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Improving the inflammatory-associated corrosion behavior of magnesium alloys by Mn₃O₄ incorporated plasma electrolytic oxidation coatings

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ABSTRACT

Biodegradable magnesium alloys for orthopedic bone fixation have been introduced for various fields of application. The corrosion resistance of magnesium implants weakens in physicochemical environments and is further compromised during post-implantation inflammation. In this study, Mn₃O₄-incorporated plasma electrolyte oxidation (PEO) coatings were developed on Mg-Zn-Ca substrate through two approaches: the addition of KMnO₄ salt and the inclusion of Mn₃O₄ nanoparticles into the electrolyte composition. Incorporating additives into electrolytes led to a reduction in surface porosity and an increase in coating thickness in both synthesis approaches. The electrochemical and immersion corrosion tests were conducted under simulated normal conditions and inflammatory conditions, where inflammatory solutions were prepared with the addition of hydrogen peroxide (H₂O₂) and hydrochloric (HCl) acid. Both corrosion studies revealed that inflammation significantly increased the corrosion rate of the uncoated Mg-Zn-Ca biomaterial, escalating from approximately 2 mm/year to 16 mm/year. Moreover, corrosion studies showed that the composite PEO coatings, incorporating Mn₃O₄ nanoparticles (MnPR-PEO), demonstrated superior corrosion performance among all coated samples. Potentiodynamic polarization results indicated a substantial reduction in corrosion current density, decreasing from 73.9 μA·cm⁻² for basic PEO coatings to 5.5 μA·cm⁻² for MnPR-PEO coatings. The improved performance of Mn₃O₄-incorporated PEO coatings, attributed to their catalytic H₂O₂ scavenging, suggests promise for magnesium implants, offering enhanced corrosion resistance and potential biomedical application benefits.

1. Introduction

Orthopedic surgery has been greatly influenced by the substantial impact of innovative metallic implants in their development and application [1]. Magnesium-based biomaterials have been a subject of research and development in medical devices due to several advantages they offer over permanent metallic implants like stainless steel and titanium [2]. The inherent biodegradability of magnesium implants enables their absorption after fulfilling their load-bearing role, eliminating the necessity for a subsequent surgical procedure for removal [2]. Moreover, magnesium implants can possess mechanical characteristics akin to natural bone, making them a favorable option for orthopedic purposes by significantly reducing the 'stress shielding' effect [3]. Although magnesium alloys demonstrate promise as implant materials, the high degradation rate poses a substantial challenge, limiting their widespread use [3]. The corrosion challenges associated with magnesium extend beyond the field of biomedical applications, impacting a broader spectrum of chemical engineering fields, including functional roles in environmental and energy applications like sacrificial electrodes, fracture balls in the oil industry, transient electronics, and battery anodes [4].

The placement of an orthopedic device in the body typically results in initiating an inflammatory reaction [5]. This response is a natural and expected part of the body's immune system reacting to the presence of a foreign object and the invasive surgical procedure itself [5]. The inflammatory microenvironment becomes a site for the generation of reactive oxygen species (ROS) like superoxide (O₂⁻) and hydrogen peroxide (H₂O₂) due to the aerobic respiration and metabolic activity in activated macrophages [6,7]. Additionally, osteoclasts may release hypochlorous acid (HOCl) in bone tissues adjacent to an implant in
response to inflammatory conditions [7]. The release of this acid can decrease the pH levels near the recently implanted device, potentially causing it to drop to approximately 5.0 [8]. Physiological corrosion of magnesium occurs due to an electrochemical reaction between the metal and water, forming a passivating magnesium hydroxide (Mg(OH)₂) thin layer and releasing hydrogen (H₂) [9]. The Mg-O-H Pourbaix diagram indicates that the stability of the Mg(OH)₂ layer can only be maintained under an alkaline environment, typically at pH levels exceeding 10.0, whereas acidic or neutral surroundings will result in the instability of Mg(OH)₂ [10]. When the pH of the environment decreases during inflammatory conditions, it accelerates corrosion kinetics, leading to a significantly faster rate of degradation of magnesium biomaterials [10], which is further enhanced by the presence of H₂O₂ in inflammatory media, which can also trigger localized corrosion on the magnesium surface, such as pitting corrosion [11,12].

Enhancing magnesium corrosion resistance is paramount for its successful utilization in many applications, including biomaterials [2,3]. The common strategy for increasing alloys corrosion resistance involves additions of elements such as aluminum (Al), zinc (Zn), calcium (Ca), or rare earth (RE) elements, into the magnesium matrix [13], which form intermetallic phases and protective layers [13]. For example, this was demonstrated for the in vivo and in vitro biodegradation behavior of the Mg-Zn-Ca biomaterial, leading to a favorable characteristic of slow and homogeneous degradation [14]. Surface modification of magnesium including various coatings, treatments, and nanostructuring, is another highly effective strategy for enhancing its corrosion resistance by creating protective barriers mitigating exposure to corrosive environments and prevent ion penetration [15,16].

One of such treatments gaining recent attention is plasma electrolytic oxidation (PEO), sometimes referred to as micro-arc oxidation (MAO). This technology exhibits great promise with the potential to enhance the corrosion performance of magnesium implants in simulated normal and inflammatory biological settings [11,17]. In the PEO process, porous magnesium oxide (MgO) coatings are formed on magnesium surfaces through guided electro-oxidation in alkaline electrolytes, achieved through the application of voltages surpassing the dielectric strength of the passive layer [18]. Prepared coatings exhibit a dual-layer structure comprising the inner compact and outer porous layers. The effectiveness of PEO coatings in preventing corrosion relies on various characteristics, among which thickness and porosity are significant factors [18,19]. When corrosive ions infiltrate the outer porous layer containing micropores and microcracks, they may potentially target and corrode the interface between the inner barrier layer and the substrate [20]. Therefore, it is crucial to enhance the protective capabilities and biofunctionality of PEO coatings by either improving or mending their porous structures [19,21–23].

The electrolyte composition has a paramount role in shaping and modifying the characteristics of PEO coatings [18,24], and there has been growing interest in enhancing the functionality of magnesium implants by incorporating micro- and nano-additives into the electrolyte and creating composite coatings [25–27]. Diverse additives may comprise inert oxide particles or electrolyte-soluble salts, that integrate into the developing MgO coating during the PEO treatment [24,27]. The inclusion of additives in the alkaline electrolyte can influence the PEO process by modifying the electrolyte characteristics, such as pH level, conductivity, and viscosity, potentially impacting the properties of the resulting coating [24–27]. A proper integration of these additives into the electrolyte can effectively decrease imperfections in the PEO coating and increases its thickness for anti-corrosion purposes [28].

Materials with ROS-scavenging properties, which can be added to PEO process, are attractive for various biomedical and environmental applications [29]. For example, particles with ROS-scavenging properties derived from cerium (Ce) [30], silver (Ag) [31], manganese (Mn) [32], and platinum (Pt) [33] are interacting with H₂O₂ in the conditions at in vivo inflammation. Such particles can act as antioxidants by accepting electrons from ROS or by catalyzing reactions that transform ROS into less harmful compounds [30–33]. There is, however, a limited knowledge of quantitative indication of their ability to modify the surfaces of metallic implants, which may offer a promising avenue for reducing corrosion rates in inflammatory conditions. In a recent study [34], it was documented that a CeO₂ layer on anodized titanium can enhance the corrosion resistance of implants in H₂O₂-containing simulated body fluids. In our prior investigation [35] it was also observed that MnO₃ nanoparticles, applied to anodized tantalum, have exhibited increased catalase-like activity and provided protective qualities when exposed to an acidic solution containing H₂O₂. Despite the remarkable electrochemical characteristics of MnO₃, it has received limited attention in PEO coatings as a secondary oxide phase within the coatings. A preliminary investigation [36] indicated that the inclusion of KMnO₄ in the electrolyte composition enhances the electrochemical corrosion protection of PEO layers on Mg-Al-Zn alloy in a seawater environment (3.5 wt% NaCl solution). However, it is noteworthy that the specific mechanism of this enhanced protection was not reported in the study. A recent study [37] showed the introduction of Mn(NO₃)₂ to the electrolyte used in the PEO process on titanium alloys. Those findings indicated that TiO₂-MnO₃ coatings demonstrated exceptional catalytic activity and corrosion resistance but the latter was only evaluated in a simulated seawater solution rather than biological media containing H₂O₂.

In this study, we are reporting the method of introduction of MnO₃ into MgO coatings on the Mg-Zn-Ca substrate by a simple, one-step PEO process, but employing and comparing two separate methods: in-situ synthesis by KMnO₄ addition ("salt route") and via direct MnO₃ nanoparticle integration ("particle route"), followed by quantitative assessment of their corrosion resistance ability to withstand simulated inflammatory conditions through electrochemical testing.

