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# Control of the Mg alloy biodegradation via PEO and polymer-containing coatings

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## Abstract

The composite calcium-phosphate coating on MA8 Mg alloy consisting of the inorganic porous basis sealed with polymer is suggested. To control the alloy resorption kinetics, the coating obtained by plasma electrolytic oxidation is modified with superdispersed polytetrafluoroethylene using electrophoretic deposition (EPD). Protective properties and morphology evolution as a result of surface treatment and corrosion propagation are examined by EIS, PDP, hydrogen evolution tests, SEM, EDX and XRD analysis. The obtained coatings are investigated at mechanistic level using SVET and local pH measurements. EPD composite coating decreases electrochemical activity of the sample in minimum essential medium and ensures the material biocompatibility.

## 1. Introduction

In the recent years, the human society has observed the increase of traumatism (bone fractures) caused by working reasons, road accidents as well as by ageing population [1,2].
Sometimes fixation of the bone fractures by metal-based implants (screws, plates) is required to facilitate faster bone healing. Usually, permanent implants are used for bone fixation. At the same time to remove such implant material, a second surgery is required. Therefore, the application of biodegradable metallic implants is considered a good alternative in this case. It eliminates the need for the second invasive surgery and shortens the healing period.
Magnesium is a biologically compatible element and a relatively large amount of it in the body does not adversely affect the human organism [3,4]. Due to its functional role and the natural presence in the bone tissue, magnesium has a stimulating effect on the growth of new tissue [5]. Therefore, magnesium alloys are the most promising materials for biomedical application as temporary bioresorbable implants, which do not require the process of implant removal [6,7]. Such implants have mechanical properties similar to the human bones [5,8] and can reliably fix bone fragments during the period of fracture healing and then progressively degrade in the organism.

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At the same time, the degradation rate of magnesium-based materials is still considered to be too high. Given the high corrosiveness of magnesium and its alloys in various environments, the use of such materials in the media of the human body can be limited by the premature dissolution of the temporary implant until the complete rehabilitation of patient [9,10]. The presence of various phases in the composition of magnesium alloys, such as intermetallic inclusions or noble impurities with different Volta potential and electrocatalytic properties, leads to micro-galvanic corrosion. This is one of the main reasons of the low corrosion resistance [11–13]. The problems like generation of hydrogen gas bubbles and local alkalization have been reported earlier [7,14–18]. However, more recently by direct *in vivo* hydrogen measurements, it has been shown that the subcutaneous gas cavities contained only a low concentration of hydrogen. This points out to fast hydrogen exchange *in vivo* and proves that hydrogen evolution is not an insurmountable problem in practical application of Mg biomaterials [19]. Furthermore, it has also been shown recently that local pH at the interface of degrading Mg alloys typically varies between 7.8 to 8.2 (at 25$^{\circ}$C) and barely ever exceeds the value of 8.5, provided that the medium (SBF, HBSS and MEM) contains physiological concentrations of $Ca^{2+}$, $HCO_3^-$ and $HPO_4^{2-}$ [20–22]. These pH values are pre-determined by the fast formation of hydroxyapatite-like compounds that stabilize local pH and forms a protective layer capable to decelerate Mg dissolution. The most important implication of faster than necessary degradation of Mg remains the loss of mechanical integrity of an implant. Therefore, auxiliary corrosion protection of Mg implant is necessary to slow down its degradation rate preventing the loss of mechanical strength before the bone healing [10].

Nowadays scientific-engineering groups followed two main strategies in order to improve the performance of bioresorbable Mg alloy implants. The first one is related with the development of new alloys with desired composition and microstructure [8,23,24]. For biomedical applications of magnesium-based materials, Wen et al. [25] studied corrosion of Al-containing Mg alloys in simulated body fluid. Besides, new Gd [26,27], Ag [27–29], Sr [30,31] and Ca-containing Mg alloys [32,33] are considered to be good candidate for implant materials owing to their biocompatibility, mechanical and degradation profiles.

The second strategy is the formation of protective layers to slow down the degradation rate of Mg-based materials especially at the initial stage. This approach reduces the corrosion activity of magnesium alloys due to surface modification, which consists in the coating formation that temporary limits the access of active medium components to the implant material. Such coatings can provide reliable barrier properties at the initial stages after implantation and then gradually degrade. There are different ways of surface treatment, which have been developed including anodization, chemical conversion, and sol-gel coatings [34]. A promising technique to obtain coatings on magnesium alloys is plasma electrolytic oxidation (PEO), which allows to form layers with a wide variation of composition, microstructure, porosity, and roughness, using modification of aqueous electrolytes components and parameters of the PEO process [35–38].

PEO method is basically an anodization process at high voltages in an appropriate electrolyte. During this process, a large number of short-lived microdischarges form at electrolyte/electrode interface as a result of breakdown of the dielectric surface film. During PEO process, the formation of the coating is achieved due to species interaction between the components of electrolyte and the substrate [39–41]. Effect of fluoride ions addition on the corrosion resistance and biocompatibility of PEO-treated Mg-Ca alloys was studied by Mohedano et al [37]. This study showed an improvement of the corrosion resistance for samples with fluoride-containing coatings since fluoride anions are able to inhibit corrosion forming insoluble $MgF_2$ layer at the interface. PEO-layer with fluorides shows better bioactivity compared to a blank one, with a higher number of cells well attached to the PEO-surface after the same immersion time.

PEO method also makes possible obtaining the Ca-P-containing bioactive layers in one step. These kind of layers promote cell adhesion/proliferation, which is particularly important for biomedical applications. However, there are only a few studies devoted to incorporation of Ca and P from the electrolyte into PEO-coatings on Mg [42,43]. Gao et al. [44] formed MgO-$Na_4Ca(PO_3)_6$ layers by PEO method on the surface of commercially pure Mg substrates. It is well known that hydroxyapatite (HA, $Ca_{10}(PO_4)_6(OH)_2$) is the main inorganic compound of natural bone. Besides, layered magnesium-substituted hydroxyapatite-like compounds ($Ca_aMg_b(PO_4)_c(OH)_d$) with partial carbonate substitution are the typical corrosion products formed on Mg alloys either *in vivo* or *in vitro* [45,46]. Therefore, some efforts have been undertaken to form HA during the PEO process [47–49]. Yang et al. [50] fabricated PEO-coatings on Mg substrate in alkaline phosphate electrolyte with hydroxyapatite particles addition. Tang et al. [48] formed hydroxyapatite-containing coatings on the surface of the AZ31 Mg alloy by micro-arc oxidation with different applied voltages. It was shown that thickness, roughness and porosity/defect levels of the coatings increased with increase of the applied voltage. In our previous work [51] *in-situ* incorporation of HA was achieved on Mg-Mn-Ce alloy by PEO in calcium glycerophosphate electrolyte.

