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Protein interactions with corroding metal surfaces: comparison of Mg and Fe

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The influence of bovine serum albumin (BSA) on the electrochemical behaviour of pure Mg and Fe was studied in simulated body fluid (SBF), in view of the possible application of these materials as biodegradable metals. Results indicate a different trend for the BSA-effect on corrosion for the two metals: for Mg, a strong corrosion-inhibiting effect is observed in the presence of BSA in solution, especially for short-term exposure, whereas for Fe only a slight acceleration of corrosion is caused by the addition of BSA to the solution. For both metals, the protein-effect on the electrochemical behaviour shows a complex time-dependence. Surface analysis indicates that stronger BSA adsorption takes place on Mg than on Fe. Moreover, adsorption experiments with BSA and a second protein (lysozyme) were conducted. The results are discussed in view of electrostatic interactions between differently charged metal oxide/hydroxide surfaces and proteins.

1 Introduction

Low-corrosion resistant metals to be used as biodegradable implant materials have been in the focus of intensive research activities in recent years, see *e.g.* review articles.^{1–7} The seemingly simple idea is to exploit the inherent degradation of low-corrosion resistant metals and alloys in biomedical applications, where the device is only required for a certain time of healing and where permanent implants may lead to various long-term complications. Such applications could be for instance cardiovascular stenting or temporary bone healing devices. Due to the required mechanical properties of the materials used for these applications, metals instead of biodegradable polymers are in the focus of interest.

A major part of the investigations on biodegradable metals have been carried out on Mg and its alloys; much less work has been dedicated to Fe based materials. The current knowledge indicates that whereas many Mg alloys seem to show a too fast corrosion rate in biological environments, Fe based materials may

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dissolve too slowly.⁸ Hence, in both cases, the general challenge is to tailor the materials and surfaces to achieve the desired and controlled corrosion rate for the targeted applications. Therefore, a remarkable amount of work has been carried out – especially on Mg alloys – to explore various approaches of surface modification and coatings for decreased corrosion rates and/or improved biocompatibility.^{9–12} A further challenge is to elucidate the influence of the complex biological environment on the corrosion mechanisms of these materials. For instance, it has been frequently reported in the literature that the degradation rate of Mg based alloys is strikingly different in SBF solutions, mimicking the inorganic chemistry of body fluids, than in cell culture medium (*e.g.*, DMEM, with or without addition of serum) that also contains organic components, such as glucose, vitamins and amino acids. In spite of the general agreement on the very significant difference in degradation rates in these media, SBF *vs.* DMEM,^{13–15} the role of the different species in the solutions on the degradation mechanisms are far from being understood.

For Mg alloys, specific concerns on biocompatibility arise from possibly too strong hydrogen gas evolution and accompanied alkalization of the electrolyte during Mg dissolution.⁵ As these are direct consequences of chemical properties of Mg, it is not possible to completely prevent these effects, as long as Mg is corroding – however, if the temporal gas evolution is not too fast, absorption/transport of hydrogen in tissues may be possible without formation of gas pockets due to local hydrogen accumulation. A further challenge in the application of Mg alloys for biodegradable implants is the corrosion mode: mostly a rather non-uniform corrosion attack takes place, often related to galvanic coupling of the intermetallic phases with the Mg matrix. It therefore seems that the challenges in Mg alloy corrosion, including an in-depth understanding in the underlying mechanisms, are larger than initially expected.

Due to these challenges in Mg alloy corrosion, it may be of interest to look at the behaviour of Fe based alloys in biological environments in more detail. A comparison of the corrosion behaviour of Fe and Mg based alloys in simulated biological environments is not only of practical interest in view of possible biomedical applications of these materials. Also from a mechanistic point of view, this comparison may aid in elucidating mechanisms of interactions between the constituents of the biological environment and the corroding metal surfaces in more detail. It is noteworthy that no direct comparison using identical experimental conditions for biodegradation of Fe and Mg can be found in the literature. Therefore, in the current study we explored the corrosion behaviour of pure Fe and Mg (as model systems for more complex alloys) in simulated body fluid with absence and presence of proteins in the solution. Moreover, surface analytical studies on protein adsorption on Fe and Mg surfaces were carried out.

