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The effect of small-molecule bio-relevant organic components at low concentration on the corrosion of commercially pure Mg and Mg-0.8Ca alloy: An overall perspective

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Abstract

The individual and combined influence of 53 small molecule bio-relevant organic compounds on the corrosion of CP Mg and Mg-0.8Ca is investigated. The results demonstrate that tested amino acids, vitamins and saccharides, do not critically influence the *in vitro* corrosion of tested materials. The presence of penicillin and streptomycin at low concentration in MEM has no significant influence on the corrosion, while higher concentration of streptomycin accelerates degradation. The similarity between MEM and SBF as corrosive medium for *in vitro* tests is also clarified. These results contribute to understanding the influence of organic compounds on *in vitro* corrosion of Mg.

Keywords: Magnesium; Corrosion; Degradation; Small-molecule organic components;

1 Introduction

After years of research and development, magnesium and its alloys have become an important material for biodegradable implants for bone and cardiovascular applications [1-5]. For a biodegradable material, understanding its degradation mechanism and degradation rate are of paramount importance. A large number of studies focus on these aspects [6-8]. The *in vivo* corrosion tests are the most appropriate method to investigate the degradation behavior of biomedical magnesium. However, because of the limitations of *in vivo* animal trials, *in vitro* corrosion tests are indispensable [9, 10] at the preliminary stages of development. Recent reviews conclude that the *in vivo* corrosion rate of biodegradable Mg does not fully correlate with corrosion rate that obtained by the *in vitro* tests [11, 12]. Typically, slower degradation rate is observed *in vivo* compared to the same material tested *in vitro*. One of the reasons is that the existing *in vitro* test protocols were developed for the traditional inert biomaterials (i.e. stainless steels and titanium) rather than fast degrading magnesium and its alloys [11]. Although a recent standard provided suggestions about the medium selection [13], there is still no generally accepted medium for *in vitro* tests of Mg. Understanding other reasons causing the discrepancy between the corrosion rate of *in vivo* and *in vitro* is important for unravelling the details of high complexity degradation phenomena.

Initially, simple saline electrolyte was often used as the *in vitro* test medium. In a search for more appropriate testing media, a number of more complex solutions have been suggested as test

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media up to now [14, 15], including Ringer solution [16], Hank's solutions [17-21], simulated body fluid (SBF) [22-28], as well as cell culture medium (MEM, DMEM, α-MEM) [17, 29]. Besides, these media were modified by other components, for example protein, to mimic the real body fluid environment more accurately [17, 30]. However, it is still not clear if any of these complex media are more suitable for *in vitro* corrosion tests. The cost of complex media is high and the influence of bacterial multiplication in complex media could not be ignored during long-term tests in an open environment. Although penicillin-streptomycin or UV light could be used to delay the contamination, the widespread application of the complex media is still constrained [31]. An optimal test medium for screening *in vitro* corrosion tests should be easy to prepare, representative and low cost [32]. Yet, a universal testing medium can hardly be created given the variation of possible *in vivo* corrosion environments (e.g. blood plasma, interstitial fluid, bile, urine, gastrointestinal fluid or saliva).

The simplification of the real body fluid appears to be a good choice for the development of test medium. Understanding the influence of body fluid components on the corrosion behavior of magnesium is prerequisite for this approach, due to the presence of a variety of components in real body fluid, such as inorganic salts, amino acids, vitamins, saccharides and several other organic components. The impact of inorganic ions on the corrosion behavior of magnesium have been fully described by a number of papers [33-37]. In our recent work, the individual effect and synergy of the inorganic ions in SBF have been studied [18, 38]. The combination of Ca^{2+}, HPO_4^{2-} and HCO_3^- ions has been proven to slow down the corrosion rate of CP Mg. If at least one of this components is absent (in the medium), corrosion rates are several times higher [38]. This is due to the immediate formation of hydroxyapatite-like precipitates that stabilizes the local pH at the surface of degrading Mg below 8.5. In contrast to the widely spread common perception, the near surface pH of Mg degrading in physiological electrolyte is not highly alkaline [18, 38].

Through the comparison between the corrosion rate of Mg in MEM and complex saline solution, it was found that the combination of amino acids, vitamins and glucose leads to accelerated corrosion rates [20, 39]. However, the individual effect of standalone organic components have not been reported systematically. Although, there are over 20 species in human plasma or serum, only a limited amount of amino acids, such as cysteine, arginine, glycine and aspartic acid were considered in this regards in recent studies [17, 40, 41]. This is also the case for works on the influence of saccharides, only glucose was taken into account [40, 42, 43], although saccharides like galactose (for children), glucosamine and fructose also have relatively high concentration in plasma/serum. In addition, the effect of vitamins on corrosion of magnesium has not been considered systematically, even though several vitamins were found to inhibit corrosion of magnesium or other metals [44, 45]. A number of other organic components in plasma/serum which are not included in common test media have also been tested as corrosion inhibitors [45]. Although the influence of a few organic components in plasma/serum on the corrosion of magnesium have been investigated, the concentration of the most of them in plasma/serum is one, two or even three orders of magnitude lower than the concentrations tested in previous reports [45, 46]. However, it is well known that the influence of organic compounds on the corrosion of magnesium is strongly

concentration dependent [45]. Thus, the limited understanding of the influence of the organic components at low concentration on the corrosion of magnesium restricts the development of *in vitro* corrosive media.

Except these small-molecule organic components from plasma/serum, other organic components that are often included in common test media also need to be considered, such as phenol red and penicillin with streptomycin. Phenol red is a commonly used pH indicator. It is added to the MEM cell culture media at low concentration (2.82×10^{-5} M). The combination of penicillin and streptomycin is often employed to avoid or delay the bacterial contamination in the *in vitro* cytocompatibility test of magnesium [47-49]. In our previous work, both the penicillin and the streptomycin at the concentration of 0.05 M were found to have a significant accelerating effect on the corrosion of magnesium in NaCl solution [45]. This, however, does not necessarily mean that the commercially available antibiotic penicillin-streptomycin accelerates the corrosion of magnesium when it is added in the cell culture media, since only the low amount of penicillin-streptomycin (1 vol. %) typically added to MEM. Common concentrations in MEM are 100 unit/ml for penicillin and 0.1 mg/ml for streptomycin, thus, the concentrations of both penicillin and streptomycin are around 10^{-4} M.

In this study, 53 bio-relevant organic compounds constituting plasma/serum or cell culture media were selected for investigation. The hydrogen evolution tests were performed to elucidate the influence of these organic components on the corrosion of magnesium. The individual and combined influence of group of amino acids was revealed, as well as the group of vitamins and saccharides. The influence of penicillin and streptomycin at different concentration on the corrosion of magnesium in MEM and SBF was also discussed. The main purpose of this work is to elucidate the influence of individual antibiotics, amino acids, vitamins, saccharides and their combinations on the corrosion of magnesium. This might contribute to better understanding of discrepancy of the *in vivo* vs *in vitro* corrosion rate of magnesium alloys and will help to facilitate the development of an appropriate corrosive media for *in vitro* corrosion tests.

2 Experimental

As-cast commercially pure Mg (CP Mg) and Mg-0.8Ca alloy were used in this study. These two materials are commonly used in biomedical research and they are also representatives for two types of magnesium alloy: Mg-0.8Ca includes anodically active second phases, while CP Mg suffers from iron-rich impurities acting as cathodic second phases. Optical discharge emission spectroscopy (SPECTROLAB with Spark Analyser Vision software, Germany) was employed to check the elemental composition of two materials, the results are listed in **Tab. 1**. In the hydrogen evolution tests, small metallic chips (produced by milling machine), which have large surface area (CP Mg: 47.7±5.0 cm^2/g; Mg-0.8Ca: 52.3±3.8 cm^2/g), was used instead of bulk samples.

The eudiometers (Art. Nr. 2591-10-500 from Neubert-Glas, Germany) combined with an electronic balance (OHAUS, SKX series) were used to perform the hydrogen evolution tests. 0.50 g

of metallic chips were placed in a eudiometer container with 500 mL of electrolyte. During the test period, the electrolyte was constantly agitated by a magnetic stirrer. **Fig. 1** shows the schematic of a eudiometer used for H_2 evolution test. Compared with the device described earlier [45], a distinct feature of the updated setup is that the corrosion rate was recorded automatically, and hence the change of corrosion rate could be recorded in more detail. Similar with previous works [50-52], the weight of water displaced from the eudiometer by evolved hydrogen was measured by the balance. The values were recorded every 15 minutes using USB data logger (OHAUS, 30268984) which is a great advantage compared to manual data recording (especially concerning overnight measurements). To process the obtained balance data files and to draw the hydrogen evolution plots in real time an in-house Python script was developed.

