Initial formation of corrosion products on pure zinc in saline solution

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ABSTRACT

Corrosion product formed on zinc sample during 2 weeks immersion in saline solution has been investigated. The corrosion layer morphology as well as its chemical composition, was analyzed using scanning electron microscopy (SEM), x-ray diffraction (XRD), x-ray photoelectron spectroscopy (XPS) and Fourier transform infrared spectroscopy (FTIR). Electrochemical measurement was used to analyze the corrosion behavior. Zinc oxide, zinc hydroxide and zinc hydroxide chloride were formed on zinc surface in saline solution. The thickness of corrosion layer increased with the time increased. The pure Zn has an estimated corrosion rate of 0.063 mm y\textsuperscript{−1} after immersion for 336 h. Probable mechanisms of zinc corrosion products formation are presented.

1. Introduction

Metallic materials have been widely applied for biomedical applications as orthopedic implants to restore lost functions [1,2]. It is well known that stainless steel 316 L [3,4], titanium and its alloys [5,6], and cobalt-based alloy [7,8] are common selection as metallic implant materials. However, these implants sometimes need to be removed under a secondary surgery after healing. Ideally, an orthopedic implant with acceptable mechanical properties could be biodegraded in accordance with the healing process. During the degradation process, the products are supposed to be non-toxic to human body and be gradually dissolved and absorbed.

Recently, zinc (Zn) and its alloys have attracted increasing attention as new biodegradable metals due to its biological merits, appropriate degradation rate and degradation behavior [9–11]. Zinc is an essential trace element in human physiology, which is widely acknowledged as an essential element for basic biological function [12]. The recommended dietary allowance (RDA) for Zn is 2 mg d\textsuperscript{−1} for infants, 11 mg d\textsuperscript{−1} for men and 8 mg d\textsuperscript{−1} for women [13]. Besides, Hennig et al. found that zinc exhibited a strong antiatherogenic property [14]. The biological merits of zinc meet the basic requirements for biodegradable metals. Mg and Fe have been considered as potential candidate materials for biodegradable metallic [15], while Mg and its alloys show high corrosion rate and are associated with evolution of hydrogen gas [16–18], Fe and its alloys corrode too slow and the corrosion products of which repel neighboring cells and biological matrix [19,20]. From a thermodynamic point of view, i.e. Mg (−2.37 V) < Zn (−0.763 V) < Fe (−0.440 V) (all V values vs. SHE), Zn has a standard electrode potential between Fe and Mg [21], which can theoretically predict that zinc provide intermediate corrosion rate in line with clinic demand.

Bowen et al. implanted pure zinc wires into the abdominal aorta of Sprague–Dawley rats, Zn degradation proceeds in rat arteries at a rate of 10−20 μm y\textsuperscript{−1}, nearly identical to the 20 μm y\textsuperscript{−1} benchmark value for ideal bioabsorbable materials [9]. Another in vivo test revealed that Zn exhibited good hemocompatibility and products of zinc corrosion may suppress the activities of inflammatory and smooth muscle cells [22]. Drelich et al. conducted clinically long term in vivo study, zinc wires implanted in the murine artery exhibited steady corrosion without local toxicity for up to at least 20 months postimplantation [23]. One in vitro evaluation showed that Zn exhibited non-cytotoxicity to endothelial cells [24]. Moreover, Chen et al. studied Zn, Fe and Mg in a long-term course of immersion in PBS solution to trace its dynamic degradation profile and the transient electrochemical results revealed
that the electrochemical potential and corrosion rate of Zn lied between Fe and Mg [25]. However the mechanical property of pure zinc is not allowed to apply in a biodegradable stent [13]. Mg, Cu, Mn and Li were selected as alloying elements to modify the mechanical properties and corrosion properties and the biocompatibility [26–29]. And these reports strongly implied the potential of Zn-based alloys to be used for biodegradable implants.

Corrosion behavior including the corrosion rate measurement and formation of corrosion products is crucial for understanding the basic corrosion processes underpinning absorption of biodegradable metals. By systematically examining the corrosion products formed on Zn, one may understand the evolution of the corrosion products during different immersion interval. Sodium, the major cation of the extracellular fluid, functions primarily in the control of water distribution, fluid balance, and osmotic pressure of body fluids. Chloride, the major extracellular anion, closely follows the metabolism of sodium. Many inorganic ions in physiological environments exert an important impact on the corrosion products of zinc. And the chloride ion is notorious for the corrosion of zinc alloys.

