Sputtered Mg$_{100-x}$Zn$_x$ (0 ≤ x ≤ 100) systems as anode materials for a biodegradable battery aimed for transient bioelectronics

Muhammad Mudasser Khan $^{a,1}$, Zia Ur Rahman $^{a, b, 1}$, Kashif Mairaj Deen $^c$, Ishraq Shabib $^{a, b, 1}$, Waseem Haider, Ph.D. $^{a, b, *}$

$^a$ School of Engineering and Technology, Central Michigan University, Mount Pleasant, MI, United States
$^b$ Science of Advanced Materials, Central Michigan University, Mount Pleasant, MI, United States
$^c$ Department of Materials Engineering, The University of British Columbia, Vancouver, V6T 1Z4, BC, Canada

Abstract

Transient implantable medical devices are gaining research enthusiasm as an emerging technology in biomedicine. To provide on-board powering for such devices, a biodegradable battery is a promising choice. However, the anode material in such batteries, usually Mg or its alloys, suffer from parasitic corrosion and faster discharge kinetics, that limits the lifetime of these devices. In the pursuit of finding a better anode material, herein, the idea of combinatorial development is employed to fabricate a material having a good combination of corrosion resistance and discharge characteristics, by exploring a wider Mg$_{100-x}$Zn$_x$ (0 ≤ x ≤ 100 at.%) system. Using magnetron co-sputtering of Mg and Zn, six Mg$_{100-x}$Zn$_x$ (x = 0, 6, 20, 34, 41, 100) systems are synthesized. Structural characterization of these systems via X-Ray Diffraction manifests range of microstructures, from fully crystalline to fully amorphous, governed by alloy composition and sputtering conditions. The corrosion investigation of the six systems manifests a generally improving trend upon higher addition of Zn content. Additionally, the discharge performances of the systems are investigated in Phosphate Buffered Saline (PBS) solution, an in-vitro surrogate of physiological fluid, which demonstrates that discharge performances of the sputtered anode materials can be effectively tailored via a prudent design of alloy composition and microstructure.

Article Info

Article history:
Received 30 June 2019
Received in revised form 11 October 2019
Accepted 21 October 2019
Available online 24 October 2019

Keywords:
Biodegradable battery
Transient bioelectronics
Implantable medical devices
Combinatorial development
Magnetron co-sputtering

1. Introduction

Transient implantable medical devices, that dissolve upon exposure to physiological environments in a specific period of time, are gaining research enthusiasm [1–3] with applications in monitoring and treatment of transient diseases, i.e. wound healing, tissue regeneration, and traumatic brain injury, etc. These devices perform their intended function as well as dissolve with time, thus precluding the need for revision surgeries and avoiding the chronic inflammatory responses associated with permanent implantable medical devices [4,5].

For better performance of transient implantable medical devices, appropriate biodegradable energy sources are required for on-board powering, allowing self-powered electronics with greater functionality [1]. A biodegradable battery may be a promising choice to deliver on-board power for such devices in-vivo and thus, is of special interest [1,6]. The biodegradable battery must have a combination of requisite characteristics, i.e., full-scale biodegradability, compactness, longer lifetime, and biocompatibility.

There are a handful of studies conducted to develop biodegradable batteries, primarily using Mg as the anode material, owing to its attractive electrochemical properties, i.e. high specific capacity (2200 mAh-g$^{-1}$), specific energy (6800 Wh-kg$^{-1}$), biocompatibility, and high physiological tolerance (daily allowable –300 mg-day$^{-1}$). The biodegradable batteries reported are Mg–Mo [7], capable of powering a light-emitting diode; Mg–Fe [1], capable of driving a commercial pacemaker; Mg alloy (AZ-31)–silk fibroin [6]; and Mg/AZ31–Fe [8]. Despite the attractive electrochemical properties of Mg, the Mg-based batteries fail to approach the theoretical capacity (low columbic efficiency) due to high self-discharge rates and occurrence of parasitic reactions in aqueous electrolytes [9]. The main shortcomings, therefore, associated with
these batteries are low specific power, small discharge capacity, and short lifetime which make these systems unsuitable for many practical applications. The lifetime of these batteries is predominantly limited by the depletion of active anode material and/or by the formation of surface barrier films leading to premature termination. These crucial shortcomings, mostly associated with the anode materials of these batteries, necessitate the development of high-performance anodes for such biodegradable batteries to make them suitable for practical biomedical applications.