2. Materials and method

2.1. Substrates preparation

The alloy was metallurgically produced by co-melting of a mixture of pure magnesium (99.99 wt%), pure zinc (99.99 wt%), and Mg-20 wt.% Ca master alloy at 800 °C within a graphite crucible under CO₂ plus 0.8 vol% SF₆ protective gas, using an electric-resistant furnace at the University of Tehran, Iran, leading to the resulted composition of Mg-2.1 wt % Zn-0.6 wt% Ca. The melt was cast into at a reduced temperature of 400 °C to obtain minimal cast defects at a slower solidification rate. The cast alloys underwent a 24 h homogenization at 350 °C, followed by quenching in water. The ingots were machined into samples 150 × 100 × 10 mm size, which were then hot-rolled preheated at 160 °C and then at 350 °C for 15 min with a reduction in each pass of 20%. Following multiple rolling passes, sheet samples were cut into pieces 25 × 10 × 1 mm. Samples were ground with silicon carbide (SiC) emery papers with grit sizes of 320, 800, 1500, and 3000 for final surface finish. To observe the microstructure, a pical solution was utilized for etching, comprising 20 mL of deionized (DI) water, 100 mL of ethanol (Merck), 5 g of picric acid (Bicca), and 6.5 mL of acetic acid (QRec). The examination was performed using a scanning electron microscope (SEM, Hitachi TM-4000Plus-RAMI) and an optical microscope (OM, Leica DM2500S) as (supplementary Fig. S1). Figure S1 displays the prepared alloy’s microstructure, primarily characterized by a dominant α-Mg matrix, accompanied by the presence of CaMgZn₃ and distributed Mg₆Ca along grain boundaries. (Supplementary Fig. S2) depicts the phase diagram of the Mg-Zn-Ca ternary alloy, with the experimental alloy component indicated by a red star. The composition Mg-2.1 wt% Zn-0.6 wt% Ca was selected for this study due to its demonstrated controlled degradation and favorable in vitro corrosion resistance, as reported in the existing literature [38].

2.2. PEO treatment of substrates

Before the PEO process, polished substrates were cleaned during 10
min by ultrasound in acetone, followed by drying with warm air. The PEO process employed a power supply (Plasma-Pazhoulh) that delivered pulsed direct current (DC), where the Mg-Zn-Ca substrate served as the anode and a cathode was established using a stainless-steel cooling tube. During the oxidation period of 15 min, the PEO coatings were produced with a steady frequency of 1000 Hz, a duty cycle of 50 %, and a current density of 100 mA cm\(^{-2}\). The electrolyte temperature during PEO was maintained at 30 °C by circulating cold water in the cathode tube. The electrolyte used for the basic PEO coating consisted of a water-based solution comprising 5 g\(^{-1}\) of tri-potassium phosphate trihydrate (K\(_3\)PO\(_4\).3H\(_2\)O, Merck) and 2 g\(^{-1}\) of potassium hydroxide (KOH, Merck). The samples treated in this electrolyte were denoted as “BSC-type” which stands for basic PEO coating.

To prepare the composite coatings on the magnesium alloy using both particulate ("PR-type") and in-situ salt ("SL-type") methods, 4.5 g\(^{-1}\) of manganese(II,III) oxide nanoparticles (Mn\(_3\)O\(_4\) NPs, 99.95 % purity, US-Nano) and potassium permanganate (K\(_2\)MnO\(_4\), Merck) salt were individually introduced into the base electrolyte, resulting in two distinct electrolyte solutions referred to as MnPR-PEO and MnSL-PEO. The SEM (Zeiss Evo-Ma15) image of Mn\(_3\)O\(_4\) NPs is presented in the insert of Supplementary Fig. S3a. The transmission electron microscopy (TEM) micrograph and the associated selected-area electron-diffraction (SAED) pattern for Mn\(_3\)O\(_4\) NPs have been previously documented in our prior publication [35]. The ZetaSizer instrument (Malvern, ZEN3600) was employed to assess both particle size distribution and zeta potential within the standard KOH electrolyte. The results are shown in Supplementary Fig. S3. Table 1 presents the characteristics of the electrolytes. Conductivity and pH values were assessed with the aid of Mettler Toledo Inlab 730 probes and Metrohm 691 pH meters.

2.3. Coating characterization

The surface and cross-sectional morphologies were observed using SEM (Zeiss Evo-Ma15). An energy-dispersive X-ray spectrometer (EDS, Ametek, Apollo X) unit, integrated with the SEM, was employed to analyze the chemical compositions of the coatings. To prepare cross-sectional PEO-coated Mg alloys, wire electrical discharge machining (WEDM, Excetek NP600L) was employed for cutting, followed by epoxy mounting, SiC paper polishing, and thorough DI water rinse and drying. To facilitate SEM analysis, a thin gold film was sputtered onto the samples by desk sputter coater (NSC DSR1) to enhance their conductivity. SEM images of the coating surface were subject to analysis using Image J (6.0 version, National Institutes of Health) software to determine coating porosity. The average coating thickness and surface roughness were measured in ten distinct areas across the coated substrates, employing PHYNIX FN and PHYNIX TR-100 instruments, respectively. To examine coating phases, the Panalytical MPD-01 X-ray diffraction (XRD) device was employed in Bragg-Brentano geometry, featuring a copper K\(_\alpha\) radiation source with a monochromator (\(\lambda = 0.154 \text{ nm}\)). The diffractometry was conducted at 40 kV and 35 mA, with a scanning rate of 5° per min and a step size under an angle range from 20° to 80°.

Table 1

<table>
<thead>
<tr>
<th>Sample</th>
<th>Electrolyte (g L(^{-1}))</th>
<th>pI</th>
<th>Conductivity (mS cm(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>BSC-PEO</td>
<td>K(_3)PO(_4).3H(_2)O</td>
<td>2</td>
<td>12.27</td>
</tr>
<tr>
<td>MnSL-PEO</td>
<td>K(_2)MnO(_4)</td>
<td>4.5</td>
<td>12.82</td>
</tr>
<tr>
<td>MnPR-PEO</td>
<td>Mn(_3)O(_4) NPs</td>
<td>2</td>
<td>12.25</td>
</tr>
</tbody>
</table>

2.4. Electrochemical corrosion tests

Potentiodynamic polarization (PDP), and electrochemical impedance spectroscopy (EIS) tests were employed to assess the corrosion performance. These evaluations were conducted using a three-electrode setup, which consisted of a reference electrode (Ag/AgCl), an auxiliary electrode (a graphite rod in 3 mm diameter), and a working electrode (uncoated/coated magnesium alloy with a 1 cm\(^2\) exposed area). The measurements were carried out using a potentiostat (IViumStat.h standard). To create the basic solution, five phosphate-buffered saline tablets (PBS, Merck) were dissolved in 1 L of DI water, representing normal physiological conditions. Upon dissolving a single tablet in 200 mL of DI water, it resulted in a PBS solution with a composition of 0.01 M phosphate buffer, 0.0027 M potassium chloride, and 0.137 M sodium chloride, maintaining a pH of 7.34 at 25 °C. To mimic inflammatory conditions near metallic implants, a solution of 150 mM H\(_2\)O\(_2\) (30 %, Merck) was added in PBS, with the pH adjusted to 5.2 using hydrochloric acid (HCl, 37 %, Merck). The measurements were conducted within 1 L simulated solutions at a temperature of 27 ± 0.5 °C, with a controlled environment of slight anaerobic conditions achieved by continuously introducing a mixture of air and 5 % CO\(_2\) gas into the solution. Prior to conducting electrochemical measurements, the specimens were immersed in the inflammatory and normal solutions for duration of 24 h. PDP experiments followed ASTM G14-standards with a 0.1667 mV s\(^{-1}\) sweep rate.

The corrosion current density (\(i_{corr}\)), corrosion potential (\(E_{corr}\)), and cathodic branch’s slope (\(i_{corr}\)) were extracted by the Tafel extrapolation (Supplementary Fig. S4) method using CorrView (version 2.8, Scribner Associates) software. The corrosion rate of the specimens, CR\(_i\) (mm y\(^{-1}\)) can be determined from \(i_{corr}\) (mA cm\(^{-2}\)) with the following equation \([39,40]\):

\[
CR_i = 22.85 \cdot i_{corr} \quad (1)
\]

After PDP test, the SEM/EDS technique was employed to investigate and evaluate the surface morphology and chemical composition. Under steady-state conditions, a potential with a sinusoidal waveform and an amplitude of 10 mV was applied near the \(E_{corr}\) generating electrochemical impedance plots at a rate of eight points per decade across a frequency range from 100 kHz to 0.1 Hz. Equivalent circuits were utilized to analyze the experimental results, employing a fitting process facilitated via the ZView (version 4.0 h, Scribner Associates) software. The goodness of fit for the data was verified through chi-squared (\(\chi^2\)) values on the order of 10\(^{-3}\).