This paper reports the investigation of the corrosion behavior of pure zinc exposed to physiological saline solution (0.9% NaCl), which can be used to simulate the body environment [30].

2. Experimental

2.1. Electrochemical corrosion measurement

Zinc samples were cut into plates with the geometric sizes of 10 mm × 10 mm × 2 mm from 99.99% pure zinc ingot. The backside of the specimen was connected electrically with a copper wire and then was sealed with epoxy to expose the research surface (ca. 1 cm² area). Electrochemical corrosion measurements, including open circuit potential (OCP) vs. time, potentiodynamic polarization (PDP) and electrochemical impedance spectroscopy (EIS), were performed with an electrochemical workstation (ModuLab XM at 37 ± 0.1 °C in 0.9% NaCl solution. A three-electrode set-up was used, containing a working electrode (the pure Zn samples), a reference electrode (saturated calomel electrode, SCE) and counter electrode (a platinum sheet, 1 cm × 1 cm). The potentiodynamic polarization (PDP) curves were carried out at a constant scan rate of 1 mV s⁻¹. The electrochemical corrosion measurements, performed with an electrochemical workstation (ModuLab XM) at 37 ± 0.1 °C in 0.9% NaCl solution. A three-electrode set-up was used, containing a working electrode (the pure Zn samples), a reference electrode (saturated calomel electrode, SCE) and counter electrode (a platinum sheet, 1 cm × 1 cm). The potentiodynamic polarization (PDP) curves were carried out at a constant scan rate of 1 mV s⁻¹, initiating from −1.5 V SCE to −0.7 V SCE. The corrosion potential Ecorr and cathodic Tafel slope were determined by the Tafel linear extrapolation. EIS studies were carried out in a frequency range from 100 kHz to 10 mHz at 10 mV sinusoidal amplitude of open circuit potential. The impedance data were analyzed with ZsimpWin3.5 software and fitted to the equivalent curves.

2.2. Immersion test

Samples were cut into 2 mm thick discs with 10 mm diameter. Prior to immersion, samples were mechanically grounded with silicon carbide sandpapers, then polished with diamond abrasive paste, followed by ultrasonically rinsed in milli-Q water, acetone and ethanol successively to remove surface contaminants. Then, the samples were dried and stored in a vacuum oven, prepared for further investigation.

Samples were immersed in 40 mL 0.9% NaCl (saline solution) at 37 ± 0.1 °C. The samples soaking up to 2 weeks (336 h) were taken out at different temporal intervals and investigated. During the immersion, the pH value of the saline solution was recorded by the FE 20 pH meter (Mettler Toledo). The amount of released Zn²⁺ in the saline solution was evaluated by atomic absorption spectrophotometer (AAS, Thermo Scientific M Series).

For different time interval, the corrosion products on the sample surfaces were removed in the chemical cleaning solution according to ISO 8407[31]: 100 g L⁻¹ NH₄Cl for 2–5 min at 70 °C. Afterwards, the samples were rinsed by ethanol and dried before being weighted. The weight loss (mg cm⁻²) was calculated using the following equation [32]:

\[ \text{Mass loss} = \frac{m_i - m_f}{A} \]

where \( m_i \) is the initial weight of the sample before immersion (mg), \( m_f \) is the final weight of each sample after immersion (mg), \( A \) is the sample surface area exposed to r-SBF (cm²). Also the corrosion rate (CR, mm y⁻¹) of pure Zn can be calculated by the following equation according to ASTM G31-72 [33]:

\[ CR = 87.4 \times \frac{m_i - m_f}{A D t} \]

where \( m_i \) is the initial weight of the sample before immersion (in mg), \( m_f \) is the final weight of each sample after immersion (in mg), \( A \) is the exposed area (cm²); \( D \) is the alloy density (in g cm⁻³); \( t \) is the immersion time (in h).

