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# Application-Driven Review of PEO/MAO-Based Composite Coatings for Magnesium Alloys: Functional Architectures, Failure Mechanisms and Validation Strategies

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## Abstract

Magnesium alloys are used or considered for lightweight structures and biodegradable implants, but high electrochemical activity, limited wear resistance, and localized corrosion still limit their service reliability. Plasma electrolytic oxidation (PEO), also called micro-arc oxidation (MAO), forms an adherent ceramic scaffold. Discharge channels, interconnected pores, thermal cracks, and a mechanically weak outer layer mean that the as-formed coating is rarely a complete protective system. This review examines advanced PEO/MAO-based composite coatings through a process–structure–function lens and develops an application-oriented design framework. The discussion covers PEO/MAO process-window control, electrolyte and particle engineering, sol–gel and polymer sealing, layered double hydroxide/inhibitor systems, self-healing reservoirs, superhydrophobic and slippery interfaces, Ca-P/hydroxyapatite and polymer biofunctionalization, and duplex coatings for wear, electrical, and thermal functions. Emphasis is placed on how these modules regulate defect connectivity, mass transport, interfacial stability, damage response, tribocorrosion, and biodegradation, as well as on the evidence needed to support each claimed function. The analysis indicates that coating performance is governed not by multilayer complexity alone, but by the compatibility among the ceramic scaffold, functional module, dominant failure mode, and service-specific validation protocol. Chloride-exposed structures require durable pore sealing and active inhibition; wear-critical components require coupled corrosion–wear assessment; and biodegradable implants require a degradation window that balances corrosion moderation, cytocompatibility, biofunctionality, and residual mechanical integrity. Remaining challenges include interfacial durability, finite inhibitor reservoirs, wetting-state instability, process reproducibility, scale-up, and life-cycle impacts. The proposed process maps and validation criteria are intended to support modular, testable, and application-specific PEO/MAO surface systems for magnesium alloys.

**Keywords:** magnesium alloy; plasma electrolytic oxidation; micro-arc oxidation; composite coatings; corrosion protection; self-healing coatings; biodegradable magnesium; validation strategy



Academic Editor: Arvaidas Galdikas

Received: 30 June 2026
Revised: 17 July 2026
Accepted: 20 July 2026
Published: 24 July 2026

## 1. Introduction

Magnesium alloys combine attractive performance with difficult surface degradation. Their low density, high specific strength and potential biodegradability make them appealing for lightweight transport components, electronic housings and temporary orthopedic devices, yet the electrochemical activity that makes them degradable also causes rapid corrosion, local alkalization, $H_2$ evolution and weak wear resistance in chloride-containing or physiological environments [1–7]. Surface treatment is not a cosmetic final step. It determines whether a magnesium alloy can remain dimensionally stable in transport service, retain coating adhesion under cyclic loading, or degrade at a useful rate during bone healing.

Useful reviews in this field usually separate the corrosion problem from the coating recipe. Foundational reviews on protective coatings and magnesium corrosion first define the instability of the Mg substrate, micro-galvanic effects, electrolyte chemistry and film breakdown before comparing coating routes [1–3,6]. PEO/MAO-focused reviews then organize the field around discharge behaviour, coating growth, electrolyte chemistry, phase formation and the compact inner/porous outer layer structure [8–11]. Biomedical coating reviews use a different logic: they ask how surface modification controls degradation, bioactivity, cytocompatibility and tissue response rather than how to maximize passivation [4,5,7,12–14]. Recent reviews on LDH, inhibitors, superhydrophobicity, self-healing and PEO/polymer systems add another lesson: a coating route is useful only when its claimed function is matched by a specific mechanism and by a test that can reveal failure [15–24].

Here, the question is narrowed further. The review is not a catalogue of all magnesium surface treatments, such as laser treatment, broad conversion coatings or other non-PEO corrosion-protection strategies [25,26]. Its focus is advanced PEO/MAO-based process design, because PEO/MAO gives magnesium alloys a strong starting scaffold, but is rarely sufficient by itself. During PEO/MAO, plasma-assisted anodic reactions create a ceramic oxide layer that can contain MgO, silicates, phosphates, aluminates, fluorides or Ca/P-containing phases, depending on the electrolyte and alloy. The same discharge process that gives high adhesion and hardness also creates open pores, discharge channels, surface roughness and thermal cracks. These features can anchor a sealant, LDH layer, polymer, hydroxyapatite or low-energy top layer, but they become harmful when they remain connected to chloride pathways [9–11,18,27–32].

This article treats PEO/MAO-based coatings as an application-driven design problem rather than as another survey of PEO/MAO chemistry. Recent reviews have summarized corrosion-resistant PEO coatings, particle-assisted PEO, layered double hydroxide (LDH)-based protection, smart container/self-healing systems, superhydrophobic magnesium coatings and biomedical Mg surface modification, but a practical process-selection framework is still needed.

This review reorganizes PEO/MAO-based composite coatings according to functional architecture and proof burden. Each module is evaluated by asking whether it changes defect connectivity, transport resistance, mechanical durability, wetting stability, active inhibitor response, or biomedical degradation behaviour, and whether the reported tests can verify that claimed function.

Here, an advanced process is defined in an engineering sense. A process is advanced if it changes the failure pathway, adds a function that the PEO scaffold cannot provide alone, or changes the validation package required to prove application value. Adding a nanoparticle or topcoat is not enough. A particle-assisted bath should show stable incorporation and a measurable change in phase, porosity, wear or degradation response. A polymer sealant should show pore closure, adhesion and swelling resistance. An LDH/inhibitor layer

should show loading, release and local suppression after damage. A superhydrophobic layer should show whether the wetting state survives abrasion, immersion and contamination. A biomedical layer should show controlled pH, $H_2$ evolution, ion release, cell response and residual mechanical function [15,17–23,33–44].

The article offers a process map rather than a publication map. Each section asks what the process module is, which defect or failure mode it addresses, which parameters decide success, and which tests make the claim credible. This structure is useful for coatings because the journal often receives papers that combine PEO/MAO with sealing, inhibitors, particles, polymers, superhydrophobic chemistry or biomedical phases. In such papers, the main risk is not limited novelty but an unclear link between process design and service function.

Throughout the review, structural and biomedical services are kept separate. For automotive, aerospace, marine and electronic applications, coating design usually aims to slow chloride penetration, preserve adhesion and resist coupled wear/corrosion. For temporary implants, the target is not permanent isolation from body fluid. The target is a degradation window in which the coating moderates early corrosion and $H_2$ evolution while still allowing eventual resorption and tissue integration. This distinction changes how PEO/MAO, Ca-P/HA, polymers, inhibitors and wetting-control layers should be judged.

## 2. Review Scope and Evidence Selection

This article is a critical narrative review with an application-oriented classification strategy, not a PRISMA-style systematic review or a meta-analysis. The source corpus was assembled to represent the PEO/MAO-based magnesium coating modules discussed here: ceramic scaffold control, electrolyte and particle engineering, sealing and polymer hybridization, LDH/inhibitor systems, self-healing reservoirs, superhydrophobic or slippery top layers, biomedical Ca-P/HA and polymer functionalization, and duplex wear, conductive or thermal layers.

The relevant literature was identified using combinations of search terms that included magnesium alloy, plasma electrolytic oxidation, micro-arc oxidation, PEO, MAO, composite coating, corrosion, sealing, layered double hydroxide, inhibitor, self-healing, superhydrophobic, slippery surface, hydroxyapatite, biodegradable implant, wear and tribocorrosion. Searches were centred on Web of Science, Scopus, and PubMed for biomedical topics, and Google Scholar for citation chasing and recent online-first papers. Foundational corrosion and coating reviews were retained when they defined mechanisms or reporting standards needed to interpret recent studies.

Inclusion required magnesium or magnesium-alloy substrates and the use of PEO/MAO as the ceramic scaffold or a directly related precursor to a functional coating stack. Priority was given to papers that reported process parameters, coating architecture, mechanistic characterization and application-relevant validation. Studies were excluded from detailed discussion when the substrate was not magnesium-based, when PEO/MAO was not part of the coating architecture, or when the claimed function was supported only by a weak screening result without structural or durability evidence. This selection strategy favours mechanistic and application relevance over exhaustive enumeration.

To make the review process more transparent, the working search window used to assemble this critical narrative corpus was January 2002 to June 2026. The core search strings, with database-specific syntax adjustments, were: (“magnesium alloy” OR “Mg alloy” OR AZ31 OR AZ91 OR WE43 OR “Mg-Ca” OR “Mg-Li-Ca”) AND (“plasma electrolytic oxidation” OR PEO OR “micro-arc oxidation” OR MAO) AND (coating OR composite OR sealing OR “layered double hydroxide” OR LDH OR inhibitor OR “self-healing” OR superhydrophobic OR SLIPS OR hydroxyapatite OR “Ca-P” OR tribocorrosion OR

biomedical OR implant). Targeted follow-up strings paired PEO/MAO with electrochemical impedance spectroscopy, potentiodynamic polarization, coating thickness, adhesion, scratch, wear rate, corrosion–wear, $H_2$ evolution, pH evolution, ion release, cytotoxicity and antibacterial performance.

Screening followed four practical steps: database search and backward/forward citation chasing; duplicate and off-topic removal; title/abstract screening for Mg or Mg-alloy substrates and PEO/MAO-based coating architecture; and full-text screening for process details, coating structure, failure mechanism and application-relevant validation. The final source corpus retained 106 references after relevance-based selection. Because this is a critical narrative review rather than a PRISMA meta-analysis, the corpus should be read as a transparent and reproducible evidence base for process comparison, not as a complete bibliometric census. Extracted fields included alloy grade, surface preparation, electrolyte chemistry and pH, current/voltage waveform, treatment time, coating thickness, phase composition, porosity or pore connectivity, post-treatment route, corrosion metrics, impedance evolution, adhesion or scratch response, wear rate, $H_2$ evolution, pH, ion release and biological indicators.

## 3. Advanced PEO/MAO Process Modules and Engineering Functions

PEO/MAO coatings are better treated as modular engineering systems than as a single coating category. The ceramic scaffold provides adhesion, roughness, hardness and a partial barrier, but application value comes from the functional module added to that scaffold and from the validation method used to prove its role. Table 1 summarizes the main advanced PEO/MAO process modules, their practical functions, typical risks and representative evidence bases.

