasma electrolytic oxidation coatings on AZ91 Mg alloy. *Surf. Coat. Technol.* 2021, 417, 127220. [CrossRef]

280. Mohedano, M.; Blawert, C.; Zheludkevich, M.L. Cerium-based sealing of PEO coated AM50 magnesium alloy. *Surf. Coat. Technol.* 2015, 269, 145–154. [CrossRef]
281. Mohedano, M.; Pérez, P.; Matykina, E.; Pillado, B.; García, G.; Arrabal, R. PEO coating with Ce-sealing for corrosion protection of LPSO Mg–Y–Zn alloy. Surf. Coat. Technol. 2020, 383, 125253. [CrossRef]

282. Zhang, M.; Chen, R.; Liu, X.; Liu, Q.; Li; J.; Yu; J.; Liu, P.; Gao, L.; Wang, J. Anticorrosion study of phytic acid ligand binding with exceptional self-sealing functionality. J. Alloys Compd. 2020, 818, 152875. [CrossRef]

283. Pezzato, L.; Babboni, R.; Cerchier, P.; Marigo, M.; Dolcet, P.; Dabalá, M.; Brunelli, K. Sealing of PEO coated AZ91 magnesium alloy using solutions containing neodymium. Corros. Sci. 2020, 173, 108741. [CrossRef]

284. Sun, P.; Lu; Y.; Yuan, Y.; Jing, X.; Zhang, M. Preparation and characterization of duplex PEO/MoC coatings on Mg–Li alloy. Surf. Coat. Technol. 2011, 205, 4500–4506. [CrossRef]

285. Laleh, M.; Kargar, F.; Rouhaghdam, A.S. Improvement in corrosion resistance of micro arc oxidation coating formed on AZ91D magnesium alloy via applying a nano-crystalline sol–gel layer. J. Sol-Gel Sci. Technol. 2011, 59, 297–303. [CrossRef]

286. Shang, W.; Chen, B.; Shi, X.; Chen, Y.; Xiao, X. Electrochemical corrosion behavior of composite MAO/sol–gel coatings on magnesium alloy AZ91D using combined micro-arc oxidation and sol–gel technique. J. Alloys Compd. 2009, 474, 541–545. [CrossRef]

287. Shi, P.; Ng, W.F.; Wong, M.H.; Cheng, F.T. Improvement of corrosion resistance of pure magnesium in Hanks’ solution by microarc oxidation with sol–gel TiO2 sealing. J. Alloys Compd. 2009, 469, 286–292. [CrossRef]

288. Peng, F.; Wang, D.; Tian, Y.; Cao, H.; Qiao, Y.; Liu, X. Sealing the Pores of PEO Coating with Mg-Al Layered Double Hydroxide: Enhanced Corrosion Resistance, Cytocompatibility and Drug Delivery Ability. Sci. Rep. 2017, 7, 8167. [CrossRef] [PubMed]

289. Mohedano, M.; Serdechnova, M.; Starykevich, M.; Karpushenkov, S.; Bouali, A.C.; Ferreira, M.G.S.; Zheludkevich, M.L. Active protective PEO coatings on AA2024: Role of voltage on in-situ LDH growth. Mater. Des. 2017, 120, 36–46. [CrossRef]

290. Petrova, E.; Serdechnova, M.; Shulha, T.; Lamaka, S.V.; Wieland, D.C.F.; Karlova, P.; Blawert, C.; Starykevich, M.; Zheludkevich, M.L. Use of synergistic mixture of chelating agents for in situ LDH growth on the surface of PEO-treated AZ91. Sci. Rep. 2020, 10, 8645. [CrossRef]

291. Wang, Z.H.; Zhang, J.M.; Li, Y.; Bai, L.J.; Zhang, G.J. Corrosion Resistance Enhancement of Micro-Arc Oxidation Ceramic Layer by Mg-Al-Co Layered Double Hydroxide Coating. Trans. Indian Ceram. Soc. 2020, 79, 59–66. [CrossRef]

292. Zheng, G.; Wu, L.; Tang, A.; Ma, Y.; Song, G.-L.; Zheng, D.; Jiang, B.; Atrens, A.; Pan, F. Active corrosion protection by a smart coating based on a MgAl-layered double hydroxide on a cerium-modified plasma electrolytic oxidation coating on Mg alloy AZ31. Corros. Sci. 2018, 139, 370–382. [CrossRef]

