Author: Wang, Xiaojian; Wen, Cuie
Title: Corrosion protection of mesoporous bioactive glass coating on biodegradable magnesium
Year: 2014
Journal: Applied Surface Science
Volume: 303
Pages: 196-204
URL: http://doi.org/10.1016/j.apsusc.2014.02.147

Copyright: Copyright © 2014 Elsevier. NOTICE: this is the author's version of a work that was accepted for publication in Applied Surface Science. Changes resulting from the publishing process, such as peer review, editing, corrections, structural formatting, and other quality control mechanisms may not be reflected in this document. Changes may have been made to this work since it was submitted for publication. A definitive version was subsequently published in Applied Surface Science, [VOL 303, (June 2014)] DOI http://doi.org/10.1016/j.apsusc.2014.02.147

This is the author's version of the work, posted here with the permission of the publisher for your personal use. No further distribution is permitted. You may also be able to access the published version from your library.

The definitive version is available at: http://doi.org/10.1016/j.apsusc.2014.02.147
Corrosion protection of mesoporous bioactive glass coating on biodegradable magnesium

Xiaojian Wang, Cuie Wen

Faculty of Engineering and Industrial Science, Swinburne University of Technology, Hawthorn, Victoria 3122, Australia

1 Corresponding author. Tel.: +61 3 92145651; Fax: +61 3 92145050
E-mail address: cwen@swin.edu.au (C. Wen).

Highlights

A mesoporous bioactive glass (MBG) coating was prepared on pure Mg substrate. The MBG coating showed a high specific surface area of 280.6 m²/g and ordered mesopores of 4 nm. The MBG coated Mg samples showed superior corrosion resistance to the bioactive glass (BG) coated and uncoated Mg samples over the immersion period of 14 days in simulated body fluid (SBF). The corrosion rate of the MBG coated Mg samples decreased with immersion time, as evidenced by an increased charge transfer resistance (R_{ct}) in SBF.

Abstract

A mesoporous bioactive glass (MBG) coating was synthesized and coated on pure Mg substrate using a sol-gel dip-coating method. The MBG coating uniformly covered the Mg substrate with a thickness of ~1.5 µm. Electrochemical and immersion tests were performed in order to investigate the biodegradation performance of Mg with and without different surface coatings in simulated body fluids (SBF) at 37 °C. Results revealed that the MBG coated Mg displayed a significantly lower biodegradation rate, in comparison with normal bioactive glass (BG) coated and uncoated Mg samples.

Keywords: Biomaterials; Magnesium; Biodegradable; Mesoporous

1. Introduction

For many years, metallic biomaterials such as titanium alloys, stainless steels and cobalt-based alloys have been successfully applied as orthopedic implants. In general, the implants stay in the human body permanently and later on may cause adverse reactions due to ion release [1-3]. Recently, magnesium alloys have been proposed as promising biodegradable metal based implants [4-12]. Magnesium alloy implants are particularly interested because of their comparable mechanical properties to natural bone and the biodegradability in the biological system. However,
the clinical applications of Mg based implants at present are still limited by their relatively high degradation rate under physiological conditions, which is accompanied by large volume of hydrogen gas evolution [4, 5]. To improve the corrosion resistance of magnesium based biomaterials, one method is to develop novel corrosion resistant alloys or amorphous structures. As an example, MgZnCa metallic glasses have been reported having improved degradation characteristics with a reduction in hydrogen gas evolution and the same good tissue compatibility, in comparison with crystalline Mg alloy implants [5, 10, 13]. Other Mg alloys such as WE43 (Mg-4Y-3RE), Mg-Zn-Mn, Mg-Zr-Sr and Mg-Ca alloys also have been extensively studied for biomedical applications [9, 12, 14, 15]. In addition to developing new Mg based alloys, another approach to reduce the corrosion of Mg alloys is by applying organic or inorganic coatings [16-25]. Distinct modification of the implant surface may lead to different surface properties that eventually could lead to better bone-to-implant interfaces. Tailoring of the surface of biomaterial with a suitable inorganic or organic coating may lead to the decreasing of corrosion rate, the increasing of biocompatibility and osteo-conductivity. A series of methods have already been developed for surface modification of Mg alloys, such as hydroxyapatite coating [16, 18], anodization [20], alkali-heat-treatment [22], fluoride conversion coating [23] and polymer coatings [24, 25]. By applying coatings, the corrosion rate of Mg can be significantly reduced. The mass loss of hydroxyapatite (HA) coated AZ31 Mg alloy was reported as 20% less compared to the uncoated samples, after 15 days immersion in 3 wt.% NaCl solution [26]. The use of bioactive coatings, such as CaSiO$_3$ and CaHPO$_4$$\cdot$$2$H$_2$O, could provide corrosion protection to the Mg alloy, meanwhile promote cell attachment and proliferation to the coated Mg alloy [27].