Proteins in solution can have multiple effects on corrosion reactions: on the one side, protein adsorption layers can block electrochemically active surface sites and therefore slow down corrosion.^{16–18} Protein adsorption will be influenced by the surface chemistry of the metals (*e.g.*, type of oxides/hydroxides formed on the surface and the resulting surface wettability and surface charges). It is generally acknowledged that protein adsorption is stronger on hydrophobic than hydrophilic surfaces. However, on hydrophilic surfaces – such as OH[−] terminated metal oxides – electrostatic interactions, due to surface charges of the metal oxide and the protein, become more important. On the other side, complexation of

metal cations can take place by proteins (and amino acids), thereby reducing the free cation concentration and possibly accelerating corrosion. Also this effect depends on the nature of the metal cations; for Fe and Mg dissolution products a different strength of interactions can be expected.

For Mg, the effect of proteins on the corrosion behaviour has been studied by many authors,^{14,19–27} but the results do not show a straightforward trend in that both acceleration and inhibition of corrosion has been observed. Moreover, a complex time-dependent influence on the corrosion rate has been observed:²² for short-term experiments, modest inhibition of corrosion was observed by albumin in SBF, but after longer exposure times to an albumin-containing solution, an opposite effect of corrosion-acceleration by the presence of albumin in solution was observed. The results suggest that the corrosion-protection effect in the early immersion is due to adsorption of the proteins to the surface blocking the active sites, but this blocking effect is not long-term stable. As the various experiments were carried out on different alloys and using different experimental approaches (for instance, studying the effects of a single protein, such as albumin, or studying the effect of serum addition in simulated body fluids), it is difficult to speculate on the origin of the different findings.

For pure iron, the influence of proteins on corrosion has been less studied than for pure Mg. The effect of proteins on iron released from stainless steels (or generally on corrosion behaviour of stainless steels) has been much more frequently studied than in the case of pure iron,^{17,18,28–32} as stainless steels already find applications in biomedicine (and in other applications, where proteins are of relevance). However, as the surface chemistries of stainless steels and iron are far from identical, the relevant protein-induced metal release mechanisms may vary considerably for the two materials. Milosev *et al.* show an increase of corrosion of pure Fe in the presence of a number of bovine serum proteins, whereas the significance of the effect depends on the particular protein.²⁹ In contrast to this, Hedberg *et al.* have reported on an enhanced release of iron from stainless steel in the presence of albumin or lysozyme, but for the iron metal reduced corrosion rates were observed (it should be noted though that for pure Fe in general a much higher iron release was observed than that for stainless steel, due to the lack of passivity of Fe in the solutions used for the studies).¹⁷

The available literature hence clearly indicates controversial observations on the influence of proteins on corrosion of metals. A comparison of the findings between the different studies is very difficult, due to different experimental approaches. In the present study, the influence of albumin (BSA) on the electrochemical behaviour of Fe and Mg in simulated body fluids was investigated. In addition, surface analytical studies on adsorption of proteins on Fe and Mg surfaces were carried out. In order to get some insight into the role of surface charges or electrostatic interactions between metal surfaces and proteins, we used two proteins with different isoelectric points and therefore different resulting surface charges, namely albumin (IEP: 4.7–5.2)³³ and lysozyme (IEP: 10.5–11.8).^{34–37} For iron oxides/hydroxides IEPs between 6.6 and 8.6, and for Mg oxides/hydroxides IEPs between 10.8 and 14 have been reported.³⁸ In a neutral simulated body fluid, different electrostatic interactions may therefore be expected between the negatively charged BSA and the positively charged lysozyme, with the rather neutral surface of Fe or with the more strongly positively charged Mg surface. In addition, binding of Fe cations by albumin has been reported to be weak,³⁹ in

contrast to strong binding of Mg cations to albumin.⁴⁰ The aim of these experiments is therefore to achieve a better understanding on possible interaction modes of proteins and the corroding Mg and Fe surfaces by carrying out electrochemical and surface analytical studies for both metals exposed to identical conditions.

