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Electrochemical behaviors and discharge performance of Mg-Sn binary alloys as anodes for Mg-air batteries

Lu Han1,2, Yuwenxi Zhang1,2, Yangyang Guo3, Yangjie Wan1,2, Lingling Fan1,2, Mingyang Zhou4 and Gaofeng Quan1,2 ⋆

1 Key Laboratory of Advanced Technologies of Materials, Ministry of Education, Southwest Jiaotong University, Chengdu, 610031, People’s Republic of China
2 School of Materials Science and Engineering, Southwest Jiaotong University, Chengdu, 610031, People’s Republic of China
3 Xi’an Rare Metal Materials Institute Co. Ltd, Xi’an, 710021, People’s Republic of China
4 Science and Technology on Reactor System Design Technology Laboratory, Nuclear Power Institute of China, Chengdu, 610213, People’s Republic of China

E-mail: quangf@swjtu.edu.cn

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Abstract

In this work, the self-corrosion and discharge performance of the as-cast Mg-xSn (x = 1, 5, 9 wt%) anodes for primary Mg-air batteries were studied through microstructure characterization, electrochemical testing and discharge experiments. With the increase of Sn content, the volume fraction of the Mg₂Sn phase increases, promoting dendrite refining. According to the electrochemical test, the Mg-1Sn anode shows a higher open circuit potential, resulting in a stronger electrochemical activity. The polarization curve and electrochemical impedance spectra show the corrosion resistance order as Mg-1Sn > Mg-5Sn > Mg-9Sn. In the discharge measurement, the Mg-1Sn anode achieves the best average discharge voltage, anode efficiency, specific capacity, and energy density under all current densities tested. At 10 mA cm⁻², the energy density of Mg-1Sn is 1239.621 mWh g⁻¹, which is higher than the Mg-5Sn anode and Mg-9Sn anode, 37% and 25%, respectively. The optimal discharge performance of the Mg-1Sn anode is mainly attributed to the high electrochemical activity and the micron-sized Mg₂Sn phase dispersed in the matrix, which facilitates more uniform dissolution.

1. Introduction

As the promising electrochemical energy storage and conversion equipment, metal-air batteries receive widespread attention in consumer electronics, electric vehicles and stationary power plants due to their higher theoretical energy density [1, 2]. Generally, metal-air batteries are composed of a metal anode, an air cathode and an aqueous or non-aqueous electrolyte. The oxygen in the air is the reactant of cathode reaction, and the electrolytes providing a zone for ion exchange are usually alkaline, saline, or aprotic [3]. The metal anode, as the only active component, plays a vital role in metal-air batteries. According to the invention date, these metals are zinc (Zn), aluminum (Al), magnesium (Mg), iron (Fe), lithium (Li), sodium (Na), and potassium (K) [4]. Among them, Mg is considered as a potential anode material for metal-air batteries due to the high specific energy density (6.8 kW h kg⁻¹), high theoretical specific capacity (2.2 A h g⁻¹), a negative standard electrode potential (−2.37 V versus standard hydrogen electrode, SHE), and relatively low density (1.74 g cm⁻³) [5, 6]. However, the practical application of Mg-air batteries is still limited because some key issues have not been resolved [3]. In the aqueous electrolyte, the Mg anode has a severe hydrogen evolution reaction (HER), which reduces the anode efficiency and discharge capacity [7]. The Mg(OH)₂ generated by HER and battery discharge easily agglomerates on the surface of the Mg anode, which leads to the anode polarization and the electrode reaction sluggish kinetics [8, 9]. Another is the specific negative difference effect (NDE) of Mg that the anode current and the cathode current increase with increased applied potential, accelerating the hydrogen evolution and corrosion rate [3].

In order to find a suitable Mg anode and promote the application of Mg-air batteries, alloying is an effective and economical method to improve the discharge performance and suppress the self-corrosion. The common
added alloying elements include Al [8, 10], Zn [11, 12], Pb [7, 13, 14], Li [15–17], Ca [6, 8, 18], Sn [8, 9, 19, 20], In [21, 22], Mn [8, 19], rare earths (RE) [7, 17, 23], etc. Among these elements, Li has been proved can effectively improve the discharge performance of Mg anodes [15, 17]. In α-Mg and β-Li based Mg alloys, the β-Li phase can weaken the HER reaction that often plagues α-Mg based alloy [15]. Wang et al [13] reported that there is an activation mechanism of dissolution-recrystallization between Pb and Al in the Mg-Al-Pb series alloy. Specifically, the precipitation of Pb2+ can destroy the structure of the discharge products layer, while the precipitation of Al3+ can promote the shedding of Mg(OH)2. As a result, Mg-Al-Pb series alloys as anodes for Mg-air batteries exhibit a higher discharge activity than pure Mg and AZ31 alloys [7]. Although these alloys show better discharge performance in Mg-air batteries, Li has higher costs and potential safety hazards in the manufacturing process due to its high activity. Pb is a toxic and heavy metal element that seriously endanger human health.