Mesoporous bioactive glass (MBG) has a highly ordered mesoporous channel structure with pore sizes ranging from a few nanometers [28]. A major feature of MBG is that it possesses an increased specific surface area and pore volume, which leads to superior bioactivity in comparison with nonporous bioactive glass [28]. Yan et al. [28, 29] demonstrated that a layer of apatite could be induced on the surface of MBG in a short time of 4-8 h in simulated body fluid (SBF). Bioactive
scaffolds made of MBG have been shown having improved in vitro and in vivo biological properties, compared with their solid counterpart [30]. In order to improve implant-bone integration, MBG coatings were applied on stainless steel plate. The mesoporous texture and release of bioactive ions from the coating improved the protein adsorption, osteoblastic MC3T3-E1 cell proliferation, differentiation, cytoskeletal organization and the immobilization of AsMg [31]. The modification of metallic implant with bioactive coatings might result in superior performance in particular during the early stage of post-implantation. Despite recent advances in the application of mesoporous bioactive glass on metallic implants, only limited study has been carried out on Mg and its alloys [32]. The corrosion behavior of MBG coated Mg alloys is still unclear. In the present work, mesoporous bioactive glass coatings were synthesized on commercially available pure Mg substrate using a sol–gel dip-coating method. The non-mesoporous bioactive glass (BG) coating was also synthesized as a comparison. The morphologies of BG and MBG coatings were characterized by scanning electron microscopy (SEM). The corrosion mechanism and the electrochemical behavior of the uncoated, BG and MBG coated pure Mg in SBF were evaluated using potentiodynamic polarization, electrochemical impedance spectroscopy (EIS) and immersion tests.

2. Materials & Methods

2.1. Preparation of MBG and BG coatings

The synthesis of MBG sol (Si/Ca/P molar ratio 80/15/5) was detailed in previous publications [28, 29]. In a typical synthesis, 4.0 g of Poly(ethylene glycol)-block-poly(propylene glycol)-block-poly(ethylene glycol) (P123, Mw 5800, Sigma–Aldrich) were dissolved in 60 g ethanol first, then 6.7 g of tetraethyl orthosilicate (TEOS) (98% purity, Sigma–Aldrich), 0.73 g of triethyl phosphate (TEP) (99.8% purity, Sigma–Aldrich), 1.4 g of Ca(NO₃)₂•4H₂O (Sigma–Aldrich), and 1.0 g of 0.5 M HNO₃ were added consequently and stirred at room temperature for 24 h. The BG sol was prepared with the same procedure without the addition of molecular template P123. Commercially
available pure Mg was machined to obtain substrates with a diameter of 10 mm and a thickness of 3.0 mm, which were then ground with SiC papers progressively to 2000 grit, then ultrasonically cleaned in acetone, ethanol and distilled water for 10 min at each step. Subsequently, Mg substrates were dried and dipped into the MBG and BG sol for 60 s, aged at room temperature for 24 h. To obtain thick coating, this process was carried out 3 times, after which, the coated samples were dried at 60 °C and heat treated at 500 °C for 1 h with a heating rate of 1 °C per minute. The mesoporous bioactive glass coated samples were denoted MBG, and the non-mesoporous bioactive glass coated samples were referred to BG. Pure Mg discs without coatings were used as the control.

2.2. Characterizations of BG and MBG coatings

The morphology of cross-section and surface morphology of the BG and MBG coatings were observed using a field-emission scanning electron microscope (FE-SEM, Zeiss 40VP), and the chemical composition of the samples were investigated by energy dispersive spectroscopy (EDS, Oxford Instruments Inca X-act). The Brunauer-Emmett-Teller (BET) of the BG and MBG powders, synthesized using the same process as described above, were measured using nitrogen (N₂) sorption analyses (Micromeritics Tristar 3020). Prior to the measurement, the samples were degassed at 150 °C on a vacuum line for 18 h. A transmission electron microscope (TEM) was used to observe the structure of MBG coatings (FEI Tecnai F20).