2.3. Materials characterization

Surface morphology of Zn samples after immersion was investigated by a scanning electron microscope (SEM, FEI Quanta 200) coupled with an Oxford Instrument INCA X-max³-sight EDX analyzer. X-ray photoelectron spectroscopy (PHI 5600 XPS spectrometer) was used to characterize the surface chemical states of samples after immersion. The XPS spectra were recorded using Al Kα radiation (1486.6 eV) as excitation source. The chemical groups of the corrosion products were characterized by Fourier transform infrared spectrometer (FTIR, Nicolet 5700) in the wave number ranging from 600 to 4000 cm⁻¹. X-ray diffraction (XRD) was conducted on the Smart Lab X-ray diffractometer (Rigaku) with Cu Kα radiation. The XRD spectra were collected at angles between 10° and 90° at a rate of 20° min⁻¹.

3. Results and discussion

3.1. Surface morphology

Fig. 1 portrays the surface of pure Zn taken from saline solution at different time during immersion. The samples still had metallic luster shortly after immersion up to 6 h (Fig. 1a). Then the metallic luster disappeared. Although there is severe corrosion sign on the samples immersed after 24 h and 48 h, it was because of the wire which hanged the samples to keep it vertical during the immersion. It is can be seen that localized whitish corrosion product appears on the sample surface after immersion up to 120 h. With the extension of immersion time, the corrosion products increased, which could be attributed to the corrosion products precipitated continuously during immersion (Fig. 1e and h).

Fig. 2 illustrates the corroded surface morphology of zinc after immersion for different periods and the inserts of each image show the magnified feature in the squared area. It can be seen that the surface keeps almost no change up to 48 h immersion with some grain boundary appearing (Fig. 2a and d). By observing the magnified feature, one can see that the nano-roses appear shortly after 6 h immersion on the surface. By extending the immersion time, the nano-roses covered the entire surface. The corrosion product showed clusters distribution after immersion in saline solution for 168 h (Fig. 2e). It also can be observed that there was a primary layer of corrosion products, over which another layer of nano-roses grew (Fig. 2e). And these re-

Fig. 3 were acquired from the cross-sectional observation and line-scan of Zn samples immersed for 120 h, 240 h and 336 h. It can be observed
that the thickness of the corrosion layer increased with the immersion time (Fig. 3a and c). A thin layer (ca. 1.5 μm) was formed on the sample surface after immersion for 120 h (Fig. 3a). With the prolonging of immersion time to 240 h, a compact corrosion layer with thickness of ca. 3 μm was formed (Fig. 3b). The thickness of corrosion product reached a maximum value to 6 μm when the immersion time was prolonged to 336 h (Fig. 3c). And the surface after immersion 336 h was covered by rod-like corrosion products. According to the EDS line scan profiles, it can be observed that the corrosion product layer was mainly consisted of Zn, Cl and O (Fig. 3d and f). It can be seen that the intensity of Zn and O in the corrosion layer enhanced along with the immersion time. The O was enriched in the corrosion layer after immersion for 240 h and the intensity of O become quite stronger than the initial immersion time after 336 h, indicating that corrosion layer was mainly composed by oxygen-containing products.

### 3.2. XRD, XPS and FTIR analysis

Fig. 4 describes the XRD spectra of Zn immersed in saline solution for different time. In addition to the dominant peaks corresponding to Zn phase, the peak of ZnO appeared since the initial immersion stage and its intensity strengthened on the profile with the extension of immersion time, which became the dominant peak when the immersion time extended to 336 h. Number of peaks with relative low intensity for Zn5(OH)8Cl2·H2O were detected on the samples after immersion for 12 h. The peaks for this species also became stronger with the prolonging of time, which indicated the amount of Zn5(OH)8Cl2·H2O increasing in the corrosion products. The peaks for Zn(OH)2 were only detected on the samples after immersion for 336 h, which could be attributed to their low contents that cannot be detected during the initial immersion stage. The results were coincident with the XPS data, clearly testifying the compositions of the corrosion products.

Fig. 5 shows the FTIR spectra of pure Zn sample immersed in saline solution for different time. Peaks at 1640 cm⁻¹ were attributed to H2O bending vibration [34] and rotation modes manifested the existence of crystal water [35]. The broad absorption from 3600 to 3100 cm⁻¹ was attributed to the OH stretching bond [34]. The peak at 868 cm⁻¹ was attributed to Zn-Cl [36]. It can be observed that Zn-Cl was hardly to be detected until after immersion for 120 h. And the intensity of Zn-Cl peak became stronger with the extension of time. The results indicated that more chlorides formed on Zn sample surfaces by extending the soaking time, which verified the presence of chloride species in the corrosion products. FTIR spectra on the species is well in agreement with the analysis retrieved from XRD results.

