

Article

Surface Modification with Phosphate and Hydroxyapatite of Porous Magnesium Scaffolds Fabricated by Binder Jet Additive Manufacturing

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Abstract: The presence of porosity within magnesium-based orthopaedic implants is known to be beneficial, promoting cell proliferation and vascularisation. However, the presence of porosity increases the surface area available for corrosion, compounding the issue of high corrosion rates which has long been plaguing magnesium-based materials. This work looks at the influence of hydroxyapatite and phosphate conversion coatings on the corrosion performance of conventionally cast, dense Mg-Zn-Zr alloys and binder jet additive manufactured porous Mg-Zn-Zr scaffolds. The performance of coating on dense Mg-Zn-Zr was found to be more effective than the coating on the porous Mg-Zn-Zr scaffold, with the discrepancies attributed to both the microstructure and geometric influence of the binder jet additive manufactured, porous Mg-Zn-Zr scaffold, which not only increases the rate of hydrogen evolution but also reduces the ability of the hydrogen gas generated within the pore channels to escape to the sample's surface. This restricts the effectiveness of coating application for porous Mg scaffold. Furthermore, the limited diffusion within the pore channels can also result in differing localized corrosion environments, causing discrepancies between the localised corrosion environment within the pore channels and that at the bulk electrolyte.

Keywords: magnesium; binder jetting; additive manufacturing; coating; corrosion



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1. Introduction

The prominent emergence of 3-dimensional (3D) porous structures in recent times cannot be overlooked, providing a special niche for applications. For orthopaedic applications, 3D porous structures are often deemed as an essential property for tissue scaffold engineering [1], which is well known to improve cell proliferation [2] and vascularisation [3]. In recent times, research into magnesium-based 3D porous structures has been gaining traction, due to their well-known biocompatibility and biodegradability [4–7]. The ability of such Mg porous structures to release essential bodily nutrients during service has also been proposed to aid in the healing process [8]. However, the relatively high degradation rate of Mg has always been its Achilles heel, which is compounded by the increased surface area of any 3D porous structure [9,10], which further increases corrosion. The reduction in the corrosion rate of Mg can be achieved either through material design [11,12] and/or the application of coatings [13].

The coatings for Mg often specifically target a single property or a combination of properties, typically in the form of improved chemical and/or mechanical properties of the Mg substrate [14–16]. Research into coating technologies can be separated into two main categories, the type of coatings and their application techniques. Coatings for biomedical Mg alloys often are phosphate [6,17–19] or hydroxyapatite [6,20,21] based due

to their demonstrated good bone compatibility [6] and osteogenesis [22]. Similarly, the coating application techniques used on Mg can also be physical (e.g., cold sprayed) [23,24], electrodeposited [21,25], or chemical [20,26] based. The majority of the coating formulation and application techniques target 2-dimensional (2D) structures, i.e., flat substrates [27,28]. When dealing with coating applications on porous structures with micron-sized pores, the lack of line-of-sight for the physical spraying method or the limited reach of the electric field during electrodeposition can result in the coating only having a limited penetration depth into the porous structure. This limits the available coating techniques. Shirokova et al. [29] demonstrated the potential of vacuum infiltration of the coating of porous titanium and nickel structures; however, its effectiveness on corrosion has yet to be investigated, especially when applied to porous Mg structures. With studies on the corrosion protection of porous Mg structures or scaffolds [26,30] remaining limited, the performance of coatings during the transfer of formulation from dense to porous structure remains of great interest.

The performance of the different coatings can be determined by electrochemical corrosion testing. Often, the preferred method of testing choice is potentiodynamic polarisation [20], due to its ability to provide informative insights into the change in the cathodic and anodic kinetics of the coating. Alternatively, measurement of the rate of hydrogen evolution from the coated sample [31,32] can also be carried out for the corrosion of coatings targeting biomedical applications. However, the shortcomings of hydrogen evolution measurements are apparent, as they provide only a limited understanding of the corrosion kinetics mechanisms [33]. Although the potentiodynamic polarisation testing of coated porous structures (scaffolds) has been attempted [26], it was reported that the penetration of the electric field into porous structures is limited [34]. As such, the effectiveness and results of the potentiodynamic polarisation when used for the determination of a 3D porous scaffold are limited.

Conventional manufacturing technologies based on powder metallurgy and casting have been used to fabricate the porous structures of Mg alloys [35–38]. These conventional approaches are useful within their boundaries. However, their applications are restricted by the limitations of conventional manufacturing methods to produce porous Mg structures with simple geometry. These restrictions are targets to be addressed by additive manufacturing technologies. In previous studies [39–42], we developed the binder-jet additive manufacturing method for fabricating interconnected porous Mg structures. This study aimed to conduct a comparative study between the corrosion characteristics of Mg alloys in 3D (3D printed porous Mg-Zn-Zr scaffolds) and 2D structures (dense Mg-Zn-Zr substrate). In this regard, electrodeless deposition and conversion coating techniques were used to form/deposit hydroxyapatite and phosphate-based conversion coating on dense Mg substrates (2D structure) and binder-jet printed porous scaffolds (3D structure). Then, the corrosion performance of these structures was investigated using potentiodynamic polarisation (for 2D Mg-Zn-Zr substrate) and hydrogen evolution measurements (for 3D porous Mg-Zn-Zr scaffold).

2. Materials and Methods

2.1. Fabrication of Dense and Porous Mg Samples

In this work, the 2D, dense Mg-Zn-Zr alloy samples for coating application were gravity cast in steel moulds at 750 °C; after cooling, the oxide-coated surface layer was machined away. Binder jetting was used to fabricate the porous samples. Detailed descriptions of the binder jetting and sintering of Mg alloys can be found in our earlier work [39–42]. The printed green sample was then sintered at the elevated temperature of 615 °C. The microstructure and composition of both the as-casted and binder jet printed (BJP) Mg-Zn-Zr sample will be reported in the results section.