2.3. Electrochemical tests

The corrosion behavior of the uncoated, BG and MBG coated Mg discs in SBF was investigated using potentiodynamic polarization tests and electrochemical impedance spectroscopy (EIS) analyses (PAR 2273, Princeton Applied Research). A three-electrode cell was employed, with a platinum electrode as the counter electrode, a saturated calomel electrode (SCE) as the reference electrode, and the uncoated and coated Mg samples with an exposed area of 0.28 cm² as the working electrode. Before commencing the potentiodynamic polarization and EIS tests, the working
electrode was stabilized in SBF for 10 min. The potentiodynamic polarization tests were recorded at a rate of 1.0 mV/s, and the frequency range used for impedance spectra was 100 kHz to 0.01 Hz.

2.4. Immersion tests

In order to verify the long term corrosion resistance, the uncoated, BG coated and MBG coated Mg samples were immersed in SBF for different periods (3, 7, 14 d) at 37 °C. The SBF volume-to-sample area ratio was 100 mL per cm². At the end of each time points, two samples were taken from the SBF for the SEM observation and five samples were collected for evaluating the average weight loss. All samples collected from SBF were ultrasonically cleaned in distilled water and dried in the air. All the corrosion products were removed by chromic acid before the normalized weight loss (n=5) was calculated.

3. Results and discussion

3.1. Coating characteristics

Fig. 1 (a)-(e) present the surface morphology and cross-section of the uncoated, BG coated and MBG coated Mg substrates. As shown in Fig. 1 (a), the surface marks from the sample preparation were observed on the surface of uncoated Mg. After being coated with BG (Fig. 1 (b)) or MBG (Fig. 1(d)), the surface morphology was changed with less scratch seen on the surface. The thickness of the BG and MBG coatings were similar at around 1.5 µm (Fig. 1(c) and (e)). The MBG coating was observed crack free. The formation of cracks is commonly observed in sol-gel coatings, due to the mismatch of thermal expansion coefficients between the substrate and the coating material, which leads to residual stress in the coating material, and subsequently the cracking of the coating [33]. However, the cracks did not form on the MBG coating, possibly because the molecular template P123 inhibited the agglomeration of the colloidal particles in the MBG sol, afterwards reducing surface tension in synthesizing coating materials. At high magnification, the BG coating showed a porous structure, with a pore diameter of around 200 nm.
In contrast, there were no such large pores to be observed on the surface of the MBG coating. The periodicity of the lattice in MBG is approximately 7 nm in the case of lamellar ordering, with a pore diameter of approximately 4 nm. N\textsubscript{2} sorption of the MBG coating showed a type IV isotherm and pore size distribution in the range of 3-5 nm (Fig. 2), typical characteristics of a mesoporous structure [34]. The TEM image (Fig. 2 (c)) shows that the MBG coating exhibits an ordered mesoporous channel structure. The result of the TEM observation is consistent with the N\textsubscript{2} sorption analysis. The measured Brunauer-Emmett-Teller (BET) surface area was 280.6 m\textsuperscript{2}/g and 50.6 m\textsuperscript{2}/g for MBG and BG coating, respectively. The high surface area of the MBG coating is attributed to the existence of ordered mesochannels [28, 35].