As an environmentally friendly element, Sn with a high hydrogen evolution overpotential, a large solubility in Mg and low cost, has attracted considerable attention in the field of corrosion and battery discharge [17, 18, 24]. Gu et al [20] studied the discharge performance of extruded Mg-Sn-Zn-Ag alloys with Sn content between 2 wt% and 8 wt% as anodes for Mg-air batteries. And Mg-4Sn-4Zn-1Ag anode with a high proportion of dynamic recrystallization and the dispersive nanometer-scale Mg2Sn phase, promoting the dissolution of the Mg matrix uniformly and providing a relatively high battery voltage and energy density. Song et al [25] reported that Sn modified AM70 alloy significantly reduces its sensitivity to local corrosion, which is accompanied by corrosion pits or corrosion grooves of large sizes and depth, causing metal blocks to fall off without participating in the discharge, significantly reducing anode efficiency [26]. In addition to the above advantages, Cain et al [27] reported that Mg-Sn alloys with different Sn content have a smaller cathode current density than AZ31B and high-purity Mg in the polarization curve test, which means that Mg-Sn alloys have a lower HER reaction rate. Mg-Sn alloys might be the candidate materials for primary Mg-air batteries anode, but there is no systematic study on their discharge properties in 3.5 wt% NaCl electrolyte. This work can provide valuable basic data for Mg-Sn binary anodes for primary Mg-air batteries.

### 2. Materials and methods

#### 2.1. Materials preparation

The anode materials Mg-xSn (x = 1, 5, 9 wt%) alloys were obtained by melting pure Mg (99.9%) and pure Sn (99.99%). When the well-type resistance furnace temperature was 300 °C, the raw materials were put into a low-carbon steel crucible with a protective atmosphere composed of CO2 and SF6 (CO2: SF6 = 100:1). Next, the raw materials were melted entirely at 730 °C and kept isothermally for 15 min. When the temperature down to 710 °C, slag scraping and stirring were performed. Then, it was poured into a mild steel mold preheated at 200 °C over 2h to obtain a cylindrical ingot with a diameter of 95 mm and cooled in the air. The chemical composition of the as-cast Mg-xSn alloy was analyzed by inductively coupled plasma emission spectrometer (ICP-OES), as shown in table 1.

| Alloy | Sn (wt%) | Mg (wt%) |
|-------|----------|----------|
| Mg-1Sn | 0.95     | Bal.     |
| Mg-5Sn | 5.43     | Bal.     |
| Mg-9Sn | 9.22     | Bal.     |

#### 2.2. Microstructure characterization

The phase identification of Mg-Sn alloys was identified by x-ray diffractometer (XRD; Empyrean). In this test, Cu Kα x-ray radiation was used to scan from 10° to 90°, and the scanning speed was 0.26° per second. Then the measured XRD curves were analyzed via Jade software. The Mg-Sn alloys were ground to 3000 grits with SiC sandpaper and polished with oxide polishing suspension (OPS) to remove most scratches. And supersaturated picric acid was used to etch the grain boundary. The microstructure of the samples prepared was observed using an optical microscope (OM, Zeiss Axio Lab. A1) and scanning electron microscopy (SEM, Quanta FEG 250 SEM). The X-max energy dispersive x-ray spectrometer (EDS) was used to determine the distribution of elements.
2.3. Electrochemical tests
The CorrTest electrochemistry workstation was used to measure the open circuit potential (OCP) and polarization curve, and the ZahnerZennium electrochemical workstation to measure the electrochemical impedance spectroscopy (EIS). Typical three-electrode system was used to test the electrochemical performance. The saturated calomel electrode (SCE) served as the reference electrode, the counter electrode was a platinum electrode (specification: 10 × 10 × 0.1 mm), and Mg-xSn alloys were used as the working electrode. Samples with an area of 10 mm × 10 mm were ground with sandpaper up to 2000 grit. Before polarization curve testing, the sample was immersed in the 3.5 wt% NaCl solution for 10 min to obtain a stable OCP and tested in the potential range of −500 mV to 500 mV (versus OCP) with a scan rate of 0.5 mV s⁻¹. The corrosion current density was calculated by extrapolating the cathodic branch to the corrosion potential. The EIS test was performed under a stable OCP with the scanning frequency from 100 kHz to 0.04 Hz. When it was greater than 66 Hz, the number of the steps per decade was 10, and at low frequencies was 5. The voltage amplitude was 10 mV. Then Zahner analysis was used to fit EIS curves. The reference electrode of this test was 0 V relative to the reversible hydrogen electrode. All electrochemical tests were repeated at least five times to ensure repeatability.