The set of samples which were immersed after 6 h, 48 h, 120 h, 240 h and 336 h were analyzed by means of XPS in order to evaluate the elemental and chemical compositions of and the results were shown in Fig. 6a. By analyzing the spectra, the corrosion product was mainly composed by Zn, O, Cl elements. There was no significant difference in elemental composition of the corrosion products after different immersion time. Corresponding high resolution spectra of Zn and Cl was collected in order to obtain detailed information about the corrosion products.

The Cl 2p spectra are depicted in Fig. 6b. There is only one chemical status of Cl 2p located at 198.8 eV, which is corresponding to Zn5(OH)8Cl2·H2O species [37]. The peak intensity increased significantly with the time prolonged, indicating that formation of Zn5(OH)8Cl2·H2O in surface is apparent after immersion for longer time. The Zn-2p3/2 spectra are depicted in Fig. 6c. The deconvoluted spectra clearly demonstrated the composition of the corrosion products with the prolonging of immersion time. There were two chemical status when the pure zinc immersed after different times, ZnO/Zn(OH)2 located at 1022.26 eV [38] and Zn5(OH)8Cl2·H2O located at 1021.8 eV [37] (Fig. 6d-g). With the extension of immersion time, the proportion of Zn5(OH)8Cl2·H2O in the corrosion product increased when the immersion time extended. The result of Zn 2p3/2 showed the same trend of corrosion products as Cl 2p and confirmed the presence of Zn5(OH)8Cl2·H2O/ZnO and Zn(OH)2 in corrosion products.

According to the results from FTIR, XPS and XRD, it is confirmed that the predominant components of the corrosion products were zinc oxides (ZnO), zinc hydroxide (Zn(OH)2) and zinc hydroxide chloride (Zn5(OH)8Cl2·H2O). With the immersion time increased, corrosion products precipitated continuously on the surfaces.

### 3.3. pH assessment, dissolution and weight loss test

pH values of the saline solution during zinc immersion as a function of immersion time is shown in Fig. 7a. The pH value increased monotonically with extended time and reached 7.61 after 336 h immersion, owing to the base corrosion reactions of producing OH⁻ anion. Although the increasing tendency of the pH value were different before and after immersion in 120 h, the value generally changed mildly, which could not induce much change to the surrounding culture. Fig. 7b shows the accumulated Zn²⁺ ion of immersed Zn samples as a
function of immersion time. It was obvious that the dissolution of Zn took place consistently as the time prolonged. The release rate of Zn$^{2+}$ increased after 120 h immersion, which was in accordance with the trend of weight loss (Fig. 7c). The slow increase of pH value is likely because of the consumption of products and less generation of OH$^-$, as shown in XRD profile that there were more Zn(OH)$_2$ and Zn$_5$(OH)$_8$Cl$_2$·H$_2$O formed after relatively longer time immersion than those formed at initial stage. Besides, Yadav et al. [39] mentioned that reduction of oxygen was inhibited when there was a thick corrosion layer on zinc, which may reduce the dissolution rate of Zn$^{2+}$. After 336 h, the accumulated release Zn$^{2+}$ was about 210 mg L$^{-1}$. Thus, the average Zn$^{2+}$ release rate was about 0.03 mg cm$^{-2}$ d$^{-1}$. And according to equation (2), the CR of Zn after immersion for 336 h was about 0.063 mm y$^{-1}$.

3.4. Micrograph of corroded Zn sample

Fig. 8 shows optical images of pure Zn samples after soaking in saline solution and removing the corrosion product in order to unveil the underneath corrosion attack. The top view showed uniform corrosion on zinc. Corrosion attack and products formation that underwent homogenously on the whole surface. However, it seems that some voids could be observed (Fig. 8b and c), indicating a tendency of localized corrosion after immersion in saline solution. Boshkov et al. [40] reported that chloride ions (Cl$^-$) participated in the reaction to form zinc hydroxide chloride in the pits and their neighborhood areas. And the localized corrosion in saline solution was in accordance with some research about the in vitro test of Zn. Cheng et al. [21] reported that pure Zn was attacked under localized corrosion in Hank’s solution; and Chen et al. [24] reported that Zn presented apparently cavity/hole- and groove-like morphology underneath the product layer after immersion in PBS for 21 d. Our results confirmed that pure Zn may encounter localized corrosion after immersion in Cl$^-$ containing solution. Thus, pure Zn may not be a promising material for practical application. However, alloy design may be a promising approach to enhance the localized corrosion resistance of zinc.
3.5. Potentiodynamic polarization measurements