**Table 1.** Advanced PEO/MAO process modules, engineering functions and evidence-based.

| Process Module | Practical Purpose | Key Process Choices | What It Solves | Main Risk | References |
|---|---|---|---|---|---|
| Dense PEO/MAO scaffold | build an adherent ceramic base layer | current mode, duty cycle, treatment time, bath anions | hardness, partial barrier, adhesion | connected pores and destructive arcs | [9–11,27,31,32,45,46] |
| Electrolyte/particle engineering | tune phase, porosity and hardness during PEO | silicate/phosphate/aluminate/fluoride; $ZrO_2$, $TiO_2$, ZnO, GO | stronger ceramic, wear resistance, bioactivity | unstable dispersion and arc intensification | [18,28,29,47–55] |
| Sol–gel/polymer sealing | close PEO pores after oxidation | sol–gel, silane, PMTMS, PLA/PLLA/PCL, epoxy | chloride blocking and topcoat compatibility | swelling, cracking or poor adhesion | [23,56–64] |
| LDH/inhibitor active layer | add ion exchange and inhibitor storage | MgAl-LDH, Ce, 8-HQ, BTA, phytic acid, GO/MOF/LDH | active corrosion protection after local attack | overclaiming self-healing without release evidence | [16,20,33,35,65–72] |
| Self-healing containers | restore the local barrier after damage | halloysite, micro/nano-containers, inhibitor-loaded LDH, polymer reservoirs | damage tolerance | finite reservoir and unclear recovery mechanism | [17,35,36,67,73–80] |
| Superhydrophobic or slippery top layer | delay wetting and fouling | nano/MOF texture, ZIF-8, stearic acid, silane, SLIPS | water delay, anti-soiling, salt splash protection | loss under abrasion, immersion or contamination | [15,21,37–43] |

**Table 1.** *Cont.*

| Process Module | Practical Purpose | Key Process Choices | What It Solves | Main Risk | References |
| --- | --- | --- | --- | --- | --- |
| Ca-P/HA/polymer biofunctional layer | control biodegradation and tissue response | Ca-P/HA, MgP/ZnP/CaP, PLLA/PCL, drug/antibacterial addition | implant degradation, cytocompatibility, osteogenesis | corrosion suppression may be too strong or too weak | [4,5,7,12–14,19,22,34,44,81–87] |
| Duplex wear or conductive layer | add tribological, thermal or electrical function | PVD, vapour deposition, cold spray, electroless plating, ATO-doped silane | wear/corrosion coupling, thermal management, conductivity | complex interfaces and process cost | [24,47,62,88–93] |

Design of a PEO/MAO-based coating stack begins before the electrical treatment. Grinding, polishing, alkaline cleaning, pickling and activation influence the surface defects that become discharge initiation sites. Alloy composition also matters: AZ, AM, WE, ZK, Mg-Ca and Mg-Li-Ca alloys differ in second-phase distribution, rare-earth content and galvanic heterogeneity, so the same bath and current programme can produce different pore structures and corrosion responses [27,28,30–32]. Process papers should report not only the alloy label but also surface preparation, specimen area, electrolyte age and bath temperature.

Initial surface roughness before PEO/MAO should also be reported. The literature reports, and laboratory practice often distinguish mirror-polished or sub-micrometre starting surfaces from ground or grit-blasted surfaces, but the numerical Ra range is preparation-specific rather than a universal criterion. Where values are provided, polished coupons may fall around 0.02–0.10 micrometre and mechanically roughened surfaces may reach approximately 0.2–1.0 micrometre or higher, depending on abrasive size, alloy condition and cleaning route. Because roughness changes discharge initiation, pore density, coating adhesion and wetting, authors should report the grinding/polishing sequence, final abrasive size, cleaning/activation route and Ra/Rz before oxidation, and should avoid cross-study comparisons when pre-oxidation roughness is missing.

The magnesium-alloy grade and nominal chemical composition should be reported because they determine micro-galvanic coupling and discharge behaviour. Representative substrates include AZ31 and AZ91 (Mg-Al-Zn systems), AM50/AM60 (Mg-Al-Mn systems), WE43 or WE54 (Mg-Y-rare-earth systems), ZK60 (Mg-Zn-Zr), Mg-Ca and Mg-Zn-Ca biomedical alloys, and Mg-Li-Ca lightweight/biodegradable systems. For review-level comparison, the alloy family should be linked to second phases, rare-earth content, Zn/Ca content and impurity control rather than treated as a generic “magnesium alloy”.

At the simplest level, the design logic is scaffold plus function. The PEO/MAO scaffold supplies adhesion, roughness, hardness and partial barrier behaviour; the added module should correct a specific limitation. Sealing modules reduce connected porosity. LDH and inhibitor modules add local response after damage. Particle modules tune phase composition and mechanical response during oxidation. Superhydrophobic and slippery modules delay wetting or fouling. Biomedical Ca-P/HA and polymer modules tune ion release, bioactivity and cell response. Duplex wear, conductive or thermal layers address functions that a ceramic oxide alone cannot deliver.

Choosing a module is only part of the design problem. A rough porous PEO layer helps mechanical interlocking with polymers and sol–gel networks, but excessive outer porosity can trap electrolyte and promote underfilm corrosion. LDH conversion can fill pores and introduce active protection, but aggressive hydrothermal conditions may transform or crack the PEO scaffold. Superhydrophobic chemistry benefits from hierarchical roughness, but that roughness is vulnerable to abrasion. Biomedical polymer sealing can

delay corrosion, but overly dense barriers may suppress the intended degradation of temporary implants [16,17,19,22,23,34,56–58,73].

Figure 1 should be read as a decision sequence. The dominant failure mode and service environment are defined first; the PEO/MAO process window is then chosen to give a mechanically stable scaffold; only the missing function is added; and the final stack is tested against the same failure mode used to justify the design. This sequence avoids a common weakness in the literature: a sophisticated multilayer coating validated only by a short-term polarization curve.

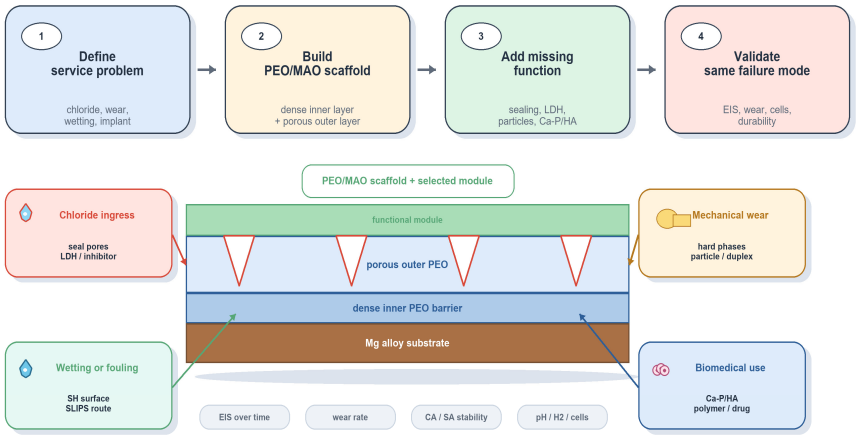


**Figure 1.** Application-driven process map for advanced PEO/MAO composite coatings on magnesium alloys.

Advanced PEO/MAO coatings are most clearly organized by failure mode. Chloride ingress through pores calls for sealing, LDH growth or inhibitor reservoirs. Mechanical wear calls for harder ceramic phases, particle incorporation or duplex wear layers. Biomedical degradation calls for Ca-P/HA, polymer or drug-loaded layers that regulate $H_2$ evolution and cell response. Superhydrophobicity is valuable when the service environment is dominated by splash, condensation or fouling; it is not automatically a long-immersion solution. Figure 1 turns this logic into a process-design map, in which the engineer identifies whether the problem is chloride penetration, wear, mechanical damage, fouling, conductivity/thermal management or biomedical degradation before selecting a PEO/MAO module. The same map also shows why every module needs a matching validation method.

The next practical question is not which process is newest, but which process solves which function. PEO-only coatings are useful baselines for hardness and adhesion, whereas active corrosion protection, wetting control and biomedical response require additional modules. Figure 2 summarizes the suitability of major PEO/MAO composite routes across key engineering functions. For Figure 2, the suitability score is defined as follows: zero means that the module is normally irrelevant or should be avoided for the function; one means optional or weakly supported; two means useful but condition-dependent; and three means a core or strongly supported route for that function. Scores were assigned by combining the mechanistic role of each module with representative evidence cited in the corresponding tables; they should be read as evidence-informed design guidance, not as averaged performance values or statistical rankings. No single coating route scores highly for every function. LDH/inhibitor and container systems are strongest for active protection; particle-assisted PEO and duplex layers are stronger for wear; superhydrophobic or slippery surfaces are strongest for wetting control; Ca-P/HA/polymer stacks are strongest for biomedical function. The matrix is intended to help build coating stacks from required functions rather than to rank papers.


**Figure 2.** Function-based matrix for advanced PEO/MAO composite coating strategies.

A unified evidence rubric was added for Figures 2, 3 and 7 to reduce subjective scoring. A score of three was assigned only when the module is mechanistically essential and repeatedly supported by direct experimental evidence for the target function; two indicates a useful but service-dependent route supported by structural evidence plus at least one quantitative performance metric; one indicates a plausible or auxiliary role with limited or indirect validation; and zero indicates no normal functional relevance or a risk of misleading overclaim. The supporting evidence was taken from the process and validation tables rather than from visual preference: corrosion and PEO scaffold evidence [1–3,6,8–11,27–29,31,32,45], LDH/self-healing evidence [16,17,20,33,35,36,65,73–80], wetting-control evidence [15,21,37–43], biomedical evidence [4,5,7,12–14,22,34,44,81–85] and wear/duplex evidence [24,47,88–94].