2.5. Immersion corrosion tests

To study the weight loss of the uncoated and coated magnesium alloys, samples with a surface area of 1 cm\(^2\) were placed into a 50 mL polyethylene container filled with 40 mL of simulated normal and inflammatory solutions. The ASTM G31-72 standard recommends using a solution-to-surface area ratio of 40 mL per cm\(^2\) for laboratory immersion corrosion testing of metals. They were subjected to dynamic conditions within a biological incubator (Noor-Sanat, TSHE 600) for 14 days at a temperature of 37 °C. The solutions were replaced with fresh solutions every 24 h to avoid appreciable changes in their corrosivity during the test. After removing samples from solutions, uncoated samples were washed with a chromate acid solution (comprising 200 g CrO\(_3\) (Sigma-Aldrich), 10 g AgNO\(_3\) (Merck), and 1 L DI water) based on the ASTM G1-03 to eliminate corrosion products. The washing process for coated samples involved employing ultrasonic (James, Sonic 4.5MX) cleaning with DI water and ethanol (Merck) to safely and effectively eliminate corrosion products, chosen to circumvent potential hazards associated with the use of chromate acid on PEO coatings. Then, the samples were dried, weighed using an electronic balance (Practum 224-1S), and returned to refreshed solutions. The calculated weight loss, \(W_i\) (mg cm\(^{-2}\) d\(^{-1}\)) can be converted to corrosion rate, \(CR_{W_i}\) (mm y\(^{-1}\))
The corrosion rate was also determined through the hydrogen evolution test. The setup employed to measure the generated hydrogen gas \((H_2)\) is illustrated in supplementary Fig. S5 [41]. The immersed uncoated and coated magnesium alloy produced hydrogen bubbles collected using a funnel and a test tube filled with a solution above the sample in beaker. The glass beaker, funnel, and burette are essential, as \(H_2\) can permeate through numerous polymer-based materials, potentially leading to inaccurate measurements. Furthermore, the beaker was sealed to prevent any loss of the solution through evaporation. The whole setup was kept in a static incubator (Noor-Sanat, TE 125) at 37 °C. The samples were immersed in the solutions for 14 days, with a ratio of 1 cm\(^2\) to 150 mL for the surface area to solution volume, a configuration chosen to minimize fluctuations in both ion concentrations and the pH value within the biological medium. The values were recorded daily from the test tube, and to reduce potential reading errors, three individuals independently conducted the readings. The dissolution of 1 mol of Mg (24.31 g) leads to the generation of one mole of \(H_2\) (22.4 L at normal conditions) through the equation \(\text{Mg} + 2\text{H}_2\text{O} \rightarrow \text{Mg(OH)}_2 + \text{H}_2\), which plays a fundamental role in magnesium corrosion in water. The formula for calculating the corrosion rate based on hydrogen evolution, \(CR_{\text{H2}}\) (mm·y\(^{-1}\)) from the released \(H_2\), \(V_{H}\) (mL·cm\(^{-2}\)·d\(^{-1}\)) was presented in [39,40]:

\[
CR_{\text{H2}} = 2.088\cdot V_{H}
\]

The solutions obtained from samples immersed for 14 days in both normal and inflammatory conditions were collected, and the concentration of released manganese ions in the collected media was measured utilizing an inductively coupled plasma mass spectrometry (ICP-OES, Perkin-Elmer DV5300). The measured levels of manganese ions were multiplied by the volume of the respective collection solutions to calculate the cumulative content of ions over the immersion duration. To maintain experimental consistency, each test described in sections 2.4 and 2.5 was conducted with three replicates. Thermodynamic computations were conducted with HSC Chemistry (version 9.0, Outotec plc.) software.

3. Results and discussion

3.1. Voltage–time response monitoring

To explore how the inclusion of \(\text{Mn}_3\text{O}_4\) NPs and \(\text{KMnO}_4\) additives in the electrolyte influences the surface events throughout the PEO method, alterations in voltage response were evaluated for oxidation time. Fig. 1 displays the voltage–time curves reflecting the voltage variations in the PEO of the magnesium alloys processed in basic electrolytes without and with additives. The PEO processing was characterized by recognizing three primary stages: (i) anodization, (ii) spark anodization, and (iii) micro-arc oxidation [18,19,24]. Throughout, the diagrams exhibit a similar overall pattern. During the initial stage, the voltage response undergoes a rapid and linear ascent characterized by a steep rise, attributed to the growth and expansion of thin passive layers on the magnesium alloy substrate. In this stage, substrate atoms dissolve and subsequently interact with electrolyte anions [18]. When the breakdown voltage \((V_b)\) is reached after the initial stage, micro-discharges or sparks appear on the substrate’s surface. During the second phase, the voltage response continues to rise, eventually reaching a point where it disrupts the dielectric or passive layer’s resistance, leading to electrical sparks at vulnerable points within the newly developed oxide coating. During the third step, the responded voltage exhibited a gradual and consistent increase to reach the final voltage \((V_f)\) [42,43]. The positions of \(V_b\) and \(V_f\) can be observed in Fig. 1, while the specific values for each sample treated in their corresponding electrolytes are detailed in Supplementary Table S1.

![Fig. 1. Voltage-time response monitoring during PEO treatment of samples in different electrolyte.](image)

Incorporation of \(\text{Mn}_3\text{O}_4\) NPs into the electrolyte leads to an elevation in \(V_b\), whereas the addition of \(\text{KMnO}_4\) reduces \(V_b\) (Table S1). The primary determinant influencing \(V_b\) is the conductivity of the electrolyte. Inclusion of \(\text{Mn}_3\text{O}_4\) NPs in the alkaline electrolyte does not have any noticeable impact on pH, indicating no reactivity between the nanoparticles and the electrolyte species (Table 1), however, they were shown to decrease the electrolyte conductivity. The ability of ions to move within an electrolyte is essential for its conductivity and may be affected by the presence of \(\text{Mn}_3\text{O}_4\) NPs. On the other hand, adding \(\text{KMnO}_4\) enhances electrolyte conductivity by releasing manganese ions (\(\text{Mn}^{2+}\)) and generating hydroxide ions (\(\text{OH}^-\) ) through partial hydrolysis, increasing the solution’s pH and conductivity. The observed decrease in \(V_b\) and \(V_f\) following the incorporation of \(\text{KMnO}_4\) into the electrolyte is in accordance with Hwang et al.’s study [36]. The deviations noted in the correlation between the breakdown voltage and electrolyte conductivity can be explained by Ikonopisov’s theoretical framework [42]:

\[
V_b = a_b + b_b\log\frac{\kappa}{\text{bb}}
\]

Here, \(V_b\) signifies the breakdown voltage, \(a_b\) represents the substrate’s constant, \(b_b\) is an electrolyte’s constant, and \(\kappa\) denotes the electrolyte’s conductivity. It can be seen that there exists an inverse correlation between the \(V_b\) and the \(\kappa\) in the PEO of metallic substrates. Studies have indicated that the \(V_b\) within a PEO process can influence the surface morphology and the thickness of the resulting coatings [44].

3.2. Structural and compositional analysis of coatings

Figs. 2 and 3 illustrate the SEM micrographs of the coated samples, showcasing both the surface and cross-sectional views, along with the respective EDS elemental distribution map images. The photographs of the coated samples are also shown in the insert of Supplementary Fig. S6a-b. The light brown color in PEO-coated samples results from \(\text{Mn}_3\text{O}_4\) incorporation, known for its natural brownish hue, altering the coating’s appearance (Fig. S6, b-c). The EDS spectra of specific areas depicted in Fig. 2, d-f are also provided in Supplementary Fig. S6, d-f. The coating’s porosity, as determined through binary surface SEM micrographs (Supplementary Fig. S6, a-b), and the recorded average thickness and roughness values are presented in Table 2. The surfaces of all three groups exhibit a distinctive porous volcano crater-like microstructure commonly seen in PEO coatings on valve metals (Fig. 2, a-c). These pores result from localized micro-discharge events during the micro-arc oxidation stage, erupting molten substrate material flowing
along discharge channels, solidifying upon electrolyte contact, and forming pores and cracks due to gas evolution. The appearance of microcracks on the coated samples’ surface is linked to the abrupt solidification during thermal shock, resulting from the electrolyte quenching of the recently melted material after discharges [45].