2.2. Coating of Dense and Porous Mg Samples

A solution of hydroxyapatite (HA) was prepared using a precipitation method [29]. Five volume parts of 0.02 M calcium hydroxide ($\text{Ca}(\text{OH})_2$) were mixed with one volume

part of 0.07 M phosphoric acid (H_3PO_4). The mixture was left to mix and precipitate on a magnetic stirring plate for 1 h, allowing the hydroxyapatite to precipitate. The precipitated hydroxyapatite was then rinsed and filtered before an equal volume was evenly spread on the surfaces of the dense Mg-Zn-Zr samples. The surfaces of the dense Mg-Zn-Zr samples were sequentially ground until they reached 1200 grit prior to coating applications. The different batches of hydroxyapatite-coated samples were dried at different temperatures of 25 °C, 40 °C, 55 °C, and 100 °C in a temperature-regulated oven.

Similarly, a series of stock solutions containing H_3PO_4 and magnesium hydroxide ($\text{Mg}(\text{OH})_2$) was also prepared. The eventual stock solutions contained 0.1 M $\text{Mg}(\text{OH})_2$, with varying concentrations of H_3PO_4 (0.12 M, 0.16 M, and 0.24 M). The pH of the stock solutions was determined to be approximately 5.15, 3.48, and 2.62, respectively. The samples were immersed in the stock solution for a duration of 1 h, eventually removed, rinsed with deionised water, and dried with nitrogen gas.

For the coating of porous Mg-Zn-Zr scaffolds, the use of a vacuum pump was introduced. The vacuum pump removes the air from the pore channels of the porous substrate. With the release of vacuum, a negative pressure is generated within the pores of the porous substrate, which allows the atmospheric pressure to aid penetrating the coating deeper into the pore channels. The use of the vacuum pump aided the penetration of the stock solutions (both HA and phosphate conversion coating) into the interconnected porous structure of Mg-Zn-Zr scaffolds. The processing steps of the coating process remained the same for consistency.

2.3. Materials Characterisation

SEM and EDX characterisations were conducted with a Zeiss Sigma 300 Fe-SEM (Zeiss, Oberkochen, Germany), with an accelerating voltage of 15 keV. Phase composition was obtained using a Bruker D8 Discover XRD (Bruker, Billerica, MA, USA) with $\text{Cu-K}\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$). The XRD profiles were collected in step sizes of 0.1° , with a dwell time of 3 s. The elemental composition of the samples was determined with a Perkin Elmer Optima 4300 DV (PerkinElmer, Waltham, MA, USA) inductive coupled plasma optical emission spectroscopy (ICP-OES), with the oxygen content determined with inert gas fusion infrared absorbance. The densities of the dense and porous specimens were measured by Archimedes' principle, according to ASTM B962. The internal structure of the porous Mg-Zn-Zr scaffold was characterised by Nanotom M180 X-ray (General Electric, Boston, MA, USA) computed tomography system (XCT), with a resolution of $3.5 \mu\text{m}$. The post-processing of the tomograms was done with computational analysis software provided by the system.

2.4. Corrosion Study

The corrosion performance of the coated and uncoated dense Mg samples was investigated in 0.1 M sodium chloride. Afterward, for 30 min under open-circuit conditions, potentiodynamic polarisation tests were carried out at a scan speed of 1 mV s^{-1} against a saturated calomel reference electrode (SCE) with a graphite rod counter electrode. The corrosion performance of the coated and uncoated 3D porous scaffold was investigated through hydrogen evolution measurements. The hydrogen evolution measurement was carried out in Phosphate Buffered Saline (PBS), maintained at 37 °C using a water bath. Figure 1 shows a schematic of the hydrogen evolution setup, consisting of an inverted funnel and burette, similar to the one proposed in the work of Song et al. [43].

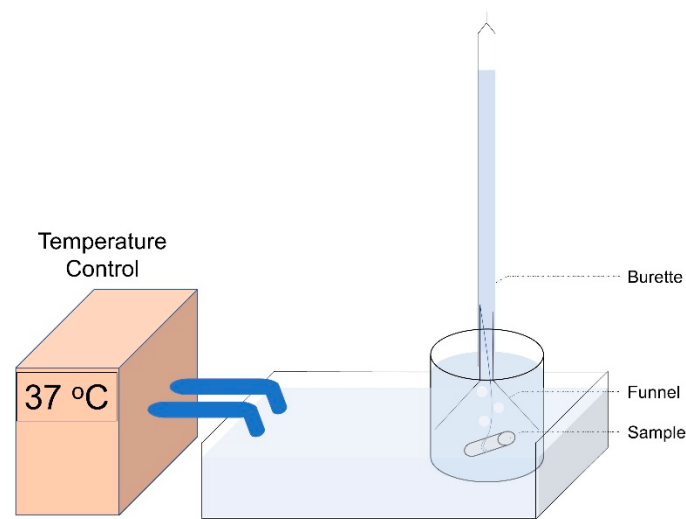


Figure 1. Schematic of the hydrogen evolution setup for Mg samples, maintained at 37 °C with a water bath.

3. Results and Discussions

3.1. Characterisation of Dense and Porous Mg-Zn-Zr Samples

Figure 2a shows SEM and EDX images of a polished cross-section of the dense Mg-Zn-Zr sample. The dense Mg-Zn-Zr sample demonstrates a microstructure with precipitation of zinc-rich secondary phases along the grain boundaries of Mg-rich matrices. Table 1 shows the elemental composition of the as-casted Mg-Zn-Zr alloy, determined from ICP-OES to be 5.49 wt.% Zn, 0.73 wt.% Zr, and Bal. Mg.