To address the aforementioned shortcomings associated with Mg-based anodes, various alloying additions have been investigated, for instance, Mg-Al-Pb [10], Mg-Al-Mn-Ca [11], Mg–Li–Al–Zn–Y [12] etc., in attempts to achieve better anodic performances. However, for anode materials aimed for biomedical applications, the choice of alloying elements reduces to few species, governed by biocompatibility considerations. Previous studies demonstrate that the addition of Zn to Mg can improve its corrosion resistance [13–15]. Additionally, Zn, owing to its large over-potential for H₂ evolution, can also modify the overall discharge performance of Mg-based anodes. However, in the addition of Zn to Mg, a crucial shortcoming is the possibility of formation of secondary phases in a wider compositional range of Mg–Zn binary phase diagram [16], which may lead to accelerated corrosion rates. This necessitates the use of non-equilibrium fabrication methods that can avoid the development of multi-phase systems in order to decrease the tendency of possible detrimental corrosion reactions. Thus, to explore a range of Mg–Zn binary systems, as well as ensuring single-phase microstructures, combinatorial development via co-sputtering may be a robust option. Using this fabrication method, the thermodynamical constraints associated with the Mg-Zn solid solubility limits can be avoided and single-phase structures can be developed [17–19]. In addition, the flexibility to vary composition in a wider range further facilitates the screening of anode materials having better combination of desired properties.

In the progress to develop an efficient biodegradable battery, herein we explore a binary Mg_{100-x}Zn_{x} (0 ≤ x ≤ 100 at.%) system. Various combinations of Mg–Zn anode systems are developed via combinatorial magnetron co-sputtering of pure Mg and Zn in order to identify the optimum combination that would provide better electrochemical performance and longevity for applications involving long-term in-vivo diagnosis, as discussed [20]. Since the biodegradable battery leads to the consumption of anode material during discharge reaction, a Mg-rich system is purposely chosen as anode material for this study, owing to its higher physiological tolerance in human body [21–23]. Comapartively less electroactive sputtered Fe, with lower hydrogen overpotential than Zn, is selected as the cathode material [1]. Phosphate Buffered Saline (PBS) solution, because of its similar ionic constituents to human’s physiological fluid, is used as the electrolyte. The sputtered anode systems are investigated for their prospective applications in biodegradable batteries using detailed microstructural, electrochemical and discharge characterization.

2. Materials and methods

Pure targets of Mg (99.95%) and Zn (99.95%) are individually sputtered as well as co-sputtered using Nano-36 sputterer (Kurt J Lesker Company) to develop thin films on glass substrates. The sputtering is carried out in a base pressure <1 × 10⁻⁶ Torr and a working pressure of ~8 × 10⁻³ Torr. DC and RF guns, employed for Zn and Mg, respectively, are operated at different power levels to develop different systems. Pure Mg, pure Zn and co-sputtered Mg–Zn systems (abbreviated as MZ-X, X = 1–6) are sputtered under various experimental conditions and designated as summarized in Table 1.

Grazing-Incidence X-Ray Diffraction (GI-XRD) is conducted using a Rigaku SmartLab Diffractometer equipped with 1.54 Å Cu Kα radiation source. The diffraction patterns are processed via Fourier Transformation and interpreted using PANalytical X’Pert HighScore.

Electrochemical characterization is done in two phases: First, the corrosion behavior of MZ-X systems is investigated, and second, the discharge characteristics of the cell (MZ-X coupled with Fe) are probed. Accordingly, the testing is carried out in both three-electrode-cell setup (Potentiodynamic polarization & Electrochemical Impedance Spectroscopy, EIS) and two-electrode-cell setup (Galvanostatic discharge & EIS).

In the first phase, the electrochemical testing of MZ-X systems is carried out in PBS solution (composition in g/L: NaCl (8.0), KCl (0.4), NaHCO₃ (0.35), Na₂HPO₄ (0.06), KH₂PO₄ (0.06), MgSiO₄ (0.2), CaCl₂ (0.14)) in a three-electrode-cell connected to a Reference 1000 Potentiostat (Gamry Instruments). The Saturated Calomel Electrode (SCE, +0.240 V vs SHE) and graphite are used as reference and counter electrode, respectively, while the Mg-ZX systems are used as working electrodes. The working electrodes are first exposed to PBS solution for 30 min to achieve a relatively stable open circuit potential (OCP) prior to potentiodynamic polarization. Potentiodynamic polarization scans are obtained within ±0.3 V potential range (vs. OCP) by using a sweep rate of 1 mV s⁻¹. The electrochemical impedance spectra (EIS) are obtained by exerting 10 mVms (at DC = 0 V, vs OCP) AC potential perturbation and impedance behaviors are registered within 100 kHz–10 mHz frequency range.

In the second phase, the discharge capacity and electrochemical performance of MZ-X systems coupled with Fe, are probed from galvanostatic discharge profiles (at 10 μA cm⁻²) and EIS (AC potential = 10 mVms at DC = 0 V vs. OCP) in a two-electrode-cell setup. In the two-electrode setup, the sputtered MZ-X systems (where, X = 1, 2 … 6) and Fe are used as the negative and positive electrodes, respectively, akin to a battery setup. In the case of galvanostatic discharge, the exposed reaction regions of the anodes and cathodes are kept 1-cm² while the anode-cathode spacings are kept constant at 2 mm for all cases.