293. Zhang, G.; Wu, L.; Tang, A.; Han, H.; Ma, Y.; Zhan, Q.; Tan, Q.; Pan, F.; Atrens, A. Effect of Micro-Arc Oxidation Coatings Formed at Different Voltages on the In Situ Growth of Layered Double Hydroxides and Their Corrosion Protection. J. Electrochem. Soc. 2018, 165, C317–C327. [CrossRef]

294. Chen, J.; Lin, W.; Liang, S.; Zou, L.; Wang, C.; Wang, B.; Yan, M.; Cui, X. Effect of alloy cations on corrosion resistance of LDH/MAO coating on magnesium alloy. Appl. Surf. Sci. 2019, 463, 535–544. [CrossRef]

295. Chen, J.; Liang, S.; Fu, D.; Fan, W.; Lin, W.; Ren, W.; Zou, L.; Cui, X. Design and in situ prepare a novel composite coating on Mg alloy for active anti-corrosion protection. J. Alloys Compd. 2020, 831, 154580. [CrossRef]

296. Zhang, J.-M.; Wang, K.; Duan, X.; Zhang, Y.; Cai, H.; Wang, Z.-H. Effect of Hydrothermal Treatment Time on Microstructure and Corrosion Behavior of Micro-arc Oxidation/Layered Double Hydroxide Composite Coatings on LA103Z Mg–Li Alloy in 3.5 wt.% NaCl Solution. J. Mater. Eng. Perform. 2020, 29, 4032–4039. [CrossRef]

297. Kaseem, M.; Ramachandraiah, K.; Hossain, S.; Dikici, B. A Review on LDH-Smart Functionalization of Anodic Films of Mg Alloys. Nanomaterials 2021, 11, 536. [CrossRef] [PubMed]

298. Asl, V.Z.; Chini, S.F.; Zhao, J.; Palizdar, Y.; Shaker, M.; Sadeghi, A. Corrosion properties and surface free energy of the ZnAl LDH/rGO coating on MAO pretreated AZ31 magnesium alloy. Surf. Coat. Technol. 2021, 426, 127764.

299. Li, Y.; Lu, X.; Serdechnova, M.; Blawert, C.; Zheludkevich, M.L.; Qian, K.; Zhang, T.; Wang, F. Incorporation of LDH nanocontainers into plasma electrolytic oxidation coatings on Mg alloy. J. Magnes. Alloys 2021. [CrossRef]

300. Zhang, D.; Peng, F.; Qiu; J.; Tan, J.; Zhang, X.; Chen, S.; Qian, S.; Liu, X. Regulating corrosion reactions to enhance the anti-corrosion and self-healing abilities of PEO coating on magnesium. Corros. Sci. 2021, 192, 109840. [CrossRef]

301. Jiang, D.; Zhou, H.; Wan, S.; Cai, G.-Y.; Dong, Z.-H. Fabrication of superhydrophobic coating on magnesium alloy with improved corrosion resistance by combining micro-arc oxidation and cyclic assembly. Surf. Coat. Technol. 2018, 339, 155–166. [CrossRef]

302. Liu, A.-H.; Xu, J.-L. Preparation and corrosion resistance of superhydrophobic coatings on AZ31 magnesium alloy. Trans. Nonferrous Met. Soc. China 2018, 28, 2287–2293. [CrossRef]

303. Li, Z.; Yu, Q.; Zhang, C.; Liu, Y.; Liang, J.; Wang, D.; Zhou, F. Synergistic effect of hydrophobic film and porous MAO membrane containing alkynol inhibitor for enhanced corrosion resistance of magnesium alloy. Surf. Coat. Technol. 2019, 357, 515–525. [CrossRef]

304. Joo, J.; Kim, D.; Moon, H.-S.; Kim, K.; Lee, J. Durable anti-corrosive oil-impregnated porous surface of magnesium alloy by plasma electrolytic oxidation with hydrothermal treatment. Appl. Surf. Sci. 2020, 508, 145361. [CrossRef]

305. Jiang, D.; Xia, X.; Hou; J.; Cai, G.; Zhang, X.; Dong, Z. A novel coating system with self-reparable slippery surface and active corrosion inhibition for reliable protection of Mg alloy. Chem. Eng. J. 2019, 373, 285–297. [CrossRef]