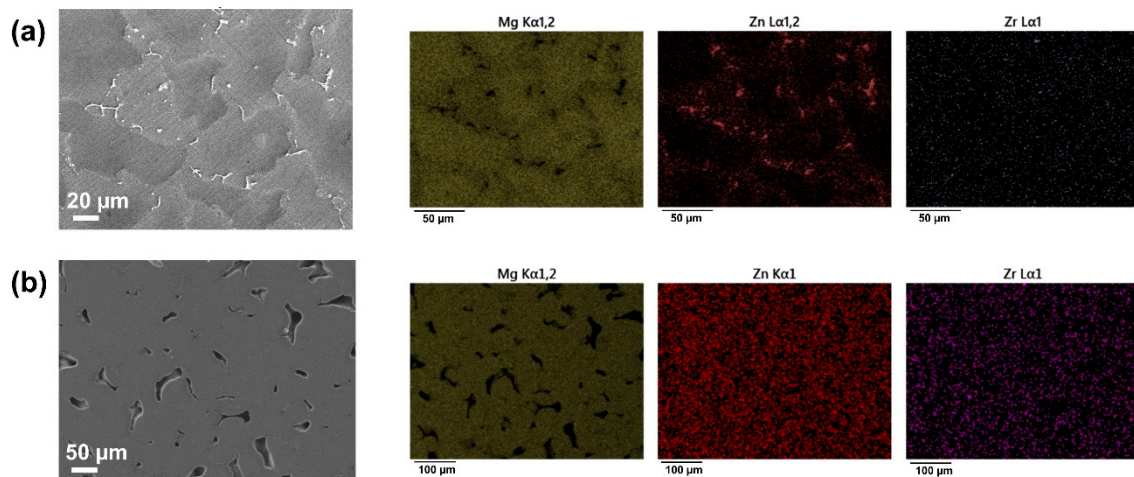


Figure 2. SEM micrographs and EDX elemental mappings for the samples, (a) dense and (b) porous Mg-Zn-Zr scaffold.

Table 1. Chemical composition of dense and porous Mg-Zn-Zr samples as determined from ICP-OES. The oxygen content of the porous sample was determined from inert gas fusion infrared absorbance. ICP was also used to analyse a range of additional metallic elements including Al, As, B, Be, Ca, Cd, Cr, Co, Cu, Fe, Hf, Mo, Mn, Nb, Ni, P, Pb, Re, Sb, Si, Sn, Ta, Ti, Y, V and W, none of which were found to exceed 0.01 wt.% in any of the alloys.

Sample	Zn (wt.%)	Zr (wt.%)	O (wt.%)	Mg (wt.%)
As cased dense	5.49	0.73	-	Bal.
BJP porous	5.16	0.18	0.12	Bal.

Figure 2b shows SEM and EDX images of a cross-section of the porous Mg-Zn-Zr scaffold manufactured via binder jet additive manufacturing. Its cross-sectional microstructure demonstrated evenly distributed pores with evenly dispersed elements of magnesium, zinc, and zirconium. The oxygen-rich regions correspond to MgO; identified later via XRD (Figure 3b). These MgO inclusions were introduced during the high-temperature sintering of the green samples, which oxidises the surface of the Mg powders [44,45]. Table 1 shows the elemental composition of the BJP Mg alloy, determined from ICP-OES and inert gas fusion infrared absorbance. The composition is reported to be 5.16 wt.% Zn, 0.18 wt.% Zr, 0.12 wt.% O, and Bal. Mg. The chemical composition of the porous Mg-Zn-Zr scaffold manufactured via binder jet additive manufacturing is similar to that of the dense Mg-Zn-Zr sample provided in the same table. One subtle difference in the elemental compositions is in the zirconium concentration, with the dense Mg-Zn-Zr sample having a higher (0.73 vs. 0.18 wt%) concentration of zirconium than the porous Mg-Zn-Zr scaffold. The addition of zirconium is known to serve as a grain refiner [46] during the manufacturing process of Mg. It is also known to possibly worsen (increase) the corrosion rate of Mg-based alloys due to the formation of zirconium secondary phases [47]. Zinc is added to the Mg matrix for mechanical properties, in particular, it has an age-hardening effect [48,49]. Similar to Zr, the formation of Mg_xZn_y secondary phases is also known to serve as local cathodes during the corrosion of Mg [46]. This means that an increase in the Zn concentration can decrease the overall corrosion resistance of the Mg alloy due to detrimental galvanic interactions from the increased Mg_xZn_y secondary phase formation. However, this paper does not intend to discuss the difference in the corrosion mechanisms of the base sample.

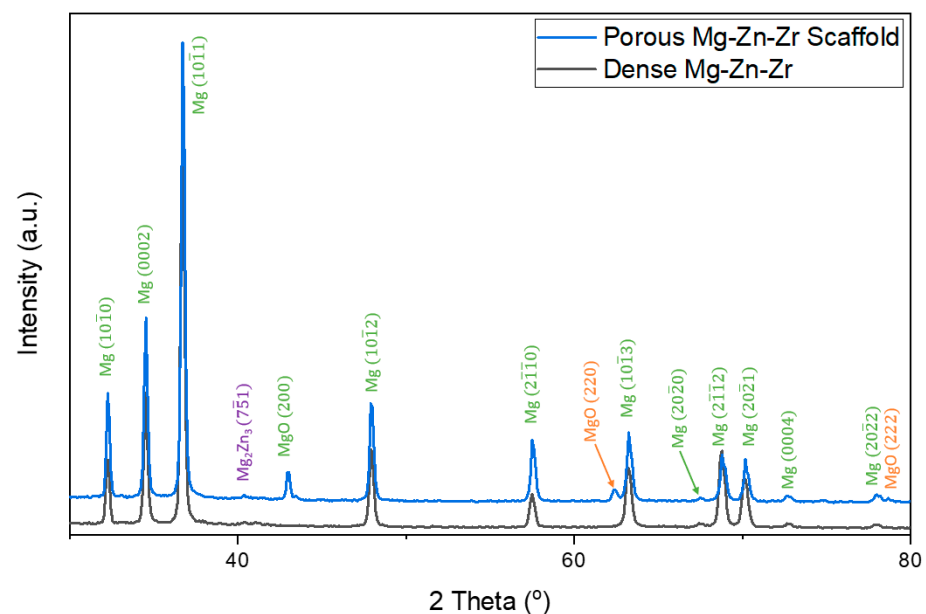


Figure 3. XRD characterisation of dense Mg-Zn-Zr and porous Mg-Zn-Zr scaffold.

Figure 3 shows the phase composition of a dense Mg-Zn-Zr sample. The phases available in the microstructure of Mg-Zn-Zr are also confirmed to consist of α -Mg and minute Mg_2Zn_3 secondary phases, which are believed to be the identities of the magnesium and zinc-rich regions identified in the EDX (Figure 2a). Figure 3 also shows the XRD pattern of the BJP Mg-Zn-Zr alloy, from which can be derived that the main phase constituents are α -Mg matrix, Mg_2Zn_3 secondary phase, and MgO inclusions. The MgO inclusions originate from the sintering process and are incorporated within the microstructure during the sintering process, as previously mentioned. From the ratios of the α -Mg and Mg_2Zn_3 peaks in Figure 3, it can be concluded that the fraction of the secondary phase in the dense and porous samples is approximately the same. Thus, other than the MgO, the phase composition of the porous and dense Mg-Zn-Zr samples can be considered almost identical.