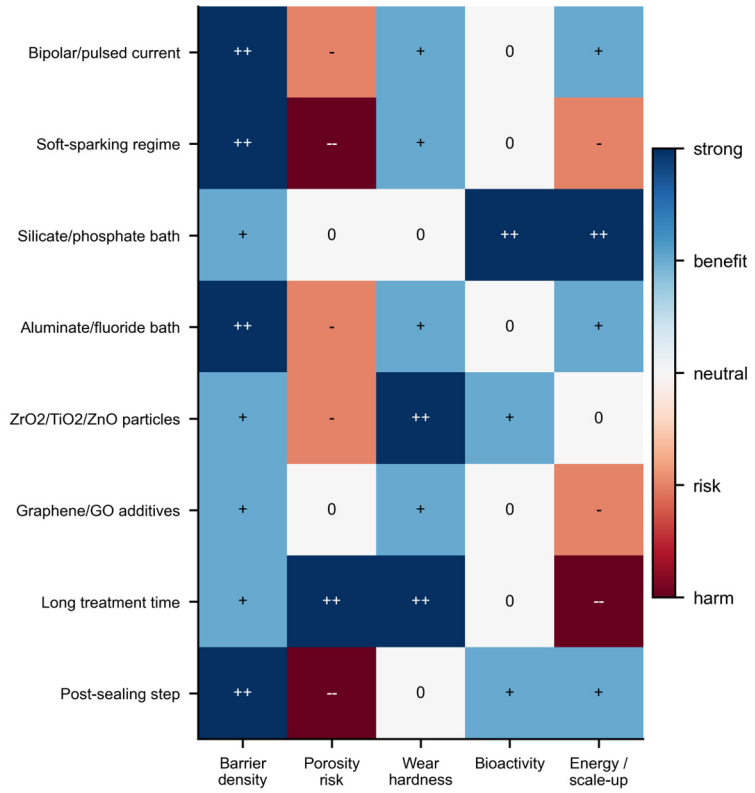


**Figure 3.** Qualitative process−response window for PEO/MAO coating design.

## 4. Engineering the PEO/MAO Ceramic Scaffold

PEO/MAO quality is largely decided before any post-treatment is added. Current density, waveform, duty cycle, frequency, treatment time, bath conductivity, electrolyte anions, bath temperature and alloy composition determine discharge intensity and the balance between a compact inner layer and a porous outer layer [10,11,27–32,45,48–50,95,96]. Advanced composite coatings fail when the underlying ceramic scaffold is too porous, weakly adherent or cracked. Post-sealing cannot reliably correct destructive arc damage or poor interfacial integrity.

PEO/MAO growth is governed by anodic oxide formation, dielectric breakdown, localized plasma discharge, melting/solidification and electrolyte-assisted incorporation. At low energy, the coating is usually thin and may contain fewer large defects, but it may not provide enough load-bearing capacity or phase development. At high energy, the coating grows faster and can become harder, yet destructive arcs, thermal cracks and connected pores can reduce barrier performance. Current density, voltage limit, duty cycle, frequency and treatment time therefore need to be discussed as coupled variables rather than isolated optimization factors [9–11,31,32,45].

The inner/outer layer distinction matters for engineering performance. The inner layer is generally denser and more relevant to barrier properties, whereas the outer layer is thicker, rougher and more porous. Many papers report coating thickness as a positive result, but a thick porous outer layer can increase electrolyte uptake and reduce reproducibility. EIS is useful here because it can separate coating resistance and charge-transfer processes over time, but interpretation requires equivalent-circuit transparency and post-immersion cross-sections [27–31,49,50].

Electrolyte composition controls both the discharge regime and the coating chemistry. Silicate-containing baths can support $Mg_2SiO_4$-related phases and relatively strong ceramic networks. Phosphate-containing baths are attractive for corrosion and biomedical applications because phosphate species can enter the coating and support Ca/P functionalization. Aluminate and fluoride species may promote densification or improve corrosion response, but environmental and biomedical acceptability must be considered. The same additive can help one application and complicate another if it changes toxicity, residual fluoride content or disposal requirements [28,29,48–52,96].

Convincing PEO/MAO papers connect process parameters to discharge morphology, phase structure and long-term performance. Optical emission or voltage–time behaviour can indicate discharge stability; SEM and cross-section images reveal pores and cracks; XRD, Raman or XPS identify phases; EIS and immersion tests show whether the layer remains protective after electrolyte penetration. Without this chain, a claim such as “improved corrosion resistance” is too thin to guide process design.

Residual stress should be treated as a coating-specific risk rather than as a universal constant. PEO/MAO layers can contain tensile or compressive residual stresses produced by rapid melting/solidification, thermal mismatch and growth defects. Because reported values depend strongly on measurement method, substrate geometry, coating thickness, phase composition, discharge intensity and post-treatment, this review treats tens to several hundreds of MPa only as an order-of-magnitude warning reported in some coating systems, not as a general design value. XRD $\sin^2\psi$, curvature or other stress measurements should be reported when cracking, delamination, thick coatings or load-bearing implants are discussed.

For magnesium alloys, practical PEO/MAO electrolytes are often alkaline to maintain Mg surface stability and stable discharge behaviour. An approximate pH 9–13 interval should be read as a common reporting window for many silicate, phosphate and aluminate baths, not as a universal optimization target; near-neutral Ca/P-containing biomedical

baths may be used when biological compatibility or apatite-forming chemistry is the priority. Strongly acidic or chloride-rich electrolytes are generally unsuitable for stable Mg PEO because they accelerate substrate dissolution. The initial and final pH, buffering capacity and bath ageing should therefore be reported.

The main process trade-off is not simply "thicker coating is better". Higher energy and longer treatment usually increase thickness and hardness, but they can also increase pore connectivity and cracking. Pulsed or bipolar regimes can moderate discharge behaviour, but they add process complexity. Electrolyte chemistry can improve barrier density or bioactivity, but fluoride or aggressive additives may create environmental or biomedical concerns. Figure 3 summarizes these trade-offs as a process-response window. It uses the same 0–3 logic as Figure 2, but the scores describe process-response tendencies rather than final coating superiority. Barrier density, porosity risk, wear hardness, bioactivity and energy or scale-up burden are read together. Positive scores identify routes that can support a target response under controlled conditions; low or negative scores mark recurring risks that should be checked experimentally, such as destructive arcs, particle sedimentation, fluorinated-waste concerns or excessive energy demand. Table 2 lists process variables, useful targets and reporting requirements. The underlying point is interaction: a particle-filled bath can improve hardness but destabilize discharges if dispersion is poor, and a long treatment can increase load-bearing capacity while leaving a porous outer layer vulnerable in chloride service. Post-sealing targets connected porosity, but it does not compensate for an unstable PEO scaffold. Authors should report waveform, final voltage, duty cycle, frequency, electrolyte composition, bath pH, temperature, treatment time, particle size and dispersion method.

**Table 2.** PEO/MAO process variables, useful targets and reporting requirements.

| Variable | Low or Mild Setting | High or Aggressive Setting | Useful Target | Engineering Note | References |
|---|---|---|---|---|---|
| Current density/voltage | thinner, lower energy, fewer large arcs | thicker oxide but more discharge defects | dense inner layer with limited outer porosity | report waveform, frequency, duty cycle and final voltage, not only treatment time | [31,32,45] |
| Current mode | DC or simple unipolar modes are simple | bipolar/pulsed modes can control discharge better | stable arcs and lower defect connectivity | mode choice should be linked to EIS evolution and cross-section | [45,96] |
| Electrolyte anions | phosphate/silicate can support bioactivity and barrier growth | aluminate/fluoride can densify, but may raise toxicity or environmental concerns | phase chemistry matched to service | avoid comparing coatings without bath composition and pH | [28,29,49–51] |
| Treatment time | lower roughness and thinner layer | higher roughness, higher hardness, higher risk of cracks | thickness sufficient for wear but not over-porous | long treatment is not automatically better | [9,11,32] |
| Bath temperature and ageing | more stable early bath | changed conductivity and particle dispersion after use | reproducible discharge regime | rarely reported, but important for scale-up | [10,11] |
| Particle loading | a modest addition can fill pores or change phase | excessive addition can agglomerate and disturb arcs | stable dispersion with functional incorporation | include particle size, dispersion method and bath stability | [18,54,55] |

For Figure 3 specifically, process-response scores were assigned from reported trends in coating thickness, pore connectivity, compact-layer formation, hardness or wear response, EIS retention and process burden. Thus, high thickness alone did not receive a high

score unless it was accompanied by evidence of lower defect connectivity or improved application performance.

## 5. Electrolyte and Particle Engineering

Table 3 organizes the main electrolyte and particle-engineering routes by intended function, evidence requirement and the literature support. This is the most direct route for changing the ceramic scaffold during PEO/MAO. Silicate, phosphate, aluminate and fluoride-containing baths have been widely used to change the oxide phase, coating thickness, porosity and corrosion response [28,29,47–52]. Particle addition extends the same route: $ZrO_2$, $TiO_2$, ZnO, $CeO_2$, graphene oxide and related additives can modify discharge channels, local melting and the final ceramic network [18,53–55,88,95,97–99]. The advantage is that functionality is introduced in one process step; the trade-off is reproducibility.

**Table 3.** Electrolyte and particle routes for functional PEO/MAO coating design.

| Additive Route | Examples | Intended Function | Evidence That Should Be Shown | Typical Limitation | References |
|---|---|---|---|---|---|
| Ceramic nanoparticles | $ZrO_2$, $TiO_2$, ZnO, $CeO_2$ | hardness, barrier densification, bioactivity or antibacterial effect | cross-section incorporation, phase data, EIS, wear or cell test | particles may sit on the surface rather than enter the layer | [18,53–55] |
| Carbonaceous additives | graphene oxide, graphene derivatives | barrier tortuosity, wear reduction, electrical/thermal function | Raman/XPS support, dispersion evidence, tribology and corrosion–wear | agglomeration and galvanic concerns if poorly controlled | [88,97–99] |
| Rare-earth or inhibitor species | Ce, La, 8-HQ, BTA, phytic acid | active inhibition and re-passivation | release/precipitation evidence and damaged-coating tests | the inhibitor effect may be confused with pore sealing | [20,33,35,66,67,74] |
| Ca/P-containing electrolytes | calcium phosphate, hydroxyapatite-related baths | bioactivity and degradation moderation | Ca/P ratio, apatite formation, pH/$H_2$/cell response | a good SBF response does not prove implant performance | [12,19,22,44,82–87] |
| Conductive or functional fillers | ATO, MOF-derived structures, MXene-related systems | conductivity, active storage, surface function | conductivity or release measurements linked to corrosion | high novelty but often weak scale-up evidence | [62,71,80,93] |

Particle and electrolyte engineering is attractive because it introduces function during the PEO/MAO step rather than through a separate post-treatment. Ceramic particles such as $ZrO_2$, $TiO_2$, ZnO and $CeO_2$ can increase hardness, modify discharge behaviour, support antibacterial activity or introduce corrosion-inhibiting species. Carbonaceous additives such as graphene oxide can increase tortuosity and improve tribological response. Ca/P-containing species can support bioactivity and apatite formation. These effects should be tied to cross-section mapping, phase analysis or chemical evidence rather than assumed from the bath recipe [18,19,53–55,88,97,98].