As depicted in Fig. 2b and 2c, introducing KMnO₄ salt and Mn₃O₄ NPs into the electrolyte resulted in a reduction in pore size compared to PEO coatings formed in the base electrolyte without additives (Fig. 2a). This observation implies that these additives influence the dimensions of the discharge channels and the volume of O₂ gas expelled from them [25]. A comparison of the coatings’ relative porosity presented in Table 1 also reveals that the introduction of Mn₃O₄ NPs and KMnO₄ to the base electrolyte led to a reduction in the coatings’ porosity. The decrease in relative porosity in the MnSL-PEO coating may be attributed to the reduced plasma discharge energy, which results from the lowered Vₚ and Vₗ due to the inclusion of KMnO₄, as indicated in Supplementary Table S1. The MnSL-PEO coatings contain some particles distributed on the surface compared to the PEO coatings obtained from the base electrolyte without KMnO₄ addition. SEM micrographs in Fig. 2b at high magnification reveal the presence of agglomerates of precipitated particles inside the coating close to the discharge channel. In MnPR-PEO coatings, while the introduction of Mn₃O₄ NPs to the electrolyte leads to a reduction in Vₚ and Vₗ, the presence of these nanoparticles (confirmed by EDS) is evident as they become closely adhered to coatings surface and are incorporated into their structure, subsequently reducing surface porosity by filling defects such as pores and cracks, as depicted in Fig. 2c. Close inspection of SEM images at high magnification shows Mn₃O₄ NPs accumulating within pores, driven by their high surface area, promoting agglomeration. The surface structure of MnPR-PEO coatings displayed interconnected pores, resulting from heightened discharge intensity and interference of discharge channel fields [46].

As depicted in Figs. 2 and 3, d-f and Supplementary Fig. S6, d-f, all coatings exhibited the existence of elements such as Mg, Zn, Ca, O, phosphorus (P), and potassium (K). The presence of Mg, Zn, and Ca elements can be attributed to the magnesium alloy substrate, O results from oxidation during the PEO process, and K and P originate from the base electrolyte, comprising K₃PO₄ and KOH. The noticeably higher K element content in the MnSL-PEO coating is a direct result of the inclusion of KMnO₄ in the base electrolyte. The presence and distribution of the Mn element in both the surface and cross-section of MnSL-PEO and MnPR-PEO coatings confirm the effective integration of Mn-based additives into the layers. When examining the Mn content in composite coatings, a notable Mn concentration was observed in MnPR-PEO samples, signifying a greater inclusion of Mn₃O₄ nanoparticles into the layers during the oxidation process.

From Fig. 3 and Table 2, it is evident that the addition of KMnO₄ to the electrolyte resulted in a slight increase in coating thickness, while the incorporation of Mn₃O₄ NPs led to a significant approximately 50% increase in thickness compared to PEO coatings. These variations are attributed to the influence of additives on the gradient of voltage-time diagrams during the anodization step, as well as the values of Vₚ and Vₗ (Fig. 1), which exert a significant influence on the characteristics of the coatings [44]. The presence of Mn₃O₄ nanoparticles in the electrolyte increases Vₚ and Vₗ, leading to an elevated energy input [25]. Consequently, a larger volume of substrate material liquefies and subsequently solidifies within each microdischarge. The addition of KMnO₄ in the PEO process resulted in a lowered in breakdown voltage and final voltage, implying lower energy deposition, but this did not lead to a reduction in coating thickness. The phenomenon could be attributed to the intricate interplay of factors, including altered discharge dynamics, ionic concentration changes in the electrolyte, and possible thermal effects, ultimately influencing the PEO coating characteristics. The alterations in surface roughness within MnSL-PEO coatings may stem from a reduction in plasma discharge energy, which is influenced by the presence of KMnO₄ in the base electrolyte [47]. As microdischarge intensity decreases with KMnO₄, the pores in discharge channels become smaller, leading to a decrease in surface undulation between peaks and valleys. The existence of Mn₃O₄ nanoparticles inside the pores, which occupy the internal spaces, also reduces surface roughness, consistent with the SEM images in Fig. 2c.

XRD analysis was utilized to identify the constituent phases to examine the impact of incorporating KMnO₄ and Mn₃O₄ NPs on the phases within the PEO coatings (Fig. 4). The porous structure of layers resulted in characteristic peaks from the underlying magnesium (JCPDS card #04–006-2605) substrate in all diffraction patterns [48]. The phase
composition of the basic and composite coatings featured MgO peaks (JCPDS card #01–076-2583), consistent with prior studies, affirming that the electrolyte additives did not modify MgO’s crystal structure in the PEO process [49]. In MnSL-PEO and MnPR-PEO coatings, besides Mg and MgO peaks, a notable presence of Mn$_3$O$_4$ peaks (JCPDS card #080–0382) is observed, indicating the successful integration of manganese-based additives into the coatings. Interestingly, a discernible dissimilarity arises in the intensity of the Mn$_3$O$_4$ peaks between MnSL-PEO and MnPR-PEO coatings. This difference may be attributed to multiple factors, including the nature of the precursors employed. In the case of MnSL-PEO coatings, where KMnO$_4$ serves as the precursor, its chemical transformation during the PEO likely results in the synthesis of Mn$_3$O$_4$, albeit with a somewhat lower intensity, as evidenced by slight particulate inclusions observed in Fig. 2b, which were subsequently identified as Mn$_3$O$_4$ through XRD and EDS analyses.

In MnPR-PEO coatings, where Mn$_3$O$_4$ NPs are utilized as the precursor, the direct inclusion of nanoparticles leads to a higher and more pronounced intensity of Mn$_3$O$_4$ peaks. The variation in peak intensity between MnSL-PEO and MnPR-PEO coatings is influenced by the formation method and underlying mechanisms discussed in the next section. The speed of physical incorporation, together with factors like nanoparticle size, charge, and interactions with the evolving PEO layer, contributes to higher Mn$_3$O$_4$ peak intensities in MnPR-PEO. The consistent XRD patterns in Mn$_3$O$_4$-incorporated PEO coatings, despite diverse synthesis methods, confirm structural uniformity, highlighting the robustness of the PEO process in preserving Mn$_3$O$_4$’s crystal structure, whether chemically synthesized within the discharge channel or

![Cross-sectional SEM micrographs and the corresponding EDS elemental maps for (a,d) BSC-PEO, (b,e) MnSL-PEO, (c,f) MnPR-PEO coatings on magnesium alloy.](image)

**Table 2**  
Average values and standard deviations for relative surface porosity, coating thickness, and surface roughness.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Relative surface porosity (%)</th>
<th>Thickness (μm)</th>
<th>Roughness (μm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BSC-PEO</td>
<td>41.2 ± 3.0</td>
<td>8.5 ± 2.1</td>
<td>1.72 ± 0.41</td>
</tr>
<tr>
<td>MnSL-PEO</td>
<td>32.6 ± 1.4</td>
<td>10.1 ± 1.7</td>
<td>0.91 ± 0.15</td>
</tr>
<tr>
<td>MnPR-PEO</td>
<td>26.9 ± 2.5</td>
<td>16.8 ± 1.3</td>
<td>0.74 ± 0.25</td>
</tr>
</tbody>
</table>
introduced as commercial nanoparticles in MnPR-PEO.

3.3. Formation mechanisms of coatings

Fig. 5a and 5b schematically represent the mechanisms through which composite coatings are generated upon introducing KMnO₄ and Mn₃O₄ NPs into the electrolyte, respectively. As seen in Fig. 5a, during the beginning phase of the PEO (anodization), under the effect of an external electric field, O₂⁻ ions combine with Mg²⁺ ions to produce a dense MgO layer [19]. Considering the potential for electron resonance capture, there is a likelihood of dissociation into O and O⁻ species, which then diffuse into the oxide phase and facilitate the oxidation of the metal. When the external voltage exceeds the dielectric breakdown threshold of MgO, it can lead to the release of substantial energy through micro-arc discharges [18]. Micro-arc discharge additionally leads to the creation of discharge channels, as the release of oxygen generates enough pressure to expel the molten MgO [24]. Based on spectroscopic investigations during the PEO process, it has been observed that the electron temperature inside and outside of the discharge channel can exceed 2000–6000 K (about 0.2–0.6 eV) [50–52]. The electrochemical oxidation of magnesium inside the discharge channel and the reaction with oxygen are monitored through the decomposition of water in the discharge channel, resulting in the formation of hydroxyl radicals (OH*) and the generation of oxygen molecules (O₂).