Three different basic electrolytes were used in this study, namely 0.85 wt. % NaCl solution (isotonic solution), complex saline solution (SBF, refer to [53] without Tris/HCl buffer) and Minimum Essential Media (MEM, Thermofisher, 61100-103). The detailed composition of these electrolytes is listed in **Tab. 2**. The HBSS (Hank's balance salt solution) is also shown for comparison since it is often used for corrosion testing of magnesium. Although SBF was used in this study instead of HBSS, based on published works [18, 38, 45] and our research result, the corrosion behavior of magnesium in these two media is comparable to their similar composition. To test the influence of individual organic components, 0.85 wt. % NaCl solution was used. Organic components were used as additives dissolved in NaCl, SBF or MEM and tested at initial pH of 6.8±0.5 adjusted by NaOH or HCl. According to ref. [46, 54, 55], the concentration of each organic component was chosen so as to correspond to the concentration of this component in the blood plasma or MEM electrolyte. The individual and then combined influence of 20 common amino acids, 9 water-soluble vitamins, 4 saccharides were tested in NaCl and subsequently in SBF at initial pH of 7.1±0.3 adjusted by NaOH/HCl. The influence of penicillin and streptomycin of three different concentrations was tested in MEM and SBF (where they are typically added to prevent the microbial growth). The impact of the investigated additives on the corrosion of magnesium is described by the inhibition efficiency (IE/ %), calculated according to H_2 evolution values after 20 h by the following equation:

$$\mathrm{IE}/\,\% = \frac{V_{Reference} - V_{Additive}}{V_{Reference}} \times 100\,\%$$

Hydrogen evolution tests in reference solutions were repeated 3-6 times for reliability. The influence of groups or part of individual tests (which impact is relatively high) were repeated 2 or 3 times to verify the reproducibility.

For the electrochemical impedance spectroscopy (EIS) measurements, a conventional three-electrode setup was used, including of a working electrode (exposure area of 0.5 cm^2, electrolyte volume of 330 mL), a Pt wire coil counter electrode and a saturated Ag/AgCl reference electrode. Bulk samples (13x13x4 mm for CP Mg and 15x15x4 mm for Mg-0.8Ca) were used for the EIS. The samples were ground to 1200 grit with SiC paper before measurement, cleaned with ethanol and dried by pressurized air stream. EIS measurements were performed at open circuit potential (OCP), applying a sinusoidal perturbation with an amplitude of 10 mV RMS over a frequency range from

100 kHz to 0.1 Hz. The EIS curves were obtained by using a Gamry Interface 1000 potentiostat/galvanostat under constant steering condition at room temperature.

A scanning electron microscopy (TESCAN, Vega3 SB) was used to observe the surface morphologies of corroded magnesium and the chemical composition was obtained by the equipped energy dispersive X-ray spectrometer (EDS).

3 Results

3.1 The hydrogen evolution tests in three reference solutions

Fig. 2 shows the comparison of H_2 evolution curves of CP Mg by using automated and manual recording. The two curves in the same electrolyte are close to identical. It indicates that the automated recording function of the H_2 evolution test device works well. The average volume of evolved H_2 after 20 h immersion in each of these three electrolytes are listed in **Tab. 3** and used as the references in the following work.

The corrosion rate for both investigated materials increases in the order SBF < MEM < NaCl, whereas the impact on the corrosion rate of CP Mg is significantly higher. These results are in good agreement with a study by Yamamoto [20] et al. In SBF, the combination of Ca^{2+}, Mg^{2+}, HPO_4^{2-} and HCO_3^- ions stimulates the formation of thin protective layer of hydroxyapatite-like compounds on the surface of Mg [38]. Compared with the corrosion rate of magnesium in SBF, CP Mg degraded more than 10 times faster in the NaCl solution. The corrosion rate of Mg-0.8Ca in NaCl solution was also two times faster compared to that in SBF. In MEM, the presence of organic components (amino acids, vitamins, glucose) led to a slight acceleration of the corrosion rate. It is noteworthy that, a great difference of corrosion rates of Mg-0.8Ca and CP Mg was observed in simple NaCl solution while the corrosion rate of the two tested materials is virtually identical in SBF and MEM electrolytes. This highlights the dominating role of the electrolyte on the degradation rate of magnesium.

3.2 Influence of amino acids on the corrosion of Mg-0.8Ca and CP Mg

The individual influence and the group effect of 20 amino acids which take part in the formation of protein [56] on the corrosion of CP Mg and Mg-0.8Ca is listed in **Tab. 4.** Additional four amino acids of relatively higher concentration in plasma or serum were also tested.

It is found that almost all of the amino acids accelerate the corrosion of Mg-0.8Ca, but the acceleration effect is not significant. 13 amino acids out of tested 24 exhibited weak inhibiting effect for the corrosion of CP Mg. The insignificant effects can be attributed to the low concentration of all the amino acids. In the case of Mg-0.8Ca alloy, the Mg_2Ca phase being the anode in the micro-galvanic coupling to the alloy matrix. In the early published works, Mg_2Ca phase was once regarded as cathodic phase in the galvanic couple between Mg_2Ca and α-Mg [57-59]. However, as the understanding deepens, more detail investigations prove the more negative corrosion potential of Mg_2Ca compared to Mg matrix [60-65]. The different corrosion mechanisms of Mg-0.8Ca and CP Mg lead to the dissimilar influence of amino acids on the corrosion of Mg-0.8Ca and CP Mg. The

combination of the amino acids dissolved in NaCl has an additive effect. Corrosion of Mg-0.8Ca was accelerated by 70%, while corrosion of CP Mg was inhibited by 26% on average. However, the group effect of amino acids approaches zero when both Mg materials are exposed to SBF.

In this section, corrosion acceleration (for Mg-0.8Ca) and inhibition (for CP Mg) induced by the combination of amino acids observed in NaCl solution is leveled out once the same materials are exposed to SBF electrolytes containing the same combination of the amino acids.

Although most of amino acids tested individually have no significant influence on the corrosion of CP Mg, cysteine that forms complexes with Fe^{3+} characterized by high stability constants [66, 67], demonstrates moderate inhibition effect on the corrosion of CP Mg. This is in good agreement with recent studies on the inhibition effect of iron complexing agents on the corrosion of pure Mg [68, 69]. On the contrary, cysteine accelerates the corrosion of Mg-0.8Ca. This can be explained by the weaker influence of iron impurities on the corrosion of Mg-0.8Ca in conjunction with the ability of cysteine to bind with Ca^{2+} and Mg^{2+} [67] which is the predominant factor concerning this alloy. Hence, Mg-0.8Ca corrodes at higher rates in the presence of cysteine.

3.3 Influence of vitamins on the corrosion of Mg-0.8Ca and CP Mg

In this part, nine water soluble vitamins, namely ascorbic acid and eight different B vitamins, were tested. The results are listed in **Tab. 5**.

The individual and cumulative effect of nine tested vitamins on the corrosion of CP Mg and Mg-0.8Ca in NaCl solution was low in both NaCl and SBF solutions. This is most likely due to the very low concentration of the vitamins in the testing solutions. It has been shown earlier, that 0.05 M solutions of folic and ascorbic acids possess high inhibiting effect to several magnesium alloys, including CP Mg [45].

3.4 Influence of saccharides on the corrosion of Mg-0.8Ca and CP Mg

In this section, four monosaccharides (glucose, galactose, glucosamine and fructose) were tested. The results are listed in **Tab. 6**.

Glucosamine was found to cause a significant acceleration effect concerning the corrosion of Mg-0.8Ca alloy. This has also impacted the cumulative effect of saccharides measured in NaCl solution, while the acceleration waned in SBF. The group effect of saccharides was low on the corrosion of CP Mg in NaCl solution, which is in line with negligible influence of four individual saccharides. Surprisingly, the mixture of saccharides caused a strong acceleration of corrosion of CP Mg when added to SBF. This might be attributed to the complexation reaction between glucosamine and Ca^{2+} contained in SBF. A reasonable assumption is that the reaction leads to depletion of Ca^{2+} in SBF solution and this retards the formation of hydroxyapatite-like protective layer. Similarly, the acceleration effect of glucosamine on the corrosion of Mg-0.8Ca might be associated with the reaction between glucosamine and Ca^{2+} dissolved from the alloy. However, the stability constant of the complexes formed by Ca^{2+} and glucosamine is not available and fully grounded conclusion cannot be drawn.

Barring glucosamine, the other tested saccharides only influence the corrosion of Mg-0.8Ca and CP Mg slightly. Glucose is a component in common corrosive media, such as HBSS solution [70] and cell culture media [71]. It has been found to accelerate the corrosion of pure Mg and several Mg alloys [40, 42, 43, 45]. However, the test concentration of glucose (2 g/L-50 g/L) in previous works were higher than the concentration in this work (1 g/L equal 5.5 mM contained in HBSS), while concentration of glucose in blood plasma varies around 0.6-1 mM for healthy adults. In a recent work, glucose with the concentration of 1 g/L was found to decrease the corrosion rate of AZ31 [72]. Comparing the published results and the results of this work, we conclude that the influence of glucose on the corrosion of magnesium is typically weak but concentration and alloy dependent.

3.5 Influence of several organic compounds from Krebs cycle and other organic components on the corrosion of Mg-0.8Ca and CP Mg

In this section, several compounds participating in the Krebs cycle as well as other organic components present in plasma/serum and MEM were tested. The individual influence of these organic components on the corrosion of CP Mg and Mg-0.8Ca is listed in **Tab. 7**. Part of them have been previously tested as corrosion inhibitors for magnesium alloys [45]. Similar to the results in other sections, most of the chemicals of low concentration have minor influence on the corrosion of Mg-0.8Ca and CP Mg.

The influence of phenol red, a commonly used pH indicator, is rather weak. This supports the applicability of phenol red in cell culture media. Unlike the other chemicals, lecithin, a type of surfactant, emulsifies in aqueous solution and possesses certain inhibiting effect for both alloys. Similarly, uric acid in low concentration is also a weak corrosion inhibitor for both alloys.