The mechanism is not simple mechanical mixing. Particles may be electrophoretically transported, trapped in molten oxide, sintered into the discharge channel, adsorbed on the outer surface or partially reacted with electrolyte species. Each pathway produces a different coating architecture. A particle that sits mainly on the outer surface may improve roughness or wetting but may not improve the inner barrier. A particle that enters discharge channels may increase hardness but can also intensify local arcing if dispersion is unstable.

This helps explain why some particle-assisted coatings improve wear without necessarily improving long-term immersion performance.

Dispersion control is missing from many process descriptions. Nominal particle concentration is not enough. Particle size distribution, zeta potential, ultrasonic treatment, stirring rate, surfactant use, pH, bath ageing and sedimentation should be reported, especially when the route is proposed for scale-up. Reproducibility becomes difficult when early specimens are treated in a freshly dispersed bath and later specimens are treated after particle settling or electrolyte heating.

For application-oriented work, the evidence package should match the intended particle function. A $ZrO_2$ or $TiO_2$ route for wear should include hardness, friction coefficient, wear-track morphology and corrosion–wear coupling. A ZnO or antibacterial route should include ion release and cytocompatibility in addition to bacterial inhibition. A graphene or GO route should include Raman/XPS support and a discussion of galvanic risk. A Ca/P route should go beyond SBF apatite formation and include pH, $H_2$ evolution and cell response when biomedical relevance is claimed.

## 6. Sealing, Sol–Gel and Polymer Hybridization

Table 4 lists sealing and hybridization routes that convert porous PEO/MAO into serviceable composite coatings. Because PEO/MAO coatings often fail through connected pores, sealing is not a decorative secondary step. It is a direct way to turn a porous ceramic scaffold into a barrier layer. Early sealed-MAO studies demonstrated improved corrosion response on AZ91D [59]. Sol–gel coatings, silanes, PMTMS, PLA, PLLA, PCL, epoxy and other polymer layers have since been used to close pores, improve topcoat compatibility or tailor biomedical degradation [23,56–58,60–64].

**Table 4.** Sealing, sol–gel and polymer hybridization routes for PEO/MAO-coated magnesium alloys.

| Sealing Process | Best Use Case | Process Benefit | Failure Mode to Check | References |
|---|---|---|---|---|
| Hydrothermal or inorganic sealing | chloride barrier on PEO pores | converts or blocks open porosity | cracking during drying and incomplete pore closure | [59,61] |
| Sol–gel/silane sealing | thin corrosion barrier and paint-compatible interface | penetrates pores and forms a hybrid inorganic–organic network | shrinkage cracks and poor adhesion under scratch | [57,62,64] |
| Polymer sealing | biomedical or flexible barrier function | slows electrolyte transport and improves toughness | swelling, delamination and loss of wear resistance | [23,58,63] |
| Epoxy/topcoat over PEO/silane | industrial corrosion protection | combines adhesion, barrier and inhibitor options | the coating stack may fail at the PEO/polymer interface | [23,60] |
| Graphene oxide composite sealing | barrier tortuosity and wear improvement | fills paths and can improve tribology | dispersion, galvanic coupling and reproducibility | [88,97–99] |

Because connected porosity is the main weakness of PEO/MAO, sealing is often the most useful post-treatment. Hydrothermal sealing, sol–gel networks, silanes, PMTMS, epoxy, PLA, PLLA, PCL and related polymers can reduce electrolyte access by filling pores, forming a continuous top layer, or improving compatibility with paints and organic coatings [23,56–64]. The engineering purpose is not to hide the PEO structure; it is to convert a high-adhesion porous ceramic scaffold into a lower-permeability composite coating.

Sol–gel and silane systems are useful when a thin, conformal and chemically bonded layer is needed. They can penetrate pores and form hybrid inorganic–organic networks, but shrinkage during drying, incomplete hydrolysis/condensation and interfacial defects can create new crack paths. Polymer sealing can provide stronger transport resistance and mechanical compliance, but swelling, solvent retention, thermal mismatch and low

scratch resistance still need to be checked. Epoxy or paint systems are relevant for industrial protection, where PEO/MAO may function mainly as an adhesion-promoting pretreatment.

Biomedical polymer layers need a different interpretation. A degradable polymer on PEO/MAO can slow initial corrosion and provide a drug reservoir, but the correct target is a controlled degradation profile, not maximum impedance. For example, a PLLA/PCL or PLA-based system may improve early barrier behaviour while allowing gradual water uptake and polymer degradation. The risk is delamination under $H_2$ evolution, trapped corrosion products or excessive suppression of degradation in a temporary implant [7,22,34,58,63].

Sealing studies need layer-by-layer controls. Bare alloy, PEO-only, sealant-only where feasible, PEO plus sealant and the final functional system should be compared. Cross-sections after sealing, adhesion tests, scratch or pull-off results, time-dependent EIS and post-corrosion morphology are more informative than a single corrosion-current value. For industrial service, salt spray or cyclic corrosion and adhesion after exposure are more meaningful than short immersion alone.

## 7. LDH, Inhibitors and Active Protection

LDH/inhibitor systems address a limitation that passive barriers cannot avoid: local damage and chloride ingress. LDH layers can provide physical blocking, anion exchange and inhibitor storage. MgAl-LDH, Ce-modified PEO, 8-hydroxyquinoline, benzotriazole, phytic acid, GO/LDH hybrids and metal–organic framework (MOF)-decorated LDH systems have all been explored on PEO/MAO-treated magnesium alloys [16,20,33,35,65–72,74]. This family is most relevant to marine, automotive and severe chloride conditions where defects cannot be fully eliminated.

On PEO/MAO-treated magnesium, LDH growth can occur through hydrothermal conversion, in situ growth or post-treatment in nitrate, carbonate or inhibitor-containing solutions. MgAl-LDH systems are common, but Ce species, 8-hydroxyquinoline, benzotriazole, phytic acid, graphene oxide and MOF/LDH hybrids can add active corrosion-protection behaviour [16,20,33,35,65,67–72,74]. Their value is highest when local damage, chloride ingress or coating defects remain likely in service.

The process window for LDH formation is narrow. Temperature, pH, solution composition and treatment time influence platelet morphology, crystallinity, interlayer anions and pore filling. A mild treatment may leave insufficient LDH coverage; an aggressive treatment can attack the PEO layer or create brittle deposits. The PEO composition itself affects LDH nucleation and conversion behaviour, so LDH growth should not be discussed as an independent topcoat detached from the scaffold chemistry [20,33,65,69].

Active protection requires more evidence than a lower corrosion current. A credible inhibitor-based LDH coating should demonstrate inhibitor loading, chloride-triggered exchange or pH-triggered release, and local suppression after damage. Damaged-coating EIS, localized electrochemical testing, release kinetics, surface chemistry after corrosion and cross-section images near scratches are stronger than intact-coating polarization. Without these tests, the improvement may simply reflect better sealing rather than smart protection.

A practical weakness of many LDH studies is the absence of reservoir accounting. Inhibitor amount, release rate, repeated exposure and long-term stability decide whether the coating can survive real service. If all inhibitors are released early, the coating may show excellent short-term performance but weak damage tolerance later. For severe chloride applications, future LDH work should report both initial barrier properties and the time-dependent active response after artificial damage.

Active protection must be separated from simple sealing. An LDH-coated sample is not self-healing merely because its corrosion current is lower. It becomes active only

when an inhibitor is stored, triggered, released and linked to local corrosion suppression. Figure 4 shows this process logic and the required evidence chain. The PEO layer supplies adhesion and ceramic support. The LDH or active conversion layer stores inhibitor species and reduces connected porosity. When chloride or a scratch creates a local corrosion path, pH and ion exchange can trigger inhibitor release and local precipitation. To support this claim, authors should measure inhibitor loading, release kinetics, damaged-coating EIS and chemical evidence of film reformation. Table 5 compares representative active-layer designs and the minimum proof needed to separate active protection from ordinary pore sealing.