In the fabrication of the MnSL-PEO coating, the added KMnO₄ salt undergoes decomposition, leading to the formation of permanganate ions (MnO₄²⁻) and potassium ions (K⁺). The stable MnO₄ ions migrate towards the discharge channel on the magnesium anode under the influence of strong electric fields in highly alkaline solutions. By taking into account the thermodynamic evaluation of potential chemical

Fig. 4. XRD patterns of (a) BSC-PEO, (b) MnSL-PEO, and (c) MnPR-PEO coatings on magnesium alloy with JCPDS reference lines for each phase.
chemical reactions occurring within the discharge channel, at the electrode layer, and at the oxide/electrolyte interface in the presence of permanganate anions, it is plausible to propose the formation mechanism as depicted in Fig. 5a. The MnO$_4^-$ ions can undergo a direct reaction with pre-existing protons (H$^+$) in the electrolyte, resulting in the formation of Mn$_3$O$_4$ and water molecules through the following reaction:

$$3\text{MnO}_4^- + 16\text{H}^+ \rightarrow \text{Mn}_3\text{O}_4 + 8\text{H}_2\text{O} \quad (5)$$

Concurrently, intramolecular oxidation–reduction reactions take place with MnO$_4^-$ ions, and unstable MnO$_4^{2-}$ anions transform through the following reaction:

$$2\text{MnO}_4^- \rightarrow \text{MnO}_4^{2-} + \text{MnO}_2 + \text{O}_2 \quad (6)$$

The manganese dioxide (pyrolusite phase MnO$_2$) produced in processes can be subjected to a series of redox reactions, leading to the formation of psylomelane Mn$_2$O$_3$ phase and hausmanite phase Mn$_3$O$_4$ [37,53] although it was noted that exact temperatures and kinetics depend very much on local partial pressure of oxygen [54,55]:

$$\text{MnO}_2 \rightarrow \text{Mn}_2\text{O}_3 \rightarrow \text{Mn}_3\text{O}_4 \quad (7)$$

The Mn$_3$O$_4$, synthesized in-situ, is deposited both within and around the pores (Fig. 2b) as part of the growing oxide layer, resulting in a composite structure that incorporates both the base oxide (MgO) and the introduced Mn$_3$O$_4$. In contrast to Hwang et al. [36], who observed the in-situ synthesis of Mn$_3$O$_4$ NPs and MgO on Mg-Al-Zn alloy by incorporating KMnO$_4$ into the electrolyte composition, our study yielded the synthesis of Mn$_3$O$_4$. A comparative analysis reveals that their study’s ratio of permanganate to electrolyte additives was 38%, which is 90% in our research. Their oxidation time was 5 min, whereas ours extended to 15 min. Despite maintaining the same current density in both studies, excluding the substrate’s influence, electrical parameters, and other additives, it can be inferred that an increased concentration of permanganate in the electrolyte and prolonged oxidation time contribute to the advancement of reactions (5)–(7) and the conversion of Mn$_3$O$_4$ to Mn$_3$O$_4$ in our experimental setup. In the context of the in-situ synthesis of other oxide phases and the simultaneous growth of MgO on the magnesium substrate during PEO, it is noteworthy to highlight a recent study that explores the synthesis of MgO-ZrO$_2$ coatings on Mg-Al-Zn [56]. Through the addition of K$_2$ZrF$_6$ to the electrolyte composition, ZrO$_2$ was deposited near the pores and effectively filled them, contributing to the formation of a composite structure.

In terms of the MnPR-PEO mechanism, it is important to note that Mn$_3$O$_4$ NPs do not dissolve into aqueous electrolytes, retaining a negative charge when dispersed in the alkaline electrolyte (Supplementary Fig. S3b). The anticipated phenomenon might involve the electrophoretic force drawing Mn$_3$O$_4$ NPs toward the positively charged magnesium alloy anode during PEO (Fig. 5b). Following the dielectric breakdown and sparking onset, nanoparticles adhere to the generated oxide coating, gathering in channels due to elevated surface energy propelled by electrophoretic forces. During the microdischarges, the expulsion of molten oxide causes the confinement of some nanoparticles near the discharge channel, exemplified by nanoparticles trapped within the pore in Fig. 2c. The turbulence and motion of the materials during sparking cause the mixing of Mn$_3$O$_4$ NPs from the electrolyte near the site of electrical discharge, followed by their trapping into the surface of the MgO coating, as seen in Fig. 2c. Thus, the inference is that the inclusion of Mn$_3$O$_4$ NPs into oxide layers in the PEO of magnesium alloy arises from a combination of their electrostatic adherence to the substrate through electrophoresis and their physical mixing driven by the perturbations created during microdischarges, which analogous findings have also been observed in prior investigations [57,58].

### 3.4. Electrochemical corrosion tests

#### 3.4.1. PDP measurements

Fig. 6 presents the PDP curves for uncoated and coated Mg-Zn-Ca alloy samples following a 1 h exposure to normal and inflammatory conditions. The values of $E_{corr}$, $i_{corr}$, $j_{corr}$, and CR$_i$ as previously detailed in section 2.4 on how to derive them from the PDP curves, are presented in Table 3. A decrease in $i_{corr}$ generally implies a slower CR$_i$, indicating that the material corrodes at a reduced pace [59,60]. Conversely, a higher $E_{corr}$ signifies lower susceptibility to corrosion, indicating a more passive and corrosion-resistant material surface [59,60]. The $E_{corr}$ values for the

![Fig. 5. Schematic representation of formation mechanism of (a) MnSL-PEO coating in electrolyte containing KMnO$_4$, (b) MnPR-PEO coating in electrolyte containing Mn$_3$O$_4$ NPs.](image-url)
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interplay. In a highly oxidative inflammatory environment, the Mn$_3$O$_4$ PEO coatings. Hence, MnPR-PEO and MnSL-PEO coatings exhibited electrochemical characteristics by changing the chemical composition of phase, renowned for its inherent ROS-scavenging properties, improves and elevated $E_{corr}$, are well-founded and supported by this intricate comparison characteristics of PEO coatings, enhancing the coating thickness compared to the uncoated magnesium alloy, accompanied by a corresponding decrease in their $i_{corr}$ values [40,59,60]. This shift is attributed to ceramic PEO-based coatings, which effectively hinder the transport of aggressive ions such as H$_2$O$_2$, Cl$^-$, and O$_2$ molecules in both test solutions [61–63].

As widely recognized, the anti-corrosion characteristics of PEO-treated surfaces are determined through the combined influence of their chemical composition, porosity, and thickness [18,19,25,61]. In a normal corrosive medium, the introduction of Mn$_3$O$_4$, whether through nanoparticles or KMnO$_4$, elicits a multifaceted influence on the corrosion characteristics of PEO coatings, enhancing the coating thickness while concurrently reducing the porosity. Utilization of Mn$_3$O$_4$ NPs amplifies this effect, resulting in a more pronounced thickness increase and porosity reduction. The observed trends, with MnPR-PEO outperforming MnSL-PEO and BSC-PEO coatings, regarding reduced $i_{corr}$ and elevated $E_{corr}$, are well-founded and supported by this intricate interplay. In a highly oxidative inflammatory environment, the Mn$_3$O$_4$ phase, renowned for its inherent ROS-scavenging properties, improves electrochemical characteristics by changing the chemical composition of PEO coatings. Hence, MnPR-PEO and MnSL-PEO coatings exhibited significantly lower values of $i_{corr}$ and $CR_i$ compared to the BSC-PEO when subjected to an inflammatory medium, similar to their performance in normal conditions.

Our results align with previous investigations, underscoring the advantageous effect of introducing additional oxide phases on the electrochemical corrosion behavior of PEO-treated magnesium alloys [25–27,57,58]. To provide a comprehensive overview, we have compiled corrosion study results from various composite coatings created by incorporating solid particles within electrolytes during the PEO process for magnesium alloys, as summarized in Supplementary Table S2. Our results pertain specifically to testing in a PBS (pH 7.4) solution, as there is limited available data on corrosion tests of composite PEO coatings in solutions containing H$_2$O$_2$. Despite variations in electrical/power supply characteristics, electrolyte compositions, and corrosion test solutions observed in different studies, the composite coating developed in this study exhibits satisfactory corrosion performance in comparison to other instances. It is important to note that the decision to conduct corrosion tests after a one-day immersion may have influenced the $i_{corr}$ in our study in contrast to studies with shorter exposure time. Moreover, the elevated $E_{corr}$ observed in PEO-coated magnesium alloy in this study, compared to previous research, can be attributed to prolonged immersion time. This extended exposure may induce changes in the PEO coating, leading to the formation of a more protective passive film on the magnesium alloy surface. This film acts as a barrier, reducing corrosion rates and shifting the corrosion potential to a more positive value. Extended immersion may also trigger surface modifications, such as a thicker or denser oxide layer, influencing the electrochemical behavior and corrosion potential. Equilibrium with the environment and ion diffusion during immersion time can further impact the corrosion potential by affecting the electrochemical reactions and species concentration. Additionally, the stabilization of surface layers after 24 h of immersion contributes to a more consistent and protective state. Telmenbayar et al. recently reported a similar higher $E_{corr}$ for PEO-coated Mg-Al-Zn alloy after one-day immersion [21]. This approach, however, offers valuable insights into the corrosion behavior of materials implanted within the body [65].