### Table 1

<table>
<thead>
<tr>
<th>Designation</th>
<th>Power (W)</th>
<th>Deposition Time (min)</th>
<th>Thickness (nm)</th>
<th>Mg (at.%)</th>
<th>Zn (at.%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MZ-1</td>
<td>160</td>
<td>0</td>
<td>605 ± 36</td>
<td>100</td>
<td>0</td>
</tr>
<tr>
<td>MZ-2</td>
<td>160</td>
<td>30</td>
<td>511 ± 19</td>
<td>94</td>
<td>6</td>
</tr>
<tr>
<td>MZ-3</td>
<td>160</td>
<td>60</td>
<td>538 ± 30</td>
<td>80</td>
<td>20</td>
</tr>
<tr>
<td>MZ-4</td>
<td>160</td>
<td>90</td>
<td>661 ± 16</td>
<td>66</td>
<td>34</td>
</tr>
<tr>
<td>MZ-5</td>
<td>160</td>
<td>120</td>
<td>648 ± 15</td>
<td>59</td>
<td>41</td>
</tr>
<tr>
<td>MZ-6</td>
<td>0</td>
<td>160</td>
<td>554 ± 32</td>
<td>0</td>
<td>100</td>
</tr>
</tbody>
</table>
3. Results and discussion

3.1. Microstructural characterization

Microstructural characterization is conducted to link the phase microstructures of the MZ-X systems to their electrochemical characteristics, i.e. corrosion and discharge behavior. Fig. 1 shows the GI-XRD patterns of the six MZ-X systems. Three different types of structure formation are revealed by the GI-XRD analysis, i.e. single-component fully crystalline, binary solid solution and amorphous. The single-component systems, i.e. MZ-1 (pure Mg) and MZ-6 (pure Zn) demonstrate full-scale crystallinity as shown by their diffraction patterns, Fig. 1. The binary systems, however, exhibit different microstructures. Upon the addition of Zn to Mg, i.e. MZ-2 (6 at.% Zn) and MZ-3 (20 at.% Zn), some peaks of Mg correspondingly disappear (more so in MZ-3 than MZ-2), indicating a corresponding loss of full-scale crystallinity. However, no diffraction peak representative of Zn and/or any other intermetallic in both MZ-2 and MZ-3 systems, suggests the formation of single-phase structures, i.e. solid solution of Mg and Zn. Upon the addition of higher Zn concentrations, i.e. MZ-4 (34 at.% Zn) and MZ-5 (41 at.% Zn), Bragg’s peaks completely disappear and instead, broad peaks are observed in the diffraction patterns, indicating the formation of amorphous single-phase structures.

The formation mechanisms of these structures are related to the sputtering parameters (substrate temperature, adatom arrival rate, adatom mobility) and material properties (number of alloying constituents, their atomic size differences and heats of mixing [18,24]). Sputter deposition process is a non-equilibrium process characterized by a vapor-solid transformation and thus, inherently possesses high quench rates [25]. That being so, the formation of fully crystalline phases, otherwise expected in equilibrium fabrication methods, is not usual. Nonetheless, despite a high-quench-rate deposition method, single-component systems can proceed to form fully crystalline structures when sputtered individually [26,27], as is observed in case of pure Mg (MZ-1) and pure Zn (MZ-6). However, the incorporation of another species (Zn to Mg in this study, or vice versa) in the form of co-sputtering can affect the crystallinity of the resulting binary system, depending on the species type and deposition rate. In the stated settings of MZ-2 and MZ-3, Mg with a much higher deposition rate (governed by RF deposition power, 160 W in both systems) can proceed to nucleate and grow forming an hcp-lattice, while Zn with a comparatively lower deposition rate (governed by DC power, 30 & 60 W for MZ-2 and MZ-3, respectively), can substitute the Mg atoms overall forming solid solution. Moreover, since sputtering is characterized by limited adatom mobility under ambient-substrate temperatures, the formation of single-phase systems is highly probable, as reported for binary Mg–Ti [28] and Mg–Zr [29] systems. In MZ-4 and MZ-5, the Zn contents are increased to 34 and 41 at.%, respectively, by increasing the DC gun deposition power from 90 W to 120 W. The increased deposition rate of Zn is expected to result in a competing effect between Mg and Zn adatoms on the substrate that would likely suppress the long-range crystallinity on the grounds of much higher adatom arrival rate. Consequently, under the applied settings of MZ-4 and MZ-5, the growth of the nucleating phase of the majority species (Mg) is intercepted at short distances, disrupting the establishment of a full-scale crystallinity and leading towards amorphization. The occurrence of amorphization is also widely reported for other binary systems fabricated via co-sputtering, even in immiscible systems having positive enthalpy of mixing, i.e. Cu-Nb [30], Ag-Fe [31], and Cu–Ta [32]. It is worth mentioning however, that while the GI-XRD analysis demonstrates single-phase structures, the possibility of formation of intermetallics at very minute scales may not be altogether eliminated, given the fact that XRD may not be helpful in revealing such nanoscale features. Thus, further investigations via high-resolution Transmission Electron Microscopy may be considered in future work.