2 Experimental

The materials used for the experiments were commercially pure Mg (99.9%, Chempur) and commercially pure Fe (99.8%, Chempur). Samples were ground with SiC abrasive paper up to a grid size of 1200 and afterwards sonicated in ethanol and dried with air. In case of Mg, a water free lubricant was used in order to prevent corrosion during sample preparation.

As model proteins, bovine serum albumin (BSA, Sigma) and hen egg white lysozyme (LYS, Sigma) were used, with IEPs of 4.7–5.3 and 11.35 according to the manufacturer.

The SBF solution used for the experiments was “SBF5”, according to Müller *et al.*⁴¹

For the electrochemical measurements, 100 ml of SBF was used as a reference electrolyte. In order to investigate the influence of proteins on the corrosion behaviour of Mg and Fe, 10 g l⁻¹ BSA was added to the SBF solution. Mg and Fe were analysed in both different electrolytes.

The electrochemical characterization took place by open circuit potential measurements (OCP), electrochemical impedance spectroscopy (EIS) and polarisation curves (IE). All measurements were conducted by using an electrochemical workstation “IM6eX”, a potentiostat, “XPot”, and the corresponding “Thales”-Software (Zahner-Elektrik GmbH & Co. KG, Kronach, Germany). The experiments were carried out in an electrochemical cell with a three electrode set-up. The material being analysed acted as working electrode. As counter electrode, a platinum sheet and, as reference, an Ag/AgCl electrode with 3 M KCl were used. The OCP was recorded for 15 min. Afterwards, the impedance was measured at the particular OCP of the samples in the range of 100 kHz to 10 mHz with an excitation amplitude of ± 10 mV. Afterwards, polarization curves were recorded, starting -300 mV relative to the particular OCP of each sample. The potential was increased up to 0 V with a slope rate of 3 mV s⁻¹. As abort criterion, a current of 10 mA was used.

For the protein coating experiments, the Mg and Fe samples were passivated by soaking in boiling 1 M NaOH solution for 20 min.

The coating took place in 0.1 mM BSA/SBF solution and in 0.1 mM LYS/SBF solution. Each sample was immersed in 50 ml stirred protein solution for 1 h. As reference, Mg and Fe were stored in pure SBF for 1 h. The pH-values of all solutions were measured before and after immersion.

The surfaces after immersion in the protein solution and in pure SBF, were characterised *via* XPS and ToF-SIMS.

XPS measurements were carried out on a high-resolution X-ray photoelectron spectrometer (PHI 5600 USA) using aluminum K α radiation (1486.6 eV, 300 W) for excitation. The binding energy of the target elements was determined at a pass energy of 23.5 eV with a resolution of <0.4 eV (values were measured every 0.2 eV for the high resolution spectra and 0.8 for surveying) and a takeoff angle of 45°

with respect to the surface normal. The binding energy of the C1s signal was used to correct the spectra for charging. The background was subtracted using the Shirley method in all spectra. To obtain the molar fractions of each species, the peak areas of the measured XPS spectra were corrected with the photoionization cross sections of Scofield,⁴² σ , and the asymmetry parameter, β (orbital geometry),⁴³ which are contained in the sensitivity factors of the acquisition software (MultiPakV6.1A, 99 June 16, copyright Physical Electronics Inc., 1994–1999).