3.6 Influence of antibiotics on the corrosion of Mg-0.8Ca and CP Mg

Penicillin and streptomycin are common antibiotics which are typically used in cell culture media to prevent the growth of bacteria but do not occur in the human body. Typically used concentration of penicillin-streptomycin in cell culture media is around 10^{-4} M. In our previous work, both of them (at high concentration of 0.05 M) were found to lead to serious corrosion for tested magnesium alloys in NaCl solution [45]. Only the corrosion of CP Mg with active iron-rich intermetallic particles was inhibited [45]. Three different concentrations of streptomycin and penicillin added either to SBF or MEM were tested. The results are listed in **Tab. 8**.

The influence of penicillin and streptomycin is alloy and concentration dependent. In general, they have similar influence on the corrosion of Mg in both electrolytes. This highlights the similarities of MEM and SBF as the media for the *in vitro* tests. As shown in **Tab. 8**, the combined effect of penicillin and streptomycin on the corrosion of CP Mg and Mg-0.8Ca in MEM and SBF are less than 30% at operating concentration of 10^{-4} M. The acceleration effect of streptomycin at higher concentrations (10^{-3} M or 10^{-2} M) on both alloys is rather significant. Streptomycin has been found to inhibit the corrosion of carbon-steel in seawater [73]. It was also shown to slightly inhibit the corrosion of CP Mg in NaCl solution [45]. However, when it is tested in MEM and SBF, the reactions

between streptomycin and components of the used media should be taken into account. In clinical practice, calcium gluconate or other calcium salts are commonly used in the treatment of streptomycin poisoning based on the affinity of streptomycin for Ca^{2+}. Thus, the complexation reaction decreases the concentration of Ca^{2+} in used media. This accelerates the corrosion of magnesium. In case of Mg-0.8Ca alloy, streptomycin promotes the corrosion by binding with Ca^{2+} from alloy and media.

4 Discussion

The main purpose of this work is to establish an overview on the influence of small-molecule bio-relevant organic compounds on the corrosion of magnesium rather than to investigate the corrosion mechanism of magnesium in solutions containing organic components. Although most of tested organic components at low concentration have no significant influence on the corrosion of CP Mg and Mg-0.8Ca, a number of interesting findings emerge from the results.

4.1 Influence of selected additives at higher concentration

The influence of individual amino acids on corrosion is somewhat different compared to the data previously reported [45, 74]. Helal [74] et al. reported the inhibiting effect of a number of amino acids (tested at the concentration of 10^{-3} M) in chloride-free phthalate electrolyte measured for AZ71 alloy. In our previous paper, much higher concentrations of amino acids, namely 0.05M, have been tested [45]. A decline in IE was clearly observed with decreasing concentration of amino acid. Among the amino acids tested in this study, cysteine at low concentration has relatively significant inhibition effect on the corrosion of CP Mg. Thus, its inhibition effect at higher concentration for CP Mg and Mg-0.8Ca was also tested (as shown in **Tab. 9**). It could be shown that the increase of the cysteine concentration led to an increase of IE for CP Mg. However, further increase in cysteine concentration (10 mM) lowers its IE. A similar result for Zn alloy was found by Shkirskiy et al. [75]. However, its effect on Mg-0.8Ca corrosion becomes more negative with the increase of concentration.

Selected organic compounds were also tested at higher concentrations, the results are shown in **Tab. 9**. All tested compounds exhibit a higher corrosion inhibition effect for CP Mg than for Mg-0.8Ca alloy. Lecithin at high concentration demonstrated limited corrosion inhibition effect owing to its emulsification rather than solubility. The ascorbic acid was the most effective corrosion inhibitor for both alloys with highest inhibiting efficiency reaching 79%.

4.2 The similar corrosion behaviors of Mg alloys in both MEM and SBF

Apart from the inorganic components common for SBF and MEM, the latter contains a variety of organic components, including amino acids, vitamins and glucose, which are mandatory for cell growth. In this study, it could be found that the organic compounds tested at physiological concentrations have no significant influence on the corrosion rate of magnesium. The addition of

low concentration of antibiotics in both MEM and SBF also has limited influence on the corrosion of magnesium. This fact indicates the similarity of magnesium corrosion in both MEM and SBF.

The evolution of EIS spectra of CP Mg and Mg-0.8Ca was investigated in 0.85 wt. % NaCl, MEM and SBF for 24 h. **Fig. 3** shows the Bode plots of CP Mg and Mg-0.8Ca after different immersion duration in three electrolytes. An interesting finding is that the hydrogen evolution and the evolution of impedance spectra are very similar for both alloys in MEM and SBF. However, the EIS spectra of two tested materials differ significantly in NaCl solution. When both alloys were immersed either in MEM or in SBF electrolytes, the additional time constant at high frequencies (about 10 kHz) continuously grew as the immersion time elapsed. This fact evidences the formation of an additional partially protective layer on the surface. This is not the case for the Bode plot evolutions of CP Mg and Mg-0.8Ca in NaCl as no additional time constant appeared at high frequency range. Furthermore, the EIS evolution of both materials in MEM and SBF at first 7 h were almost the same, while the evolutions of two materials in NaCl deviate significantly. This result provides a strong support on the applicability and representativeness of SBF for the *in vitro* corrosion tests. Nevertheless, the EIS curves after 24 h immersion have differences. It could be attributed to the consumption and depletion of Ca^{2+}, HPO_4^{2-} and HCO_3^- ions in electrolytes (EIS was done in stirred electrolyte, but the medium was not refreshed). This emphasizes the notion that maintaining constant composition of the electrolyte is necessary throughout the duration of the immersion tests.

Fig. 4 shows the morphologies of corroded CP Mg and Mg-0.8Ca after 24 h immersion in MEM and SBF. The elemental compositions of corrosion products in **Fig. 4** given by EDS is listed in **Tab. 10**. From the morphology and EDS results, it is clear that the products formed on different alloys in these two media have similar features, low Ca-P content product layer combined with the clusters of product with higher Ca-P content. The similar dense layer of corrosion products is in agreement with similar corrosion rate of Mg in MEM and in SBF. These results indicate that the precipitates with similar protection effect were formed on different magnesium alloys in the same electrolyte. This is also in line with our previous work [18], similar local pH values were found during immersion of four different Mg alloys in HBSS electrolyte. The bulk pH changes of media after hydrogen evolution are shown in **Fig. 5**. It could be found that, even without pH buffer, the bulk pH changes of SBF and MEM after hydrogen evolution test are significantly lower than that of NaCl. The high final pH value of NaCl solution originates from the formation of $Mg(OH)_2$ products, however, it has poor blocking or passivation effect. For SBF and MEM, similar bulk pH changes reflect similar composition of main corrosion products. Fast formation of protective products layer in SBF and MEM inhibits further corrosion of magnesium and slows down the increase of pH value of media [18, 38]. Similar corrosion behavior in both SBF and MEM points out the interchangeability between them. It should be noticed that the change of bulk pH of medium does not always have a direct relevance for the corrosion behavior of magnesium. For example, high corrosion rate of CP Mg has been found in the Tris-buffered SBF, even though the bulk pH change after hydrogen evolution test was low [38]. It was explained by the continuous active surface reaction of Mg caused by Tris [38].

Our results show that the corrosion rates of tested materials in SBF and MEM are similar. However, several published works reported different results [12, 76-78]. First of all, this can be explained by the fact that different materials and different test methods were used. In some cases, the corrosive media that used in published works are different with the media in this work, even though they have similar name, like SBF, m-SBF and r-SBF. HEPES and Tris, as the main components of other types of SBF, inhibit the formation of protective products layer and accelerate the corrosion of magnesium significantly [18, 38, 79]. In addition, cell culture media was used for the long-term *in vitro* tests at open environment, but the risk of media contamination was not always taken into account. All the above points can give rise to significantly faster degradation of Mg. This discrepancy points out to the urgent need for standardization of *in vitro* test protocols for biodegradable magnesium [80].

In this work, SBF (without synthetic pH buffer) was selected as the representative of inorganic simulated body fluids to be used. But it does not mean that the obtained results only could be applied to explain the phenomena in SBF. Other types of the inorganic simulated body fluid, like HBSS (with Ca^{2+} and Mg^{2+}, listed in **Tab. 2**) and EBSS [20], possess similar concentration of inorganic components. As we mentioned in experimental part, based on published works [18, 38, 45] and our research results, we believe that the corrosion behavior of magnesium in these inorganic simulated body fluid media is comparable. Therefore, the small-molecule organic components at low concentration should have similar influence on magnesium corrosion in SBF, HBSS and EBSS. In other words, the effect of small organic molecules of corrosion of Mg exposed to SBF are also relevant to the influence of these organic molecules on corrosion of Mg exposed to other inorganic simulated body fluids.