3.2. Electrochemical characterization (three-electrode-cell setup)

3.2.1. Potentiodynamic polarization

The major limitation associated with the biodegradable batteries is the rapid degradation of Mg anodes in physiological media. Therefore, it is important to tune the degradation rate of these anode materials to enhance the performance of biodegradable batteries. Improvement in the corrosion resistance of Mg, with the addition of Al and Zn (AZ-31 alloy), is reported in literature, leading to better discharge characteristics [8]. Herein, the electrochemical behavior of the six MZ-X sputtered systems, with varying concentrations of Zn, is investigated in simulated physiological solution (PBS) to explore their potential as anode materials for primary biodegradable batteries.

Potentiodynamic polarization tests are conducted to evaluate the electrochemical response of the sputtered MZ-X systems as shown in Fig. 2. At more negative potentials than OCP, the polarization trends demonstrate the kinetics of reduction reactions i.e., H2 evolution due to H2O dissociation and/or the reduction of any dissolved O2 in the PBS solution. MZ-1 (Pure Mg) exhibits a highly negative corrosion potential (Ecorr of −1.96 V vs SCE) in PBS solution. At such negative potential, the dissolution of Mg is controlled by the H2 evolution reaction, which is thermodynamically favourable. With the addition of 6 at.% Zn to Mg, the potentiodynamic polarization scan of the binary system MZ-2 demonstrates a shift in Ecorr towards less negative values (−1.47 V vs SCE), becomes nobler than Ecorr of MZ-1). Both cathodic and anodic polarization trends are changed due to the relatively positive reduction potential of Zn than Mg and limited kinetics of H2 evolution on Zn. In simple words, in MZ-2, the H2 evolution on Zn is kinetically slow and may control the anodic dissolution of Mg. Under oxidizing conditions, the Mg and its alloys generally exhibit high dissolution rates and are described by the negative difference effect [33,34]. This is associated with the relatively negative redox potential of Mg/Mg2+ reaction compared to the thermodynamic stability of H2O. Therefore, the formation of Mg2+ ions and their reaction with water may lead to hydrogen gas evolution according to reaction 1.
with an increase in Zn contents in the MZ-X sputtered systems, the $E_{\text{corr}}$ shifts to relatively less negative values. This indicates that the $H_2$ evolution tendency may decrease at the surface of Mg–Zn co-sputtered systems. For instance, the $E_{\text{corr}}$ of MZ-4 (−1.23) and MZ-5 (−1.24 vs SCE) approaches the value of pure Zn.  

$$\text{Mg} + 2\text{H}_2\text{O} \rightarrow \text{HO.Mg}^2+ + \text{OH}^- + H_2 \uparrow$$ (1)

Similarly, a noticeable change in the cathodic polarization trends (cathodic Tafel slope; $\beta_c$) is observed with the increase in Zn content in MZ-X systems. As evident from these results, it is estimated that a change in composition and corresponding microstructure can affect the reduction processes on the MZ-X systems.  

Following the application of anodic potentials on MZ-X systems, metal oxidation dominates the anodic current in all cases. All the scans associated with co-sputtered systems initially demonstrate faster anodic dissolution in comparison to pure Mg (MZ-1) before reaching a point of slower dissolution (at higher anodic potentials). Additionally, despite varying concentrations of Zn in the MZ-X systems, there is no considerable change in the anodic Tafel slopes (almost same $\beta_a$ range of 27.8–47.3 mV/dec). Anodic branches of the polarization scans may offer one approach to judge the discharge activity of these anodes in actual battery setup [10]. As seen during the anodic polarization of MZ-X ($X = 3, 4, 5, 6$), the current peak at approximately −1.13 V (vs. SCE) corresponds to the formation of corrosion product layer and the current density at this peak is designated as critical current density ($I_{\text{crit}}$). Thermodynamically, the conversion of Zn into Zn(OH)$_2$ is possible with the presence of $H_2$ evolution at this potential on the surface of Zn-enriched sputtered systems according to reaction 2 and 3.

$$\text{Zn} + 2\text{H}_2\text{O} \rightarrow \text{Zn(OH)}_2 + 2H^+ + 2e^-$$ (2)

$$2H^+ + 2e^- \rightarrow H_2 \uparrow$$ (3)

The appearance of this current peak at higher anodic potentials in the case of MZ-6 system also validates the formation of Zn(OH)$_2$ species on co-sputtered systems having relatively higher Zn concentrations. The decrease in current at potentials higher than −1.15 V (vs. SCE) represents a hindrance in the dissolution of underlying systems due to surface coverage by the corrosion product layer. This may, in turn, contribute in prohibiting the systems from self-discharge [35].