Due to its surface sensitivity the ToF-SIMS analysis is a predestined method for the characterization of protein adsorption.^{44,45} A TOF.SIMS 5 from ION-TOF (Münster) was used for surface analysis. The Mg samples were irradiated with a pulsed Bi_3^+ liquid metal ion beam ($E = 25$ keV) that was electro dynamically bunched down to <1 ns in order to increase the mass resolution. Thus, positive and negative spectra were recorded in high resolution mode ($\Delta m/m > 8000$ at ^{29}Si). The rastered area was $100 \times 100 \mu\text{m}^2$ with 5 measurement spots per sample and polarity. To ensure static conditions, the primary ion dose density (PIDD) was kept at 5×10^{11} ions per cm^2 . Signals were identified using the accurate mass as well as the isotopic pattern and calibrated to C^+ , CH^+ , CH_2^+ , CH_3^+ and C_7H_7^+ for the positive and CH_2^- , C_2^- , CN^- and CNO^- for the negative spectra. For the integration of the signals, Poisson correction was used.²⁷

3 Results and discussion

Fig. 1–5 show a comparison of the electrochemical behaviour of Fe and Mg in SBF, in the absence and presence of albumin. Typical open-circuit potential vs. time curves (Fig. 1) show an increase of OCP with time for Mg (Fig. 1a), as frequently found for magnesium and related to the formation of corrosion product layers on the surface. For Fe (Fig. 1b), the decrease of OCP with time indicates the breakdown of the air-formed native passive film on the iron surface in SBF. The OCP behaviour indicates a significant influence of the addition of BSA in SBF in the case of Mg, whereas for Fe, the effect of the BSA addition is very minor.

Potentiodynamic polarization curves indicate that for Mg active dissolution takes place in SBF, both in the absence and presence of BSA (Fig. 2). In the absence of BSA in solution (Fig. 2a), the anodic current densities decrease with longer immersion times before the measurement; this is accompanied with a shift of the corrosion potential to more positive values, which is in agreement

Fig. 1 OCP for Mg (a) and Fe (b) measured for 24 h in SBF and in SBF + BSA.

Fig. 2 Polarization curves of Mg after 0.25 h, 1 h, 3 h and 24 h immersion in SBF (a) and SBF + BSA (b).

with the OCP measurements. The corresponding curves measured in SBF + BSA indicate lower i_{corr} values and a more positive E_{corr} from the beginning of exposure, as compared to the SBF solution without BSA addition. Fig. 4a clearly indicates lower corrosion rates for 1 h immersed samples in the SBF + BSA solution. For Fe, an active/passive-transition with a short passive range is observed in SBF, both in the absence and presence of BSA (Fig. 3). Spontaneous passivation is not possible for Fe under the here used experimental conditions. The polarization curves are almost independent of the immersion time as well as of the presence of BSA in solution. This can as well be seen in Fig. 4b, where 1 h immersion in SBF and SBF + BSA is compared.

Impedance spectra measured after various immersion times at the particular OCP show the typical features of two capacitive loops and an inductive loop in the Nyquist plots for Mg (Fig. 5). The shape of the impedance spectra remains similar for all immersion times and independent of the presence of BSA in solution; however, the charge-transfer resistance values and their time-dependence strongly change upon addition of BSA to the solution. The time-dependence of R_{ct} will be discussed in more detail below. For Fe, only one time-constant is seen in the Nyquist plots (Fig. 6). The impedance spectra indicate a significantly lower corrosion rate for Fe as compared to Mg, especially in SBF without the addition of BSA.

Fig. 3 Polarization curves of Fe after 0.25 h, 1 h, 3 h and 24 h immersion in SBF (a) and SBF + BSA (b).

Fig. 4 Comparison of the polarization curves after an immersion time of 1 h in SBF with and without BSA for Mg (a) and Fe (b).

The time-dependence of the R_{ct} -values determined from the impedance spectra is summarized in Fig. 7. For Mg, the addition of BSA in solution leads to a significant increase in the R_{ct} -values, especially in the early stages of immersion (Fig. 7a). Similar to previous findings on a Mg alloy, the corrosion inhibiting effect of BSA in SBF decreases with time.²¹ In the case of Fe (Fig. 7b), the effect of BSA addition is much less significant than for Mg. Interestingly, for short-term exposure, the presence of BSA in solution slightly accelerates corrosion of Fe, in contrast to the BSA-inhibiting effect observed for Mg.