In general, the components of the electrolytes participate in the formation of the precipitates on the surface of corroded magnesium during the corrosion process. The alloy characteristics, such as composition, processing and grain orientation, obviously influences the degradation rate, while having only a limited influence on the composition and the protective ability of the precipitation layer. Two latter parameters are dominated by the electrolyte components. Therefore, the differences in degradation rate of magnesium alloys (caused by the elemental composition, phases and microstructural features of the materials) are best distinguished by the corrosion tests conducted in NaCl solution. These differences are leveled off during the immersion in simulated body fluids (such as SBF, HBSS, EBSS and MEM) because degradation is dominated by precipitation/conversion products especially at relatively early stages of corrosion. In line with this, similar corrosion behavior was observed for different magnesium alloys exposed either to MEM or to SBF. Although, from our results, the corrosion rate of CP Mg and Mg-0.8Ca in SBF or MEM is very similar, this might not hold true for all the magnesium alloys. However, it could be confirmed that the great difference in corrosion rate of different Mg alloys observed in simple NaCl solution is levelled off in SBF or MEM electrolytes.

4.3 The influence of streptomycin

Zhen [81] et al. reported the high corrosion rate of magnesium leads to the cells death. The corrosion rates of magnesium exposed to MEM and SBF are rather slow, but the influence of exogenous additives should be taken into account because of their potential corrosion acceleration effect. The test results indicate that addition of penicillin-streptomycin (at operating concentration) to MEM or SBF has no significant influence on the corrosion of magnesium. The cytocompatibility tests of Mg that performed presence of penicillin-streptomycin are not affected by these two antibiotics.

However, at high concentration (10^{-2} M) streptomycin significantly accelerate the corrosion of both tested materials. **Fig. 6** shows the corrosion morphologies of corroded CP Mg and Mg-0.8Ca after 24 h immersion in MEM with streptomycin at the concentration of 10^{-4} M and 10^{-2} M. The compositions of corrosion products in **Fig. 6** determined by EDS are listed in **Tab. 11**. It is clear that the corrosion morphologies and chemical compositions in MEM with low streptomycin concentration are similar to those in blank MEM, while the thick products and many deeper cracks appeared in the corrosion products in MEM with high streptomycin concentration (indicating poor corrosion resistance in this medium). This morphology is in good agreement with the conducted hydrogen evolution results. The evolution of EIS spectra of CP Mg and Mg-0.8Ca was investigated in MEM with streptomycin at concentration of 10^{-2} M and is shown in **Fig. 7**. Although the Ca-P content of corrosion products is also relatively high after 24 h immersion in MEM with high streptomycin concentration (shown in **Tab. 11**), there is no evident additional time constant observed at the high frequency range (shown in **Fig. 7**). Only after 24 h, a very diffusive relaxation response with minor barrier properties can be evidenced. Besides, the values of the low frequency impedance for both alloys at the earlier hours of immersion were one order of magnitude lower than that when the alloys were exposed to streptomycin-free SBF and MEM, compare to **Fig. 3**. This means that the formation of Ca-containing protective layer is delayed significantly suggesting possible complex formation between Ca^{2+} and streptomycin. This decreases the concentration of free Ca^{2+} in MEM and delays the formation of initially partially protective layer which is critical for the corrosion protection of magnesium in these media [38]. Apart from complex formation between streptomycin and Ca^{2+}, the possible complexation reactions between antibiotics and other metal ions might influence the corrosion behavior of other Mg alloys more significantly. Therefore, moderate caution is still necessary when adding antibiotics in the various tests media. Consequently, the affinity of antibiotics for ions like Ca^{2+} needs to be taken into account for future studies.

4.4 Additional remarks and outlook

All the tests in this work were carried out at ambient temperature (AT), while bio-degradation tests are usually done at 37°C. Typically, the higher temperature leads to faster corrosion and can also shift chemical equilibria. However, Wagener et al. [32] compared the corrosion behavior of CP Mg in DMEM and SBF at AT and 37°C. They concluded that the temperature only shows minor influence during the *in vitro* corrosion tests.

In this work, we have tested 53 chemicals, focusing only on the influence of small-molecule organic components on the corrosion of magnesium. The results shows that they have no critical influence on the corrosion of tested materials. A number of studies, which investigated the structure and chemical composition of Mg corrosion products exposed to cell culture media, suggested that the organic molecules influence the formation of corrosion products on magnesium [17, 82]. Therefore, it is important to clarify our opinion in this case. From the research results in this work, although it could be found that the products formed on tested material in SBF and MEM have similar features. But the amount of product clusters (with higher Ca-P content) on the corroded Mg in MEM is less than that in SBF (as show in **Fig. 4**). It could be attributed to the presence of small-molecule organic components in MEM. Several organic components in MEM, like amino acids, were found to bind Ca^{2+} and Mg^{2+} [66]. Thus, the potential complexation reactions might influence the formation of product clusters with higher Ca-P content to certain extent. However, based on the results in this work, it could be concluded that the presence of organic compounds at low concentration does not critically influence the final corrosion rate. Similarly, streptomycin at low concentration has only low effect on degradation rate of Mg. Although the complexation effect between Ca^{2+} and streptomycin is explicit, its negative influence on corrosion rate is still not obvious at low concentration of antibiotics.

Previously, macromolecule organic components, like proteins, have been proven to have various stronger or weaker effects on the corrosion of magnesium [17, 39, 83-85]. These discrepancies could be attributed to the diversity of tested alloys, proteins and concentrations. Thus, the influence of protein on magnesium corrosion seems still worthy to be investigated in the future. Especially, in a recent review, Höhn [86] et al. pointed out that the interaction of protein on the surface of Mg and its effect on the formation of calcium phosphate containing products during the magnesium corrosion should be explored in more details.

The establishment of a set of appropriate *in vitro* test protocols is the target of many scientists who are working in this field. Many corrosion influencing factors have been considered, such as inorganic ions, organic compounds and macromolecules as well as medium sterilization [2, 8, 31, 48, 80, 86, 87]. In our recent work, we showed significant oxygen consumption as a result of cathodic oxygen reduction reaction during the corrosion of Mg [88]. The influence of oxygen might be another latent factor which leads to the discrepancy of magnesium corrosion rate measured *in vivo* and *in vitro*. Obviously, cell viability can be significantly influenced by concentration of dissolved oxygen.

Considering the diversity of *in vitro* test methods, the optimal corrosive media should be designed separately for different corrosion test methods. A single investigation does not suffice for predicting the overarching corrosion process, while a variety of *in vitro* corrosion test methods should be applied for comprehensively evaluation. In addition, because of the variety of physiological environment, different test methods or media should be employed for the implant materials that will be used in different part of body. Even so, the corrosion behavior of implant in human body is still difficult to be mimicked completely by the *in vitro* corrosion tests at present stage. In human body, a number of factors may influence the corrosion behavior, such as local

inflammation (accompanied by the changes of local physiological environment) and the interaction between tissue and implant. These are difficult to mimic by *in vitro* corrosion tests. Although the experimental condition of *in vitro* corrosion tests can be made closer to the environment of real body, the *in vivo* animal trials are still irreplaceable in the developing magnesium for biomedical applications.

5 Conclusion

In this work, an automated logging of hydrogen evolution was established and experimentally tested. The individual influence and group effect of 53 bio-relevant organic components on the corrosion of Mg-0.8Ca and CP Mg was investigated. The obtained results led us to the conclusion, that:

(1) The small-molecule organic components do not have a critical influence on the corrosion of Mg-0.8Ca and CP Mg *in vitro*. In general, the individual influence of small-molecule organic components at low concentration is not significant in NaCl solution. None of the cumulative effects of group of amino acids, vitamins and saccharides is significant when added in SBF.

(2) The addition of penicillin and streptomycin combination at 10^{-4} M in MEM also has no obvious effect on the corrosion of tested materials. However, the affinity of ions to antibiotics needs to be taken into account. Decreased concentration of free Ca^{2+} due to binding with the antibiotic results in higher corrosion rates of Mg.

(3) The individual test results point out promising corrosion inhibitors for Mg. Such as uric acid (for CP Mg) and ascorbic acid (for both CP Mg and Mg-Ca).

(4) Different magnesium alloys were found to have similar corrosion rate in the same medium (SBF or MEM). Similar corrosion behavior of the same alloy in SBF and MEM was also observed. These phenomena indicate that the corrosion of Mg in simulated body fluids (such as SBF, HBSS and MEM) is controlled by precipitation of the protective layer of corrosion products which is mainly controlled by the inorganic components of the electrolyte.

(5) The relatively simple solutions that contain all inorganic constituents (like SBF and HBSS) might be suitable *in vitro* test media for magnesium at open environment.

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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Tab. 1 The elemental composition of commercial pure Mg (CP Mg) and Mg-0.8Ca alloy.

	Element content/ wt. %										
	Fe	**Cu**	**Ni**	**Al**	**Mn**	**Ce**	**Zn**	**Si**	**Ca**	**Zr**	**Mg**
CP Mg	0.0342	0.00037	<0.0002	0.00402	0.00237	0.0007	0.00046	0.00071	<0.0001	<0.0005	Bal.
Mg-0.8Ca	0.0046	0.0021	0.0019	0.024	0.052	0.001	0.0052	0.045	0.83	0.0035	Bal.

Tab. 2 The compositions of three basic electrolytes. (HBSS is also listed for comparison.)