The corrosion current densities ($I_{\text{corr}}$) are calculated from the extrapolation of the linear Tafel regions (±50 mV away from OCP) in the potentiodynamic scans, as given in Table 2. The $I_{\text{corr}}$ decreases significantly with the addition of Zn content. Approximately one order magnitude lower $I_{\text{corr}}$ of MZ-3, MZ-4 and MZ-5 indicates appreciable decrease in the degradation tendency of these systems.  

From these results, it is evaluated that the dissolution tendency of the sputtered MZ-X systems depends on the concentration of Zn as well as the resulting microstructure. The addition of Zn considerably influences the kinetics of reduction processes, particularly $H_2$ evolution. The role of microstructure may be ascribed to the single-phase structures that avoid galvanic coupling of electrochemically dissimilar phases, and hence avoids detrimental corrosion rates. The addition of Zn content in these sputtered systems shifted the $E_{\text{corr}}$ to positive potentials and their dissolution is controlled by the cathodic $H_2$ evolution reaction as indicated from the positive shift of $E_{\text{corr}}$ and decrease in $I_{\text{corr}}$ with increase in Zn contents. Although, the $\beta_a$ is appreciably decreased with the increase in Zn concentration in MZ-X (i.e., $X = 3, 4, 5$), the correspondingly lower $I_{\text{corr}}$ values suggest the decrease in dissolution tendency of Mg–Zn sputtered systems, particularly controlled by the restricted $H_2$ evolution. Additionally, the slower anodic kinetics popping up in the regions of higher anodic potentials (−1.15 V vs SCE) in MZ-X ($X = 3, 4, 5$) may help in ensuring slower discharge kinetics of these materials as anodes, through protective corrosion layers.

### 3.2.2. Electrochemical Impedance Spectroscopy of MZ-X anodes

It is intriguing to further investigate the dissolution tendency and/or the formation of corrosion product layers on the MZ-X systems, via EIS. The small potential perturbation (10 mVrms vs OCP) will oscillate the surface potential in a sinusoidal mode which is considered sufficient to evaluate the kinetic behavior of these systems without deteriorating the surface. Fig. 3 shows the EIS spectra of the six MZ-X systems obtained in PBS solution. From the Nyquist plots, Fig. 3(c), MZ-1, MZ-2 and MZ-3 exhibit similar trends, characterized by depressed semicircles, however, MZ-4, MZ-5, and MZ-6 exhibit incomplete semicircles.  

In order to estimate the dissolution tendencies of the MZ-X systems, the spectra are simulated using a two-time-constant equivalent electrical circuit (EEC) model as shown in Fig. 3(d). The two-time constant model is proposed based on the phase angle shift as a function of applied frequency (Fig. 3(b)). Two capacitive loops at high and medium frequency ranges are evident in the

<table>
<thead>
<tr>
<th>System ID</th>
<th>$E_{\text{corr}}$ (V vs SCE)</th>
<th>$I_{\text{corr}}$ (µA.cm$^{-2}$)</th>
<th>$I_{\text{lim}}$ (mA.cm$^{-2}$)</th>
<th>$\beta_c$ (mV.dec$^{-1}$)</th>
<th>$\beta_a$ (mV.dec$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MZ-1</td>
<td>−1.96</td>
<td>27.2</td>
<td>—</td>
<td>478.6</td>
<td>415.4</td>
</tr>
<tr>
<td>MZ-2</td>
<td>−1.47</td>
<td>19.5</td>
<td>—</td>
<td>27.8</td>
<td>446.8</td>
</tr>
<tr>
<td>MZ-3</td>
<td>−1.29</td>
<td>2.16</td>
<td>2.8</td>
<td>39.7</td>
<td>143.6</td>
</tr>
<tr>
<td>MZ-4</td>
<td>−1.23</td>
<td>5.16</td>
<td>0.23</td>
<td>40.8</td>
<td>109</td>
</tr>
<tr>
<td>MZ-5</td>
<td>−1.24</td>
<td>3.95</td>
<td>0.24</td>
<td>47.3</td>
<td>103.4</td>
</tr>
<tr>
<td>MZ-6</td>
<td>NA*</td>
<td>—</td>
<td>0.35</td>
<td>—</td>
<td>—</td>
</tr>
</tbody>
</table>