3.2. Corrosion resistance of the uncoated, BG coated and MBG coated Mg in SBF

EIS and potentiodynamic polarization tests were performed in order to evaluate the corrosion protection of the BG and MBG coatings. The values of the corrosion potential (E\text{corr}) and corrosion current density (i\text{corr}) were derived from the polarization plots (Fig. 3(a)). Nyquist plots of the uncoated and coated samples are shown in Fig. 3(b). The real impedance could to be referred to the charge transfer resistance - R\text{ct}, and is an indicator of corrosion resistance [36]. low corrosion current density - i\text{corr}, high charge transfer resistance - R\text{ct}, and high corrosion potential - E\text{corr}, indicate good corrosion resistance [20, 37]. The electrochemical corrosion parameters of the uncoated, BG coated and MBG coated Mg samples are listed in Table 1. In comparison with the uncoated Mg (-2.03 V), the E\text{corr} value of the BG coated sample showed a shift of 10 mV to -2.01 V. However, the E\text{corr} value exhibited a substantial shift of 620 mV to -1.71 V for the MBG coated sample, which indicates that MBG coating significantly improved the corrosion resistance of the sample. By applying coatings, the corrosion current density (i\text{corr}) also reduced from 2.8 x 10\textsuperscript{-3} A/cm\textsuperscript{2} for the uncoated Mg to 7.8 x 10\textsuperscript{-5} A/cm\textsuperscript{2} and 1.1 x 10\textsuperscript{-6} A/cm\textsuperscript{2} for the BG and MBG coated samples respectively (Table 1). Fig. 3 (b) revealed that the R\text{ct} value changed from 0.65 k\textOmega cm\textsuperscript{2} (uncoated Mg) to 0.63 k\textOmega cm\textsuperscript{2} and 1.05 k\textOmega cm\textsuperscript{2} for BG and MBG coated samples, respectively. The
results of electrochemical tests revealed the enhanced corrosion resistance provided by the BG and MBG coatings, compared to the uncoated Mg substrate.

Previous research has shown that electrochemical corrosion measurement of Mg alloys is accompanied by breaking up of the metal into fine particles, thus the electrochemical corrosion measurement needs to be further verified by the direct mass losses in media. The corrosion rate calculated by the weight loss method and the electrochemical method can be different by one magnitude [38]. To better understand the corrosion process of the uncoated and coated samples in SBF, immersion tests were carried out. The corrosion of Mg in aqueous solution includes the chemical reactions as follows [7, 37]:

\[
\begin{align*}
\text{Mg} & \rightarrow \text{Mg}^{2+} + 2e^- \quad \text{(anodic reaction)} \quad (1) \\
2\text{H}_2\text{O} + 2e^- & \rightarrow \text{H}_2 + 2\text{OH}^- \quad \text{(cathodic reaction)} \quad (2)
\end{align*}
\]

According to Eqs. (1) and (2), the anodic dissolution of Mg would lead to the weight loss of the Mg substrate. Fig. 4 (a) presents the pH changes vs immersion time for the uncoated, BG coated and MBG coated Mg samples in SBF. It can be seen that the immersion of the uncoated Mg showed stronger alkalization than those of the BG and MBG coated Mg. As the corrosion of Mg in SBF introduces OH\(^-\), stronger alkalization indicates a higher corrosion process. The normalized weight loss of uncoated, BG and MBG coated Mg samples is shown in Fig. 4 (b). The weight losses of the uncoated Mg were 10.3%, 36.5% and 57.1% after 3, 7, and 14 days immersion in SBF, respectively.

The thickness of naturally formed oxide film on Mg is around \(~10\) nm [39]. When Mg is immersed in SBF, magnesium hydroxide (Mg(OH)\(_2\)) rapidly deposited on the surface of the substrate. The magnesium hydroxide would further react with chloride ions to form the soluble MgCl\(_2\) [37, 39,
Corrosion cracks were observed on the uncoated Mg and the cracks grew larger with an increase in time, as shown in Fig. 5 (a) and (b). The EDS result showed that the corrosion product of pure Mg, after soaking in SBF for 14 d, is mainly Mg(OH)₂ or MgO with a small amount of CaP precipitate, as shown in the insert of Fig. 5 (b). Witte et al. [41] assumed that the corrosion layer of Mg alloys in body fluid was composed of magnesium oxide or magnesium hydroxide and CaP compounds. Thus, it is reasonable to assume that a protective layer with similar compositions was formed in this study.