When comparing the $i_{corr}$ and $CR_i$ values, the addition of H$_2$O$_2$ and HCl into PBS to simulate the post-implantation inflammatory environment results in a significant increase in both $i_{corr}$ and CR$$_i$ values. Introducing H$_2$O$_2$ and HCl to corrosion test solutions amplifies magnesium’s CR$$i$$ due to their strong oxidative and acidic properties [11,12,66]. H$_2$O$_2$, an oxidizing agent, spurs the oxidation of magnesium,
generating Mg\(^{2+}\) and releasing electrons, thus expediting the corrosion process within an electrochemical cell [67]. On the other hand, HCl induces a strong acidic environment, further promoting magnesium localized corrosion [66]. Although the inflammatory environment increases the metal’s corrosion rate, it is noteworthy that a notable shift toward a more noble corrosion potential \(E_{corr}\) is observed in the samples rather than a reduction. The electropositive shift in the \(E_{corr}\) when \(H_2O_2\) is introduced can be attributed to several factors. Firstly, \(H_2O_2\) undergoes decomposition to form \(H_2\) and \(O_2\), thereby acting as an additional cathodic reaction that influences the electrochemical behavior [68,69]. In electrochemical systems, cathodic reactions involve reductions, and \(H_2O_2\) can serve as a source of oxygen for these reduction reactions. Secondly, earlier studies showed that the positive \(E_{corr}\) values in \(H_2O_2\)-containing solutions from intermediates for these reduction reactions. 

### 3.4.2. EIS studies

To gain insights into the influence of Mn\(_3\)O\(_4\) integration on electrochemical corrosion performance, samples underwent AC electroimpedance measurements. Fig. 7(a-c) and (d-f) showcase the Nyquist, Bode modulus/phase diagrams for the uncoated and coated Mg-Zn-Ca alloy under simulated normal and inflammatory conditions, respectively. Across all diagrams, the data dots correspond to the EIS records, the solid lines represent the fitted results, and the dashed arrows indicate specific frequencies in the Nyquist plots. Typically, enhanced corrosion resistance is associated with larger semicircles in Nyquist plots, along with an elevated impedance modulus \(|Z|\), noted at the low frequencies in the Bode spectra [71]. Upon evaluating the semicircle diameters in both test conditions, the coated samples demonstrated increased capacitive loop radii and elevated \(|Z|\) values, underscoring their superior protective performance compared to the uncoated magnesium alloy [72,73]. Notably, in direct comparison to the BSC-PEO and MnSL-PEO samples, the MnPR-PEO sample exhibited even more substantial capacitive loop radii and higher \(|Z|\) values, signaling a notable further enhancement in its corrosion resistance. In addition, the higher \(|Z|\) value of the MnPR-PEO than that of the MnSL-PEO in inflammatory conditions means that the Mn\(_3\)O\(_4\) NPs in the MnPR-PEO coating can effectively decrease the corrosion rate. In the Nyquist plots of the uncoated magnesium alloy (Fig. 7a and d insets), the presence of inductive loops indicates the initiation of substrate corrosion by aggressive species [59,60,71]. The inductive response was attributed to the relaxation of the intermediate Mg\(^{2+}\) product within the corrosion pits. The hypothesis regarding the existence of Mg\(^{2+}\) has been justified, as it offered a satisfactory rationale for the negative difference effect (NDE) observed in magnesium corrosion [74].

On the other hand, there were no discernible inductive loops in the Nyquist plots of the PEO-coated magnesium samples in both environments. PEO coatings serve as protective barriers against corrosive ions, forming oxide layers that impede local corrosion sites. These coatings modify the magnesium substrate’s electrochemical behavior, leading to a distinct impedance response that mitigates inductive loops with protective films [18,19,25,64]. The uniform and passive nature of PEO coatings contributes to reliable and consistent electrochemical performance, highlighting their effectiveness in safeguarding the substrate from corrosion [18,19,23]. In EIS, phase angles also indicate corrosion resistance, with a high phase angle near −90° signifying capacitive behavior associated with protective films [59,60,71]. The MnPR-PEO coating exhibits the highest phase angle, indicating superior corrosion resistance (Fig. 7c and f).

The EIS records underwent fitting procedures employing suitable equivalent circuit (EC) models to gain deeper insights into the physicochemical characteristics of coatings. Fig. 8 displays the EC models for both uncoated magnesium alloy (Model a) and coated specimens (Model b) in both test solutions. Within both circuits, the notation “RC” designates the resistance attributed to the corrosive solution present in an electrochemical cell containing the working and reference electrodes. Using a Constant Phase Element (CPE) in EIS analysis is a valid approach, especially for materials like magnesium alloy and PEO coatings with complex electrode/electrolyte interfaces. PEO layers often have rough surfaces, and CPE accommodates a broader range of behaviors compared to ideal capacitors, making it suitable for capturing non-ideal responses due to factors like roughness and pore structures, offering a more realistic representation of complex electrical processes [75]:

![Fig. 7. EIS analyses: (a) Nyquist plots, (b) Bode modulus plots, and (c) Bode phase plots for uncoated and coated samples under normal conditions; (d) Nyquist plots, (e) Bode modulus plots, and (f) Bode phase plots for uncoated and coated samples in an inflammatory environment.](attachment:image.png)
The condition of EIS test & Samples & $R_S$ ($\Omega \cdot \text{cm}^2$) & (CPE-T)$_{\text{PEO}}$ ($\Omega^{-1} \cdot \text{cm}^2$) ($\times 10^6$) & $\eta_{\text{PEO}}$ & $R_{\text{PEO}}$ ($k\Omega \cdot \text{cm}^2$) & $R_{\text{ct}}$ ($k\Omega$) & (CPE-T)$_{\text{ad}}$ ($S^0 \cdot \Omega^{-1} \cdot \text{cm}^2$) ($\times 10^6$) & $n_{\text{ad}}$ & $L$ ($\text{H} \cdot \text{cm}^2$) & $R_L$ ($k\Omega$) & $R_T$ ($k\Omega$) & $\tau$ ($\text{s}$)

<table>
<thead>
<tr>
<th>Normal</th>
<th>Mg-Zn-Ca</th>
<th>44.79 ± 0.01</th>
<th>6.33 ± 0.15</th>
<th>0.95</th>
<th>8.94 ± 0.25</th>
<th>3.53 ± 0.29</th>
<th>0.94</th>
<th>320 ± 0.9</th>
<th>0.17 ± 0.16</th>
</tr>
</thead>
<tbody>
<tr>
<td>BSC-PEO</td>
<td>46.14 ± 0.10</td>
<td>6.33 ± 0.15</td>
<td>0.95</td>
<td>8.94 ± 0.25</td>
<td>3.53 ± 0.29</td>
<td>0.94</td>
<td>320 ± 0.9</td>
<td>0.17 ± 0.16</td>
<td></td>
</tr>
<tr>
<td>MnSL-PEO</td>
<td>44.34 ± 0.04</td>
<td>6.33 ± 0.15</td>
<td>0.95</td>
<td>8.94 ± 0.25</td>
<td>3.53 ± 0.29</td>
<td>0.94</td>
<td>320 ± 0.9</td>
<td>0.17 ± 0.16</td>
<td></td>
</tr>
<tr>
<td>MnPR-PEO</td>
<td>43.21 ± 0.03</td>
<td>6.33 ± 0.15</td>
<td>0.95</td>
<td>8.94 ± 0.25</td>
<td>3.53 ± 0.29</td>
<td>0.94</td>
<td>320 ± 0.9</td>
<td>0.17 ± 0.16</td>
<td></td>
</tr>
<tr>
<td>Mg-Zn-Ca</td>
<td>21.17 ± 0.04</td>
<td>6.33 ± 0.15</td>
<td>0.95</td>
<td>8.94 ± 0.25</td>
<td>3.53 ± 0.29</td>
<td>0.94</td>
<td>320 ± 0.9</td>
<td>0.17 ± 0.16</td>
<td></td>
</tr>
</tbody>
</table>

The details regarding the obtained values from fitting the elements of the equivalent circuits, as well as the calculated $R_T$ values, can be found in Table 4. Initially, a noticeable trend is the reduction in $R_T$ values when comparing the inflammation state with the normal physiological condition. These findings imply that inflammation after implantation elevates the susceptibility to corrosion in all specimens.

The $R_{\text{ct}}$ in EIS represents the resistance to the transfer of charge at the electrode-electrolyte interface, typically at the interface between the coating or passive layer with the substrate beneath. Higher $R_{\text{ct}}$ signifies superior corrosion protection by slowing charge transfer kinetics [59,60,71]. The decrease in the $R_{\text{ct}}$ value for the uncoated Mg-Zn-Ca alloy sample within the inflammatory environment represents the
deterioration of the passive film, likely due to the harsh, corrosive nature of the acidic environment. The ranking of $R_c$ values for the coated samples in both conditions follows the order of MnPR-PEO, MnSL-PEO, and BSC-PEO.

This suggests a reduction in the electrochemical degradation by MnO$_2$ NPs incorporation. In the coated samples, the higher $R_c$ values compared to $R_{PEO}$ indicate a likely dominance of the charge transfer phenomenon at the electrolyte–electrode boundary ($R_C$) in shaping the overall impedance characteristics. Indeed, the higher $R_c$ compared to the $R_{PEO}$ could be attributed to the accumulation of corrosive media under the coating within localized corrosion sites. When localized corrosion occurs, it can create pathways for corrosive media to penetrate beneath the protective layer and reach the substrate [78]. This localized attack can result in higher resistance to charge transfer at the electrolyte/electrode interface arising from electrochemical reactions associated with corrosion processes [79]. In such cases, $R_c$ may represent the impedance associated with charge transfer processes occurring at the corroding sites. The higher $R_C$ value can reflect the electrochemical response associated with localized corrosion. At the same time, $R_{PEO}$ represents the resistance related to the penetration of corrosive ions through pores of PEO coating, which may be less affected by the localized corrosion sites.