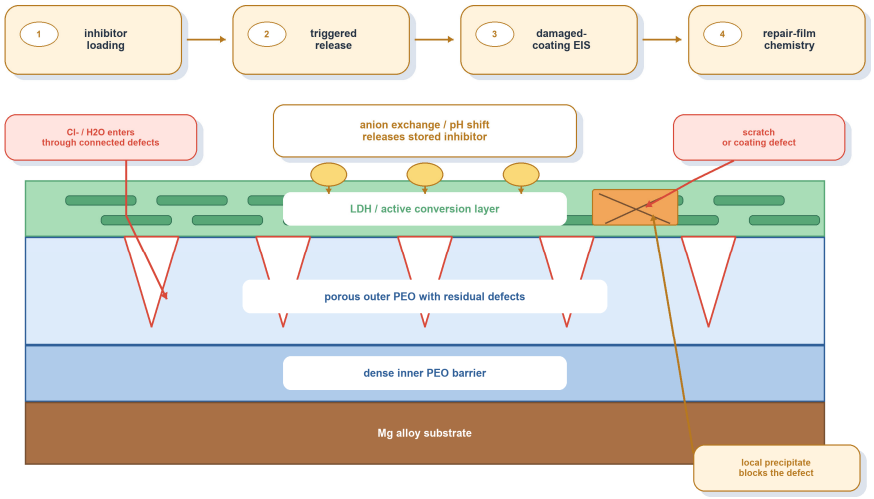


**Figure 4.** LDH/inhibitor and self-healing mechanism for PEO/MAO-based magnesium-alloy coatings.

**Table 5.** LDH, inhibitor and active-layer process designs for PEO/MAO magnesium coatings.

| Active-Layer Design | Process Route | Function Added Beyond Baseline PEO/MAO | Minimum Proof Needed | References |
|---|---|---|---|---|
| PEO/Ce/LDH | PEO followed by Ce modification and LDH growth | combines a ceramic barrier, rare-earth inhibition and anion exchange | LDH morphology, Ce chemistry, EIS after immersion and damaged-coating response | [20,33,66] |
| PEO/MgAl-LDH/inhibitor | in situ LDH growth with 8-HQ, BTA or other inhibitors | stores inhibitors near connected defects | loading amount, release kinetics and comparison with inhibitor-free LDH | [16,35,65,69,72] |
| GO/LDH hybrid layer | graphene oxide as a carrier or barrier support with LDH | increases tortuosity and can host inhibitor molecules | proof of GO location, LDH growth and active-release effect | [35,69,71] |
| MOF/GO/LDH layer | MOF-decorated GO/LDH on MAO | high storage area and tunable chemistry | stability in chloride solution and no loss of adhesion | [39,71] |
| Phytic acid/Ce coating | reactive organic/rare-earth conversion over MAO | lower-temperature active sealing route | chemical state, self-healing test and long-term EIS | [67,100] |

## 8. Self-Healing Coatings: Useful Concept, Strict Evidence

Table 6 sets stricter criteria for deciding whether a coating should be described as self-healing rather than merely corrosion-resistant. The concept is attractive because real coatings are scratched, abraded and locally damaged. Halloysite nanotubes, micro/nano-containers, inhibitor-loaded LDH, polymer reservoirs and dual-function hydrophobic/self-healing layers have been reported for magnesium alloy protection [17,35,36,56,67,73–80]. The application value is clearest for components exposed to handling damage, stone impact, machining marks or cyclic chloride environments.

**Table 6.** Evidence criteria for self-healing claims in PEO/MAO-based magnesium coatings.

| Claim | Weak Evidence | Strong Evidence | Recommendation | References | Quantitative Comparison to Report |
|---|---|---|---|---|---|
| Self-healing | impedance remains high during immersion | controlled scratch followed by time-resolved impedance recovery | include PEO-only, sealed-only and active-container controls | [17,35,36,73–80] | scratch width/depth; $\|Z\|$ 0.01 Hz before damage, after damage and after recovery; recovery ratio; $i_{corr}$ or corrosion rate; coating thickness; $n \geq 3$. |
| Inhibitor release | an inhibitor is listed in the bath or coating | release profile measured under pH/chloride trigger | link release to local corrosion suppression | [35,67,74,78,80] | inhibitor loading (mass or mol $cm^{-2}$), release rate, trigger pH/$Cl^-$ level, release duration and residual reservoir after exposure. |
| Barrier regeneration | corrosion current decreases | local precipitation or film reformation is chemically observed | use SEM/EDS/XPS or local electrochemical mapping | [35,67,75,79] | repair-product thickness/coverage, local chemistry by SEM/EDS/XPS, $\|Z\|$ 0.01 Hz recovery, $i_{corr}$ change and chloride content near damage. |
| Long-term durability | 24 h or 72 h corrosion test | multi-week immersion with post-corrosion cross-section | report failure mode rather than only final impedance | [17,36,73,77] | immersion duration, EIS retention percentage, mass loss or corrosion rate, cross-section after exposure and time to visible failure. |
| Repeatability | one best sample | repeated coating batches and error bars | critical for scale-up and coatings reviewers | [10,11,32] | at least three independent coating batches, mean +/− SD, batch coefficient of variation and full process parameters. |

Self-healing coatings should be described carefully. In magnesium-alloy research, the term is sometimes used when impedance increases after immersion or when corrosion products partly block pores. That behaviour may be useful, but it is not necessarily engineered self-healing. A stronger definition requires a defined damage event, a responsive storage or conversion mechanism, time-resolved recovery and a non-responsive control that separates healing from ordinary corrosion-product deposition [17,35,36,67,73–80].

Container-based systems use halloysite nanotubes, micro/nano-containers, polymer reservoirs, inhibitor-loaded LDH, GO/LDH hybrids or related structures to store active species. The trigger may be chloride ingress, pH change, local corrosion chemistry, mechanical rupture or water uptake. For PEO/MAO coatings, the porous ceramic scaffold provides anchoring and space for reservoirs, but it also complicates interpretation because pores can physically trap inhibitors even without a designed container.

The finite reservoir is the main application constraint. Self-healing is not unlimited repair. It has a loading capacity, a release threshold, a diffusion path and a consumption rate. Authors should avoid broad statements such as “permanent self-healing” unless repeated damage or long-term cycling is demonstrated. A more useful claim is that a coating delays corrosion after a defined scratch for a defined time under a defined chloride condition.

Validation should combine electrochemical and chemical evidence. A practical package includes scratch geometry, optical or SEM images before and after exposure, time-resolved EIS, local pH or scanning electrochemical measurements, inhibitor release data, chemical identification of precipitated protective products and a sealed but non-inhibiting

control. This package is demanding, but without it, self-healing becomes a label rather than an engineering property.

## 9. Superhydrophobic and Slippery PEO/MAO Surfaces

Superhydrophobic coatings use micro/nano roughness and low-surface-energy chemistry to delay water and chloride access. PEO/MAO is a natural rough scaffold for these surfaces. Recent routes include zeolitic imidazolate framework-8 (ZIF-8)/MOF-based layers, ZnO@ZIF-8 nanorods, graphene oxide/stearic acid systems, silane or fatty-acid modification and dual superhydrophobic/self-healing designs [15,21,36–43,73]. Slippery liquid-infused porous surface (SLIPS) designs are also relevant because they can reduce fouling and droplet adhesion.

These surfaces exploit two features of PEO/MAO: roughness and coating adhesion. After PEO/MAO creates micro/nano-scale texture, low-surface-energy molecules, fatty acids, silanes, MOF-derived structures, ZnO@ZIF-8 arrays, graphene oxide/stearic acid systems or liquid-infused layers can reduce water contact and delay chloride access [15,21,37–43]. The route is most appropriate for splash, condensation, anti-soiling and fouling-related service.

The mechanism is a wetting-state mechanism, not simply a corrosion-barrier mechanism. A high static contact angle indicates low apparent wettability, but protection depends on whether the surface remains in a Cassie-like state or transitions toward wetting under pressure, abrasion, salt crystallization, oil contamination or long immersion. Once water penetrates the roughness, the underlying PEO/MAO defects may again become transport paths. Contact angle alone is therefore a weak predictor of long-term corrosion protection.

Slippery liquid-infused porous surface (SLIPS)-type surfaces may reduce fouling and droplet pinning more reliably than fragile air-trapping surfaces, but they introduce another failure mode: lubricant depletion. A slippery PEO/MOF surface, for example, should show lubricant retention, sliding-angle stability, abrasion response and chemical compatibility with the service medium. For outdoor or marine components, UV ageing, salt contamination and cleaning cycles are also relevant.

The most useful wetting-control papers pair wetting data with durability data. Static contact angle, sliding angle and hysteresis should be reported before and after abrasion, immersion and contamination. EIS after forced wetting is more meaningful than EIS while the surface is still dry or air-retaining. If a coating is claimed to protect magnesium in long immersion, the study should show what happens after the trapped-air or lubricant state is partly lost.

Durability is the application question. A high static contact angle before corrosion testing has limited value if the surface loses the air layer during abrasion, immersion, acid exposure, salt crystallization or oil contamination. Figure 5 separates wetting-control routes from the durability evidence required for application claims. Superhydrophobicity is a surface-state strategy, not a universal corrosion solution. It is valuable for splash, condensation, fouling and early wetting delay, but long immersion or abrasion can remove the trapped-air state. SLIPS-type surfaces may resist fouling more effectively, but require lubricant retention evidence. For practical coatings, contact angle, sliding angle, hysteresis, abrasion, immersion, and EIS after wetting and contaminated-surface tests should be reported together. Table 7 links wetting-control routes to the durability evidence required for corrosion, fouling or splash-service claims.

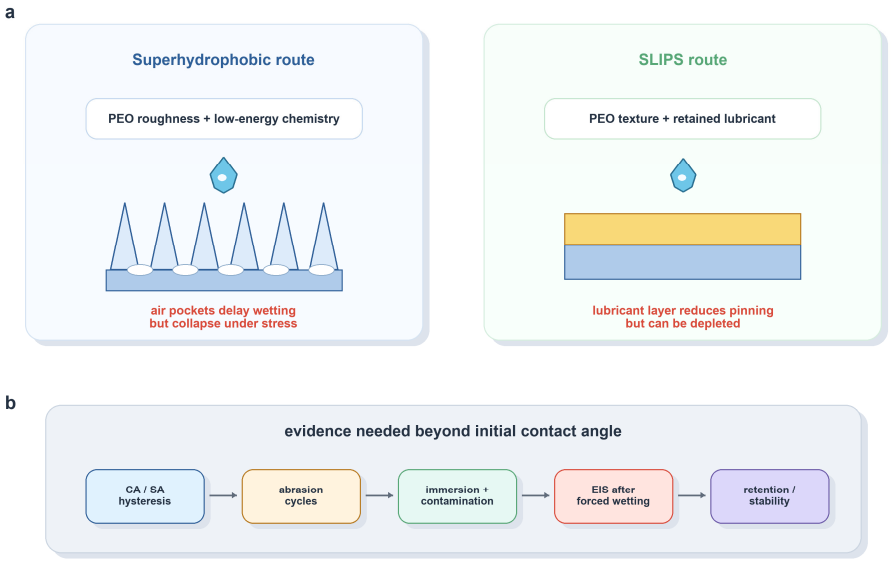


**Figure 5.** Wetting-control routes on PEO/MAO magnesium coatings and the evidence needed beyond initial contact angle: (**a**) two wetting-control routes built on PEO roughness; (**b**) evidence needed beyond contact angle.