Calcium-phosphate layers (including hydroxyapatite ones) formed using PEO technique provide improved implant biocompatibility and accelerate the osteoconduction [52–55]. Unfortunately, such Ca-P coatings do not provide sufficient protection of Mg alloy against corrosion degradation. Typically, better corrosion protection for Mg alloys is required even for biomedical implant applications. One of the ways is to modify PEO-coating to form composite corrosion resistant bioactive coating. Such hybrid layer might prevent the corrosive medium access to the Mg alloy substrate and at the same time increases the rate of bone tissue growth.

PEO-coating on Mg alloys can be used as a matrix [56] for composite coating formation due to its good adhesion to the metal and barrier properties as well as highly porous morphology, which can stimulate interaction with cells. Being a porous ceramic-like material PEO-layer is a good basis for further improving the corrosion performances using polymer to decrease the rate of material degradation [57,58]. The use of polymers as impregnation component into the pores of

outer part of the coating and as a topcoat for PEO-layer is an effective way to tune, moderate and control the kinetics of bioresorption of Mg-based implant materials in biological environments. Such coatings ensure a controllable degradation rate of Mg alloy specimens. However, there are very few reports on impregnations of PEO with bioinert polymers for biomedical use [51,59,60]. For instance, Liu et al. [60] used chitosan and poly (styrene sulfonate) polyelectrolyte multilayers for sealing the PEO-layer on WE43 Mg alloy using the layer-by-layer self-assembly technique. It was stated that such a coating can be an efficient way for surface modification of magnesium-based materials to meet the requirements of biomaterials applications. In the other work [54] calcium phosphate/chitosan composite coatings on a PEO-pretreated AZ91D alloy were prepared by electrophoretic deposition followed by immersion into a PBS. It was shown that obtained composite coating can obviously protect the Mg alloy from corrosion in the modified SBF.

Therefore, the objective of this work is to offer the method of composite bioactive coating formation to improve a control of Mg alloy resorption for personalized orthopaedics. The main idea of this work is based on the incorporation of superdispersed polytetrafluoroethylene (SPTFE) into PEO-coating containing HA. SPTFE is bio-relevant polymer [61,62] which has good compatibility with the human organism and ensures controlled degradation rate of magnesium implant. The technical approach suggested here combines modification of the magnesium alloy surface using PEO method and improving barrier properties of the PEO-layer by means of formation of composite polymer-containing coating.

Along with increasing the protective properties of the PEO-treated Mg alloy samples, it is also necessary to save the biological activity of the HA containing PEO-coatings after polymer treatment. Therefore, the method of SPTFE electrophoretic deposition (EPD), which ensures the high protection of Mg alloy specimens along with keeping the bio functionalities of HA PEO-layers, was used in this work. Previously [63] it was established that polymer-containing coatings formed by EPD on magnesium alloys provided a threefold decrease of the corrosion current density and twofold decrease of the wear, as compared to the base PEO-coating obtained in the silicate-fluoride electrolyte. In the earlier study [51], the triboelectric method was used to apply SPTFE on the surface of PEO-treated Mg alloy to improve the corrosion resistance of the material. At the same time, EPD method was not used previously for treating the active hydroxyapatite-containing PEO-layers with polymer on the Mg alloy surface. In this work, bioactive composite polymer-containing coatings formed using EPD on magnesium alloy specimen is achieved for the first time.

Electrochemical properties and level of the corrosion protection of samples were studied *in vitro* in this work. It was established in our previous studies [22,64], that taking into account features of the applied medium and different corrosion mechanisms it is reasonable to make electrochemical tests of the Mg alloy samples, which are promising for biomedical application, in physiological medium rather than in typical NaCl solution. Therefore, MEM (minimum

essential medium) – synthetic cell culture medium, which imitates the ionic composition of body plasma and includes physiological concentrations of amino acids, was used in this work. The mechanism of the corrosion degradation of the bare MA8 Mg alloy in MEM was established in [22,64]: the local pH on the surface of the sample was typically 8.5±0.6 and the main product formed on the surface was partially magnesium-substituted HA. The multifunctional active protective PEO-coatings with and without polymer treatment on Mg alloy samples is studied in the MEM for the first time in this paper.

The active control of degradation of the coated Mg alloy samples was made using integral (electrochemical impedance spectroscopy (EIS), potentiodynamic polarization (PDP), open circuit potential (OCP) evolution) and localized electrochemical methods (scanning vibrating electrode technique (SVET) and scanning ion-selective electrode technique (SIET)) in cell culture medium (MEM). Application of conventional DC and AC current electrochemical methods in combination with local scanning electrochemical methods allows to study the effect of local heterogeneous meso-sized inclusions and morphological features on the intensity of exchange processes at the interface as well as to obtain information concerning the whole electrode surface, structure of electrode surface layers and the mechanism of electrochemical reactions on the electrode surface.

The results of this work will promote the development of new protective coatings on the surface of magnesium alloys in order to introduce this technology into the bio-medical sector.

## 2. Experimental

### 2.1. Samples

Plates of wrought MA8 magnesium alloy (1.5–2.5 wt. % Mn; 0.15–0.35 wt. % Ce; 0.05 wt. % Fe; 0.1 wt. % Si; 0.007 wt. % Ni; 0.1 wt. % Al; 0.05 wt. % Cu; 0.002 wt. % Be; 0.3 wt. % Zn; balance – Mg) were used as specimens. Samples were mechanically ground with SiC papers, degreased with ethanol, polished using aluminium oxide lapping films (Thorlabs Inc., USA) with grain size decreasing down to 3 μm in ethanol as a lubrication liquid. Finally, the plates were rinsed with deionized water, degreased with ethanol and air-dried.

The samples were PEO-treated in the electrolyte containing 25 g $L^{-1}$ calcium glycerophosphate ($C_3H_7O_6PCa$), 5 g $L^{-1}$ sodium fluoride (NaF), and 7 g $L^{-1}$ sodium silicate ($Na_2SiO_3$). The PEO process was performed in the pulsed bipolar mode [51] using equipment designed by Fleron[®] on the base of commercially available thyristor power supply TER4-100 (Russia). Specimens were processed for 110 seconds. The anodic component was in the potentiostatic mode at 420 V. The cathodic component was in galvanodynamic mode in which the current was changed from 11 A up to 6 A at a rate of 0.045 A $s^{-1}$. The polarization frequency was 100 Hz (pulse duration of 10 ms, no pauses). The duration ratio of the anodic and cathodic pulses was equal to 1. The duty cycle was 50 %. The root-mean square values of the voltage were applied in the

PEO process. The electrolyte temperature was maintained at 15 ºC using ChillerSmart H150-3000 (Lab-Tech Group, UK).