Fig. 9a portrays the potentiodynamic polarization (PDP) curves of pure Zn soaking in saline solution up to 48 h. These curves can be divided into several potential domains. The cathodic domain includes potential below $-1.15$ V$_{SCCE}$ for all the curves. At potential below $-1.3$ V$_{SCCE}$, the near vertical stage of current density mainly corresponds to hydrogen generation process (Eq. (3)), whereas the slope region (mainly from $-1.3$ to $-1.2$ V$_{SCCE}$) represents the oxygen consumption process (Eq. (4) and 5).

$$2H_2O + 2e^- \rightarrow 2OH^- + H_2 \quad (3)$$

$$O_2 + H_2O + 2e^- \rightarrow HO_2^- + OH^- \quad (4)$$

$$HO_2^- + H_2O + 2e^- \rightarrow 3OH^- \quad (3)$$

The peaks at $\sim -1.2$ V$_{SCCE}$ in the cathodic branch of the PDP curves likely correspond to the mixed potential of the hydrogen evolution reaction and the anodic dissolution [41,42]. At relative higher potentials, the hydrogen evolution reaction was suppressed. Thus the peaks at $-1.1 \sim -1.0$ V$_{SCCE}$ refer to the mixed potential of oxygen reduction reaction and anodic dissolution. As the immersion time increased, the formation of corrosion product film on the zinc surface hindered the oxygen diffusion [39]. As a result, the cathodic reaction was dominated by hydrogen evolution (it was observed that the peak at cathodic branch on sample immersed for 48 h almost diminished). The anodic branches of samples immersed up to 48 h show only acceleration of anodic dissolution, implying that there is no stable corrosion product formed during the immersion at this stage.

Fig. 9b portrays the PDP curves of sample after being immersed in saline solution from 120 h to 336 h. It is apparent that all the cathodic branch experiences mixed oxygen reduction reactions and hydrogen evolution reaction. Because the corrosion product at this time stage is thicker than that immersion at 48 h, no significant dissolution peaks could be found at cathodic branch on sample immersed for 48 h almost diminished. The anodic branches of samples immersed up to 48 h show only acceleration of anodic dissolution, implying that there is no stable corrosion product formed during the immersion at this stage.

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substrate. This phenomenon demonstrates that the corrosion product formed after 120 h immersion may play a protective role for the substrate. It was reported that zinc showed passive behavior of zinc in NaCl solution attributed to the formation of zinc hydroxide and zinc oxide [43]. According to the XRD results, there were a great quantity of zinc hydroxide and zinc oxide on surface after immersion, which led to the passivation behavior. However, by extending the immersion time, the intrinsic dissolution character of the corrosion products could be revealed.

Fig. 9c summarized the value of \( E_{corr} \) and current density with respect to the immersion time. It is found that the value of \( E_{corr} \) decreases with the increasing of immersion time up to 120 h (Fig. 9c). Then the value of \( E_{corr} \) keeps almost constantly, indicating a stable tendency for long term degradation. The cathodic polarization curves were picked for current density (\( i_{corr} \)) of Zn by using linear extrapolation, which is reliable for active metals. As immersion progressed, the \( i_{corr} \) of Zn increased from 5 \( \mu \)A cm\(^{-2} \) at the initial stage to \( \sim 16 \) \( \mu \)A cm\(^{-2} \) after 336 h immersion, which is due to the formation of zinc hydroxide chloride.

EIS analysis between \( 10^{-2} \) and \( 10^{5} \) Hz with amplitude of 10 mV at the open circuit potential condition was performed on Zn after immersion from 0 to 336 h in saline solution to investigate the influence of immersion on the electrode/electrolyte interface. Fig. 10 shows a series of EIS plots of Zn immersed for different time. The Nyquist plots of sample immersed for up to 48 h was performed in Fig. 10a. It was observed two capacitive loops in Nyquist plots. Meanwhile, two peaks were also found in the Bode plots, representing two time constants. It is acknowledged that a large diameter of the capacitive loop in the Nyquist plots represents a high corrosion resistance of the working electrode [37]. The two loops likely indicated that the corrosion product might contain two distinct layers, a relative dense one and another porous one. It is obvious that the diameter of first capacitive loop increased during the first 48 h, due to the gradually formation of corrosion products to protect the surface. Fig. 10b portrays the Nyquist plot of samples immersed from 120 h to 336 h. The second capacitive loops began to diminish and merged with the first one with the extension of immersion time. There was only one apparent loop for sample immersed for 336 h, indicating the corrosion product might merge to one layer.