	Concentration/ mM			
	0.85 wt. % NaCl	SBF	MEM	HBSS
Na^+	145.4	142.0	144.4	142.5
K^+	-	5.0	5.3	5.8
Mg^{2+}	-	1.5	0.8	0.9
Ca^{2+}	-	2.5	1.8	1.3
Cl^-	145.4	147.8	126.1	146.8
HCO_3^-	-	4.2	26.2	4.2
HPO_4^{2-}/ $H_2PO_4^-$	-	1.0	1.0	0.8
SO_4^{2-}	-	0.5	0.8	0.4
Synthetic pH buffer (i.e. Tris/HCl, HEPES)	No	No	No	No
Amino acids (13 kinds)	-	-	848.0 mg/L	-
Vitamins (8 kinds)	-	-	8.1 mg/L	-
Glucose	-	-	5.5	5.5
Phenol red	-	-	10mg/L	-
Initial pH value	5.6-5.9	7.35-7.45	7.0-7.4	7.0-7.4

Tab. 3 The volumes of evolved H_2 after 20 h immersion in three reference solutions.

Reference solutions	**H_2 evolved after 20h immersion/ mL**	
	Mg-0.8Ca	**CP Mg**
0.85 wt. % NaCl	**62.8±3.4**	**386.1±22.7**
SBF	**32.1±4.5**	**32.3±6.5**
MEM	**44.4±1.3**	**43.8±1.3**

Tab. 4 The individual influence and the group effect of amino acids on the corrosion of Mg-0.8Ca and CP Mg. (Red background color means the compound accelerates corrosion, IE<0%; Yellow color means weak inhibition effect, 0%<IE<40%; Green color means relatively moderate inhibition effect, IE>40%; The same color-code is used in all the tables in this paper.)

Amino acid	Concentration/ M	Mg-0.8Ca		CP Mg		Medium (Initial pH)
		Volume of H_2 (20 h) / mL	IE/ %	Volume of H_2 (20 h) / mL	IE/ %	
Alanine	8.53×10^{-4}	65.9	-5	424.8	-10	NaCl (pH 6.8±0.5)
Serine	1.90×10^{-4}	63.4	-1	338.4	12	
Aspartic	9.01×10^{-5}	55.6	11	374.2	3	
Proline	4.95×10^{-4}	74.6	-19	403.8	-5	
Glutamic	1.90×10^{-4}	66.8	-6	391.8	-1	
Cysteine	4.13×10^{-4}	82.3±7.3	-31±11	262.2±26.5	32±7	
Glycine	7.19×10^{-4}	69.1	-10	377.1	2	
Asparagine	1.00×10^{-4}	67.9±5.5	-8±8	353.1±28.3	9±7	
Leucine	3.96×10^{-4}	64.1	-2	375.3	3	
Isoleucine	3.20×10^{-4}	68.2	-9	364.8	6	
Methionine	1.01×10^{-4}	65.1	-4	375.1	3	
Arginine	2.07×10^{-4}	70.0	-12	389.2	-1	
Histidine	2.45×10^{-4}	71.7	-14	356.1	8	
Valine	3.59×10^{-4}	78.9±6.9	-26±11	406.4±1.4	-5±1	
Tryptophan	1.47×10^{-4}	68.2	-9	403.7	-5	
Threonine	2.69×10^{-4}	70.4	-12	388.0	0	
Phenylalanine	2.42×10^{-4}	73.4	-17	377.0	2	
Glutamine	7.25×10^{-4}	78.9	-26	401.3	-4	
Lysine	3.97×10^{-4}	68.9	-10	396.6	-3	
Tyrosine	1.38×10^{-4}	78.8	-26	375.4	3	
All above listed amino acids tested together		107.6±11.3	-70±18	285.1±15.7	26±4	NaCl (pH 6.8±0.5)
		29.0±6.0	11±18	30.4±1.4	5±4	SBF (pH 7.1±0.3)
Ornithine	1.06×10^{-4}	68.1	-8	391.4	-1	NaCl (pH 6.8±0.5)
α-Aminobutyric acid	1.94×10^{-5}	62.8	0	375.1	3	
Taurine	1.68×10^{-4}	72.2	-15	396.8	-3	
Cystine	9.90×10^{-5}	83.2±5.2	-34±8	303.4±14.5	21±4	

Tab. 5 The individual influence and the group effect of vitamins on the corrosion of Mg-0.8Ca and CP Mg.

Vitamins	Concentration/ M	Mg-0.8Ca		CP Mg		Medium (Initial pH)
		Volume of H_2 (20 h) / mL	IE/ %	Volume of H_2 (20 h) / mL	IE/ %	
Ascorbic acid (VC)	1.14×10^{-4}	64.3±1.1	-2±2	333.8±5.0	14±1	NaCl (pH 6.8±0.5)
Folic acid (VB9)	2.27×10^{-6}	64.5	-3	365.4	5	
Inositol (VB8)	3.89×10^{-5}	67.2	-7	395.9	-3	
Riboflavin (VB2)	2.66×10^{-7}	68.5	-9	362.0	6	
Pyridoxine-HCl (VB6)	4.82×10^{-6}	67.2	-7	379.5	2	
Thiamine-HCl (VB1)	2.96×10^{-6}	59.7	5	363.3	6	
Nicotinamide (VB3)	8.19×10^{-6}	65.7	-5	398.3	-3	
Choline chloride (VB4)	7.16×10^{-6}	61.5	2	421.1	-9	
Calcium pantothenate (VB5)	2.10×10^{-6}	64.1	-2	401.8	-4	
All above listed vitamins tested together		68.9±1.5	-10±2	347.3±34.6	10±10	NaCl (pH 6.8±0.5)
		30.3±1.0	5±3	28.4±4.8	12±15	SBF (pH 7.1±0.3)

Tab. 6 The individual influence and the group effect of saccharides on the corrosion of Mg-0.8Ca and CP Mg.

Saccharides	Concentration/ M	Mg-0.8Ca		CP Mg		Medium (Initial pH)
		Volume of H_2 (20 h) / mL	IE/ %	Volume of H_2 (20 h) / mL	IE/ %	
Glucose	5.83×10^{-3}	76.5	-22	399.2	-3	NaCl (pH 6.8±0.5)
Galactose	1.11×10^{-3}	69.1	-10	362.8	6	
Glucosamine	4.97×10^{-3}	106.5±0.5	-69±1	386.5±0.3	0±1	
Fructose	4.44×10^{-4}	71.8	-14	374.5	3	
All above listed saccharides tested together		114.4±4.4	-82±7	369.1±7.7	4±2	NaCl (pH 6.8±0.5)
		29.7±6.4	8±20	41.2±1.6	-33±5	SBF (pH 7.1±0.3)

Tab. 7 The individual influence of several other organic components on the corrosion of Mg-0.8Ca and CP Mg.

Organic components	Concentration/ M	Mg-0.8Ca		CP Mg		Medium (Initial pH)
		Volume of H_2 (20 h) / mL	IE/ %	Volume of H_2 (20 h) / mL	IE/ %	
Phenol red	2.82×10^{-5}	66.5	-6	362.5	6	NaCl (pH 6.8±0.5)
β-Hydroxybutyric acid	9.00×10^{-6}	65.2	-4	391.4	-1	
Lactate	2.20×10^{-3}	62.6	0	395.1	-2	
Glucuronic acid	5.67×10^{-5}	66.9	-6	360.9	7	
Malic acid	6.70×10^{-5}	69.6	-11	375.3	3	
Creatinine	1.00×10^{-4}	79.5	-27	392.2	-2	
Glycerol	1.87×10^{-4}	60.2	4	399.5	-3	
Urea	6.66×10^{-3}	67.7	-8	340.1	12	
Uric acid	4.82×10^{-4}	51.9±4.4	17±7	294.8±23.2	24±6	
Citric acid	1.66×10^{-4}	60.3	4	356.9	8	
Succinic acid	4.23×10^{-5}	68.4	-9	397.2	-3	
Acetone	3.44×10^{-4}	65.0	-3	377.2	2	
Pyruvic acid	1.40×10^{-4}	72.7	-16	426.5	-10	
Lecithin	2.25 g/L	53.1±6.3	14±1	267.4±3.9	31±1	NaCl (pH 6.8±0.5) (emulsion)

Tab. 8 The influence of antibiotics on the corrosion of Mg-0.8Ca and CP Mg.

Antibiotics	Concentration/ M	Mg-0.8Ca		CP Mg		Medium (Initial pH)
		Volume of H_2 (20 h) / mL	IE/ %	Volume of H_2 (20 h) / mL	IE/ %	
Penicillin (Penicillin G sodium salt)	1×10^{-4} (0.036 g/L)	40.9±1.8	8±4	33.3±3.5	25±8	MEM (pH 7.1±0.3)
	1×10^{-3} (0.356 g/L)	29.7±5.7	33±13	43.4±4.4	1±11	
	1×10^{-2} (3.563 g/L)	34.6±5.3	23±12	43.4±9.2	3±21	
Streptomycin (Streptomycin sulfate salt)	1×10^{-4} (0.073 g/L)	36.3±1.3	18±3	40.3±2.7	8±6	
	1×10^{-3} (0.729 g/L)	79.9±2.6	-80±6	38.5±1.2	13±3	
	1×10^{-2} (7.287 g/L)	93.8±17.6	-115±40	95.5±17.9	-127±40	
Penicillin + Streptomycin	$1 \times 10^{-4} + 1 \times 10^{-4}$ (0.036 g/L + 0.073g/L)	36.9±1.3	17±3	33.9±1.9	23±4	
Penicillin (Penicillin G sodium salt)	1×10^{-4} (0.036 g/L)	23.9±7.5	26±23	17.7±0.5	45±2	SBF (pH 7.1±0.3)
	1×10^{-3} (0.356 g/L)	17.8±0.6	45±2	24.8±4.8	23±14	
	1×10^{-2} (3.563 g/L)	20.4±1.5	36±5	15.9±0.8	51±2	
Streptomycin (Streptomycin sulfate salt)	1×10^{-4} (0.073 g/L)	29.5±4.7	8±15	28.4±6.1	12±18	
	1×10^{-3} (0.729 g/L)	22.0±0.3	31±1	24.1±2.9	25±9	
	1×10^{-2} (7.287 g/L)	57.0±8.5	-78±26	45.3±0.8	-40±3	
Penicillin + Streptomycin	$1 \times 10^{-4} + 1 \times 10^{-4}$ (0.036 g/L + 0.073g/L)	26.0±1.5	19±5	28.5±7.4	12±23	

Tab. 9 The individual influence of selected organic compounds (at higher concentration) on the corrosion of Mg-0.8Ca and CP Mg.