Archimedes' density of the dense and porous samples was measured to be 99.5% and 87%. Figure 4 shows the 3D reconstruction of the porous Mg-Zn-Zr scaffold manufactured via binder jet additive manufacturing. The computational software analysis shows that the pore channels within the structure can be characterised, with the relative porosity being approximately 13%, possessing an open porosity index of >95%. With open porosity of the porous Mg-Zn-Zr scaffold >95%, the electrolytes are aided (through a vacuum) into the interconnected pore channels, before being deposited on the internal walls of the porous structure, either through precipitation (in the case of HA) or conversion (phosphate conversion coating), achieving corrosion protection.

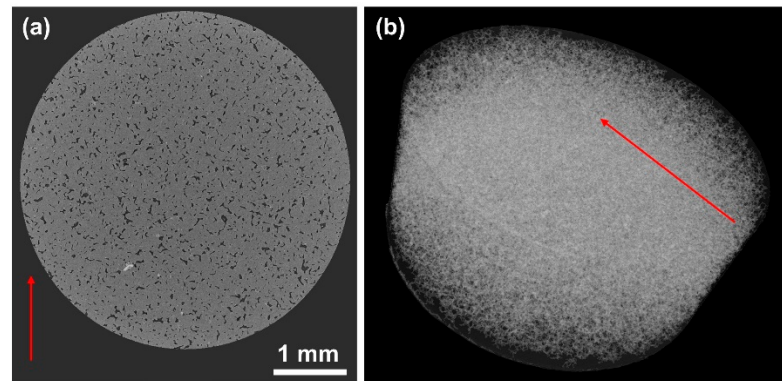


Figure 4. X-Ray Computed Tomography. (a) 2-dimensional (2d) and (b) 3-dimensional (3d) recreation of the porous Mg-Zn-Zr scaffold manufactured via binder jet printing. The red arrows indicate the building direction (stacking direction of the powder).

3.2. Coating of Dense Samples

As there is still excess liquid upon applying the stock solution on the sample's surface, removing an excess solvent is necessary. Variations in drying temperature have been known to influence the corrosion protection properties of coatings due to the potential to form microcracks at high drying temperatures [50]. To investigate the influence of drying temperature on the corrosion properties of the applied HA coating, the dense Mg-Zn-Zr samples were coated with the same stock solution of HA and dried at temperatures of 25 °C, 40 °C, 55 °C, and 100 °C. Similarly, differences in the composition of the initial stock phosphate solution prior to the application of the conversion coating are known to induce variations in the properties of the final coated samples [27,28]. To investigate the influence of initial H_3PO_4 concentration on the corrosion protection properties of the applied phosphate conversion coatings, these were coated on dense Mg-Zn-Zr samples using initial concentrations of H_3PO_4 varying from 0.12 M, 0.16 M to 0.24 M.

Figure 5 shows SEM images of the HA (dried at 25 °C) and phosphate conversion (0.12 M, 0.16 M, and 0.24 M) coated samples. From the morphology of both the HA and phosphate conversion coated surfaces the coatings appear to be generally uniform across the surface, despite the observation of some microcracks on the coatings. Although it is known that a thicker coating layer can provide a better barrier against corrosion, thicker coatings have a greater tendency to crack (Figure 5) which nullifies the benefits of increased thickness. As such, the optimization of the process parameters can be seen as a means to minimize the influence of cracks on corrosion performance instead of varying the coating thickness to optimize corrosion performance. In view of this, the coating thicknesses were not measured. The corrosion performance of these coated samples is explored in more detail in the following section.

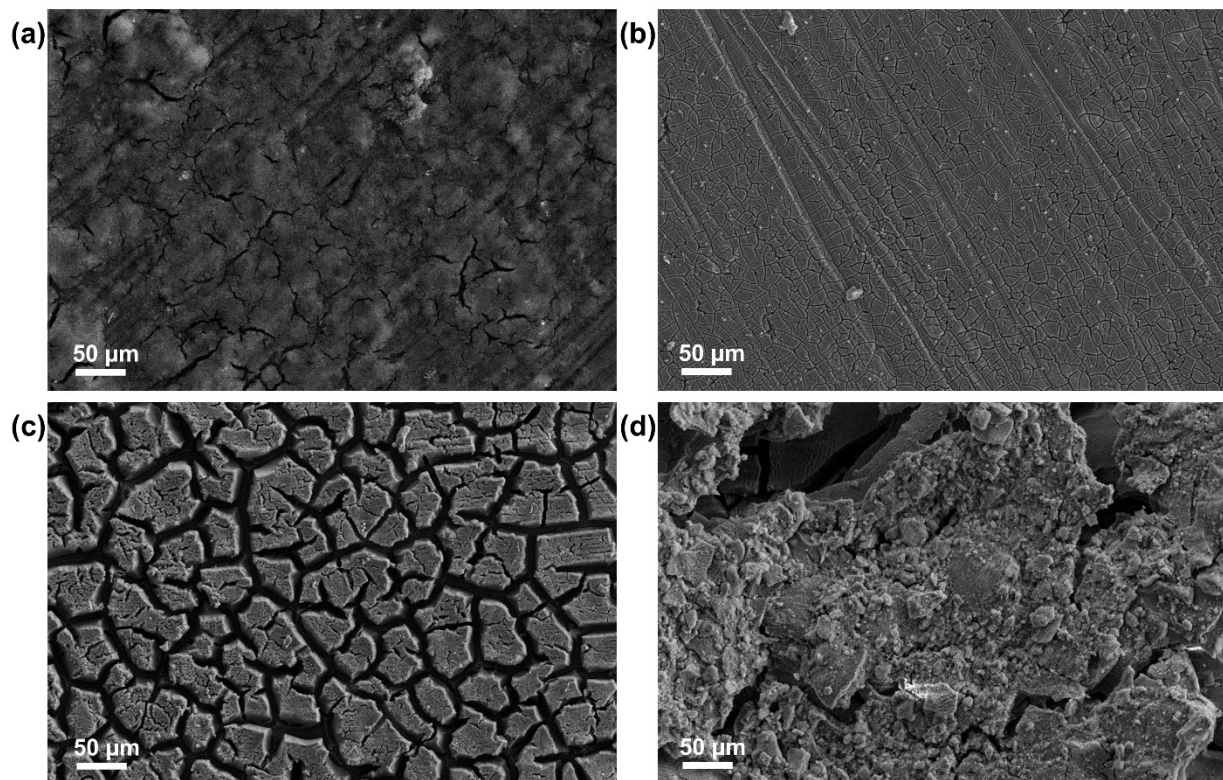


Figure 5. SEM images of the dense Mg-Zn-Zr sample after (a) hydroxyapatite coated dried at 25 °C, and phosphate conversion coated with initial concentration of (b) 0.12 M, (c) 0.16 M, and (d) 0.24 M phosphoric acid.