306. Mashtalyar, D.V.; Gnedenkov, S.V.; Sinebryukhov, S.L.; Imshenetskiy, I.M.; Gnedenkov, A.S.; Bouznik, V.M. Composite coatings formed using plasma electrolytic oxidation and fluoro-paraffin materials. J. Alloys Compd. 2018, 767, 353–360. [CrossRef]
307. Mashtalyar, D.; Nadaraya, K.; Sinebryukhov, S.; Gnedenkov, S. Polymer-Containing Layers Formed by PEO and Spray-Coating Method. Mater. Today Proc. 2019, 11, 150–154. [CrossRef]

308. Nadaraya, K.V.; Gnedenkov, S.V.; Sinebryukhov, S.L.; Mashtalyar, D.V. Protective coatings formed by PEO and fluorine-containing compound. Defect Diffus. Forum DDF 2018, 386, 343–348. [CrossRef]

309. Tsai, D.-S.; Tsai, Y.-C.; Chou, C.-C. Corrosion passivation of magnesium alloy with the duplex coatings of plasma electrolytic oxidation and tetrafluoroethylene-based polymers. Surf. Coat. Technol. 2019, 366, 15–23. [CrossRef]

310. Fattah-alhosseini, A.; Chaharmahali, R.; Babaei, K. Impressive strides in amelioration of corrosion and wear behaviors of Mg alloys using applied polymer coatings on PEO porous coatings: A review. J. Magnes. Alloy. 2022, 10, 1171–1190. [CrossRef]

311. Parichehr, R.; Dehghanian, C.; Nikbakht, A. Preparation of PEO/silane composite coating on AZ31 magnesium alloy and investigation of its properties. J. Alloys Compd. 2021, 876, 159995. [CrossRef]

312. Brady, M.P.; Leonard, D.N.; McNally, E.A.; Kish, J.R.; Meyer, H.M., III; Cakmak, E.; Davis, B. Magnesium alloy effects on plasma electrolytic oxidation electro-ceramic formation and corrosion resistance. J. Electrochem. Soc. 2019, 166, C492–C508. [CrossRef]

313. Xue, Y.; Pang, X.; Jiang, B.; Jahed, H. Corrosion and corrosion fatigue performances of micro-arc oxidation coating on AZ31B cast magnesium alloy. Mater. Corros. 2010, 61, 268–300. [CrossRef]

314. Zhang, G.; Wu, L.; Tang, A.; Ding, X.; Jiang, B.; Atrens, A.; Pan, F. Smart epoxy coating containing zeolites loaded with Ce on a plasma electrolytic oxidation coating on Mg alloy AZ31 for active corrosion protection. Prog. Org. Coat. 2019, 132, 144–147. [CrossRef]

315. Li, M.; Liu, J.; Li, J.; Li, Y.; Lu, S.; Yuan, Y. The enhanced corrosion resistance of UMAO coatings on Mg by silane treatment. Prog. Nat. Sci. Mater. Int. 2014, 24, 486–491. [CrossRef]

316. Bestetti, M.; Cavallotti, P.L.; da Forno, A.; Pozzi, S. Anodic oxidation and powder coating for corrosion protection of AM60B magnesium alloys. Trans. IMF 2007, 85, 316–319. [CrossRef]

317. Song, G.-L. An irreversible dipping sealing technique for anodized ZE41 Mg alloy. Surf. Coat. Technol. 2009, 203, 3618–3625. [CrossRef]

318. Duan, H.; Du, K.; Yan, C.; Wang, F. Electrochemical corrosion behavior of composite coatings of sealed MAO film on magnesium alloy AZ91D. Electrochim. Acta 2006, 51, 2898–2908. [CrossRef]

319. Ivanou, D.K.; Starykevich, M.; Lisenkov, A.D.; Zheludkevich, M.L.; Xue, H.B.; Lamaka, S.V.; Ferreira, M.G.S. Plasma anodized ZE41 magnesium alloy sealed with hybrid epoxy-silane coating. Corros. Sci. 2013, 73, 300–308. [CrossRef]

320. Wang, J.; Tang, J.; He, Y. Top coating of low-molecular weight polymer MALPB used for enhanced protection on anodized AZ31B Mg alloys. J. Coat. Technol. Res. 2010, 7, 737–746. [CrossRef]

321. Chen, M.-A.; Cheng, N.; Ou, Y.-C.; Li, J.-M. Corrosion performance of electroless Ni-P on polymer coating of MAO coated AZ31 magnesium alloy. Surf. Coat. Technol. 2013, 232, 726–733. [CrossRef]