In the case of the BG coated Mg substrate, the weight loss was close to that of uncoated Mg, with the loss of 10.4%, 34.6%, 38.5% after 3, 7 and 14 days immersion in SBF, respectively, which indicates that the BG coating did not provide effective protection of Mg substrate underneath. The corrosion protection of coatings is closely related to the surface morphology and the composition of the material [42]. As shown in Fig. 1 (b), there were pores observed in the BG coating. When immersed in SBF, the corrosion media easily penetrated through the BG coating and reacted with the Mg substrate underneath, producing hydrogen gas. The released hydrogen widened the gap between the cracks and broke down the coating layer, as shown in Fig. 5 (c). After 14 d immersion in SBF, larger amount of CaP precipitations were found on the corroded surface of the BG coated Mg in comparison with those on the uncoated Mg sample, insert of Fig. 5 (d). There was no coating element, such as Si, detected by EDS, which indicates that the corrosion layer was thick, and a more severe corrosion process occurred. The weight losses for the MBG coated Mg substrate were 3.7%, 7.1% and 10% after 3, 7 and 14 days immersion in SBF, respectively, which were significantly lower than those of the uncoated and BG coated Mg. This indicates that the MBG coating effectively retarded the corrosion process of the Mg substrate. The results of weight loss tests were consistent with the results of potentiodynamic polarization, where the lowest \( i_{\text{corr}} \) was observed for the MBG coated sample. The morphology of the MBG coated substrate after 3 and 14 days is shown in Fig. 5 (e) and (f). It can be seen that a corrosion layer was observable after the immersion tests. EDS results further demonstrated that 6.16 at% Ca, 6.16 at% P and 9.10 at% Mg
were found on the surface. More Ca, P and less Mg ions were detected in the corrosion layer than that of the uncoated and BG coated Mg. Elements from the MBG coating layer such as Si were also detected, which indicates that the corrosion layer is thin in nature. It was reported that the MBG could rapidly induce a CaP layer depositing on its surface, when immersed in SBF and the CaP inducing ability was attributed to its high surface area and the large amount of OH group presented on its surface [28, 29]. Therefore it is assumed that the MBG coating in the present work also induced a CaP layer on the surface. This layer was shown to provide effective protection to the substrate and slowed down the corrosion rate of Mg. It is assumed that the crack free nature of the MBG coating might also contributed to the improved corrosion protection. The uniform coating layer stopped direct contact of electrolyte and metal substrate.

EIS analysis can evaluate the barrier and the deterioration mechanism of a coating. Fig. 6 shows the Nyquist plots of the uncoated, BG and MBG coated Mg samples soaked in SBF for 3-14 d. To validate the EIS data, Kramers–Kronig transforms were calculated using the ZSimpWin software V2.0 and the results were shown in Fig. S1-S3. The real-to-imaginary axis transforms were shown in Fig. S1-S3 (a), (c), (e). The real-to-imaginary axis transforms were within the accuracy of the experimental data, but those for the imaginary-to-real axis, Fig. S1-S3 (b), (d), (f), displayed slight deviations from the experimental data at low frequencies, which might indicate the system is not completely stable when doing EIS measurement. The results suggested that the systems remained relatively stable during the EIS measurement and satisfied the constraints of Linear System Theory (LST) [43, 44].

The diameter of the semicircle in Fig. 6 gives the charge transfer resistance (Rct) at the electrode/electrolyte interface. From the Rct value, the exchange current density (j0) can be calculated using the following equation [45, 46]:

\[
    j_0 = \frac{RT}{nFR_{ct}}
\]  