Electrophoretic deposition was used to modify PEO-coating with superdispersed polytetrafluoroethylene (Forum ®). EPD was carried out in a water suspension containing SPTFE particles in concentration of 30 g $L^{-1}$. Wetting agent (OP-10 [65], 1 g $L^{-1}$) and anionic surfactant (sodium dodecyl sulfate, 0.5 g $L^{-1}$) were added to increase the wettability of SPTFE particles and stabilize the suspension. EPD was performed in potentiostatic mode at 200 V during 25 s. The EPD process was described elsewhere [63]. The final step of formation of composite polymer-containing coating was a thermal treatment of the EPD-processed samples at 315 °C for 15 min.

Coated MA8 magnesium alloy samples were investigated in MEM (# 61100-103 powder, Gibco®, Thermo Fisher Scientific, USA) [66,67] with 2.2 g $L^{-1}$ $NaHCO_3$ addition [68].

*2.2. Electrochemical measurements*

*2.2.1. Localised electrochemical studies*

The localised techniques (SVET and SIET) (Applicable Electronics, USA) were used to obtain information about the kinetics of corrosion processes on the surface of MA8 magnesium alloy with PEO-coating in MEM. These methods were used to detect the formation of defects and pitting in surface layers as well as to present a characterization of physico-chemical processes occurring in these corrosion sites. The methodology of SVET and SIET tests was described in detail elsewhere [22,69].

The SVET probe located at 100 μm ± 5 μm above the scanned surface was an insulated Pt–Ir wire with a layer of platinum black deposited on a tip. The diameter of the tip of SVET probe was 15 μm. The probe vibration amplitude was equal to 16 μm (Z-axis) and 17 μm (X-axis) peak to peak. The probe vibration frequencies were 99 Hz (Z-axis) and 160 Hz (X-axis). The data from vertical (Z-axis) component of vibration were analyzed.

The $H^+$-selective microelectrode was used for SIET measurements. It was made from single-barreled glass capillary (1.5 mm outer diameter). The diameter of the opening of the conical tip of glass capillary was 2.0 ± 0.5 μm. The silanized capillaries were backfilled with solution of 0.01 M $KH_2PO_4$ in 0.1 M KCl. Ionophore-based membrane selective for $H^+$ (Fluka, Ref. 95293) [20] was embedded in the capillary tip. A homemade silver-chloride Ag/AgCl/0.1 M KCl, 0.01 M $KH_2PO_4$ electrode was an external reference electrode.

The $H^+$-selective microelectrode was located at 40 ± 5 μm above the studied surface and was calibrated in MEM with specified pH in compliance with the Nernst equation (56.0 ± 0.7 mV $pH^{-1}$ – the Nerstian slope). The microelectrodes were mounted on the SVET/SIET dual-head

stage. The SVET/SIET measurements were controlled by means of LV-4 software (ScienceWares, USA) in quasi-simultaneous mode [69].

After isolating the sample edges with wax, the active studied area of the PEO-coated Mg MA8 alloy specimen was about 4.8 mm$^2$. The obtained results were checked twice on similar samples. All SVET and SIET maps contain 1764 points (42 × 42 grid). PEO-treated MA8 Mg alloy specimens were tested in MEM under open circuit potential conditions. SVET/SIET measurements were performed during 3 days of samples exposure to MEM. To simulate the experiment conditions to the body medium, avoid the electrolyte evaporation and the microbial growth, the solution in the SVET/SIET cell was refreshed continuously using the peristaltic pump (Medorex TL15E) at rate 1–1.5 mL min$^{-1}$ in accordance with [22].

### 2.2.2. Conventional electrochemical tests (EIS, PDP, OCP)

Electrochemical behaviour of the coated MA8 Mg alloy samples was investigated in MEM using EIS and PDP methods by means of the electrochemical system 12558WB («Solartron Analytical», UK). The description of the conventional electrochemical tests was presented elsewhere [64]. PEO-treated Mg alloy plates with a size of about 15 mm × 20 mm × 1.5 mm were tested in a three-electrode Model K0235 Flat Cell («PAR», USA) at ambient conditions. The investigated area was equal to 1 cm$^2$. Hg/Hg$_2$Cl$_2$, KCl (saturated) (SCE) was used as a reference electrode. The counter electrode was Pt mesh. Samples were exposed to MEM for 1 hour before PDP tests to reach the equilibrium.

PDP test was utilized in order to evaluate barrier properties and degradation rate of the coated Mg substrates in MEM solution. The sweep rate for PDP test was about 1 mV s$^{-1}$. PDP measurements were carried out in accordance with ASTM G5-14 [70–72]. The PEO-treated samples were polarized from $E = E_C - 350$ mV up to $E = E_C + 900$ mV. Corrosion potential, $E_C$, corrosion current density, $I_C$, were established to evaluate the corrosion properties of the materials. $I_C$ was calculated using the cathodic Tafel slope, $\beta_c$, and a straight horizontal line drawn through $E_C$ [37,73,74].

The degradation of barrier properties as well as the degradation of the coating/substrate interface was studied by means of EIS. The sinusoidal signal with 10 mV (rms) amplitude was applied. The frequency range for EIS spectra was 0.1 MHz – 0.1 Hz (logarithmic sweep 10 points per decade). Samples were kept for 1 hour in MEM to achieve the steady state, and the last OCP value was used for EIS tests. To carry out EIS, PDP, and OCP measurements CorrWare/Zplot software was applied. Experimental data were processed by means of CorrView/ZView software. EIS tests were done every 2 h within 107 h. To investigate the potential evolution under specimens exposure to MEM, OCP was recorded during 118 h. EIS, OCP, and PDP tests were repeated on the three specimens to verify the experimental data. Errors for the individual

parameters calculated using fitting the impedance data with equivalent electrical circuits (EEC) were < 5 %.

## 2.3. Immersion experiments and hydrogen evolution tests

Coated samples with a size of about 15 mm × 20 mm × 1.5 mm were immersed in MEM (pH 7.45, 500 mL). Hydrogen evolution tests were carried out using homemade eudiometer within 7 days at room temperature [75]. The bulk pH of the solution was measured every 24 h. The total surface area of samples was equal to 35 cm$^2$. To imitate the renewal of the human body medium and to decrease the rate of bacteria growth in MEM [22] the solution was manually renewed every 12 h. The glass equipment was sterilized before the test by means of dry heat sterilizing in the drying chamber at 180 ºC during 1 h [76]. MEM was stirred at $350 \pm 100$ rpm. Tests were performed in triplicates. The measurement error was 10 %. At the end of the immersion tests, specimens were removed from MEM, rinsed with deionized water, and air-dried.

In the current work, the normalized hydrogen evolution, as well as the corrosion rate evolution during Mg alloy samples exposure to MEM, were presented. The degradation rate (DR, mm year$^{-1}$) was calculated according to [77–81].

## 2.4. Cross-section preparation

Cross-sections of samples with PEO-coating and composite polymer-containing layer was made using Tegramin-25 equipment (Struers A/S, Denmark). Cross-sections contain initial specimens and samples after 7 days immersion in MEM. Specimens were fixed in SpeciFix epoxy resin. After grinding the samples were degreased with ethanol and polished with composite MD-disks (Struers, Denmark) using 3 and 1 μm diamond suspensions (DP-Suspension, Struers, Denmark), respectively. Samples were washed with deionized water, degreased with ethanol and air-dried.