The fitted models (a) \( (R_s (Q_1 R_1) (Q_2 R_2)) \) and (b)\( (R_s (Q_1 (R_1 (Q_2 R_2)))) \) in Fig. 10 gave satisfactory results to EIS. The model\( (R_s (Q_1 (Q_2 R_2))) \) was used for the immersion during 48 h and the model\( (R_s Q_1 (R_1 (Q_2 R_2))) \) was used to immersion after 120 h. Both fitted parameters were summarized in Table 1. \( R_1 \) corresponds to a charge-transfer resistance and \( R_2 \) is due to the adsorbed species that contribute to the formation of the corrosion layer. The \( R_1 \) value increased during 48 h and then decreased, the small charge-transfer resistance was due to oxidation of zinc electrode was inhibited by the corrosion products. The corrosion layer covered the whole surface of zinc electrode and its thickness also grew consequently, which was the same as shown at the cross section SEM. \( Q \) is used in place of a capacitor to compensate for the non-homogeneity of system [44]. As reported by Heakal [45], the total resistance value \( R_t \) given by \( R_t = R_1 + R_2 \), which was equal to the charge-transfer resistance. The highest \( R_t \) value appeared at 48 h, which was in accordance with \( i_{corr} \).

3.6. Mechanism of zinc corrosion in saline solution

According to the results interpreted in previous sections, the main corrosion products on zinc during immersion in saline solution are zinc oxide, zinc hydroxide and zinc hydroxide chloride. The chemical reaction process may contain the following steps [39,42,46]:

Initially, pure Zn dissolved from onset of immersion via the chemical reaction

\[
Zn \rightarrow Zn^{2+} + 2e^- \quad (4)
\]

Meanwhile, oxygen reduction carried out near the zinc surface.

\[
O_2 + H_2O + 2e^- \rightarrow 4OH^- \quad (5)
\]

The reaction (7) leaded to a local increase in pH value in the depth...
of the corrosion damages.

And Zn$^{2+}$ ions from the substrate can react with OH$^-$ to form Zn(OH)$_2$, parts of which can be dehydrated to form ZnO.

$$\text{Zn}^{2+} + 2\text{OH}^- \rightarrow \text{Zn(OH)}_2 \quad (8)$$

$$\text{Zn(OH)}_2 \rightarrow \text{ZnO} + \text{H}_2\text{O} \quad (6)$$

With the immersion time extended to 48 h (Fig. 11a), that maturing and thickening of the accumulated Zn(OH)$_2$/ZnO layer on the samples contributed to the inhibition of Zn dissolution, the whole surface of samples were nearly covered with corrosion products, which caused the lowest $i_{corr}$. With the reaction constantly happened, the pH value increased, when the pH was high enough, Part of Zn(OH)$_2$ would react with OH$^-$ to form Zn(OH)$_4^{2-}$, so the pH value may increase slowly after 48 h, just as discussed previously.

$$\text{Zn(OH)}_2 + 2\text{OH}^- \rightarrow \text{Zn(OH)}_4^{2-} \quad (7)$$

In the presence of chloride ions (Cl$^-$), the following chemical reaction occurred and Zinc chloride hydroxide is formed:

$$5\text{Zn}^{2+} + 8\text{OH}^- + 2\text{Cl}^- + \text{H}_2\text{O} \rightarrow \text{Zn}_5\text{(OH)}_8\text{Cl}_2\cdot\text{H}_2\text{O} \quad (8)$$

The Zn(OH)$_2$ could also be the precursor of Zinc chloride hydroxide. So the following chemical reaction happened:

$$5\text{Zn(OH)}_2 + 2\text{Cl}^- + \text{H}_2\text{O} \rightarrow \text{Zn}_5\text{(OH)}_8\text{Cl}_2\cdot\text{H}_2\text{O} + 2\text{OH}^- \quad (9)$$

The reaction (11) and (12) mainly occurred after 120 h immersion.
Fig. 11b). the increase in pH can promote more formation of corrosion product (Zn5(OH)8Cl2·H2O) around the pits and their neighborhood areas in neutral Cl\textsuperscript{−} containing solution, which were caused by reaction (7). But the main reaction was still to form ZnO and Zn(OH)\textsubscript{2} to contribute the thickness of oxide films. The Sites of Zn5(OH)8Cl2·H2O products can be regarded as relative severe local corrosion sites, which accelerated the corrosion rate after 48 h. In any case, the oxide films' characteristics control the rate of diffusion of zinc ions [47] and oxygen and affect corrosion rate.