322. Gnedenkov, A.S.; Sinebryukhov, S.L.; Mashtalyar, D.V.; Gnedenkov, S.V. Protective properties of inhibitor-containing composite coatings on a Mg alloy. Corros. Sci. 2016, 125, 348–354. [CrossRef]

323. Lamaka, S.V.; Knörnschild, G.; Shinohiro, D.V.; Taryba, M.G.; Zheludkevich, M.L.; Ferreira, M.G.S. Complex anticorrosion coating for ZK30 magnesium alloy. Electrochim. Acta 2009, 55, 131–141. [CrossRef]

324. Ivanou, D.K.; Yasakau, K.A.; Kallip, S.; Lisenkov, A.D.; Starykevich, M.; Lamaka, S.V.; Ferreira, M.G.S.; Zheludkevich, M.L. Active corrosion protection coating for a ZE41 magnesium alloy created by combining PEO and sol-gel techniques. RSC Adv. 2016, 6, 12553–12560. [CrossRef]

325. Chen, Y.; Lu, X.; Lamaka, S.V.; Ju, P.; Blawert, C.; Zhang, T.; Wang, F.; Zheludkevich, M.L. Active protection of Mg alloy by composite PEO coating loaded with corrosion inhibitors. Appl. Surf. Sci. 2020, 504, 144462. [CrossRef]

326. Lamaka, S.V.; Lourenço, M.M.; Ivanou, D.K.; Zheludkevich, M.L.; Ferreira, M.G.S.; Hack, T. Fault-Tolerant Composite Protective Coating for WE43 Magnesium Alloy. In Proceedings of the IMA 2014 World Annual Magnesium Conference, Munich, Germany, 1–3 June 2014.

327. Wei, H.; Wang, Y.; Guo, J.; Shen, N.Z.; Jiang, D.; Zhang, X.; Yan, X.; Zhu, J.; Wang, Q.; Shao, L.; et al. Advanced micro/nanocapsules for self-healing smart anticorrosion coatings. J. Mater. Chem. A 2015, 3, 469–480. [CrossRef]

328. Vallet-Regí, M.; Colilla, M.; Izquierdo-Barba, I.; Manzano, M. Mesoporous Silica Nanoparticles for Drug Delivery: Current Insights. Molecules 2018, 23, 47. [CrossRef] [PubMed]

329. Ouyang, Y.; Li, L.-X.; Xie, Z.-H.; Tang, L.; Wang, F.; Zhong, C.-J. A self-healing coating based on facile pH-responsive nanoccontainers for corrosion protection of magnesium alloy. J. Magnes. Alloy. 2020, 10, 836–849. [CrossRef]

330. Qiao, Y.; Li, W.; Wang, G.; Zhang, X.; Cao, N. Application of ordered mesoporous silica nanoccontainers in an anticorrosive epoxy coating on a magnesium alloy surface. RSC Adv. 2015, 5, 47778–47787. [CrossRef]

331. Kurzynowski, T.; Pawlak, A.; Smolina, I. The potential of SLm technology for processing magnesium alloys in aerospace industry. Arch. Civ. Mech. Eng. 2020, 20, 23. [CrossRef]

332. Liu, S.; Guo, H. A Review of SLMed Magnesium Alloys: Processing, Properties, Alloying Elements and Postprocessing. Metals 2020, 10, 1073. [CrossRef]

333. Zhang, W.-N.; Wang, L.-Z.; Feng, Z.-X.; Chen, Y.-M. Research progress on selective laser melting (SLM) of magnesium alloys: A review. Optik 2020, 207, 163842. [CrossRef]
334. Li, M.; Benn, F.; Derra, T.; Kröger, N.; Zinser, M.; Smeets, R.; Molina-Aldareguia, J.M.; Kopp, A.; Llorca, J. Microstructure, mechanical properties, corrosion resistance and cytocompatibility of WE43 Mg alloy scaffolds fabricated by laser powder bed fusion for biomedical applications. *Mater. Sci. Eng. C* 2021, 119, 111623. [CrossRef]

335. Kopp, A.; Derra, T.; Müther, M.; Jauer, L.; Schleifenbaum, J.H.; Voshage, M.; Jung, O.; Smeets, R.; Kröger, N. Influence of design and postprocessing parameters on the degradation behavior and mechanical properties of additively manufactured magnesium scaffolds. *Acta Biomater.* 2019, 98, 23–35. [CrossRef]