## 2.5. SEM-EDX, surface topography and XRD analyses

SEM analysis was performed of the surface morphology and its evolution for PEO-treated samples and those coated with composite coating. Cross-sectional microstructures of surface layers were observed to study the evolution of the coating morphology as a result of aggressive medium effect as well as to compare the degradation level of samples with base PEO-layer and composite polymer-containing coating. SEM-images were obtained at an accelerating voltage of 10–20 kV using Zeiss EVO 40 scanning electron microscope (Carl Zeiss Group, Germany) with Silicon Drift Detector X-Max$^N$ 80 (Oxford Instruments NanoAnalysis, USA). Energy Dispersive X-Ray analysis was used to study elements distribution in surface layers of samples. SEM-EDX measurements were controlled using AZtec 3.0 SP2 software (Oxford Instruments NanoAnalysis, USA).

The morphology and chemical composition of the degraded surface of the PEO-coated sample after SVET/SIET test was observed using scanning electron microscopy (TESCAN, Vega3 SB, Czech Republic) equipped with energy dispersive X-ray spectrometer. SEM-images were collected at an accelerating voltage of 10 kV with SE detector.

PEO-coating formed on the MA8 Mg alloy surface was studied using X-ray diffraction (XRD) analysis. XRD tests were performed using a SmartLab diffractometer (Rigaku, Japan) in $CuK_\beta$ radiation, the tube power 42 kV, 140 mA at room temperature in the range $2\theta = 4° – 85°$ with a step of $0.01°$.

The surface topography of the obtained coatings was characterized using a non-contact optical surface profiler (OSP). M370 electrochemical workstation (Princeton Applied Research, USA) with OSP370 device was used. Data analysis was carried out by means of Gwyddion 2.45 software.

## 3. Results

### 3.1. Coating characterization

In order to establish the composition of the formed PEO-layer, the XRD analysis was performed. Fig. 1 depicts the X-ray diffraction patterns of the PEO-coating. XRD test showed high intensity peaks of Mg coming from the alloy matrix. PEO-layer consisted of following crystalline phases: MgO (periclase), $Mg_2SiO_4$ (forsterite), hydroxyapatite (HA; $Ca_{10}(PO_4)_6(OH)_2$), and sodium magnesium silicate ($Na_2MgSiO_4$). Presence of HA in the PEO-coated sample indicates its potential improved bioactivity as compared to previously studied PEO-layers formed in Si-F electrolytes [82].

### 3.2. SVET/SIET studies of the local corrosion activity

SVET/SIET tests were performed during 3 days of specimen immersion in MEM. Fig. 2 displays the investigated area of the PEO-treated specimen at different stages of the material examination. Figs. 2a, 2b presents the active sample surface after wax isolation before SVET/SIET studies. The result of local electrochemical activity of the PEO-processed sample monitored on a microscale level is shown in Fig. 3. Small changes of the current density and pH were detected after 1 h of sample exposure (Figs. 3a, 3d). Local pH measurements demonstrated slightly higher sensitivity (over SVET) to detecting the initiation of the corrosion process, as shown in SVET and pH maps in Fig. 3a and 3d respectively. Interestingly the far right alkalinization peak in Fig. 3d coincides with the site of hydrogen evolution observed at the top of Fig. 2c. Local pH remained below 7.9. After 6 h more signs of coating degradation were revealed using SVET and SIET 3D maps (Figs. 3b, 3e). At the same time, there was no pits or other visible changes of PEO-coated surface, apart from small hydrogen bubble (Fig. 2c). Fig. 3c, 3f showed the sample electrochemical activity after 30 h of the test. Monitored values of the local current density and

pH continue growing during sample exposure to MEM as a result of Mg alloy corrosion in the defects appearing as a result of PEO-layer degradation. Local pH values increased to 8.4 in the most actively corroding area of the sample. After 30 h the corrosion activity of coated alloy practically did not change until the end of the experiment according to SVET/SIET data. The optical image of the sample surface after MEM removal (Fig. 2d) confirmed the corrosion attack in the lower part of the PEO-coated sample, where SVET and SIET detected high electrochemical activity. Colour heterogeneity of the pitting zone on SVET-diagram (Figs. 3b, 3c) indicates the presence of the zone with lower anodic activity inside one with higher positive values of current density as a result of micro-galvanic coupling, which accelerates the corrosion process and material degradation. The local $pH_{max}$ and $pH_{min}$ evolution determined from SIET test during 72 h are presented in Fig. 4. Before the pitting formation, the average pH was equal to 7.4±0.2. When the pitting was formed, pH values did not exceed 9.0, that is in accordance with our previous work [22] and corresponded to the pH of bare MA8 Mg alloy in MEM. Values of the $pH_{max}$ and $pH_{min}$ for PEO-treated sample in MEM varied within: 7.5–9.0 and $6.3 \pm 8.3$, respectively. Lower values of the pH for Mg alloy in MEM as compared to those, which are typical for Mg corrosion in NaCl (pH is about 10–11) is a result of hydroxyapatite-like protective layer formation, which stabilized the local pH at the value below 9.0 [20–22]. However, there might have been a microbial growth manifested by low minimal pH values below 7 in the passive areas of the sample, at ca. 50 h. This kind of microbial growth is hard to avoid in MEM, the medium developed to promote the cell growth. Typically, the antibiotics (streptomicine+peniciline) are added to MEM to control the undesired microbial growth. This acidification of the medium promoted faster magnesium degradation that resulted in higher pH values at 55–60 h.

SEM image of the most corroded area of the PEO-coated sample after 72 h SVET/SIET test presented in Fig. 5. Obtained results show the intensive pitting-like corrosion propagation and coating degradation with the formation of Ca-P-containing products in accordance with EDX data.

These results showed that PEO treatment performs two functions: decreases the electrochemical activity of the sample and ensures formation of Ca-P containing semi-protective layers. At the same time, 6 h of sample protection is not enough to provide the necessary service life of the material intended to be used as an implant.

### 3.3. Surface topography of the PEO and composite coatings (SEM and OSP data)

To improve the resistance of the material to corrosive medium, pores of PEO-coating were sealed with SPTFE using electrophoretic deposition. Fig. 6 represents SEM images of the surface of PEO-coating (a) and composite polymer-containing layer (b). As a result of polymer treatment, the surface of the coating became smoother and more homogeneous as compared to PEO-coating, which has a lot of pores – possible places of corrosion initiation. SPTFE penetrates

into the pores and forms an additional barrier, which assures the lower corrosion activity of the composite coating as compared to the base PEO-layer. The surface topographies of the PEO and composite coatings performed using OSP are presented in Fig. 7. The arithmetic mean of the height in the measured area ($S_a$) determined from Fig. 7 was $10.8 \pm 0.9$ µm for PEO-layer (Fig. 7a) and $7.8 \pm 0.5$ µm for polymer-containing coating (Fig. 7b). This result confirmed the surface smoothening after the electrophoretic deposition of SPTFE, which decreased the coating roughness.