Selected additives	Concentration/ M	Mg-0.8Ca		CP Mg		Medium (Initial pH)
		Volume of H_2 (20 h) / mL	IE/ %	Volume of H_2 (20 h) / mL	IE/ %	
Cysteine	4.13×10^{-4}	82.3±7.3	-31±11	262.2±26.5	32±7	NaCl (pH 6.8±0.5)
	5.00×10^{-3}	100.9	-61	227.5	43	
	1.00×10^{-2}	127.9	-104	269.6	30	
Uric acid	4.82×10^{-4}	51.9±4.4	17±7	294.8±23.2	24±6	
	5.00×10^{-3}	34.2	46	85.3	80	
	1.00×10^{-2}	63.42	-1.0	104.0	73.1	
Ascorbic acid (VC)	1.14×10^{-4}	64.3±1.1	-2±2	333.8±5.0	14±1	
	5.00×10^{-3}	20.1	68	104.9	73	
	1.00×10^{-2}	30.8	51	82.0	79	
Lecithin	2.25 g/L (added)	53.1±6.3	14±1	267.4±3.9	31±1	NaCl (pH 6.8±0.5) (emulsion)
	5.00 g/L (added)	52.5	16	267.9	31	
	10.00 g/L (added)	50.6	20	220.9	43	

Tab. 10 Composition of corrosion products on the CP Mg and Mg-0.8Ca given by EDS after 24h immersion in MEM and SBF.

Sample / Electrolytes	Position	Elements/ at. %						
		C	O	Na	Mg	P	Cl	Ca
CP Mg / MEM	1	9.4	52.4	2.8	2.4	13.1	2.1	17.8
	2	9.0	37.1	1.4	37.3	8.6	0.2	6.4
Mg-0.8Ca / MEM	3	21.4	46.1	0.9	4.6	12.1	0.1	14.8
	4	9.0	35.9	1.0	39.3	8.4	0.1	6.3
CP Mg / SBF	5	8.6	49.5	2.1	3.9	17.7	0.5	17.7
	6	9.9	22.0	1.8	58.2	4.7	0.2	3.2
Mg-0.8Ca / SBF	7	8.0	50.0	0.6	5.5	16.4	0.1	19.4
	8	7.1	26.9	1.2	52.0	7.1	0.1	5.6

Tab. 11 Composition of corrosion products on the CP Mg and Mg-0.8Ca given by EDS after 24h immersion in MEM with streptomycin at different concentration (10^{-4} M and 10^{-2} M).

Sample / Electrolytes	Position	Elements/ at. %						
		C	O	Na	Mg	P	Cl	Ca
CP Mg / MEM+10^{-4} M	9	10.1	52.3	2.8	5.8	12.6	1.1	15.3
	10	9.5	38.7	1.7	34.0	9.0	0.2	6.9
Mg-0.8Ca / MEM+10^{-4} M	11	15.6	57.6	0.9	4.7	9.7	0.4	11.1
	12	8.6	38.9	1.0	33.2	9.6	0.1	8.6
CP Mg / MEM+10^{-2} M	13	9.2	57.5	1.4	5.2	12.6	0.1	14.0
Mg-0.8Ca / MEM+10^{-2} M	14	8.5	56.3	0.9	6.1	13.3	0.1	14.8

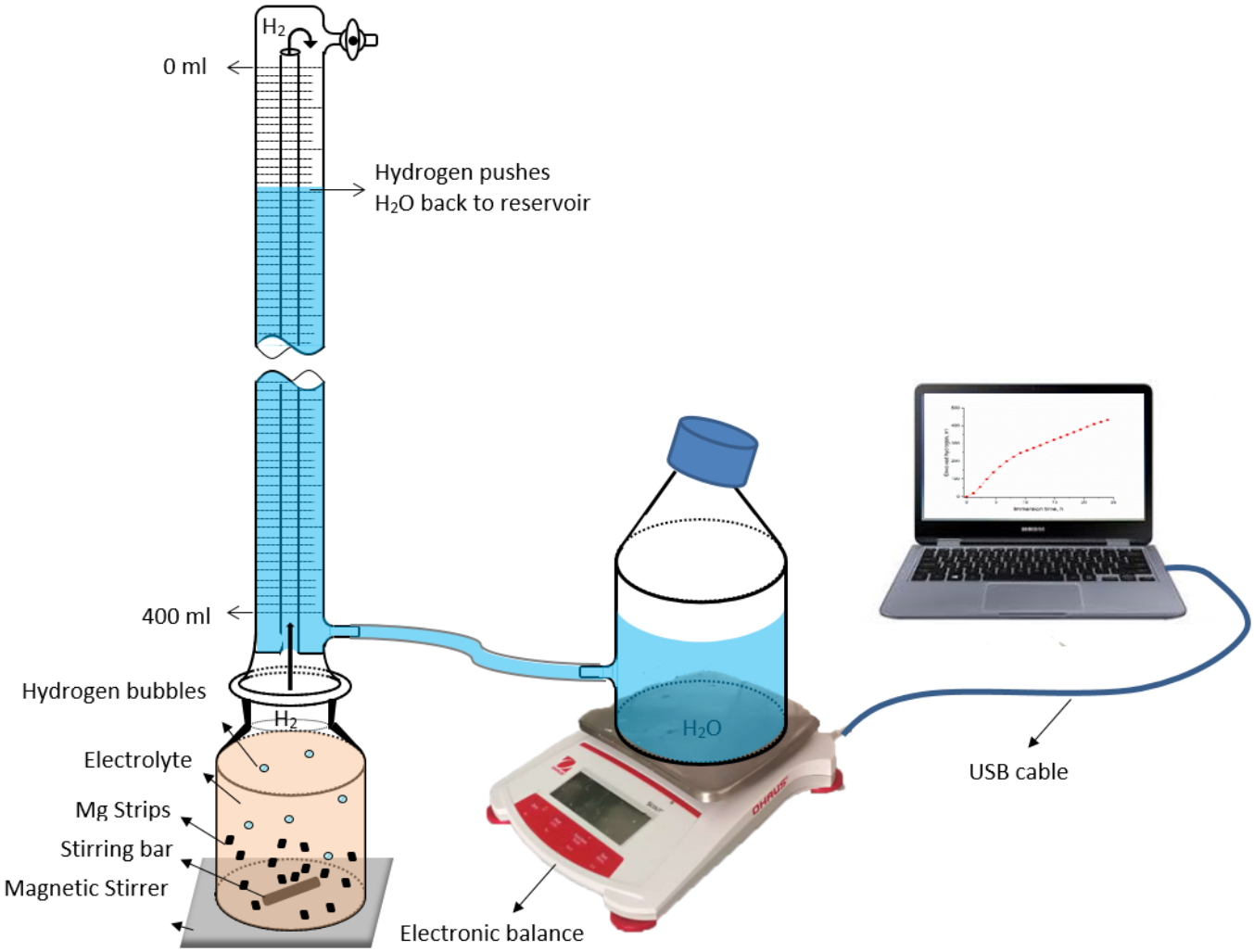

Fig. 1 The schematic setup of an eudiometer experiment used for H_2 evolution test.

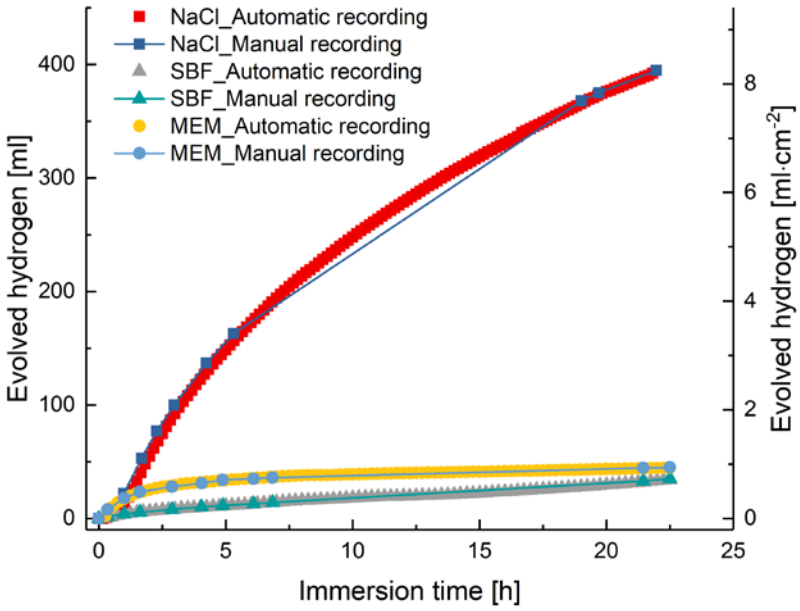

Fig. 2 Comparison of H_2 evolution test results of CP Mg by using automated recording and manual recording (in three basic electrolytes).