The results of the electrochemical characterization therefore clearly indicate that the effect of BSA addition in SBF is significantly stronger for Mg than for Fe. Moreover, the trend for the protein effect is different for both metals: for Mg, a significant corrosion-inhibiting effect is observed by protein addition, especially in the first 3 hours of immersion, whereas for Fe a short-term immersion (up to 3 h) leads to a very modest corrosion-accelerating effect. In order to elucidate the possible reasons for this behaviour, XPS measurements were carried out for samples immersed for 1 and 24 h in SBF as well as in SBF + BSA solutions; the results are summarized in Table 1 for atomic concentrations determined from the N1s, P2p and Ca2p peaks.

Fig. 5 Nyquist plots for Mg after 0.25 h, 1 h, 3 h and 24 h immersion in SBF (a) and SBF + BSA (b).

Fig. 6 Nyquist plots for Fe after 0.25 h, 1 h, 3 h and 24 h immersion in SBF (a) and SBF + BSA (b).

In the presence of BSA in solution, a significantly higher amount of N – indicative of adsorbed BSA – is detected on Mg than on Fe. Moreover, the amount of N decreases more strongly with time for Fe than for Mg. The decrease of the N-concentration with immersion time may be related to the continuous corrosion of the samples in SBF and/or to the formation of corrosion product layers on the sample surfaces, thus masking the N signal. However, as Fe corrodes slower than Mg, one would expect this effect to be less significant for Fe. Therefore, the strong decrease in the N-concentration with immersion time observed for Fe may also be an indication of comparably more weakly bound proteins. The lower N-concentration on the surface of Fe immersed in the BSA-containing solution in any case suggests that albumin adsorption is less favoured on Fe than on Mg; this could be a reason for the weak effect of albumin on the electrochemical behaviour of Fe. The P- and Ca-peaks for Mg and Fe after immersion in SBF without or with BSA addition reveal further interesting differences in the behaviour of these two metals. In the absence of BSA, Mg surface immersion in SBF leads to a significant amount of Ca and P detected on the surface, the Ca- and P-concentrations increasing with time. For Fe, on the other hand, the concentrations of Ca and P

Fig. 7 Comparison of the average charge transfer resistances calculated from the corresponding Nyquist plots; (a) R_{ct} values with the corresponding standard deviation for Mg in SBF with and without BSA; (b) R_{ct} values with the corresponding standard deviation for Fe in SBF with and without BSA.

Table 1 Atomic concentration of N1s, Ca2p and P2p for XPS measurements after 1 h and 24 h immersion of Mg and Fe in SBF with and without BSA

Atomic concentration in at%						
	N (1 h)	N (24 h)	Ca (1 h)	Ca (24 h)	P (1 h)	P (24 h)
Mg SBF	1.03	0.15	8.6	12.06	3.22	5.41
Mg SBF/BSA	16.95	13.33	1.15	1.65	0.35	0.79
Fe SBF	4.19	0	1.52	1.94	1.8	0
Fe SBF/BSA	10.87	3.29	0	0.14	0	0.44

are very low and do not significantly increase upon longer immersion times. The Mg surface hence seems to be more beneficial for precipitation of Ca-phosphate layers from SBF; this may be due to the surface alkalization by Mg dissolution, as the solubility of Ca-phosphates is strongly pH-dependent. It is further noteworthy that only minor amounts of Ca and P are found on the Mg (and Fe) surface in the presence of BSA in solution. This indicates another indirect role of proteins in influencing the corrosion behaviour of Fe and Mg; namely by influencing the formation of Ca-phosphate containing surface layers. This effect will be further investigated in future studies.