## 3.4. Electrochemical behaviour of samples in MEM

Fig. 8 depicts the OCP evolution for the bare, PEO-coated, and polymer-treated specimens during 118 h of the exposure to MEM. The sample without coating shows the lowest potential values among other samples. These values change with time, that indicates the continuous process of corrosion product layer formation and degradation [64]. For the PEO treated sample the OCP values increased and slightly changed during the immersion time. This is the result of a lower rate of the alloy dissolution as compared to bare material, which ensures the lower rate of the corrosion product formation and stability of the coating in the corrosive medium. The highest values of the OCP were registered for the sample with polymer-containing coating. Values of the potential changed during the experiment from $-0.5$ up to $0.1$ V vs SCE. The electrode potential of the sample with composite coating is governed by combination of electrochemical reactions occurred on the material surface. Higher potential of the composite coating as compared to PEO-layer and sample without coating is a result of superior barrier properties of polymer-containing coating and its differential effect on cathodic and anodic current respectively. This can also be related to different transport properties of different charged species ($Mg^{2+}$ vs $OH^-/H^+$) through a high-barrier layer. The trend of OCP evolution for composite coating corresponds to partially passing MEM through some partially sealed pores and microdefects, with limited reaching metallic magnesium. Such permeability of the coating is not significant, which is confirmed by higher potential values as compared with those for other samples. At the same time, this composite coating provides the contact of the medium with bioactive PEO-layer on the surface of the alloy, which probably can further improve the biocompatibility and provides the controlled implant degradation during the service time.

Fig. 9 presents PDP curves for studied coated and uncoated samples. PEO-coating slightly increases the protective properties of the Mg alloy, value of the corrosion current density decreased from $9.2 \times 10^{-6}$ A cm$^{-2}$ down to $5.4 \times 10^{-6}$ A cm$^{-2}$ (Table 1). However, composite coating possesses the highest protection, corrosion current density decreased down to $7.6 \times 10^{-10}$ A cm$^{-2}$. One should keep in mind that this evaluation is performed for only a semi-quantitative comparison since the Tafel law is only applicable for the situations when the current is controlled by the activated charge transfer, which is often not the case of coated substrates. For bare and PEO-treated samples the anodic curves are characterized with a sharp increase of the current density, which is the result of pitting formation in the protective layer and coating degradation

in accordance with SVET/SIET results (Figs. 2,3,5). The sample with composite coating has the anodic curve without inflexion and with very low values, which reveals its high level of barrier properties.

The EIS was applied to study the evolution of the protective properties during exposure to MEM. Impedance spectra evolution during 107 h immersion in MEM are presented in Fig. 10 for the PEO-coated specimen and in Fig. 11 for the sample with composite layer. The evolution of the impedance spectra for bare MA8 alloy in MEM was described in detail in [64]. Spectra for the PEO-treated sample at 1 h of immersion have two not well resolved time constants, which are responsible for two layers of the coating: inner dense and outer porous layers (Fig. 12a). During the immersion, impedance modulus for the sample with PEO-coating increased in the full frequency range (Figs. 10a, 10b), it is the result of formation of corrosion products and calcium-phosphate compounds on the surface and in the pores of the coating (Fig. 12b). These changes are also confirmed by evolution of the behaviour of the phase angle $\theta$ dependence on frequency (Fig. 10b), which indicates growth of Ca-P product layer that is also manifested by increase of impedance modulus at high frequency range from $10^5$ Hz to $10^2$ Hz. This is accompanied by partial degradation of the PEO-layer and partial blocking the pores by the formed corrosion products. Therefore, analysis of the EIS data indicates that after the first hours of sample immersion two separate time constants are revealed in Fig. 10 (after 24 h). The first one is responsible for capacitance of the whole coating including Ca-P layer (high frequency range) and the second one for very thin inner PEO-layer (middle and low frequency range) [83]. Due to high permeability of PEO-coating and following partial degradation, its structure was changed. The evolution of the impedance modulus measured at the lowest frequency ($|Z|_{f=0.1Hz}$) during the time of samples immersion in MEM is shown in Fig. 13. The trend of impedance modulus is similar to OCP evolution (Fig. 8). Impedance of the uncoated sample increased up to 54 h due to corrosion layer formation and then decreased due to the breakdown of the partially protective surface film. The curve for the PEO-coated sample reflects its stability in the corrosive medium as compared to the bare alloy. During 107 h values for the PEO-treated sample changed in the range from 0.7 $10^4$ $\Omega$ cm$^2$ up to 2.5 $10^4$ $\Omega$ cm$^2$. Impedance modulus for the sample with composite coating has the highest values with periods of increase (up to 5.4 $10^9$ $\Omega$ cm$^2$) and decrease (down to 1.7 $10^7$ $\Omega$ cm$^2$), which indicates the high protective properties of the sample on the one hand and ensures the penetration of the MEM through partially sealed pores down to the dense part of the PEO-coating. Figs. 10, 11 represent data points of the experimental values and fitting curves obtained using equivalent electrical circuits. In the first hour of sample exposure, EIS spectrum for the sample with composite coating contains three time constants (Figs. 11, 12c). Unresolved time constants are associated with the presence of porous and dense layers, and the third one is related to the polymer plug as a result of SPTFE layer formation on the top of the PEO-coating and in the coating pores. However, during the specimen exposure, only two time constants become visible. This is related to morphology changing of the composite coating due to corrosion product formation and deposition causing the partial pore sealing (Fig.

12d). Such morphology evolution was shown in Fig. 11b, since phase angle at the lowest frequency move to the low degree from –6° down to –31°, indicating more capacitive character of the coating due to partial closure of the surface defects. Evolution of impedance modulus with stages of decline and growth in Fig. 11 is related to the accompanying process of corrosion activation and healing of microdefects during samples immersion in MEM. Therefore, due to the protective layer degradation and to the corrosion product formation, EIS spectra for composite coating depict only two constants (Fig. 12d). However, composite coating has significantly higher stability as compared to base PEO-coating. Thereby for this protective layer, neither intensives corrosion process nor sufficient precipitation of Ca-P products is reflected in Bode plots as it was previously revealed for PEO-layer. It should be noted that these morphology changings revealed in Fig. 11 cannot be a result of swelling of the organic coating since PTFE is inert and one of the most stable polymers that is insoluble in ordinary conditions [84]. Impedance spectra presented in Figs. 10 and 11 (except the first one for the composite coating) were described using a serial-parallel connection of two $R$–$CPE$-circuits, where $R$ stands for resistance and $CPE$ is Constant Phase Element [36,58,59,64,85–91]. For the sample with PEO-coating at 1 h of immersion, $R_1$–$CPE_1$ and $R_2$–$CPE_2$ are related to unresolved time constants, which describe the whole coating and its inner dense part respectively (Fig. 12a). For the PEO-coated sample after 24 h of immersion, time constants ($R_1$–$CPE_1$ and $R_2$–$CPE_2$) correspond to entire coating (with Ca-P product layer) and degraded inner PEO-layer respectively (Fig. 12b). For the specimen with composite coating $R$–$CPE$-circuit in high frequency range is responsible for the whole coating without corrosion products (for the sample at 1 h of immersion, Fig. 12c) and with corrosion products (for the sample after 24 h of immersion, Fig. 12d) deposited in microdefects and unclosed pores ($R_1$–$CPE_1$) and second one in low frequency is related to the inner poreless part of the coating ($R_2$–$CPE_2$) including SPTFE layer inside pores (Figs. 12c, 12d). The additional time constant ($R_3$–$CPE_3$) visible at the initial stage of immersion (at 1 h) is responsible for pores sealed with polymer (Fig. 12c).