* Multiple inflection points.
Nyquist plots, Fig. 3(c). The high-frequency loop represents the impedance of corrosion film on the surface while the medium-to-low frequency loop represents the charge-transfer processes at the electrode/electrolyte interface [36]. Accordingly in the EEC model, $R_1$ and $CPE_1$ represent the film resistance and capacitance, while $R_2$ and $CPE_2$ represent the charge transfer resistance and double-layer capacitance, respectively. MZ-2 exhibits an additional low-frequency inductive loop that is generally attributed to damage in Mg(OH)$_2$ film and initiation of localized corrosion [37–39]. Some authors, however, have associated the low-frequency inductive loop to the non-stationarity during EIS measurements [36], and for these reasons, it is not included in the EEC model.

Table 3 presents the values of film resistance and charge transfer resistance of the six MZ-X systems, extracted via fitting of the experimental data with EEC model, using iterative process. Clearly, the charge-transfer resistance dominates the film resistance in all cases. This is expected since at OCP, all the systems are highly active. From the total resistance values, the binary MZ-X (X = 2, 3, 4) systems, except MZ-5, show lower but roughly similar values to that of pure Mg, though not in conformity to the corrosion current densities extracted from potentiodynamic polarization scans, a contradiction reported elsewhere [10]. However, it is suggested that the progress of both irreversible reactions i.e. Mg dissolution (oxidation) and H$_2$ evolution (H$_2$O reduction) processes will be hindered by the formation of surface film and Zn enrichment in the sputtered systems, respectively. This behaviour is evident from the overall decrease in the $I_{corr}$ (potentiodynamic scans) and increase in charge transfer resistance, $R_2$ (from EIS) with increase in Zn concentration in the sputtered systems, compared to pure Mg.

It is important to mention that the OCP stabilization of 30-min
in EIS (or even higher) may not be sufficient to achieve a fully steady state. Thus, while the EIS scan is running, it is reasonable to expect that the surface potential of the system is also changing. Additionally, the EIS of Mg-based systems is generally susceptible to degradation occurring during scanning which makes the low-frequency impedance data challenging, as active reactions continuously occur at the same time while the impedance is being recorded [40]. This is probably why the low-frequency response in some systems show “drift” behavior.

3.3. Electrochemical characterization of MZ-X/Fe cells

3.3.1. EIS

In a two-electrode-cell setup, the MZ-X systems (negative electrodes) and sputtered Fe (positive electrodes) are coupled and immersed in a PBS solution as discussed above. Fig. 4 shows the potentiostatic EIS spectra, conducted at OCP, of the MZ-X anodes (X = 1, 2,…, 6) coupled with Fe cathodes. Two time-constants, and a Warburg element, typically representing batteries configuration [41–43], are observed in the Bode and Nyquist plots, as shown in Fig. 4(a-c).

As evident from Fig. 4(c), all systems (except MZ-6) exhibit similar impedance trends in the Nyquist plots, consisting of a depressed semicircle in the medium frequency range, that is associated with charge transfer processes occurring at the electrode/electrolyte interface owing to the galvanic coupling of MZ-X and Fe electrodes [44,45]. The Warburg element appearing at low-frequency regions is associated with the diffusion-controlled processes. The high-frequency intercept at the Zreal axis represents the electrochemical series resistance (ESR) of the cells, associated with the potential drop across the electrode/electrolyte interface and the resistance of electrical connections.

By completing the depressed semicircle in the Nyquist plots to intersect the real impedance axis (Zreal to assess charge transfer resistance), it is evident that except MZ-2, all the other spectra exhibit an increase in the diameter of semicircles upon the addition of higher Zn content. The increasing trend upon increasing Zn concentration, may suggest relatively slower dissolution of anode materials when coupled with Fe cathode. Among the binary MZ-X systems, MZ-4 exhibits the highest total impedance (Ztot, 20.37kΩ cm²) in the lowest frequency region, Fig. 4(a). This represents the controlled dissolution of anode material, and the largest imaginary impedance, Zimag, exhibited by this MZ-4/Fe cell, corresponds to the distribution of ionic species across the electrode/electrolyte interface. From the EIS results it can be maintained that appropriate alloying combination in the Mg–Zn binary system can effectively control the dissolution kinetics in PBS solution, which in turn, may be beneficial in controlling the discharge process of these anodes, when coupled with cathode, in a battery like setup.