3.3. Corrosion of Coated Dense Samples

3.3.1. Hydroxyapatite Coating

Figure 6a shows potentiodynamic polarisation curves for HA-coated dense Mg-Zn-Zr samples in 0.1 M sodium chloride. The polarisation curves were obtained after a 30 min immersion at open circuit potential, with a scan rate of 1 mV s^{-1} . The corrosion current densities obtained from Tafel extrapolation of the potentiodynamic polarisations curves are tabulated in Table 2. The polarisation curve of the uncoated Mg-Zn-Zr sample (with a measured current density of $1.5 \times 10^{-5} \text{ A cm}^{-2}$) is provided as a reference. It is observed that the drying temperature of the HA coating in this work does not have a direct correlation to the measured corrosion current density. The measured current varied from $5.0 \times 10^{-6} \text{ A cm}^{-2}$ when dried at 25 °C, to $5.26 \times 10^{-5} \text{ A cm}^{-2}$ when dried at 40 °C, and $6.2 \times 10^{-6} \text{ A cm}^{-2}$ when dried at 55 °C and $2.2 \times 10^{-5} \text{ A cm}^{-2}$ when dried at 100 °C. The corrosion performance of HA coating dried at 25 °C appeared to be optimal for the coating of dense Mg-Zn-Zr sample, with this sample having both the lowest corrosion current recorded and a positive shift in its pitting potential relative to the HA coatings prepared with other parameters. As previously hypothesised, the drying temperature played an important role in the determination of the corrosion protection of the HA coating. An inappropriate coating processing parameter resulted in detrimental corrosion performance relative to the uncoated Mg-Zn-Zr sample (i.e., the samples dry at 40 °C and 100 °C).

When comparing the corrosion performance of the HA coating via the precipitation method on a dense Mg-Zn-Zr sample dried at 25 °C with the conversion-based HA coating method reported in another work by Chen et al. [20], a 16~22x reduction in corrosion current density (of coated vs. uncoated) was reported after a successful conversion coating with HA/Mg(OH)₂ on pure Mg. Although only a 3x reduction in current density (of coated vs. uncoated) was observed in this present work, it is worth noting that the eventual measured corrosion current densities reported in the two works are of the same magnitude being

$2.7 \times 10^{-6} \text{ A cm}^{-2}$ in the work of Chen et al. [20] and $5.0 \times 10^{-6} \text{ A cm}^{-2}$ in the present work. Thus, we translated this electroless precipitation parameter for the surface modification of the interior pores and exterior surface of the porous Mg samples with hydroxyapatite.

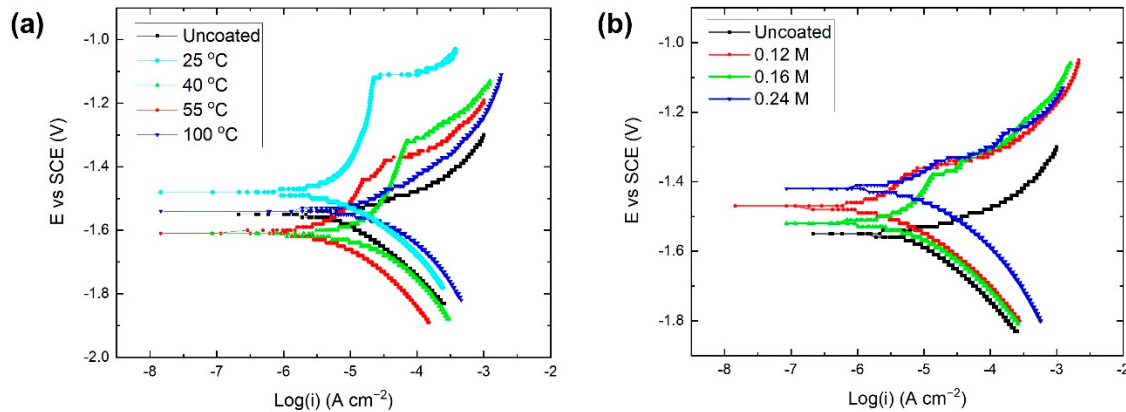


Figure 6. Potentiodynamic polarisation of dense Mg-Zn-Zr samples coated with (a) hydroxyapatite at different drying temperatures and (b) phosphoric acid conversion coating with different initial concentrations of phosphoric acid. The polarisation curves were obtained after 30 min immersion in 0.1 M NaCl at a scan rate of 1 mV s^{-1} .

Table 2. Corrosion current of uncoated 2-dimensional (dense) Mg-Zn-Zr, HA-coated dense Mg-Zn-Zr, and phosphate-coated dense Mg-Zn-Zr alloy, obtained from Tafel extrapolation of respective potentiodynamic polarisation curve in 0.1 M NaCl.