*3.5. SEM-EDX analysis of the PEO and EDP treated samples*

SEM images of the freshly prepared PEO-coated sample (a) and the sample after 7 days immersion in MEM (b) are presented in Fig. 14. Analysis of the result indicated that due to the high porosity of the coating the corrosive medium penetrates down to the substrate, which leads to its dissolution and formation of the corrosion products within and under the PEO-layer. Due to the MEM influence, the surface of the PEO-layer degrades facilitating further access of the medium to the magnesium alloy. In contrast to this, the morphology of the composite coating is affected to lesser extent (Fig. 15a, 15b). Polymer-containing coating has less defective structure, due to partial pore sealing with SPTFE, which prevented the rapid material degradation.

The elements distribution within the PEO-layer before (1a–1g) and after 7 days of exposure (2a–2g) is shown in Fig. 16. This oxide coating consists of a high amount of phosphorus, calcium and silicon. Phosphorus is uniformly distributed within the coating, whereas calcium and silicon

are more concentrated in the outer porous layer. Magnesium also can be seen in the composition of the coating, but due to its high concentration in the substrate, the colour intensity of its distribution in PEO-layer is lower. Fluorine was presented in Fig. 16 only for comparison of its concentration in PEO-layer with that in composite coating (Fig. 17). Distribution of elements and their lower colour intensity after 7 days exposure of the sample with base PEO-coating indicates the growth of the protective layer permeability and the coating degradation. Important accumulation of Ca at the metal/PEO interface is observed after immersion, supporting the notion of formation of Ca-P products during exposure of PEO-treated Mg in MEM electrolyte.

Fig. 17 depicts the element distribution for the composite coating before (1a–1h) and after 7 days of exposure to MEM (2a–2h). Polymer-containing coating as shown in Fig. 15 has fewer defects as compared to base PEO-layer, and thereby the substrate is less susceptible to corrosion degradation. Permeability of the composite coating is lower in comparison with the base PEO-layer, which is shown by the elements distribution and low free space in the coating structure even after 7 days of exposure. Carbon concentration in the composite coating (Fig. 17 1h, 2h) is related to the impregnation of polymer into the outer porous part of PEO-layer. This indicates the increasing protective properties of the coating. At the same time, polymer treatment does not fully prevent degradation due to non-completely pores sealing. This result showed that EPD of polymer does not only increase the protective properties due to blocking the pathway for the corrosive ions but also provides the contact of the medium with Ca-P bioactive layer. Pores sealing with SPTFE is also confirmed by high fluorine distribution before and after samples exposure. It should be noted that fluorine distribution in the coating duplicates the geometry of pores in the structure of the protective layer, which is shown in Figs.15, 17 (1a, 2a). Similar to PEO-layer the stripe of Ca-P compounds was revealed at the Mg alloy/composite coating interface, which indicates the identity of the corrosion processes for two types of coated samples.

*3.6. Hydrogen evolution test*

The rate of the corrosion degradation of magnesium alloy, can be estimated using the hydrogen evolution measurements. Fig. 18 depicts the behaviour of the magnesium alloy without coating, with PEO-layer, and with composite polymer-containing coating during 7 days immersion in MEM. Fig. 18a shows the evolution of normalized total volume of the evolved hydrogen, whereas Fig 18b demonstrates the evolution of degradation rate in mm per year. Obviously, that bare sample shows the highest degradation rate with the average value of $0.042 \pm 0.009$ mL cm$^{-2}$ day$^{-1}$ ($0.09 \pm 0.02$ mm year$^{-1}$). Corrosion rate decreased two folds following PEO treatment and has the average value of about $0.015 \pm 0.002$ mL cm$^{-2}$ day$^{-1}$ ($0.031 \pm 0.005$ mm year$^{-1}$). Composite coating has the lowest dissolution rate ($0.006 \pm 0.002$ mL cm$^{-2}$ day$^{-1}$; $0.013 \pm 0.003$ mm year$^{-1}$) and provides the material with the best corrosion protection. Corrosion activity of the samples with the maximum registered on the first day decreased and increased in series as a result of corrosion products deposition and degradation. DR changed from 0.14 to 0.07 mm year$^{-1}$ for the bare sample, from 0.04 to 0.02 mm year$^{-1}$ for the PEO-coated sample and from 0.02 to

0.01 mm year$^{-1}$ for the sample with composite coating. Values of the bulk pH for all the samples practically did not change due to the MEM refreshing and were $7.45 \pm 0.08$.

It should be stated, that difference in values of corrosion current density roughly estimated from PDP-curves (Table 1) and the hydrogen evolution rate can be related with two factors: contribution of oxygen reduction reaction to the total cathodic process [92,93] and the influence of a well known negative difference effect, as previously described in [94,95]. Moreover, it is important that PDP measurements take a snapshot for the sample behaviour at a certain time, while the long-term hydrogen evolution accounts for evolution of the system during days of exposure.

## 4. Discussion

The electrochemical activity of the bare MA8 Mg alloy in MEM was studied previously in [22,64]. It was stated that formation of protective coating is necessary to prolong the mechanical integrity of magnesium samples. The method of plasma electrolytic oxidation was chosen since it one of the most promising and claimed ways of forming oxide/hydroxide layers with a wide range of functional properties [34]. Application of PEO method enables one to form calcium phosphate layers (including those containing hydroxyapatite), which allows to achieve the necessary biocompatibility of the implant and to increase the osteoconductivity [18]. Therefore, PEO method was applied to reduce the corrosion of Mg alloy and as a consequence to maintain the mechanical strength and integrity of the implant during the time required for bone healing and restoration of its functions.