\( (3) \)
where $n$ is the number of transferred charges, $F$ is the Faraday constant. Apparently, $j_0$ is inversely proportional to $R_{ct}$ [46]. Consequently, charge transfer resistance could be used to evaluate the corrosion property of the material. For the all three samples, the capacitive loop enlarged with the increase of the immersion time. The enlarged capacitive loops indicated the charge transfer resistance ($R_{ct}$) increased with immersion time, namely an increase in corrosion protection provided by the deposition of corrosion products or the coating itself. This observation is consistent with findings in other Mg alloys [36, 40]. The $R_{CT}$ value at day 14 for the MBG coated samples was 28.91 k$\Omega$ cm$^2$, in comparison with 21.01 k$\Omega$ cm$^2$ for the uncoated sample, and 17.45 k$\Omega$ cm$^2$ for the BG coated sample. The Bode plots and fitted results of the uncoated, BG and MBG coated Mg samples after soaking in SBF are shown in Fig. 7 (a) - (c). The equivalent circuit (EC) proposed to analyze the spectra are shown in Fig. 7 (d), where $R_s$ represents the resistance of SBF, As all the samples were measured after SBF immersion, there was a layer of CaP/Mg(OH)$_2$ detected on top of the coating film. Therefore, $R_{L1}$ is the resistance of the corrosion product layer, which was mainly composed of CaP and Mg(OH)$_2$. $R_L$ is the layer resistance and $R_{ct}$ is the charge transfer resistance of the coating film. $Q_{L1}$ and $Q_{dl}$ are the constant phase elements (CPE) which correspond to the CaP/Mg(OH)$_2$ layer, coating film, respectively [47-49]. The inductive behavior characterized by resistance $R_L$ and inductance $L$ indicated the existence of metastable Mg$^+$ during the dissolution of magnesium substrate (the low frequency inductance loop). The low frequency inductive loop may also be related to the relaxation reaction of the adsorbed species from SBF such as chloride ions [50]. The fitted EIS spectra of the un-coated and coated samples are presented in Table 2. The polarization resistance ($R_P$) of the samples was obtained by adding $R_L$ and $R_{CT}$. It was shown that the polarization resistance increased with the immersion time, which means the corrosion rate decreased with the time. After immersion in SBF for 14 d, the $R_P$ values were recorded to be 31.52 k$\Omega$ cm$^2$, 38.06 k$\Omega$ cm$^2$ and 48.97 k$\Omega$ cm$^2$ for the uncoated Mg, BG and MBG coated samples. The observation of increased $R_{ct}$ and $R_P$ value of the MBG coated sample indicates that the coating retarded the corrosion rate of Mg.
4. Conclusions

A mesoporous bioactive glass (MBG) coating was prepared on pure Mg substrate by using a sol–gel dip-coating technique. The corrosion behavior of the uncoated, bioactive glass (BG) coated and MBG coated Mg was investigated. Conclusions can be summarized as follows:

1. Electron microscopy revealed that the MBG coating uniformly covered the substrate, with mesopores of 4 nm presented in the coating. The thickness of the coating was ~ 1.5 µm. The measured Brunauer-Emmett-Teller (BET) surface area for the MBG was 280.6 m²/g. The high surface area of the MBG coating is attributed to the existence of ordered mesochannels.

2. The MBG coated samples showed better corrosion resistance to the bioactive glass (BG) coated and uncoated Mg samples over the immersion period of 14 days in SBF. The weight loss of the MBG coated samples lost 10% of its original weight, while the uncoated Mg showed a weight loss of 57%.

3. After an immersion in SBF for 14 days, a larger amount of CaP compounds were found on the MBG coated substrates in comparison with the BG and uncoated Mg samples.

Supporting information available: Kramers–Kronig validations of the impedance data were shown in Fig. S1-S3. This material is available free of charge.

Acknowledgments

This research is financially supported by the Australian Research Council (ARC) through the ARC Discovery Project DP110101974.

References


Captions of Figures:

**Fig. 1.** Surface morphology of (a) the uncoated Mg, (b) the BG coated Mg substrate, insert is enlarged view of (b), (c) cross-section of the BG coated Mg substrate, (d) the MBG coated Mg substrate, insert is the enlarged view of (d), and (e) cross-section of the MBG coated Mg substrate.

**Fig. 2.** (a) Nitrogen sorption isotherms of BG and MBG coating, (b) pore size distribution of the BG and MBG coating, and (c) TEM image of the MBG coating.

**Fig. 3.** (a) Potentiodynamic polarization curves and (b) Nyquist plots of the uncoated, BG coated and MBG coated Mg samples in SBF.

**Fig. 4.** (a) pH values of uncoated, BG coated and MBG coated Mg immersion in SBF and (b) Weight loss of uncoated, BG and MBG coated Mg in SBF after removing corrosion products.

**Fig. 5.** SEM images of surface morphology of: (a) the uncoated Mg after 3 d and (b) 14 d immersion in SBF, insert is the EDS result of the marked area in (b); (c) the BG coated Mg after 3 d and (d) 14 d immersion in SBF, insert is the EDS result of the marked area in (d); (e) the MBG coated Mg after 3 d and (f) 14 d immersion in SBF, insert is the EDS result of the marked area in (f).

**Fig. 6.** (a)-(c) Nyquist plots of the uncoated, BG and MBG coated Mg after immersion in SBF for 3, 7, 14 d, respectively.