In both normal and inflammatory conditions, the $R_{PEO}$ values for MnPR-PEO and MnSL-PEO coatings exhibited significant increases, with MnPR-PEO showing approximately 30–40 times higher $R_{PEO}$ compared to BSC-PEO. Additionally, MnSL-PEO demonstrated about 10–20 times higher $R_{PEO}$ than the BSC-PEO coating. The $R_{PEO}$ increase in composite coatings is due to their increased thickness and reduced porosity, hindering the penetration of corrosive ions through the pores and thereby limiting their access to the substrate [80,81]. The equation that relates capacitance ($C$) and exposed surface area ($A$) in EIS is given by [75]:

$$C = \frac{\varepsilon_0 \varepsilon_r A}{d}$$

where $\varepsilon_0$ is the vacuum permittivity (a constant), $\varepsilon_r$ is the relative permittivity (dielectric constant) of the coatings, and $d$ is the thickness of the coatings. When considering the same coating material (with a constant $\varepsilon_r$), a decrease in $A$ and an increase in $d$ lead to reduced capacitance. This outcome is typically associated with lower porosity, indicating a reduction in the open space within the coating and reducing the exposed surface area in contact with the electrolyte [82].

The capacitance values presented in Table 4 reveal that all Constant Phase Elements (CPE$_{PEO}$ and CPE$_{d}$) for the MnPR-PEO coating are notably lower than other coatings, aligning with SEM observations about its low porosity.

3.4.3. Surface morphologies after corrosion

The SEM micrographs in Fig. 9 were captured to assess alterations in sample surface morphology after polarization tests conducted under both normal and inflammatory conditions after 1 h of exposure. The micrographs reveal that samples subjected to inflammatory conditions (e–h) suffered from intensified corrosion damage compared to those in normal conditions (a–d), aligning with numerical findings from PDP and EIS analyses. The presence of numerous cracks in the immersed samples is likely attributed to internal stress and dehydration resulting from the drying process upon sample removal from the test solution [111]. The SEM images in both conditions show pits on the surface of the uncoated magnesium alloy formed through localized corrosion reactions, with notably larger pit sizes observed in the inflammatory conditions, as depicted in Fig. 9a and 9e. The coated samples exhibited less corrosion damage when compared to the uncoated control, highlighting the protective effectiveness of the coatings in both media. In the inflammatory solution, the BSC-PEO coating (Fig. 9c) exhibited significantly more severe corrosion than the others. As a result, the original morphology of the coating (morphology before the immersion test) became unrecognizable and was completely obscured during the testing period due to the aggressive attacks. The MnSL-PEO sample displayed a higher incidence of corrosion attacks than the MnPR-PEO sample, as evidenced by the conspicuous presence of larger pits on the surface. Despite localized corrosion and morphological changes in specific areas in MnPR-PEO, some regions retained the original coating morphology, underscoring its enduring protective properties.

Elemental analysis via EDS was performed in the designated region of the coatings [Supplementary Fig. S7]. Upon assessing the chemical composition of the layers and comparing it with the chemical composition of the coated samples before the corrosion test [Supplementary Fig. S6], distinct alterations were observed. There was an increase in the oxygen content and the appearance of chlorine within the coating layers. These changes can be attributed to chemical reactions from exposure to the corrosive test solutions [83]. The presence of chlorine is particularly pronounced in samples tested in the inflammatory medium, where hydrochloric acid is present. This higher chlorine content directly correlates with the elevated corrosion rates experienced in the inflammatory conditions. An elevation in phosphorus and potassium levels was observed in the coatings after exposure to both test environments. This observation can be attributed to the presence of these elements in ionic form within the PBS solution, which served as the corrosion test medium. The PBS solution contains precursors such as sodium phosphate and potassium phosphate, contributing to the elevated levels of phosphorus and potassium in the coatings. The trends in chemical composition align with SEM observation in a corrosion testing context [58].

3.5. Immersion corrosion tests

Fig. 10a and b illustrate the CRWL and CRHE variations over a 14-day immersion period in normal and inflammatory solutions for uncoated and coated Mg-Zn-Ca alloy. The weight loss and hydrogen release rates of the samples follow a pattern akin to what was observed during the electrochemical tests. Importantly, coatings containing manganese oxide exhibit lower corrosion rates compared to both basic coatings and the uncoated substrate. Composite coatings formed by incorporating manganese oxide nanoparticles demonstrate even lower corrosion rates than coatings derived from manganese permanganate precursors. It is noteworthy that there is a substantial impact of the inflammatory environment, which substantially heightens the corrosion rates of the samples. An interesting trend appears when looking at the corrosion rate increase. After the 8th day of immersion, a more pronounced surge in hydrogen release and weight loss becomes apparent, aligning with findings from in vivo corrosion rate monitoring of Mg-Zn-Ca alloys [84]. Such research has consistently indicated an accelerated corrosion rate after one week of implantation. Upon comparing the various corrosion rates obtained, it becomes evident that the values determined through Tafel extrapolation do not align with corrosion rates calculated from weight loss and hydrogen release measurements. This disparity suggests that short-term electrochemical tests may not accurately reflect the corrosion rates of magnesium alloys in long-term applications. Conversely, a strong alignment between the CRHE and CRWL measurements is notably evident in both test solutions, as reported earlier [85,86].

The corrosion rate assessment of Mg-Zn-Ca alloys using various methodologies in this investigation reveals that under normal conditions, corrosion rates fall within the 2–10 mm·y$^{-1}$ range, whereas in inflammatory conditions, they increase to 6–15 mm·y$^{-1}$, depending on the immersion duration. First and foremost, the study reveals a notable difference in corrosion rates in normal and inflammatory conditions. This suggests that inflammatory responses can play a significant role in accelerating corrosion processes. Referring to MAGNEZIX® CS’s corrosion rate, a commercial magnesium implant in surgical applications (image shown in case reports [87,88]) provides practical significance to the findings presented in this study. Surgeons have observed that this implant (20 × 3.9 mm) undergoes complete absorption and dissolves within the human body in 17–24 months, exhibiting an average
Fig. 9. SEM micrographs of surface morphology for (a) uncoated magnesium alloy, (b) BSC-PEO, (c) MnSL-PEO, (d) MnPR-PEO in normal media, and (e) uncoated magnesium alloy, (f) BSC-PEO, (g) MnSL-PEO, (h) MnPR-PEO in inflammatory media.
corrosion rate of 9–13 mm·y⁻¹ [87,88]. They also noted that the corrosion rate is influenced by patients’ age, gender, metabolic factors, and underlying medical conditions. The question arises: if corrosion rates in practical service conditions correlate with the accelerated corrosion observed in the inflammatory environment in this study (ranging from 6 to 15 mm·y⁻¹), what is the purpose of developed coatings on magnesium implants to reduce corrosion rates? The answer lies in understanding the multifaceted objectives of coatings. While minimizing corrosion rates and mitigating the generation of H₂ gas are fundamental goals, coatings provide a more comprehensive approach by aiming to preserve the mechanical properties of implants over an extended period. This emphasis on sustaining mechanical integrity contributes significantly to the overall improvement of implant performance.

One significant aspect of this study’s findings is the positive effect of incorporating Mn₃O₄ into PEO coatings on magnesium. These coatings not only offer corrosion resistance but also, as observed, demonstrate remarkable behavior even in the face of inflammatory conditions. While the corrosive effects of inflammation are evident, the coatings, particularly those enriched with Mn₃O₄, counterbalance this by providing an effective barrier. These coatings serve as protective barriers during the crucial initial phases of implantation, when the implant is most susceptible to corrosion, effectively maintaining the corrosion rates at approximately 8 mm·y⁻¹ during the first week (Fig. 10 a,b) so they can modulate the degradation of the implant, aligning it with the pace of tissue healing to prevent excessive early corrosion.