Sample	Corrosion Current Density ($\times 10^{-6} \text{ A cm}^{-2}$)
Uncoated dense Mg-Zn-Zr	15.0
Hydroxyapatite dried at 25 °C	5.0
Hydroxyapatite dried at 40 °C	52.6
Hydroxyapatite dried at 55 °C	6.2
Hydroxyapatite dried at 100 °C	22.0
0.12 M H_3PO_4	3.1
0.16 M H_3PO_4	4.7
0.24 M H_3PO_4	5.9

3.3.2. Phosphate Conversion Coating

Figure 6b shows the potentiodynamic polarisation curves of the dense Mg-Zn-Zr sample after phosphate conversion coating, in 0.1 M NaCl. The phosphate conversion coating was conducted with stock solutions of premixed $\text{H}_3\text{PO}_4/\text{Mg}(\text{OH})_2$ with initial concentrations of 0.12 M, 0.16 M, and 0.24 M H_3PO_4 , respectively. The polarisation curves were obtained after 30 min of immersion under open-circuit conditions, with a scan rate of 1 mV s^{-1} . The corrosion current densities obtained from Tafel extrapolation of the potentiodynamic polarisation curves are tabulated in Table 2. Similarly, the polarisation curve of an uncoated Mg-Zn-Zr sample (with a measured current density of $1.5 \times 10^{-5} \text{ A cm}^{-2}$) is also provided as a reference. The measured current density increases from $3.1 \times 10^{-6} \text{ A cm}^{-2}$ with an initial H_3PO_4 concentration of 0.12 M to $4.7 \times 10^{-6} \text{ A cm}^{-2}$ with an initial concentration of H_3PO_4 of 0.16 M and $5.9 \times 10^{-6} \text{ A cm}^{-2}$ with an initial concentration H_3PO_4 of 0.24 M. It is observed that an increase in the initial concentration of H_3PO_4 during the coating process led to an increase in the measured corrosion current density. The corrosion performance of phosphate conversion coating with an initial concentration of 0.12 M phosphoric acid appeared to provide better corrosion resistance to the sample, relative to the conversion coatings applied with initial concentrations of either 0.16 M or 0.24 M H_3PO_4 . The result resonates with the previous finding by Jayaraj et al. [27], where a higher

pH of the phosphate conversion coating, which was done through a reduction in H_3PO_4 concentration, improved the corrosion properties of the phosphate conversion coating formed. Comparing the corrosion performance of the phosphate conversion coatings and their effectiveness in reducing the corrosion of the uncoated dense Mg-Zn-Zr alloy, a $4.8\times$ reduction in corrosion current density is found from the phosphate conversion coating in 0.12 M stock H_3PO_4 solution (relative to the uncoated dense Mg-Zn-Zr alloy). The $4.8\times$ reduction in the corrosion rate post phosphate conversion coating falls within the range reported in the work of Jayaraj et al. [27], where 3 to 15x improvements in corrosion rates were reported from the base AZ31 alloy after phosphate conversion coating. The reported corrosion density of the phosphate conversion coating in 0.12 M ($3.1 \times 10^{-6} \text{ A cm}^{-2}$) is also of the same magnitude as the corrosion current density of the magnesium phosphate conversion coating reported in the works of Phuong et al. ($6.3 \times 10^{-6} \text{ A cm}^{-2}$) [19] and Jayaraj et al. ($9 \text{ to } 49 \times 10^{-6} \text{ A cm}^{-2}$) [27].

Comparing how the optimised HA (dried at 25°C) and phosphate conversion coating (0.12 M) in this work fare against each other, the potentiodynamic polarisation of uncoated dense Mg-Zn-Zr alloy, HA coating with a drying temperature of 25°C (Figure 6a) and phosphate conversion coating with an initial concentration of 0.12 M H_3PO_4 (Figure 6b) are compared. The overall corrosion performance, as determined from the measured corrosion current density, increases in the order uncoated, to HA (25°C), to phosphoric (0.12 M) conversion coating, with the decreases in the corrosion rates for the coated samples compared to the uncoated sample being a factor of $3.0\times$ for the HA (25°C) and $4.8\times$ for the phosphoric conversion (0.12 M) coated samples (Table 2). Although the phosphoric conversion (0.12 M) coated sample displayed the lowest corrosion current density the HA (25°C) coated Mg-Zn-Zr sample had the most positive pitting potential of the three dense Mg-Zn-Zr samples; i.e., the HA (25°C) coating provided the best protection against localized pitting corrosion.

3.4. Coating of Porous Mg-Zn-Zr Scaffolds

From the studies on both the coating process optimisation and corrosion performance, both HA (25°C) and phosphoric conversion (0.12 M) coating were subsequently chosen to be applied to the porous Mg-Zn-Zr scaffold manufactured via binder jet printing (Figure 3) using vacuum impregnation. Penetration of electrolytes into the pore channels is one of the major challenges in the coating of porous structures given limited electrolyte penetration as a result of its surface tension. As such, selected coated porous samples were fractured and characterised (at their midpoint) to investigate the penetration depth and effectiveness of the coating process. Figure 7 shows SEM and EDX images of a fracture surface coated with hydroxyapatite and dried at 25°C . The main constituents of HA, calcium and phosphorous, can be observed to be evenly spread over the internal porous channels of the BJP structure. Similarly, this uniform coating can be observed in the phosphate conversion coating, with Figure 8 showing SEM and EDX images of the phosphate conversion coating after being coated in H_3PO_4 with the initial concentration of 0.12 M. The presence of phosphorous in the centre of the sample indicates that the phosphate coating successfully formed during the conversion coating process. Overall, these results show the promise of the vacuum impregnation methodology in the coating of the interiors and exteriors of porous scaffolds, resonating with the findings presented in the work of Shirokova [29].

3.5. Corrosion of Coated Porous Scaffolds

As discussed in the introduction, although polarisation tests are known to provide valuable information on corrosion kinetics, previous studies on the corrosion mechanism of porous Mg revealed the limitations of potentiodynamic polarisation test for the determination of corrosion kinetics on porous BJP alloys [34]. This limitation is attributed to the inability of the electric field to penetrate and probe deep into the pore channels, resulting in an underestimation of the actual corrosion rate. As such, the authors deem the corrosion rate determined via hydrogen evolution to be a more accurate representa-

tion of corrosion for porous samples compared to polarisation tests. Figure 9 shows the comparison of the hydrogen evolution rate of the uncoated porous Mg-Zn-Zr scaffold with those coated with HA and phosphate conversion coatings. The hydrogen evolution rates of the samples are tabulated in Table 3. The average hydrogen evolution of porous Mg-Zn-Zr scaffold decreases from $0.41 \text{ mL cm}^{-2} \text{ hr}^{-1}$ (uncoated) to $0.35 \text{ mL cm}^{-2} \text{ hr}^{-1}$ when coated with phosphate conversion coating. The samples that are coated with HA coating demonstrated the most significant decrease in the average hydrogen evolution, reduced to a rate of $0.22 \text{ mL cm}^{-2} \text{ hr}^{-1}$. This is a $1.9\times$ and $1.2\times$ decrease in the corrosion rate of the hydroxyapatite (25°C) and phosphate conversion (0.12 M) coated samples, respectively, over their uncoated counterpart.