**Table 7.** Superhydrophobic and slippery PEO/MAO surface routes and durability requirements.

| Wetting-Control Route | Process Sequence | Application Value | Mandatory Durability Evidence | References | Quantitative Comparison to Report |
|---|---|---|---|---|---|
| PEO + low-energy silane/fatty acid | rough PEO scaffold followed by chemical modification | simple water-delay route | contact-angle hysteresis, immersion and abrasion | [15,21,43] | coating/top-layer thickness; static contact angle, sliding angle and hysteresis; \|Z\|0.01 Hz and $i_{corr}$ before/after abrasion or immersion. |
| PEO + GO/stearic acid | MAO, GO deposition, stearic acid modification | anti-soiling and improved chloride delay | fouling, EIS after wetting and mechanical durability | [42] | GO or modifier loading; contact-angle retention; EIS after forced wetting; abrasion cycles/load; wear track or mass-loss data. |
| PEO + ZIF-8 or MOF layer | grow or deposit MOF/nano arrays on MAO | hierarchical roughness and possible active storage | acid/salt stability and adhesion | [37,39,40] | MOF/ZIF layer thickness, adhesion/scratch response, acid/salt stability, \|Z\|0.01 Hz retention and corrosion rate after immersion. |
| Superhydrophobic + self-healing | combine water delay with inhibitor response | dual protection under early wetting and later damage | show both wetting durability and scratch recovery | [36,73] | both wetting retention and scratch-recovery metrics: contact angle, sliding angle, damaged-coating EIS and inhibitor-release profile. |
| SLIPS on PEO texture | infuse lubricant into a rough porous layer | anti-fouling and low adhesion of droplets | lubricant retention, wear and long immersion | [39] | lubricant mass/volume retention, sliding-angle stability, immersion time, abrasion response and EIS after lubricant depletion. |

## 10. Biomedical PEO/MAO, Ca-P/HA and Polymer Functionalization

Biomedical magnesium coatings have a different objective from automotive coatings. The target is not maximum corrosion resistance, but controlled degradation, manageable $H_2$ evolution, favourable pH evolution, cytocompatibility, antibacterial or osteogenic function where needed and sufficient mechanical integrity during healing. PEO/MAO, Ca-P/HA

layers, phosphate conversion, fluoride-containing MAO coatings, PLLA/PCL polymers, drug-loaded silanes and hydroxyapatite/MgO composite coatings have all been used to tune this balance [4,5,7,12–14,19,22,34,44,81–87,101,102].

Biomedical PEO/MAO coatings require a performance vocabulary different from that used for industrial corrosion coatings. For temporary implants, the desired surface does not simply block corrosion; it shapes the early degradation response while preserving enough mechanical support during healing. The coating should moderate pH rise and $H_2$ evolution, reduce local alkalization, support bone-related cell response, and eventually allow safe degradation [4,5,7,12–14,19,22,34,44,81–87].

Ca-P, hydroxyapatite (HA), magnesium phosphate, zinc phosphate and related conversion or PEO-derived layers are attractive because they can improve bioactivity and support apatite formation. Apatite formation in simulated body fluid (SBF), however, is only a screening indicator. It does not prove osteogenesis, antibacterial performance or in vivo integration. A Ca/P-containing PEO layer should be connected to ion-release profiles, cell adhesion/proliferation, osteogenic markers where relevant and corrosion/degradation kinetics in physiologically meaningful media [12,19,44,82–87].

The evidence hierarchy for biomedical claims should be explicit. SBF apatite formation is a preliminary bioactivity screen; buffered immersion, $H_2$ evolution and ion-release tests indicate degradation control; cell viability, adhesion, osteogenic markers and antibacterial assays address biological response; and animal or ex vivo testing is needed before claims of implant-level integration or healing performance. This distinction prevents in vitro surface activity from being overinterpreted as clinical suitability.

Polymer and drug-loaded layers add another level of control. PLLA, PCL, PLA, silane and composite polymer coatings can slow water ingress and carry antibacterial or osteogenic agents. The design risk is interfacial failure caused by $H_2$ evolution, swelling or weak adhesion to the PEO scaffold. For antibacterial systems, the minimum evidence should include bacterial inhibition and cytocompatibility together; strong antibacterial activity alone is insufficient if the released species harms host cells [22,34,44,63,78].

The degradation window in Figure 6 should guide experiment design. A coating that keeps residual barrier function very high may be unsuitable for an implant intended to resorb. A coating that loses function too fast may expose the substrate before tissue healing begins. Biomedical studies should report pH, $H_2$ evolution, mass loss or ion release, surface morphology, corrosion products, cell response and residual mechanical integrity over time. Strong papers also compare the same coating in SBF, phosphate-buffered saline (PBS) or cell culture media because proteins, chloride, phosphate and buffering capacity change degradation behaviour.

The degradation mechanism of coated magnesium implants is not simple dissolution of a stable oxide. Although $MgO/Mg(OH)_2$ and Ca-P/HA phases can be relatively stable locally, body fluid enters through pores, cracks, coating defects and the coating/substrate interface. Magnesium then dissolves anodically under the coating, $H_2$ is produced cathodically, $Mg(OH)_2$ forms, but can be destabilized by chloride to soluble $MgCl_2$, and interfacial alkalization, gas accumulation and corrosion-product wedging can undermine the coating. Ca-P/HA or polymer layers slow this sequence and promote bioactivity, but they do not eliminate underfilm degradation if connected pathways remain.

There is no single permissible load range for all PEO/MAO-coated magnesium implants, because the allowable load depends on implant geometry, alloy, defect tolerance, implantation site and healing time. Review papers should therefore avoid a universal load claim and instead require residual mechanical validation under the intended device condition. For temporary orthopedic fixation, coating studies should report bending, com-

pression, torsion or fatigue retention during degradation and should not claim load-bearing suitability from corrosion data alone.

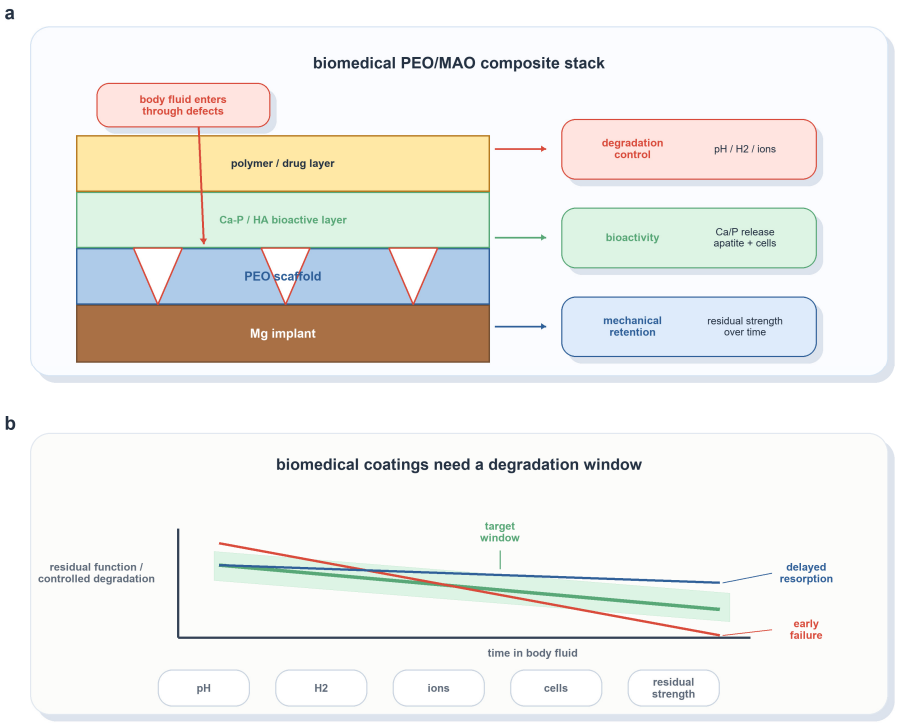


**Figure 6.** Biomedical PEO/MAO composite coating logic for magnesium alloys: (**a**) biomedical PEO/MAO composite stack; (**b**) biomedical coatings need a degradation window.

The advanced-process problem is a window problem. If the coating dissolves too fast, the implant loses mechanical function and produces excessive $H_2$. If the coating blocks corrosion too strongly, the implant may not degrade as intended. Figure 6 presents this target window and the multilayer process stack used to approach it. A PEO scaffold can moderate initial degradation and provide roughness. Ca-P/HA or magnesium phosphate layers can improve bioactivity. A polymer or drug layer can regulate ion release, antibacterial activity or cell response. The coating should be judged by time-dependent pH, $H_2$ evolution, ion release, cytocompatibility, antibacterial activity, where relevant and residual mechanical integrity, not only by polarization resistance. Table 8 summarizes biomedical coating targets and the minimum evidence needed to support degradation-control, osteogenic or antibacterial claims.

**Table 8.** Biomedical PEO/MAO, Ca-P/HA and polymer functionalization targets for magnesium alloys.

| Biomedical Target | Useful Coating Stack | Key Process Control | Required Evidence | References | Quantitative Biomedical Metrics to Report |
|---|---|---|---|---|---|
| Orthopedic temporary fixation | Mg alloy + PEO/MAO + Ca-P/HA or PLLA/PCL | degradation rate and interfacial adhesion | SBF/PBS immersion, pH, $H_2$, ion release, cell viability and residual strength | [4,5,7,12–14,34] | coating thickness; $H_2$ evolution rate; pH drift; $Mg^{2+}$/$Ca^{2+}$/P release; cell viability; residual bending/compression strength over time. |
| Osteogenic surface | PEO with Ca/P-containing bath or post-HA layer | Ca/P ratio, apatite formation and roughness | apatite growth, osteoblast response and corrosion rate | [19,44,82,85–87] | Ca/P ratio; apatite coverage; corrosion rate; ALP/osteogenic markers; cell adhesion/proliferation; ion-release profile. |

**Table 8.** *Cont.*

| Biomedical Target | Useful Coating Stack | Key Process Control | Required Evidence | References | Quantitative Biomedical Metrics to Report |
|---|---|---|---|---|---|
| Antibacterial implant | PEO/polymer/drug or $TiO_2$/HA composite | drug loading and release without cytotoxicity | antibacterial assay, cell compatibility and release profile | [22,78,83] | drug/ion loading and release; antibacterial reduction; mammalian-cell viability; pH and $H_2$ evolution in relevant medium. |
| Low-temperature active protection | MAO + in situ Mg-Al LDH or polymer layer | avoid damaging the biodegradable alloy microstructure | degradation, cytocompatibility and LDH stability | [22,63,68] | degradation rate, extract cytotoxicity, hemolysis or inflammatory markers when relevant; residual mechanical integrity. |
| Balanced degradation | multilayer PEO/polymer/Ca-P | avoid both rapid failure and over-passivation | time-dependent pH/$H_2$ and mechanical retention | [19,22,34,44,63] | coating adhesion/scratch response, sterilization effect, extract ratio, cell line, medium composition and replicate number. |

## 11. Application-Oriented Selection of Coating Stacks

A process has application value only when it maps onto a real service condition. Automotive and aerospace magnesium parts need coating adhesion, cyclic corrosion resistance and paint compatibility. Electronics housings may require thinness, conductivity or heat dissipation in addition to corrosion control. Marine or severe salt service needs active inhibition and damage tolerance. Wear parts need corrosion–wear tests. Orthopedic implants need degradation and biological evidence.