A possible reason for the different protein effects on the corrosion of Mg and Fe may be different electrostatic interactions between the negatively charged BSA and the differently charged metal oxide/hydroxide surfaces (see Table 2), which in turn could lead to different amounts of protein adsorption on the surface. In order to study this effect further, additional surface analytical experiments for protein adsorption were carried out with two different proteins, BSA and lysozyme (LYS), which show different surface charges in neutral solutions (Table 2). As the surface analytical data presented above is complicated by simultaneously occurring albumin adsorption and metal dissolution reactions, together with the precipitation of corrosion product layers, these additional surface analyses were carried out on Mg and Fe samples pre-passivated in NaOH. The pre-passivation treatment on the one side leads to a similar surface chemistry on both materials (hydroxide terminated metal oxides) and therefore similar wettability (hydrophilic surfaces). This is advantageous for the elucidation of the role of electrostatic interactions on protein adsorption, as surface wettability is another important factor influencing protein adsorption. On the other side, pre-passivation reduces the reactivity of the Mg and Fe surfaces during immersion in the SBF + protein solutions.

The XPS data for BSA and lysozyme adsorption on passivated Mg and Fe are shown in Fig. 8. Additional results after passivation of the metals in NaOH are shown to elucidate the effect of SBF immersion without proteins. For both metals, an increase of Ca and P can be observed accompanied by a decrease of O, Mg and

Table 2 IEPs for the oxides/hydroxides of Mg and Fe and the proteins, BSA and LYS

	MgO/Mg(OH) ₂	FeO/Fe(OH) ₂	BSA	LYS
IEP	10.8–14	6.6–8.6	4.8–5.2	10.5–11.8

Fig. 8 Results of the XPS measurements of the adsorption experiments. Atomic concentration of several signals after passivation, after immersion in pure SBF and after immersion in SBF with BSA and LYS for Mg (a) and Fe (b).

Fe after SBF treatment, indicating a partial coverage with calcium phosphate compounds of the metal oxide surfaces. Ca and P signals increase much stronger for magnesium than for iron, suggesting a favoured formation of calcium phosphate compounds on magnesium, as was already mentioned above.

As the C1s signal contains contributions from surface contamination as well as from possible carbonate and protein layers on the surface, the amount of protein on the surface can be better determined from the N1s signal. Comparing the atomic concentration of N for Mg immersed in the two protein-containing solutions shows a significantly higher amount of BSA than of lysozyme adsorbed on the surface. For Fe, the trend is reversed in that a higher N-concentration is measured in the lysozyme-containing solution as compared to the BSA-containing solution. Looking at the data in Table 2, the amount of proteins adsorbed indeed seems to follow the expectations based on considering electrostatic interactions: for the strongly positively charged Mg surface, the negatively charged BSA adsorbs in larger amounts than the positively charged lysozyme, whereas for Fe oxides/

Fig. 9 Peak area ratios calculated from three characteristic protein signals and the substrate signals (Mg and Fe). As signals characterize proteins on the surface, peaks at $m/z = 72$, $m/z = 110$ and $m/z = 120$ corresponding to $C_3H_6NO^+$ (Asn) and $C_4H_{10}N^+$ (Val), $C_5H_8N^+$ (His) and $C_8H_{10}N^+$ (Phe), respectively, were used; (a) peak area ratios for Mg after immersion in pure SBF and after immersion in SBF with addition of BSA and LYS; (b) peak area ratios for Fe after immersion in pure SBF and after immersion in SBF with addition of BSA and LYS.

hydroxides, a stronger electrostatic attraction is expected for lysozyme and indeed a higher amount of protein adsorption is indicated by the XPS data.