### Table 1

Equivalent electrical circuit parameters of the pure Zn at different immersion periods in saline solution.

| Immersion time | \( R_s \) (\( \Omega \text{ cm}^2 \)) | \( Q_1 \) (\( \mu\Omega^{-1} \text{ s}^{-1} \text{ cm}^{-2} \)) | \( n \) | \( R_1 \) (\( \Omega \text{ cm}^2 \)) | \( R_2 \) (\( \Omega \text{ cm}^2 \)) | \( Q_2 \) (\( \mu\Omega^{-1} \text{ s}^{-1} \text{ cm}^{-2} \)) |
|----------------|-------------------------------|-----------------|---|----------------|----------------|-------------------------------|
| 0 h            | 15.2 ± 0.4 (1.8 ± 0.2) \times 10^{-5} | 0.82 ± 0.02    |   | 1380 ± 160     | 1780 ± 100     | (1.7 ± 0.1) \times 10^{-5}    |
| 6 h            | 15.5 ± 0.6 (1.1 ± 0.1) \times 10^{-5} | 0.84 ± 0.05    |   | 1880 ± 60      | 1810 ± 80      | (1.7 ± 0.4) \times 10^{-5}    |
| 12 h           | 13.5 ± 1.4 (1.4 ± 0.2) \times 10^{-5} | 0.76 ± 0.04    |   | 2510 ± 80      | 2020 ± 280     | (2.2 ± 0.6) \times 10^{-5}    |
| 24 h           | 13.6 ± 0.5 (1.8 ± 0.5) \times 10^{-5} | 0.79 ± 0.01    |   | 2680 ± 90      | 2110 ± 170     | (2.3 ± 0.1) \times 10^{-5}    |
| 48 h           | 15.2 ± 0.3 (2.1 ± 0.8) \times 10^{-5} | 0.77 ± 0.01    |   | 3850 ± 250     | 3570 ± 360     | (2.0 ± 0.8) \times 10^{-5}    |
| 120 h          | 15.6 ± 1.2 (1.0 ± 0.1) \times 10^{-5} | 0.81 ± 0.07    |   | 530 ± 180      | 6270 ± 140     | (5.2 ± 0.7) \times 10^{-4}    |
| 168 h          | 15.4 ± 0.6 (1.1 ± 0.4) \times 10^{-5} | 0.81 ± 0.03    |   | 780 ± 40       | 7000 ± 550     | (5.5 ± 0.8) \times 10^{-4}    |
| 240 h          | 15.0 ± 0.8 (1.0 ± 0.4) \times 10^{-5} | 0.80 ± 0.06    |   | 1150 ± 170     | 5260 ± 350     | (8.9 ± 2.2) \times 10^{-4}    |
| 336 h          | 14.8 ± 0.5 (0.8 ± 0.2) \times 10^{-5} | 0.84 ± 0.02    |   | 1230 ± 130     | 4650 ± 210     | (4.2 ± 1.0) \times 10^{-4}    |

4. Conclusions

The initial corrosion behavior and corrosion products of pure Zn in saline solution have been investigated to trace details regarding the degradation profile. It is thought that this fundamental understanding of degradation studies is of utmost importance for research on biodegradation of Zn-based materials. Following conclusions can be drawn:

1. The pure Zn displayed uniform corrosion and homogeneous-distributed corrosion products on surfaces during the immersion for 336 h.
2. The initial corrosion products formed on pure Zn mainly consisted of
ZnO, Zn(OH)₂ and Zn₂(OH)₃Cl·H₂O. And the proportion Zn₂(OH)₃Cl·H₂O increased with time prolonged. 
3 The degradation of Zn in saline solution didn’t lead to much change to the surrounding culture. 
4 The passivation of zinc occurred after 120 h immersion due to the stable corrosion products and the corrosion rate increased after 120 h.

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