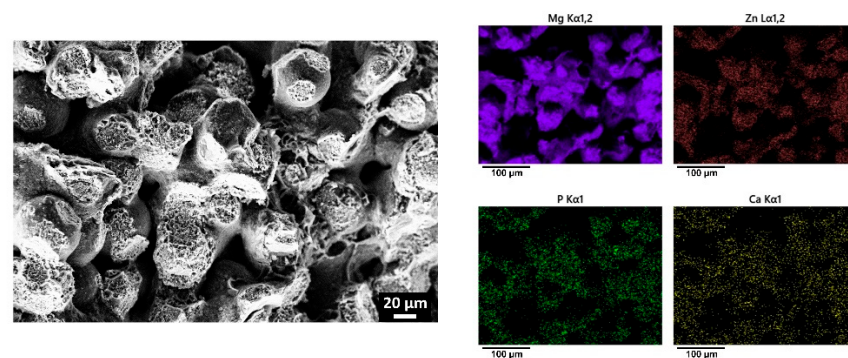


Figure 7. SEM and EDX images of the porous Mg-Zn-Zr scaffold's fracture surface coated with hydroxyapatite.

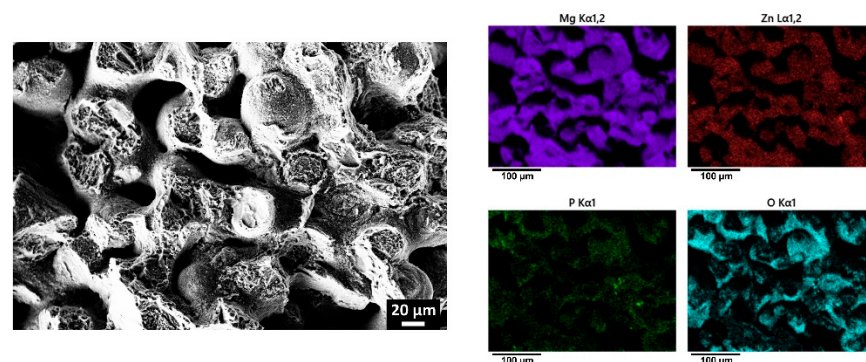


Figure 8. SEM and EDX images of the porous Mg-Zn-Zr scaffold's fracture surface coated with phosphate conversion coating.

Table 3. Tabulated average hydrogen evolution rate of uncoated and coated porous Mg-Zn-Zr samples with hydroxyapatite and phosphate conversion coating in PBS maintained at 37°C .

Sample	Average Hydrogen Evolution Rate ($\text{mL cm}^{-2} \text{ hr}^{-1}$)
Uncoated porous	0.41 ± 0.09
Phosphate Conversion Coating	0.35 ± 0.03
Hydroxyapatite Coating	0.22 ± 0.03

It is notable that no direct comparison has been made between the two samples, i.e., coated dense Mg-Zn-Zr samples vs. coated porous Mg-Zn-Zr scaffold. In the authors' previous work, it was found that the uncoated porous Mg-Zn-Zr scaffold demonstrated a higher corrosion rate than that of a dense Mg-Zn-Zr sample [34,45]. As such, there is no basis for comparison. Instead, the corrosion results are better presented as the improvement in the corrosion performance of the coated samples relative to their uncoated counterpart.

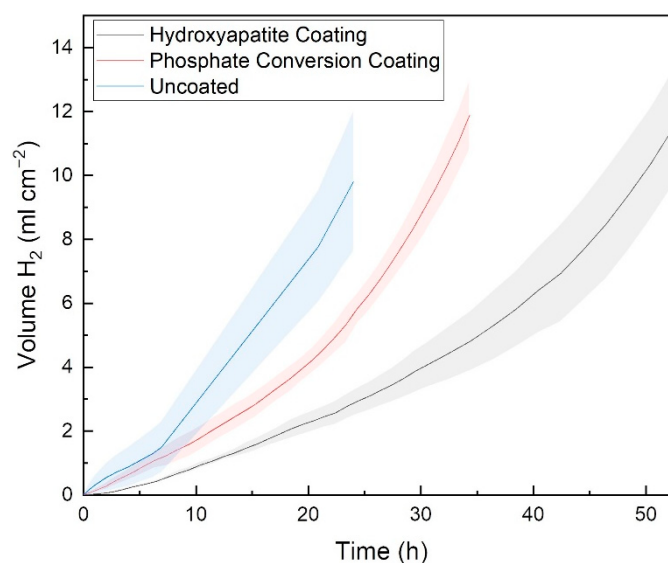


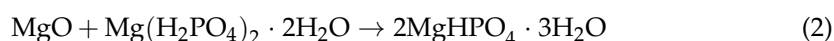
Figure 9. Hydrogen evolution comparison between uncoated, hydroxyapatite-coated, and phosphoric conversion coated porous Mg-Zn-Zr scaffolds. The shaded regions represent the standard deviation of the respective hydrogen evolution collection data.

4. Challenges of Coating and Corrosion Testing of Porous Mg-Zn-Zr Scaffolds

Upon further analysis, it is hypothesised that the restricted geometry within the pore channels of the porous Mg-Zn-Zr alloy may have contributed to the discrepancies with the performance of HA and phosphate conversion coatings, in particular, the significant reduction in the effectiveness of the phosphate conversion coating when applied to the porous sample in this work.

4.1. Influence of H₂ Evolution during Coating Process

Equations (1) and (2) show the reaction mechanism for the phosphate conversion coating on an Mg surface [51]. Despite no change in pH being proposed from the reaction, the dissolution of the Mg in the acidic media cannot be avoided. It is known that the dissolution of Mg in acidic media is accompanied by the release of hydrogen gas (Equation (3)) [46]. Figure 10 shows the schematic of the phosphate conversion coating forming process of the dense Mg sample and porous Mg scaffold. Due to restricted geometry within the pore channels of the porous structure, the hydrogen gas formed from the dissolution of Mg may accumulate, isolating the surfaces from the electrolyte and preventing further formation of phosphate coating, which may result in an uneven coating layer. This contrasts with the dense sample where the hydrogen gas evolved can freely detach from the sample surface due to buoyancy force, allowing a more even coating across the sample surface.