3.3.2. Galvanostatic discharge

To assess the discharge performance of the sputtered MZ-X systems coupled with Fe in PBS solution, galvanostatic discharge profiles are obtained in a two-electrode-cell setup by applying 10 μA cm⁻² current density. The MZ-X systems and Fe are employed as the negative and positive electrodes, respectively. During discharge, the anodic dissolution of MZ-X (reaction 4 & 5) is supported by the reduction reactions i.e., reduction of H₂O and/or any dissolved O₂ according to reactions 6 & 7.

At anode (during discharge), i.e. MZ-X:

\[
\text{Mg} \rightarrow \text{Mg}^{2+} + 2e^- \tag{4}
\]

Or

\[
\text{Mg} + \text{H}_2\text{O} \rightarrow \text{Mg(OH)}_2 + 2\text{H}^+ + 2e^- \tag{5}
\]

At cathode (during discharge), i.e. on Fe:

\[
\text{O}_2 + 2\text{H}_2\text{O} + 4\text{e}^- \rightarrow 4\text{OH}^- \tag{6}
\]
Apart from MZ-1 (pure Mg), in all other MZ-X systems (X = 2, …, 6), dissolution of Zn is possible according to reaction 2 and 8 as follows:

\[
\text{Zn} \rightarrow \text{Zn}^{2+} + 2e^- \tag{8}
\]

Fig. 5 shows the galvanostatic discharge profiles of the six MZ-X systems. In all cases, the cell potential drops immediately upon the application of discharge current density which is associated with the kinetic limitation of the electrochemical reactions. MZ-1 (pure Mg) shows the highest output voltage. With the addition of 6 at.% Zn to Mg (MZ-2), the voltage decreases slightly, accompanied by a slight increase in discharge time at the same applied discharge current density (10 \(\mu\)A cm\(^{-2}\)). However, both MZ-1 and MZ-2 show complete dissolution before reaching the cut-off potential (indicated by arrows; wide fluctuations and high rate of potential drop at the tail end of the discharge curves), Fig. 5. The other binary systems, MZ-X (X = 3, 4, 5) show no such signs of complete dissolution, rather an overall drop in discharge voltages with time are registered. Among the binary systems, MZ-3 and MZ-5, unexpectedly, shows a quick drop in discharge potential while MZ-4 demonstrates the longest discharge time. MZ-6 (Pure Zn), due to much nobler electrochemical potential, quickly drops to cut-off potential, demonstrating its main shortcoming as an anode material for such applications.

The discharge behavior of the MZ-X systems may be explained in terms of three different aspects: 1) The microstructure, 2) the composition, and 3) the formation of surface products, predominantly hydroxides. In terms of microstructures, all the six systems are single-phase species, as validated by X-ray Diffraction, so any possibility of the interplay of electrochemically dissimilar phases in the form of microscale galvanic corrosion can be excluded. The role of composition and surface hydroxides, on the other hand, can strongly influence the battery characteristics and will be discussed in detail. Generally, a potential drop during discharge is usually contributed by charge transfer overpotential \((\eta_{ct})\), diffusional overpotential, \((\eta_{diff})\) and IR drop, where “\(I\)” the discharge current and “\(R\)” is the applied load. The surface hydroxides, depending on how much they inhibit the mass diffusion process, would cause a corresponding diffusional overpotential.

MZ-1, owing to its high electrochemical reactivity, demonstrate complete depletion of anodic film upon discharge, displaying its main limitation for such applications. So does MZ-2, where a small addition of Zn (6 at.%) to Mg slightly lowered the discharge potential plateau to approximately 1.2 V from ~1.5 V (in case of MZ-1). However, the potential plateau extends slightly corresponding to increase in discharge capacity. MZ-3 exhibits large potential decay and presents small plateau at 0.95 V followed by decay to cut-off potential. Generally, at low discharge currents, the rate of hydroxide formation may exceed the rate of film breakdown, which results in premature termination of the battery. In other words, a rapid production rate of Mg(OH)\(_2\) and/or Zn(OH)\(_2\) may deteriorate the cell discharge performance, owing to the surface-shielding effects by these hydroxides. Due to the formation of such hydroxide layers, the fresh metallic system loses its contact with the electrolyte that leads to a drop in the cell potential (potential drop due to limitation in mass transfer). Analogous to MZ-3, the MZ-4 and MZ-5 are also most likely influenced by the formation of surface hydroxides. This is expected as seen from the passivation regions in passivity-dynamic polarization upon the application of higher anodic potentials, where the anodic dissolution slows down, hindered by surface products. Given that both systems (MZ-4 and MZ-5) are amorphous and having better corrosion resistance properties, the behavior of MZ-5 seems rather peculiar. One reason, however, could be the higher Zn content (41 at.%), that favors the formation Zn(OH)\(_2\) resulting in the quicker drop in potential compared to MZ-4. In this case the kinetic overpotential might dominate the overall decrease in discharge potential. Under similar applied conditions, the MZ-4 provides the longest discharge plateau at 0.8 V for ~300 min and the cell potential drops gradually to cut-off potential in approximately 490 min. It is noticed that with increase in Zn contents in the MZ-X systems, the potential plateau of the cell decreases gradually, which is attributed to the hindered dissolution kinetics of Mg in the presence of Zn, due to the formation of corrosion products on their surface.