Application-oriented selection translates laboratory functions into service conditions. Automotive and aerospace parts usually require adhesion, cyclic corrosion resistance, paint compatibility and tolerance to mechanical damage. Marine and severe chloride service requires active protection and long immersion or salt-spray durability. Electronics housings may need corrosion resistance without sacrificing electrical or thermal function. Wear parts require hardness and low friction, but also corrosion–wear coupling because wear can expose fresh magnesium and accelerate localized attack [24,47,60,62,89–94].

For structural applications, the best coating is rarely the most complex coating. A dense PEO scaffold plus a stable sealant may outperform a highly functional multilayer if the latter cracks, delaminates or cannot be scaled to complex geometry. Industrial routes must consider power consumption, bath lifetime, edge effects, internal corners, threaded holes, masking, repairability and compatibility with primers or paints. A coating that works on a flat coupon may fail on a component with sharp edges because discharge density and coating thickness are not uniform.

Moving from coupon-scale PEO/MAO studies to components also requires attention to geometry and manufacturing constraints. Edge effects, threaded holes, internal corners, masking, current density non-uniformity, bath ageing, particle sedimentation, power consumption, repairability and compatibility with primers or paints can decide whether a coating that performs well on a flat coupon remains useful on a real part, especially for additively manufactured or geometrically complex magnesium components [103].

For biomedical applications, module selection is governed by healing time and biological risk. A temporary bone implant may need a PEO/Ca-P/polymer stack, whereas an antibacterial implant may need an additional drug or ion-release layer. Such additions must be balanced against cytocompatibility and degradation. Biomedical coating design is

therefore a trade-off among corrosion moderation, biological function and residual strength, not a race toward maximum impedance.

Figure 7 converts process modules into an application-selection matrix rather than a universal ranking. In this matrix, three means that the module is normally core to the application claim, two means useful under defined service conditions, one means optional or secondary, and zero means unnecessary or potentially distracting for that application. The scores are qualitative guidance: they ask authors to justify each layer by a measurable function and a matching validation test. Table 9 translates this logic into recommended coating stacks and common overclaims to avoid. A single "best" coating does not exist. Dense PEO scaffolds and polymer sealing are core for many corrosion applications; LDH/inhibitor layers become core when damage and chloride exposure are expected; superhydrophobic or slippery surfaces are useful for wetting and fouling control but are not enough for long immersion by themselves; Ca-P/HA is central for implants but irrelevant for electronics housings; and duplex wear layers are essential for tribological service but unnecessary for degradable implants.

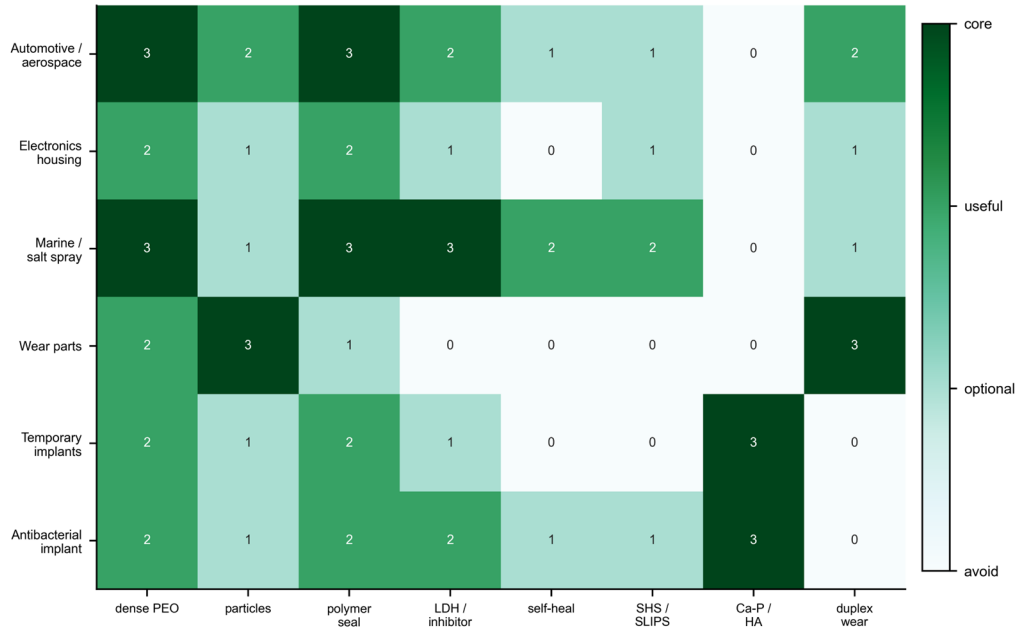


**Figure 7.** Application-oriented module selection matrix for PEO/MAO-based composite coatings on magnesium alloys.

**Table 9.** Application-oriented selection of PEO/MAO-based coating stacks.

| Application | Recommended Stack | Why This Stack | Avoid This Overclaim | References |
|---|---|---|---|---|
| Automotive or aerospace Mg components | dense PEO + sol–gel/polymer seal + optional inhibitor | balances adhesion, chloride barrier and coating compatibility | do not infer cyclic corrosion life from one polarization scan | [1,9,23,60,104] |
| Electronics housing | thin PEO + conductive or thin polymer/silane seal | protects while preserving dimensional and possible electrical/thermal needs | do not ignore conductivity, heat dissipation or coating thickness | [62,93] |
| Marine or severe salt exposure | dense PEO + LDH/inhibitor + durable topcoat | needs both barrier and active response | contact-angle-only evidence is not enough | [16,20,33,60,65] |
| Wear or sliding parts | PEO + ceramic particles or duplex wear layer + sealed pores | combines hardness with corrosion–wear resistance | wear data without corrosion–wear coupling is incomplete | [24,47,88–93] |

**Table 9.** *Cont.*

| Application | Recommended Stack | Why This Stack | Avoid This Overclaim | References |
| --- | --- | --- | --- | --- |
| Biodegradable orthopedic implant | PEO + Ca-P/HA + degradable polymer or drug layer | controls degradation while improving tissue response | maximum corrosion resistance is not automatically the best outcome | [4,5,7,12–14,19,22,34,44,81–85] |
| Antibacterial temporary implant | PEO + Ca-P/HA or polymer + antibacterial component | combines degradation control and infection control | the antibacterial effect must be checked with cytocompatibility | [22,78,83] |

For Figure 7, the application score was assigned by matching each module to the minimum evidence required by the service condition. For example, LDH/inhibitor layers receive high scores only where damage-tolerant chloride protection is required; Ca-P/HA and degradable polymers receive high scores only for biomedical service; and superhydrophobic/SLIPS layers are scored as auxiliary for immersion corrosion unless wetting durability and post-wetting EIS are demonstrated.

## 12. Validation Protocols That Make Advanced Processes Useful

Many advanced coating papers are limited less by novelty than by weak verification. A paper may combine PEO, LDH, inhibitor, polymer and superhydrophobic chemistry, but without layer-by-layer controls, it is impossible to know which component solved which problem. The minimum useful control sequence is bare alloy, PEO-only, PEO plus one module and the final composite. For self-healing or active inhibition, a non-responsive sealed control is also needed.

Validation is where process-driven reviews become useful to experimental authors. Magnesium coatings are often screened by potentiodynamic polarization, but polarization alone can overstate protection because it is short, destructive and sensitive to surface condition. EIS over immersion time, $H_2$ evolution, pH tracking, mass loss, cross-sectional morphology and post-corrosion chemistry are more informative for long-term behaviour. When a coating claims active protection or self-healing, intact-coating data are not enough.

Equivalent-circuit fitting should be handled cautiously. A fitted resistance value is meaningful only when the circuit is physically justified, a fitting error is reported, and the result is checked against morphology. For porous PEO/MAO coatings, water uptake and pore resistance can change during immersion, so a single EIS spectrum after a short exposure does not reveal service durability. Longitudinal EIS with post-test cross-sections is a stronger design tool.

Mechanical and interfacial tests are also needed. Adhesion, scratch resistance, hardness and wear response decide whether a coating survives handling, assembly and service. For duplex or particle-assisted coatings, corrosion and wear should be coupled rather than tested separately. A coating that reduces friction in dry sliding may still fail rapidly if wear exposes fresh magnesium in a chloride solution.

Statistical and reproducibility reporting remain common weak points. Batch-to-batch repeatability, specimen area, edge sealing, bath temperature, stirring, treatment time, particle dispersion and surface preparation should be documented. For biomedical work, the biological replicate definition, extract ratio, medium composition and sterilization method should be stated. These details may look routine, but they decide whether another laboratory can reproduce the coating. Table 10 gives the minimum and stronger test packages needed to make advanced-process claims useful rather than decorative.

The validation package should also specify the standard or standard-like method used for each claim. Corrosion studies should report exposed area, edge sealing, electrolyte

composition, temperature, immersion duration and whether corrosion rate was calculated from mass loss or electrochemical current. Adhesion and wear studies should report loading geometry, counter-body, sliding speed, distance, humidity and coating thickness. Biomedical studies should report sterilization, extraction ratio, medium composition, biological replicate definition and the acceptance criterion used for cytocompatibility.