Conversely, the HA coating was precipitated, filtered, and rinsed before deposition on the Mg-Zn-Zr surfaces. Despite the expectation of hydrogen evolution from the Mg surface during the coating process, due to the availability of the aqueous environment, the lower aggressiveness of the HA solution relative to its phosphate conversion coating counterpart means that less hydrogen evolution can be expected to have occurred during the coating process. Thus, the lowered aggressiveness of the HA deposition solutions may result in a more uniform coating layer and the eventual coating providing better corrosion resistance.

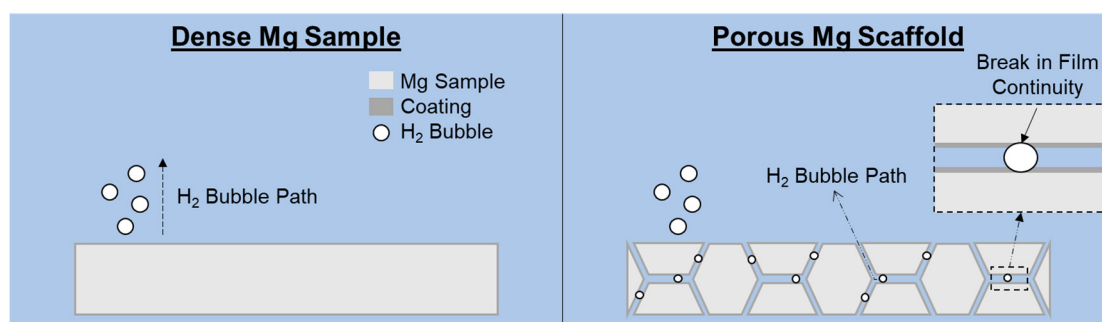


Figure 10. Schematic of the phosphate conversion coating forming process of both dense Mg sample and porous Mg scaffold. As the hydrogen gas that evolves within the pore channels is unable to escape freely, its accumulation leads to a break in film continuity during the film formation process.

Furthermore, it is known that a compact phosphate conversion coating is required for optimal corrosion protection. Zhou et al. [52] extensively discussed the cracking of chemical conversion coatings on Mg alloys, in particular, the defects caused by the entrapment of H₂ bubbles within the coating. From our previous study [45], it is found that there is a significant increase in the cathodic kinetics of the uncoated porous sample over the dense Mg-Zn-Zr sample used in this work due to the presence of MgO. The difference in the hydrogen evolution rate of the porous and dense Mg-Zn-Zr samples may contribute to the increased trapping of hydrogen inside the coating, causing increased hydrogen-induced cracking of the coating and reducing the protection offered, as observed from the discrepancies between the reduction in corrosion offered by the phosphate conversion coating of the porous and dense Mg-Zn-Zr samples in this work.

4.2. Limited Diffusion within the Pore Channel during the Coating and Corrosion Processes

During the coating of porous Mg-Zn-Zr scaffolds, the limited material transport within the porous channels may also result in a high concentration difference between the electrolyte in the bulk solution and that in the pore channels. This contrasts with the coating process of the dense sample where the relatively higher diffusion rate can compensate quickly for variations in localised concentration gradients. This difference may influence the properties of the coating formed. This hypothesis is supported by previously reported findings of variations in coating properties formed under different pH conditions [27,28].

Similarly, the restricted material transport during corrosion, due to limited diffusion within the pore channels, can also result in discrepancies in coating performance. The corrosion performances of coatings are well known to vary with changes in the corroding environment [53,54]. The limited material transport within the pore channels during corrosion can lead to the accumulation of corrosion by-products and local variation of pH, resulting in the alteration of the localised environment affecting the corrosion protection effectiveness of the coating, especially within the channels of the porous Mg-Zn-Zr scaffold.

The combination of possible implications of hydrogen evolution and limited material transport during the coating and corrosion processes means that the quality of applied coatings may perform better or worse in porous Mg structures relative to their dense Mg counterpart. Other than the type of formulation of coating, the extent of performance may vary across structures based on the inherent properties of the pore channels, such as degree of porosity, pore sizes, and tortuosity, which will all affect material transport rates.

In summary, a combination of accumulation of H₂ gas during the coating process and the development of different localised conditions within the pore channels compared to the external surface results in an inability to directly translate the corrosion protection performance of coatings from dense solids to porous Mg structures. This means that more focus is needed on the understanding of coating technologies applicable to the corrosion protection of porous Mg structures. The proportionate H₂ evolution that occurs from the corrosion of Mg alloys at high rates is known to result in post-implantation

mortality [55]. Therefore, improvements in coating knowledge and techniques will allow for better retardation of the corrosion rate of Mg alloys, pushing the boundary for the use of Mg in biomedical applications. In addition, the reduction in the corrosion rate of Mg is also known to positively influence cell adhesion [56], coupled with improved cell proliferation [2] and vascularisation [3] from the porous geometry of the Mg structure. Consequently, the future of Mg as the next-generation biomaterial has never been brighter.

5. Conclusions

In this work, the influence of hydroxyapatite and phosphate conversion coatings on the corrosion performance of conventionally cast, dense Mg-Zn-Zr alloy and binder jet additive manufactured porous Mg-Zn-Zr scaffold was investigated. It was found that the optimum hydroxyapatite and phosphate conversion coatings resulted in a 3x and 4.8x reduction in the corrosion rate of dense Mg-Zn-Zr samples, respectively, and a 1.9x and 1.2x reduction in the corrosion rate of porous Mg-Zn-Zr scaffold, respectively. The discrepancies between the corrosion performance of hydroxyapatite and phosphate conversion coating, when applied to dense and porous Mg-Zn-Zr samples, can be attributed to both the microstructure and the geometry's influence on the binder jet additive manufactured porous Mg-Zn-Zr scaffold, which not only increases the rate of hydrogen evolution but also reduces the ability of the hydrogen gas generated within the pore channels to escape to the sample surface. This restricts the effectiveness of the coating application for porous Mg scaffolds. The limited diffusion within the pore channels can also result in differing localized corrosion environments, causing discrepancies between the localised corrosion environment within the pore channels and those at the bulk electrolyte.

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