Fig. 6 shows the average decreasing rate of discharge voltage (\(\Delta V/t, \text{mV.hr}^{-1}\)) as well as the open-circuit voltage just after the cell assembly. Owing to the more negative OCP of pure Mg (MZ-1) in PBS, the large cell potential (~1.6 V) is observed that decreases to approximately 1.3 V with the addition of Zn (in case of MZ-2, MZ-3, MZ-4 and MZ-5). The cell potential after assembly is the maximum potential difference between the positive and negative electrodes. Upon discharge, the overpotentials caused by charge transfer processes and diffusional processes may contribute to decrease in discharge potential under applied load. The rate of change in discharge potential as a function of Zn contents in the negative MZ-

\[
2\text{H}_2\text{O} + 2e^- \rightarrow \text{H}_2\uparrow + 2\text{OH}^- \tag{7}
\]
X electrodes is also shown in Fig. 6.

Among the six MZ-X systems, pure Mg (MZ-1) has the highest and most stable output voltage. However, its faster dissolution causes the shorter potential plateau (small discharge capacity) under similar applied conditions. The highest voltage output in the case of Mg, nevertheless, may be beneficial for high energy output but the progress of other parasitic reactions (i.e. H₂ evolution) and shorter service life are the major concerns. Though the existing cells with binary Mg–Zn anodes possess relatively lower cell potential and current outputs, the two issues may be overcome, respectively, by integrating stacks of cells in series or usage of larger electrode area [46].

These MZ-X systems can provide large open-circuit potential in the range of 1.6–0.9 V that may be sufficient for low-power medical devices in the range of micro-to milli-watts [47]. Among the low-power consumption devices, for instance, Xue et al. have reported a blood flow rate sensing system with total power consumption of 21.6 mW [48]. The shelf life of these batteries is expected to be appreciable on the grounds of a reasonable resistance to Mg oxidation in air [46]. The thin-film nature of the electrodes in this work can, in future, be exploited for developing flexible implantable batteries [49].

4. Conclusions

The following conclusions may be drawn:

1. Single-phase Mg₁₀₀₋ₓZnx systems, over a wider compositional range \(x = 0, 6, 20, 34, 41, 100\), are fabricated via magnetron sputtering. GI-XRD demonstrates the formation of fully crystalline systems (MZ-1 and MZ-6) for pure elemental species. Formation of binary solid solutions occur upon the addition of Zn to Mg at low concentrations (i.e. MZ-2 and MZ-3), however, at higher Zn concentration, fully amorphous structures dominate (i.e. MZ-4 and MZ-5).

2. Upon addition of Zn to Mg via co-sputtering, the binary systems exhibit a positive shift in \(E_{corr}\) towards nobler values and decrease in \(I_{corr}\). The MZ-X systems \((x = 3, 4, 5)\) exhibit faster anodic dissolution compared to pure Mg, but passive upon increasingly higher anodic potentials, due to the formation of Mg(OH)₂ and Zn(OH)₂.

3. The discharge behavior of the MZ-X systems does not vary monotonically with the addition of Zn, which confirms that apart from the compositional differences, the roles of microstructure and surface hydroxides are also influential in controlling the discharge kinetics.

4. Pure Mg and pure Zn manifest major shortcomings as anode materials for biodegradable batteries on the grounds of high electrochemical reactivity (in case of Mg) and noble electrode potential (in case of Zn), however, combinational development of the two systems (Mg–Zn) via co-sputtering can tune the degradation rate and discharge characteristics in the battery setups.

5. Longest discharge time (approx. twice as much pure Mg) is registered by MZ-4, that may be attributed to the combined effect of amorphous structure and optimized combination of alloying constituents.

Declaration of competing interest

Authors would like to confirm that submission of this article implies that the work described has not been published previously. This article is not under consideration for publication elsewhere. Moreover, this publication is approved by all authors and tacitly or explicitly by the responsible authorities where the work was carried out, and that, if accepted, it will not be published elsewhere in the same form, in English or in any other language, including electronically without the written consent of the copyright-holder.

References


[16] H. Okamoto, Supplemental literature review of binary phase diagrams: Cs-In, Cs-K, Cs-Rb, Eu-In, Ho-Mn, K-Rb, Li-Mg, Mg-Nd, Mg-Zn, Mn-Sm, O-Sb, and Si-Sr, J. Phase Equilibria Diffusion 34 (3) (Jun. 2013) 251–263.