**Table 10.** Validation packages required for advanced PEO/MAO-based magnesium coating claims.

| Claimed Advantage | Minimum Test Package | Stronger Application-Level Package | References | Relevant Standards, Test Conditions, Sample Preparation and Statistics |
|---|---|---|---|---|
| Corrosion protection | OCP, polarization, EIS over time, immersion morphology | multi-week immersion, cross-section after corrosion, salt spray or cyclic corrosion | [1–3,6,8,9,11] | ASTM G31 [105] immersion; ASTM G59 [106] or ASTM G5 [107] polarization; ASTM G102 [108] corrosion-rate calculation; ISO 16773-2 [109] EIS; ASTM B117 [110] or ISO 9227 [111] salt spray, where relevant. Reporting: Report alloy grade/composition, roughness, exposed area, edge sealing, coating thickness, immersion volume, temperature, n $\geq$ 3 and mean +/− SD. |
| Pore sealing | porosity/morphology, EIS before and after sealing | dye penetration or local electrochemistry plus adhesion and scratch | [23,57,59,61,64] | cross-section SEM/EDS, dye penetration or local electrochemistry; ISO 16773-2 [109] EIS; ASTM D3359 [112] tape or ASTM D4541 [113] pull-off adhesion, where applicable. Reporting: Report surface roughness before PEO, sealant thickness/curing, adhesion failure mode, n $\geq$ 3 and post-test cross-section. |
| Active inhibition | damaged-coating EIS and inhibitor release | local pH/chloride response, chemical proof of precipitation and repeated batches | [16,20,33,35,65] | artificial scratch with defined width/depth; chloride or pH trigger; inhibitor loading/release kinetics; damaged-coating EIS and local chemical mapping. Reporting: Report defect size, inhibitor amount, release medium, pH/$Cl^-$ condition, repeated exposure and control coatings. |
| Self-healing | controlled scratch and time-resolved recovery | mechanistic release/repair evidence and non-responsive controls | [17,35,36,73–80] | defined scratch geometry; time-resolved EIS; optical/SEM observation before and after exposure; non-responsive sealed control. Reporting: Report scratch tool, load, recovery time, repeated damage cycles, recovery ratio and independent coating batches. |
| Superhydrophobic protection | static angle, sliding angle, EIS | abrasion, immersion, contamination, acid/salt and recovery of wetting state | [15,21,37–43] | static/dynamic contact angle, sliding angle and hysteresis before/after abrasion, immersion, salt contamination and forced wetting; post-wetting EIS. Reporting: Report abrasion load/path/cycles, droplet volume, contamination medium, immersion time and wetting-state failure criterion. |

**Table 10.** *Cont.*

| Claimed Advantage | Minimum Test Package | Stronger Application-Level Package | References | Relevant Standards, Test Conditions, Sample Preparation and Statistics |
|---|---|---|---|---|
| Biomedical performance | SBF/PBS, pH, $H_2$, ion release, cell viability | antibacterial tests, mechanical retention, animal or ex vivo validation, where appropriate | [4,5,7,12–14,22,34,44,81–85] | ISO 10993-5 [114] cytotoxicity and ISO 10993-12 [115] sample preparation; SBF/PBS/cell medium composition; $H_2$ evolution, pH, ion release and residual strength. Reporting: Report sterilization method, extract ratio, cell line, medium, incubation time, biological replicates, viability threshold and residual mechanical data. |
| Wear/corrosion durability | hardness, friction and wear tracks | corrosion–wear coupling and post-test cross-section | [24,47,88–93] | ASTM G99 [116] pin-on-disc or equivalent tribology protocol; load, speed, distance, counter-body, environment and wear-rate calculation; corrosion–wear when service involves electrolyte. Reporting: Report hardness, coating thickness, normal load, sliding speed, track radius, sliding distance, coefficient of friction, wear volume/rate and $n \geq 3$. |

As a minimum statistical requirement, quantitative comparisons should be reported as mean +/− standard deviation from at least three independently prepared specimens or independent coating batches unless a standard or device-specific protocol requires more. For EIS fitting, equivalent-circuit choice, fitting error and raw spectra should be reported; for biological assays, both technical and biological replicates should be distinguished.

Table 10 can also be used as an application-claim checklist before a PEO/MAO composite coating is described as advanced.

For corrosion protection, the coating should show time-dependent electrochemical and morphological evidence. For pore sealing, it should show pore closure and adhesion after exposure. For active inhibition or self-healing, it should show loading, trigger, release and local recovery. For wetting control, it should show contact-angle stability after abrasion, immersion and contamination. For biomedical use, it should show degradation, biological response and residual mechanical relevance. For wear service, it should include corrosion–wear coupling rather than dry wear alone.

## 13. Research Gaps with Direct Application Value

One unresolved gap is scale-up. Many advanced PEO/MAO composite coatings are demonstrated on small flat coupons, whereas real components have edges, holes, threads, variable thickness and non-uniform current distribution. Future work should report coating uniformity on complex shapes, bath ageing, power consumption and maintenance of particle or inhibitor dispersion over repeated processing.

A second gap is mechanism-resolved validation. Advanced coatings often combine PEO, particles, LDH, inhibitors, polymers and hydrophobic chemistry in one stack. Without layer-by-layer controls, the contribution of each module is unclear. Future papers should include subtractive designs: PEO-only, PEO plus one module, PEO plus two modules and final stack. This is the only way to judge whether complexity is justified.

A third gap is coupled with degradation testing. Structural components experience chloride, stress, abrasion, temperature changes and coating damage together. Implants

experience body-fluid chemistry, proteins, cells, mechanical load and time-dependent corrosion together. Single-factor tests are useful for screening, but application claims require coupled protocols.

Data standardization is another gap. PEO/MAO papers should report enough process detail to reproduce the coating: waveform, current density, final voltage, duty cycle, frequency, bath composition, pH, conductivity, temperature, treatment time, specimen area, surface preparation, particle dispersion and post-treatment conditions. A shared reporting checklist would make future quantitative synthesis more reliable.

Service-specific failure language is still weak. Many papers use general claims such as high corrosion resistance, excellent self-healing or good biocompatibility, but these phrases do not identify a service condition. A stronger paper should state whether the coating is designed for splash corrosion, long immersion, cyclic salt exposure, corrosion–wear, damage tolerance, bacterial challenge or temporary implantation. Each service condition demands a different validation package.

Life-cycle and environmental assessment also need more attention. PEO/MAO is often described as environmentally favourable compared with chromate-based treatments, but advanced processes may introduce fluorides, rare-earth salts, organic solvents, inhibitors, fluorosilanes or high-energy post-treatments. Future studies should include bath durability, waste treatment, energy demand and safe chemistry choices when industrial translation is claimed.

The most useful next step is not simply adding more layers. It is designing fewer, better-justified layers that solve known failure modes. A useful coating stack for magnesium alloys should be modular, testable and application-specific.

## 14. Limitations of the Present Review

This review has three limitations. As a critical narrative review rather than a systematic review, it uses the selective literature corpus organized by application logic and should not be read as a complete bibliometric map of all PEO/MAO studies. The suitability matrices are qualitative tools based on mechanism-service matching and representative evidence, not meta-analytic effect-size estimates. Rapidly developing areas, including MOF/LDH hybrids, MXene-containing coatings, multifunctional biomedical coatings and industrial scale-up, will also require periodic updating as longer-term durability and reproducibility data become available. Recent reviews of MAO functionalization and modern PEO applications also show why this field will require periodic updating as hybrid architectures and validation practices evolve [117,118].

## 15. Conclusions

PEO/MAO remains a central process for magnesium-alloy surface engineering because it creates an adherent ceramic scaffold that can accept further functionalization. Its value is not that it produces a universally protective coating. Its value lies in the combination of adhesion, roughness, ceramic load support and electrolyte-derived chemistry that can serve as a platform for sealing, active protection, wetting control, biomedical function or wear resistance.

The main practical conclusion is that advanced coating design should start from the failure mode. Chloride ingress requires pore sealing, active LDH/inhibitor response or both. Wear service requires ceramic load support, particle or duplex strengthening and corrosion–wear verification. Damage-prone service requires controlled scratch tests and evidence of inhibitor release or repair. Splash, fouling and condensation conditions may justify superhydrophobic or slippery layers, but long immersion requires proof that the wetting state survives. Temporary implants require a degradation window in which

corrosion, biological response and residual mechanical integrity are balanced rather than maximally suppressed.

Multilayer complexity also needs layer-by-layer evidence. Adding particles, polymers, LDH, inhibitors and hydrophobic chemistry can produce impressive short-term results, but it can also create brittle interfaces, swelling layers, unstable reservoirs, lubricant loss or over-passivation. Strong future PEO/MAO papers will use fewer, better-explained modules and prove each module with a matching test.

For coatings readers, the reporting standard can be simple: describe the PEO/MAO process completely, state the target failure mode, explain why each added module is necessary, and validate the coating under conditions that reproduce the claimed service. This process-driven logic turns magnesium-alloy surface treatment from a list of recipes into an engineering design framework.

**Author Contributions:** Conceptualization, L.L. and X.Y.; methodology, X.Y. and L.L.; validation and evidence classification, L.L., X.Y. and K.X.; formal analysis, L.L. and X.Y.; investigation, X.Y.; resources, D.Z.; data curation, L.L. and X.Y.; writing—original draft preparation, L.L.; writing—review and editing, X.Y., Y.X., D.Z. and K.X.; visualization, Y.X.; supervision, X.Y.; project administration, X.Y.; funding acquisition, L.L. and X.Y. All authors have read and agreed to the published version of the manuscript.

**Funding:** This research was funded by the Scientific Research Programme, the Education Department of the Shaanxi Provincial Government, grant number 23JP087.

**Institutional Review Board Statement:** Not applicable. This review did not involve human participants, animals or new biological experiments.

**Data Availability Statement:** No new data were created or analyzed in this study. Data sharing is not applicable to this article. All cited information is available in the published literature referenced in the manuscript.

**Conflicts of Interest:** The authors declare no conflicts of interest.

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