Results of this work showed that PEO-layer formed on MA8 Mg alloy improves the corrosion resistance of the material, the initial values of the impedance modulus measured at the lowest frequency slightly increased from $5.5 \times 10^3$ Ω cm$^2$ up to $6.9 \times 10^3$ Ω cm$^2$ (Fig. 13) as compared to bare alloy. This increase is only incremental due to high porosity of PEO-layer, typically formed by this method on Mg. The electrochemical activity measured at a microscale level using SVET/SIET showed pitting formation after 6 h of sample exposure to MEM (Fig. 3). Therefore, additional surface treatment must be applied in order to ensure a proper tuning of the degradation rate of the magnesium alloy especially during the most critical initial period.

To create a reliable protective layer that preserves the bioactive properties of the Mg-containing material, it is necessary to control the process of pore narrowing and their sealing in the outer part of the PEO-coating. One of the ways to solve this problem is to modify the PEO-layer, which ensures the formation of a composite corrosion-resistant bioactive coating, which limits the access of the corrosive environment to the material, on the one hand, and accelerates the growth of bone tissue, on the other. In this case, EPD treatment of PEO-coating using SPTFE was suggested and applied to form the barrier in pores. It increases the protective corrosion properties of coatings on the magnesium substrate.

Fig. 12 depicts schemes of the electrolyte/electrode interface and used EEC for base PEO-layer (a, b) and polymer-containing coating (c, d) at various stages of their degradation. Results of the EIS fitting (Figs. 10, 11) are shown in Tables 2 and 3. The capacitive behaviour of the aforementioned (in Section 3.4, Fig. 12) parts of protective coatings was described using corresponded parameters CPE. CPE was used instead of an ideal capacity [57,80,87,96–99]. Thus, for example, $CPE_1$ is responsible for the capacitive behaviour of the whole coating, including its porous (outer) and poreless (inner) parts. The outer porous layer is connected to the substrate through the microdefects in the inner barrier layer, described using $CPE_2$ (Fig. 12). The corrosive solution penetrates inside the coating through pores exist in PEO-coatings. $CPE_3$ is assigned to capacitive parameter of the sealed pores. $Q$ and $n$ were CPE coefficient and exponential quantity of $CPE$, respectively. $R_1$, $R_2$ and $R_3$, were the resistance of electrolyte in pores, resistance of inner PEO-layer and resistance of pores sealed with polymer, respectively. $R_s$ in Fig. 12 is solution resistance. All impedance spectra were fitted with low chi-square value ($\chi^2 = 1 \times 10^{-4}$). Impedance spectra of PEO-coated samples can be described using one time constant, however, the goodness of fit significantly decreased ($\chi^2 = 1 \times 10^{-3}$) as compared with fitting using two time constants. This simulation confirmed the presence of inner dense layer. To show the behaviour of PEO and composite coatings during immersion in MEM, parameter $Q$ was recalculated to real capacitance ($C$) in accordance with equation (1) suggested in [64,100,101], which is suitable for normal distribution of time constants.

$$C = Q^{\frac{1}{n}}(R_i^{\frac{1-n}{n}}),$$ (1)

where $C$ and $R_i$ are the capacitance (F cm$^{-2}$) and resistance of protective layer, respectively. The thickness of this layer can be calculated using equation for a parallel-plate capacitor (2).

$$C = (\varepsilon\varepsilon_0 S)/d,$$ (2)

where $\varepsilon$ is the dielectric constant, $\varepsilon_0$ is the permittivity of vacuum (8.854 $10^{-14}$ F cm$^{-1}$), $S$ is the area and $d$ is the thickness of the layer. According to this formula, the lower value of the capacitance can be related to a thicker layer [102]. However, this equation is true only for homogeneous poreless layer and due to high porosity of the obtained calcium-phosphate PEO-coating (Fig. 14) its high roughness and low compactness the thickness estimation cannot be accurately completed [101,103]. Moreover, PEO-layer consists of various components (MgO, $Mg_2SiO_4$, $Ca_{10}(PO_4)_6(OH)_2$, $Na_2MgSiO_4$) and therefore real dielectric constant is hard to know. The capacitance of the inner layer ($C_2$) deduced from the spectra shown in Fig. 10b is in the range of 3.2–6.8 μF cm$^{-2}$ (Table 2), which corresponds to the oxide film thickness (dielectric constant for magnesium oxide = 9.7) of 1–3 nm typically observed on the surface of Mg alloys with or without a PEO-layer [104,105].

In this work, the thickness of entire composite coating was calculated due to its more homogeneity, compactness and lower porosity as compared with PEO-layer as a result of

polymer treatment. For the whole coating, the calculated thickness is in the range of 50–100 μm (with $C_1 = 36$ pF cm$^{-2}$ and the range of $\varepsilon$ from 2.0 up to 4.0 for the components of polymer-containing coating), which is correlated with the real coating thickness presented in Fig. 15.

Changing of the electrochemical parameters $C$ and $R$ confirmed the process of pores sealing with corrosion products as well as these products degradation and removing from pores (Tables 2, 3). This process as it was shown in [64] for the bare alloy is dynamic. The periods of corrosion layer growth on the surface and inside pores at coating/substrate interface and its breakdown continue until the MEM species are depleted and corrosion occurs on the specimen just like in NaCl medium.

After 96 h of sample exposure to MEM, total resistance ($R_1 + R_2$) of the PEO-coating was equal to 22.7 kΩ cm$^2$, whereas resistance of the composite coating is more than 5 orders of magnitude higher, 4.2 GΩ cm$^2$. This result showed a sufficient increase of the protective properties of the sample after polymer treatment of the PEO-layer, which is also confirmed by PDP and hydrogen evolution tests (Figs. 9, 18). SEM and OSP analysis of the surface of the both coated samples indicates that EPD treatment decreases the coating roughness and makes the surface smoother as compared to base PEO-layer (Figs. 6, 7). Sealing the pores in the base PEO-layer with SPTFE was confirmed using SEM-EDX analysis of samples cross-section (Figs. 14-17) according to the fluorine distribution in the coating. SPTFE layer is nonuniformly distributed on the surface of coating since most of the polymer part is penetrated inside pores of the PEO-layer. Therefore, the thickness of the EPD layer on the surface of coating varies from 1 μm to 7 μm, whereas F signal can be seen through all the thickness of the composite coating. SEM-EDX data also show a high concentration in the coating composition (Figs. 16, 17) of such elements as Ca and P, which are necessary for biocompatibility. Analysis of the samples cross-sections after 7 days immersion in MEM indicates that additional Ca-rich layer growth at Mg/PEO interface supporting the EIS results. Electrodeposition of the polymer on the sample after PEO improves the coating morphology and makes the coated samples more resistant to corrosion degradation. Nevertheless, with time, the formed composite coating provides the controllable access of the active medium components to the substrate due to dosed pore sealing (Figs. 14–17). Therefore, polymer treatment does not absolutely isolate the implant making it bioinert. Rather, it partially limits the contact of the medium to the material ensuring the necessary rate of its degradation.