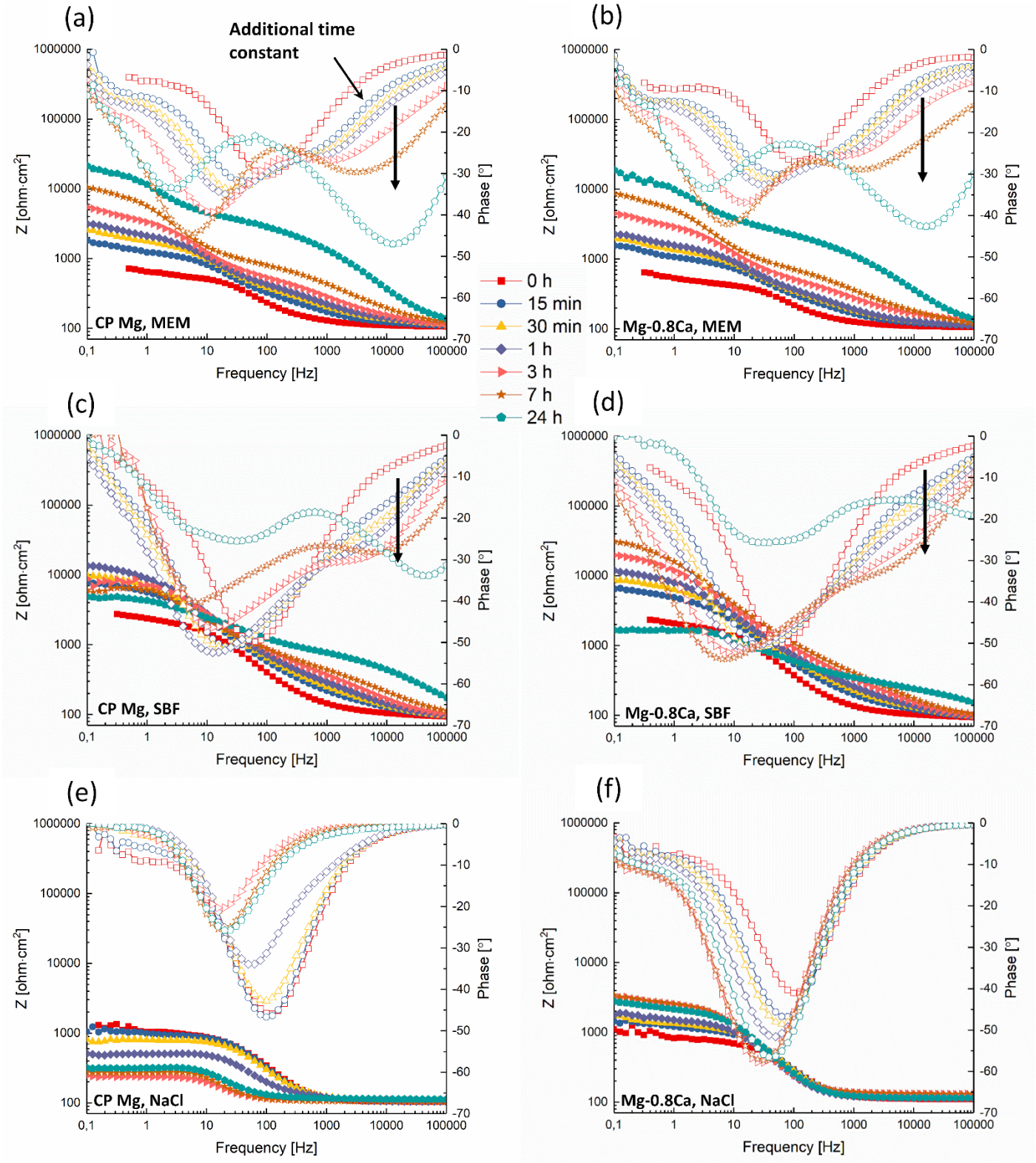

Fig. 3 Evolution of Bode plots for CP Mg (a, c, e) and Mg-0.8Ca (b, d, f) during 24h immersion in MEM (a, b), SBF (c, d) and NaCl (e, f).

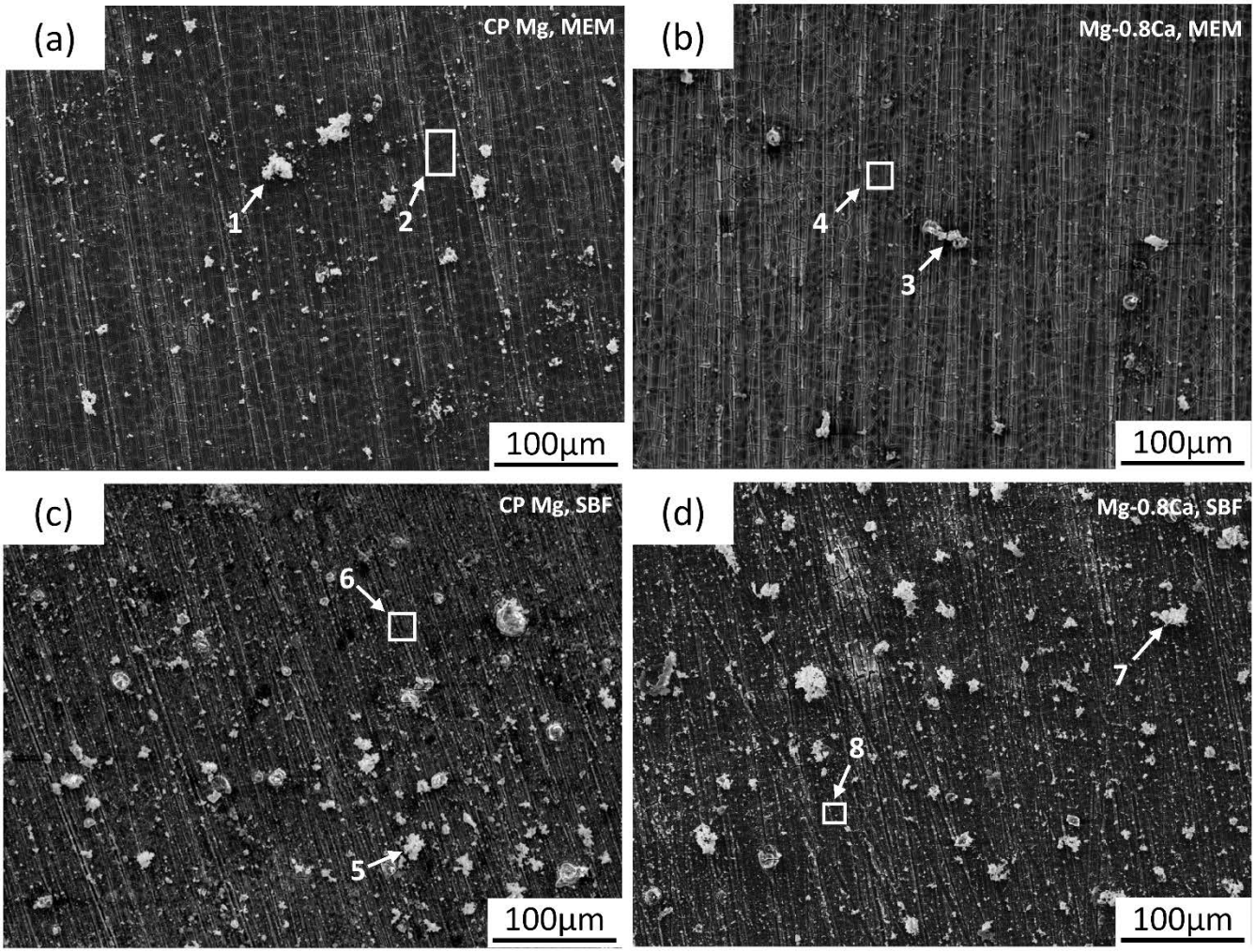

Fig. 4 Typical corrosion morphology of CP Mg (a, c) and Mg-0.8Ca (b, d) after 24h immersion in MEM (a, b) and SBF (c, d).