The presence of protein adsorption layers on the Mg and Fe surfaces was verified by ToF-SIMS measurements. Fig. 9 shows the peak area ratios of 3 characteristic protein signals and the signals of the particular substrate (Mg respectively Fe). Signals at $m/z = 72$, corresponding to $C_3H_6NO^+$ and $C_4H_{10}N^+$, at $m/z \sim 110$, corresponding to $C_5H_8N^+$ (Asn and Val), at $m/z \sim 110$, corresponding to $C_5H_8N^+$ (His), and at $m/z \sim 120$, corresponding to $C_8H_{10}N^+$ (Phe), were chosen to verify the protein adsorption on the Mg and Fe surfaces. The described peaks are shown in Fig. 10 and 11. For Mg, it can be seen that all peak area ratios increase significantly after immersion in the BSA containing solution compared to the immersion in pure SBF (Fig. 9a). For the immersion in SBF + LYS, only a slight increase of the peak area ratios compared to Mg in pure SBF is detectable, indicating less protein adsorption for LYS than for BSA on Mg. Fig. 10 confirms these results, showing no protein peaks for Mg immersed in pure SBF, clear protein peaks for the addition of BSA to SBF and only small protein peaks for the addition of LYS to SBF.

Fig. 10 Signals used for the calculation of the peak area ratios for Mg after immersion in pure SBF and in SBF with BSA and LYS. $m/z = 24$, $m/z = 25$ and $m/z = 26$ corresponding to Mg^+ , $^{25}Mg^+$ and $^{26}Mg^+$, respectively, were used as the substrate signals. The amino acid residues at $m/z = 72.05$ (Asn), $m/z = 72.09$ (Val), $m/z = 110.07$ (His) and $m/z = 120.08$ (Phe) were chosen as the characteristic protein signals.

Fig. 11 Signals used for the calculation of the peak area ratios for Fe after immersion in pure SBF and in SBF with BSA and LYS. $m/z = 55.93$ corresponding to Fe^+ was used as the substrate signal. The amino acid residues at $m/z = 72.05$ (Asn), $m/z = 72.09$ (Val), $m/z = 110.07$ (His) and $m/z = 120.08$ (Phe) were chosen as the characteristic protein signals.

For Fe, the peak area ratios (Fig. 9b) also show a significant increase after the addition of BSA to SBF. Unlike for Mg, the addition of LYS to SBF leads to a further increase in peak area ratios, indicating a higher adsorption of LYS than for BSA on the Fe surface. The peaks used for the verification of the protein adsorption on Fe are shown in Fig. 11. There are no characteristic protein peaks visible for the immersion of Fe in pure SBF. For the addition of BSA as well as for the addition of LYS, clear protein peaks can be detected, showing more or less the same intensity for both proteins. A difference for BSA and LYS is the intensity of the Fe signal, indicating a higher surface coverage of Fe by LYS, especially if the fact is taken into account that LYS is a much smaller molecule than BSA.

For Mg as well as for Fe, the ToF-SIMS results verify the presence of protein adsorption on the surface. Even though a direct comparison of Mg and Fe with ToF-SIMS is not possible due to the fact that ToF-SIMS is a semi-quantitative method, the results for Mg and Fe correlate well with the findings of the XPS measurements.

4 Conclusions

Proteins (here: bovine serum albumin, BSA) can inhibit or accelerate metal corrosion. In the present study, the effect of BSA on Mg and Fe corrosion was investigated. The influence of BSA on the electrochemical behaviour of Fe was found to be very minor as compared with Mg. Thus, while BSA was found to show a strong inhibition of Mg corrosion, BSA caused a slight acceleration of Fe corrosion in simulated body fluid for the first hours. Surface analysis with XPS indicates that this may be related to a favoured adsorption of BSA on Mg compared to Fe.

A comparison of the adsorption behaviour of two different proteins, BSA and LYS, suggests that the adsorption behaviour can be explained by considering electrostatic interactions between the charged proteins and metal oxide/hydroxide layers of different surface charges. The extent of these effects depends on the metal cation–protein binding strengths. In the future, metal release studies may further elucidate the influence on proteins on corrosion. These findings are not only of interest in elucidating the effect of proteins on metal corrosion, but may be of general relevance for understanding the role of metal oxide surface charges in corrosion processes, such as localized breakdown of passivity.

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