In addition, the coating obtained using PEO contains the hydroxyapatite in its composition (Fig. 1), which will increase the osteoconductivity during the rehabilitation period. SIET method showed that local pH on the PEO surface was stable and did not exceed 9.0 (Figs. 3, 4) due to the hydroxyapatite-like layer formation as a result of interaction of Ca$^{2+}$, HPO$_4^{2-}$, HCO$_3^-$ ions (from MEM) and Mg$^{2+}$, OH$^-$ (from corroded Mg alloy), which was also reported previously for bare Mg alloys exposed to SBF and MEM [20–22,66]. EDX analysis of the corrosion products formed as a result of degradation of PEO-coated Mg sample in MEM showed the presence of Ca and P at a ratio close to HA (Fig. 5). The presence and formation of bioactive component

such as hydroxyapatite will contribute to the growth of bone tissue and improve the biocompatibility of the implantable material in the human body [18,106].

To sum up, this work intended to reduce the rate of biodegradation of Mg-containing materials by means of protective layer formation. Relationship between the coatings structure, morphology, composition and their corrosion protection properties was established. The modified layer on the surface of the bioresorbable material has a potential to protect temporary implants for a certain fixed period, intended for the treatment of a specific injury. The service life of such a product will depend on the severity of the fracture and will be governed by the technological features of the protective coating.

## 5. Conclusions

The functional porous calcium phosphate PEO-coating, which possesses limited barrier properties, was formed on MA8 magnesium alloy. SEM-EDX analysis of the protective coating cross-section showed a high concentration of Ca and P and their distribution within the coating. Hydroxyapatite was found in the composition of the protective layer using XRD. PEO-coating increases the protective properties of the magnesium alloy. In accordance with EIS and PDP tests as a result of PEO treatment $|Z|_{f=0.1\ Hz}$ increased from $5.5 \times 10^3\ \Omega\ cm^2$ up to $6.9 \times 10^3\ \Omega\ cm^2$; $I_C$ decreased from $9.2 \times 10^{-6}\ A\ cm^{-2}$ down to $5.4 \times 10^{-6}\ A\ cm^{-2}$ in comparison with uncoated sample. SVET and SIET showed the pitting formation after 6 h of sample exposure to MEM. At the same time the maximum local pH near the surface of the coating did not exceed 9.0 during 72 h, which is related to formation of hydroxyapatite-like products precipitating when the MEM components, such as $Ca^{2+}$, $HCO_3^-$ and $HPO_4^{2-}$ encounter higher concentration of $OH^-$ at corroding Mg interface.

The highest coating protection was registered for composite polymer-containing coating ($|Z|_{f=0.1\ Hz} = 1.7 \times 10^7\ \Omega\ cm^2$; $I_C = 7.6 \times 10^{-10}\ A\ cm^{-2}$), which was formed using electrophoretic deposition of superdispersed polytetrafluoroethylene on the PEO-pretreated magnesium alloy. SPTFE penetrates inside pores, forms an additional barrier and increases the surface homogeneity of the coating. The mechanism of the corrosion evolution was related to partial composite layer degradation and sealing PEO-coating pores with deposited corrosion products. Hydrogen evolution test indicates that corrosion rate of the composite coating decreased by 7.0 and 2.8 times as compared to bare and PEO-treated samples, respectively.

These results showed that PEO treatment performs two function: decreases the electrochemical activity of the sample and ensures the probable material bioactivity due to the presence of HA in the coating composition. Additional sealing of PEO-coating with SPTFE enables us to regulate the rate of sample degradation. Electrophoretic deposition of the polytetrafluoroethylene does not fully isolate the specimen making it bioinert. Rather, it provides

the limiting contact of the medium with the material to ensure the bioactivity of the implant and necessary rate of its degradation.

## Data availability

The raw/processed data required to reproduce these findings cannot be shared at this time as the data also forms part of an ongoing study.

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**Figure captions**

Fig. 1. XRD patterns of the PEO-coated MA8 Mg alloy.

Fig. 2. Optical images of the studied area of the PEO-treated specimen: after wax isolation (a), before SVET/SIET studies (the investigated area marked by frame) (b), after 3 h of sample exposure to MEM (c), at the end of the tests after MEM removal (d).

Fig. 3. SVET (a, b, c) and SIET (d, e, f) 3D maps for the sample with PEO-coating after 1 h (a, d), 6 h (b, e), and 30 h (c, f) of exposure to MEM solution.

Fig. 4. The local $pH_{max}$ and $pH_{min}$ evolution during 72 h of sample exposure to MEM.

Fig. 5. SEM image of the most affected area of the PEO-coated sample after 72 h SVET/SIET test (a) combined with EDX analysis of the formed corrosion products (b).

Fig. 6. SEM images of the PEO-coating (a) and composite coating (b).

Fig. 7. 3D topography OSP maps of the surface of PEO (a) and composite coatings (b).

Fig. 8. The evolution of the open circuit potential (118 h) for the MA8 samples without coating, with PEO-layer, and with composite polymer-containing coating in MEM solution.

Fig. 9. PDP curves for the studied coated and uncoated samples in MEM solution.

Fig. 10. Impedance spectra (Nyquist plot (a), Bode plot (b)) evolution with time of the PEO-coated MA8 magnesium alloy sample exposure to the MEM. Experimental data are presented as a scatter plot, and fitting curves obtained using equivalent electrical circuits are shown as lines.

Fig. 11. Impedance spectra (Nyquist plot (a), Bode plot (b)) evolution with time of exposure of the MA8 Mg alloy sample with composite coating to the MEM. Experimental data are presented as a scatter plot, and fitting curves obtained using equivalent electrical circuits are shown as lines.

Fig. 12. Schematics of the electrolyte/electrode interface and applied EEC for base PEO-layer (a, b) and polymer-containing coating (c, d) before (a, c) and after degradation (b, d).

Fig. 13. Impedance modulus ($|Z|_{f=0.1Hz}$) evolution during 107 h immersion of samples with and without protective coatings in MEM.

Fig. 14. SEM images of the cross-sections for the PEO-coated sample before immersion (a) and after 7 days immersion in MEM (b)

Fig. 15. SEM images of the cross-sections for the sample with composite polymer-containing coating before immersion (a) and after 7 days immersion in MEM (b)

Fig. 16. SEM-EDX maps of the distribution of Mg (b), O (c), Ca (d), P (e), Si (f), F (g) within the cross-section of the MA8 Mg alloy sample with PEO-coating before (1a-1g) and after 7 days of immersion in MEM (2a-2g).

Fig. 17. SEM-EDX maps of the distribution of Mg (b), O (c), Ca (d), P (e), Si (f), F (g), C (h) within the cross-section of the MA8 Mg alloy sample with composite coating before (1a-1h) and after 7 days of immersion in MEM (2a-2h).

Fig. 18. Normalized hydrogen evolution curves (a) and the degradation rate evolution diagrams (b) for MA8 magnesium alloy samples without and with protective coatings during 7 days immersion in MEM.