Manganese is a vital trace element within the human body, and is crucial in various physiological functions. The recommended daily intake of manganese is relatively low, and a well-balanced diet typically provides an adequate amount without posing health risks. However, excessive exposure to manganese can lead to toxicity and undesirable effects [89], so investigation of Mn ions released from Mn₃O₄-incorporated PEO coatings is of paramount importance for biomedical applications. The results, as depicted in Fig. 10c, indicate that Mn release remains within the range of 1.43 to 6.1 ppm for both coatings after 14 days of immersion, depending on the immersion media. The increased release in the MnPR-PEO sample compared to the MnSL-PEO sample can be attributed to higher initial amount of manganese element in this coating. According to the Agency for Toxic Substances and Disease Registry (ATSDR), the usual reference intervals for manganese concentrations in serum or whole blood generally fall between 1 and 15 ppm, while urinary manganese levels are typically reported in the range of 1–8 ppm per mmol creatinine. It is important to note that these values

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**Fig. 10.** Corrosion rate variations using different methods: (a) CRWL, (b) CRHE, and (c) manganese ion release from MnSL-PEO and MnPR-PEO coatings after 14-day immersion in normal and inflammatory media.
are indicative of urinary manganese concentrations relative to creatinine levels, providing insights into potential variations in renal clearance [90]. Moreover, the Recommended Dietary Allowance (RDA) for manganese considered safe and adequate, is around 1.8 mg daily for females and 2.3 mg daily for males. Daily manganese ingestion is set at 11 mg for middle-aged individuals according to the Tolerable Upper Intake Level (UL), ensuring a daily intake that is unlikely to lead to adverse health outcomes [90]. These findings showed that the manganese release levels from the PEO coatings in both normal and inflammatory conditions remain within safe reference ranges, affirming their appropriateness for biomedical applications.

3.6. Corrosion protection mechanisms

The schematic representation in Fig. 11 illustrates the protective mechanism against corrosion of the Mn3O4-incorporated coatings on a magnesium alloy under inflammatory conditions. The corrosion resistance mechanism is influenced by three key factors: increased thickness of the oxide coating, decreased coating porosity, and heightened catalytic activities resulting from incorporating the Mn3O4 phase. As mentioned earlier, the presence of manganese-based additives in the electrolyte composition is pivotal, leading to a substantial growth in the thickness of the MgO coating. This increased thickness, as a crucial component of our corrosion resistance strategy, plays a central role in altering the diffusion pathways for corrosive ions compared to the BSC-PEO coating. Specifically, the greater thickness of the Mn3O4-incorporated coatings results in significantly lengthened and more tortuous diffusion pathways for corrosive ions when compared to the BSC-PEO coating. This aspect is critical as it contributes to the observed enhanced corrosion resistance. In contrast, the inherent porosity of the BSC-PEO coating allows corrosive ions to infiltrate and dissolve the coating, potentially leading to localized pitting corrosion [91]. Here, we highlight the importance of the increased coating thickness in preventing such localized corrosion. Moreover, the Mn3O4-incorporated coatings exhibit the lowest pore density, further reducing the infiltration of ions and molecules into the coating/substrate interface. This dual effect of increased coating thickness and reduced pore density collectively enhances the corrosion protection offered by the Mn3O4-incorporated coatings under inflammatory conditions.

The anti-corrosion performance of incorporated Mn3O4 under acidified inflammatory conditions may also be influenced by its effective catalytic removal of ROS. It is established that bone tissue cells generate various ROS during an inflammatory response, which can actively engage in Fenton reactions, leading to the generation of substantial radical species [92,93]. In reactions resembling the Fenton process, the metal ion serves as an electron donor to H2O2, resulting in the creation of the OH• radical, as illustrated by the equation below:

\[
\text{Mn}^+ + \text{H}_2\text{O}_2 \rightarrow \text{M}^{n+} + \text{OH}^- + \text{OH}^* \quad (12)
\]

Here, ‘n’ corresponds to the specific valence state, while ‘M’ denotes a transitional metallic catalyst employed in Fenton reactions. Mn3O4 offers numerous notable benefits, including exceptional chemical durability, strong H2O2 adsorption capability, and minimal release of manganese ions when contrasted with typical heterogeneous Fenton catalysts like FeS2, Fe2O3, Fe3O4, and FeOOH [93,94]. As depicted in the Pourbaix diagram representing manganese behavior in water (as shown in Supplementary Fig. S8), it becomes evident that Mn3O4 exhibits instability under acidic inflammatory conditions. A hypothetical schematic representation illustrating the catalytic activity-based corrosion inhibition mechanism of the Mn3O4 is depicted in the right portion of Fig. 11. Particularly, at a pH level of 5.2, the prevailing constituents consist of MnO2 and Mn2+. The mechanism of the Fenton-mimicking catalytic process entails the creation of hydroxyl radicals through the cyclic transformations of Mn3+ to Mn2+, ultimately leading to the decomposition of H2O2 [93,95]:

\[
\text{Mn}^{2+} + \text{H}_2\text{O}_2 \rightarrow \text{Mn}^{3+} + \text{OH}^- + \text{OH}^* \quad (13)
\]

Furthermore, the catalytic efficacy of Mn3O4 NPs is impacted by the pH of the physiological environment, predominantly hinging on the adsorption of H+ and OH• ions on the catalyst’s surface. In an acidic environment, H2O2 has a proclivity to associate with H+, leading to its breakdown into H2O and OH•, as suggested by theoretical computations [96]:

![Fig. 11. Schematic representation of anti-corrosion mechanism of Mn3O4-incorporated PEO coatings on magnesium alloys in inflammatory condition.](image-url)
In an acidic environment characterized by inflammation, MnO₂ is the primary phase of Mn₃O₄, as mentioned earlier, alongside Mn₂⁺ compounds. MnO₂ can easily engage in a redox reaction that alternates between the Mn²⁺ and Mn³⁺ states, creating Mn₂O₃ [97]. As depicted in Supplementary Fig. 8B, Mn₂O₃ remains stable under acidic pH conditions. It can effectively interact with the OH⁻ generated in reactions (13) and (14) to neutralize them, resulting in the thermodynamically feasible production of H₂O₄ and H₂O₂. At 37 °C, the thermodynamic energy variation (ΔG) of equations (15) and (16) was calculated to be −69.51 kJ·mol⁻¹ and −7.71 kJ·mol⁻¹, respectively, utilizing the HSC Chemistry program. The mechanisms for scavenging H₂O₂ molecules and OH⁻ radicals can be mentioned as follows:

\[
2\text{MnO}_2 + \text{H}_2\text{O}_2 \rightarrow \text{Mn}_2\text{O}_3 + \text{H}_2\text{O} + \text{O}_2
\]

\[
3\text{Mn}_2\text{O}_3 + 2\text{OH}^- \rightarrow \text{H}_2\text{O} + 2\text{Mn}_2\text{O}_4 + 2\text{H}_2\text{O}_2
\]

Through repeated cycling of reactions (15) and (16), the manganese oxide phases can convert H₂O₂ back into H₂O and O₂, as described in equation (15), thereby reducing the potential infiltration of H₂O₂ [97]. It has been documented that the efficacy of the manganese oxide phases in their role as scavengers is most effective when the rate of decomposition of H₂O₂ equals or surpasses the rate of its production [93,96,98]. Therefore, Mn₂O₃ can be regarded as a pioneering additive for PEO coatings on metallic implants, demonstrating exceptional electrochemical corrosion performance and potent anti-inflammatory attributes.

4. Conclusion

The present study successfully demonstrated the development of Mn₃O₄-incorporated PEO coatings on Mg-Zn-Ca alloy through two distinct approaches, showcasing a reduction in surface porosity and increased coating thickness with additives. The addition of KMnO₄ resulted in a decrease in voltages, while Mn₃O₄ led to an increase in voltages in the voltage–time response diagram, directly influencing the structural characteristics of the coatings. The electrochemical and immersion corrosion tests conducted under simulated normal and inflammatory conditions highlighted the susceptibility of uncoated Mg-Zn-Ca alloy to corrosion, particularly in inflammatory environments. Notably, the composite PEO coatings, incorporating Mn₃O₄ nanoparticles, exhibited superior corrosion performance, with a significant reduction in corrosion current density and increment in total impedance resistance compared to basic PEO coatings. The enhanced performance is attributed to the catalytic activity of Mn₃O₄ in scavenging H₂O₂ in simulated inflammatory conditions, as well as to the higher thickness and lower porosity of the composite coatings compared to basic PEO, which collectively hindered the penetration of corrosive agents to the substrate. These findings suggest that Mn₃O₄-incorporated PEO coatings provide a promising system for magnesium implants, demonstrating improved inflammatory-associated corrosion behavior and a controlled release of manganese ions into the implantation site microenvironment within a safe concentration range for the human body. Future research should focus on further optimizing these coatings and exploring their biomechanical properties, as well as in vitro cell responses.

CRediT authorship contribution statement

Sara Bahrampour: Writing – original draft, Visualization, Software, Resources, Methodology, Investigation, Formal analysis. Aydin Bordbar-Khiabani: Writing – original draft, Validation, Resources, Funding acquisition, Formal analysis, Conceptualization, Supervision. M. Hossein Siadati: Writing – review & editing, Supervision. Michael Gasik: Writing – review & editing, Supervision, Funding acquisition. Masoud Mozafari: Writing – review & editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

The authors do not have permission to share data.

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Appendix A. Supplementary data

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