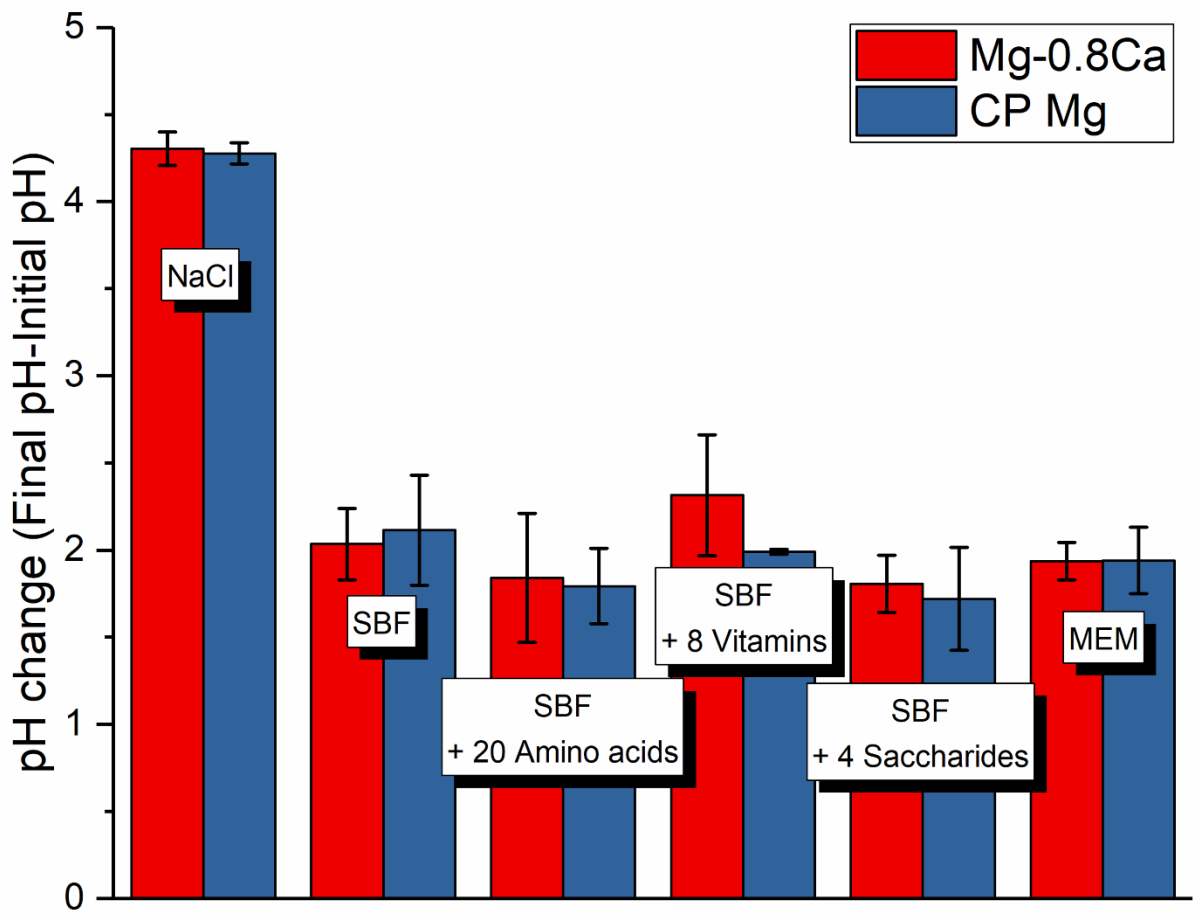

Fig. 5 The bulk pH change of selected media after hydrogen evolution test.

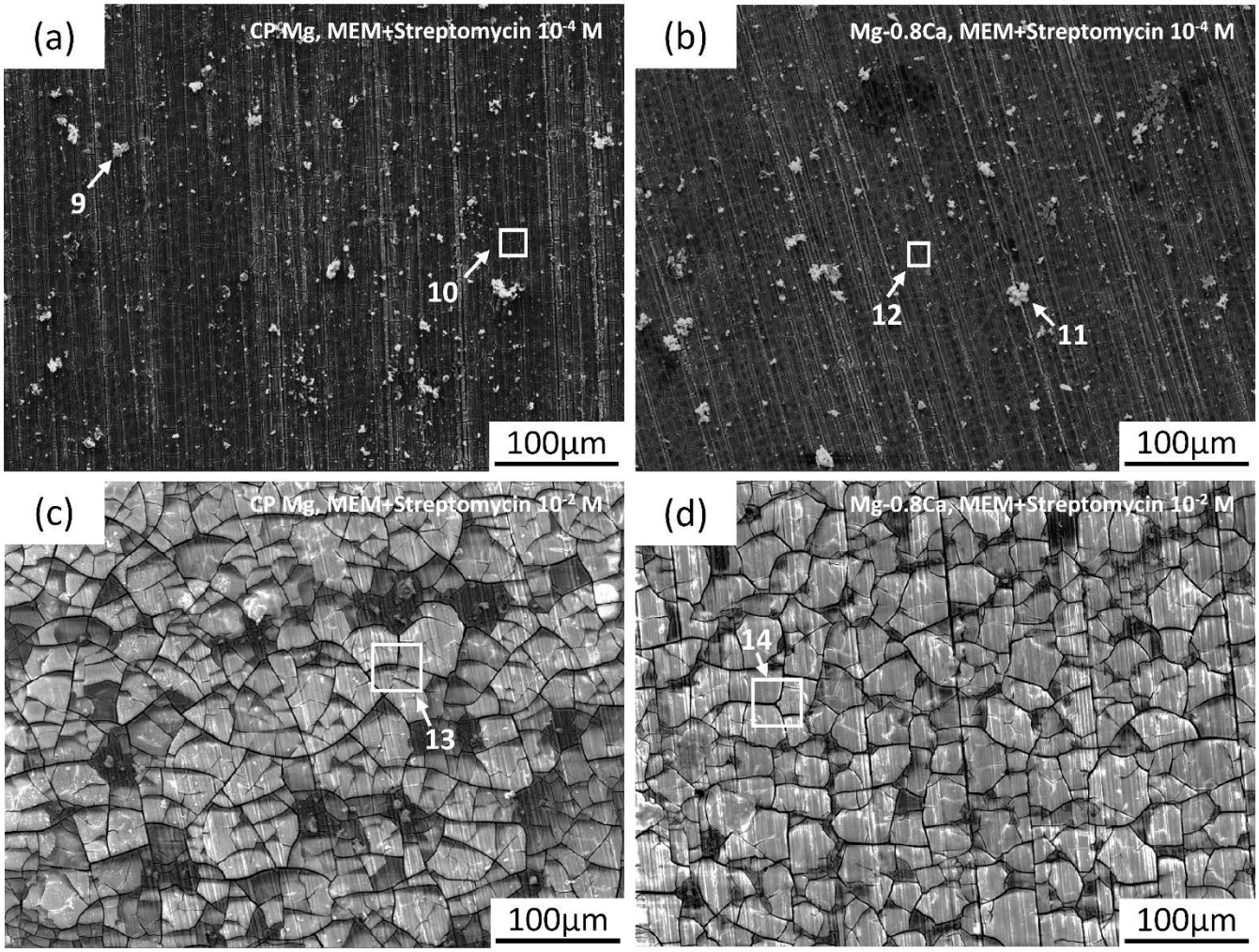

Fig. 6 Typical corrosion morphology of CP Mg (a, c) and Mg-0.8Ca (b, d) after 24h immersion in MEM with streptomycin at the concentration of 10^{-4} M (a, b) and 10^{-2} M (c, d).

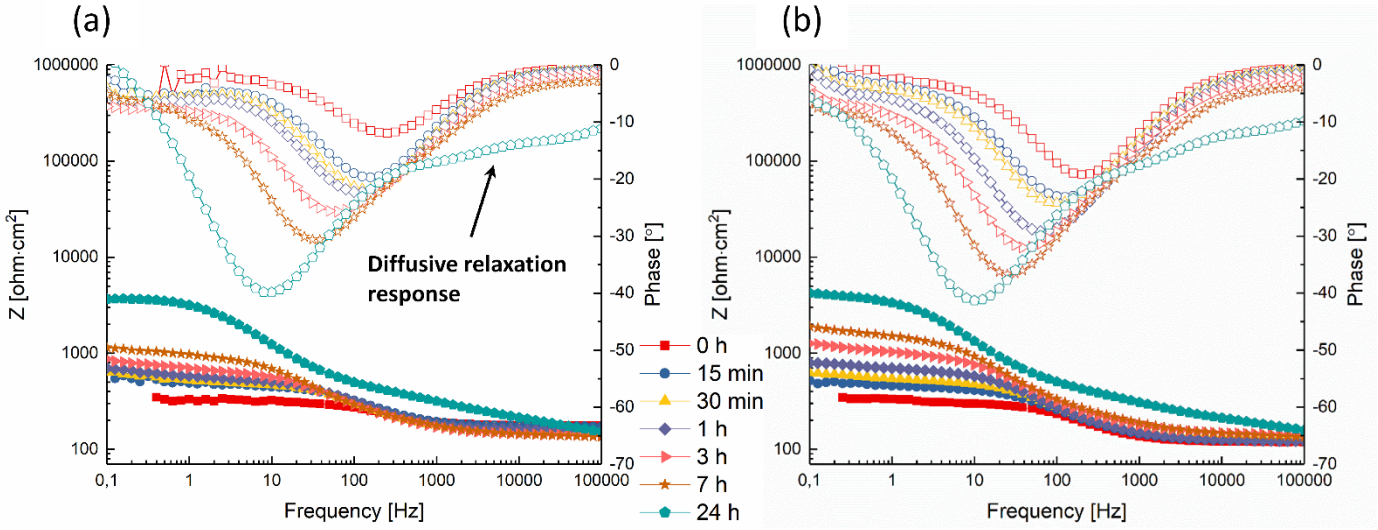

Fig. 7 Evolution of Bode plots for CP Mg (a) and Mg-0.8Ca (b) during 24h immersion in MEM with streptomycin at concentration of 10^{-2} M.