**Fig. 7.** (a)-(c) Bode plots of the uncoated, BG and MBG coated Mg after immersion in SBF for 3, 7, 14 d, respectively, and (d) Equivalent circuits used for modeling.
Tables:

**Table 1.** Corrosion properties of the uncoated, BG coated and MBG coated Mg substrates in SBF

<table>
<thead>
<tr>
<th>Samples</th>
<th>$E_{corr}$ (V vs. SCE)</th>
<th>$I_{corr}$ (A/cm$^2$)</th>
<th>$R_t$ (kΩ cm$^2$)</th>
<th>Corrosion rate (mm/year)*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Uncoated</td>
<td>-2.03</td>
<td>$2.8 \times 10^{-3}$</td>
<td>0.65</td>
<td>8.29</td>
</tr>
<tr>
<td>BG coated</td>
<td>-2.01</td>
<td>$7.8 \times 10^{-5}$</td>
<td>0.63</td>
<td>0.23</td>
</tr>
<tr>
<td>MBG coated</td>
<td>-1.71</td>
<td>$1.1 \times 10^{-6}$</td>
<td>1.05</td>
<td>$3.28 \times 10^{-3}$</td>
</tr>
</tbody>
</table>

*Corrosion rate calculated from corrosion current*
Table 2. EIS fitted results for spectra obtained from the uncoated, BG coated and MBG coated Mg substrates after immersion in SBF

<table>
<thead>
<tr>
<th>Samples</th>
<th>$R_s$ ($\Omega \text{ cm}^2$)</th>
<th>$Q_{L1}$ ($10^6 \text{F cm}^{-2}$)</th>
<th>$R_{L1}$ ($\Omega \text{ cm}^2$)</th>
<th>$Q_{dl}$ ($10^6 \text{F cm}^{-2}$)</th>
<th>$n$</th>
<th>$R_{ct}$ ($\Omega \text{ cm}^2$)</th>
<th>$R_L$ ($\Omega \text{ cm}^2$)</th>
<th>$L$ ($10^4 \text{ H cm}^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg3d</td>
<td>237</td>
<td>16.1</td>
<td>2545</td>
<td>564.5</td>
<td>0.50</td>
<td>2564</td>
<td>1556</td>
<td>4.2</td>
</tr>
<tr>
<td>BG3d</td>
<td>230.8</td>
<td>19.2</td>
<td>3195</td>
<td>954.5</td>
<td>0.87</td>
<td>1641</td>
<td>516.3</td>
<td>2.9</td>
</tr>
<tr>
<td>MBG3d</td>
<td>301.7</td>
<td>27</td>
<td>2739</td>
<td>941.1</td>
<td>0.92</td>
<td>4946</td>
<td>1664</td>
<td>64.2</td>
</tr>
<tr>
<td>Mg7d</td>
<td>342.3</td>
<td>1.26</td>
<td>140.4</td>
<td>35.3</td>
<td>0.48</td>
<td>7058</td>
<td>610</td>
<td>65.5</td>
</tr>
<tr>
<td>BG7d</td>
<td>341.9</td>
<td>22.6</td>
<td>4897</td>
<td>48.6</td>
<td>0.94</td>
<td>8430</td>
<td>6541</td>
<td>8.6</td>
</tr>
<tr>
<td>MBG7d</td>
<td>296</td>
<td>15.9</td>
<td>7849</td>
<td>65</td>
<td>0.85</td>
<td>1661</td>
<td>2464</td>
<td>15.8</td>
</tr>
<tr>
<td>Mg14d</td>
<td>150</td>
<td>42.7</td>
<td>374.4</td>
<td>1.62</td>
<td>0.86</td>
<td>10514</td>
<td>21009</td>
<td>28.7</td>
</tr>
<tr>
<td>BG14d</td>
<td>396.9</td>
<td>21.6</td>
<td>3740</td>
<td>0.42</td>
<td>0.94</td>
<td>20610</td>
<td>17450</td>
<td>21.8</td>
</tr>
<tr>
<td>MBG14d</td>
<td>306</td>
<td>52.2</td>
<td>315.3</td>
<td>1.26</td>
<td>0.76</td>
<td>28913</td>
<td>20054</td>
<td>8.09</td>
</tr>
</tbody>
</table>
Fig. 1.
Fig. 2.
Fig. 3.
Fig. 4.
Fig. 6.
Fig. 7