2.4. Mg-air battery tests
The performance of Mg-air batteries with Mg-Sn anodes was tested by a Neware battery testing system. The electrolyte used in the Mg-air battery test was 3.5 wt% NaCl solution. The air cathode used was MnO2/C catalyst, which was provided by Changzhou YOU TE KEI New Energy Technology Co., Ltd All the specimens used for the battery performance testing were polished to 2500 grit with SiC sandpaper and exposed to the electrolyte with a surface of 10 mm × 10 mm. By discharging for 10 h at current densities of 2.5 mA cm⁻², 5 mA cm⁻², 10 mA cm⁻² and 20 mA cm⁻², the potential-time curves of Mg-Sn anodes were obtained. A chromic acid aqueous solution (200 g l⁻¹ CrO₃ + 10 g l⁻¹ AgNO₃) was used to remove discharge products, then the anode efficiency was calculated by the mass loss method. The calculation formula is equations (1) and (2) [28].

\[
\text{Utilization Efficency(\%)} = \frac{W_{\text{theo}}}{\Delta W} \times 100\% \tag{1}
\]
The calculation formulas of specific capacity and specific energy density are shown in equations (3) and (4), respectively.

$$W_{\text{theo}} = \frac{I \times t}{F \times \sum n_i \times \Delta W \times m_i}$$  

Specific capacity ($\text{mAh} \cdot \text{g}^{-1}$) = \frac{I \times t}{\Delta W} \times 1000  

Specific energy ($\text{mWh} \cdot \text{g}^{-1}$) = $U \times \text{Specific capacity} (\text{mAh} \cdot \text{g}^{-1})$

Where $W_{\text{theo}}$ is the theoretical weight loss due to faradaic process (g), $\Delta W$ is the weight loss of alloys during discharge process (g), I is the discharge current (A), t is discharge time (h), F is the Faraday constant (96485C mol$^{-1}$), $x_i$ is the mass fraction, $n_i$ is the number of exchanged electrons, $m_i$ is atomic weight (g mol$^{-1}$) and U is the average discharge voltage (V) [6]. At last, the morphology of the removed surface discharge products after discharge was characterized by SEM.

3. Results and discussion

3.1. Microstructure of Mg-Sn alloys

Figure 1 shows the optical images and XRD patterns of cast Mg-xSn alloys. There is almost equiaxed grain structure in Mg-1Sn alloy (figure 1(a)), while distinct dendrites are found in the microstructure of Mg-Sn alloys with high Sn content (5 wt% and 9 wt%). The formation of dendrites is due to the composition supercooling near the solid-liquid interface when melting liquid solidified. As the content of Sn increases, it greatly promotes crystal nuclei formation, hinders the rapid growth of crystal grains, and refines the dendrites [29]. In XRD patterns, the $\alpha$-Mg solid solution is detected in alloys, while the Mg$_2$Sn intermetallic is only seen in Mg-5Sn and Mg-9Sn alloys. The SEM images and EDS analysis of Mg-Sn binary alloys are shown in figure 2. According to the inset in figure 2(a), the raised bright white points marked by the yellow arrows are the Mg$_2$Sn phase, and the area surrounding the Mg$_2$Sn particles marked by the purple arrows are the enrichment areas of Sn [22]. Whereas, the Mg$_2$Sn phase in Mg-1Sn alloy cannot be detected by XRD might be associated with the low volume fractions and

Figure 2. The secondary electron images of (a) Mg-1Sn, (b) Mg-5Sn and (c) Mg-9Sn and corresponding high-magnification pictures are embedded in them, separately; EDS images of (d) Mg-1Sn, (e) Mg-5Sn, (f) Mg-9Sn.
its small dimension. With the Sn content up to 5 wt%, the Mg2Sn is distributed in irregular bands and dispersive points. Besides, there are still some Sn-rich zones. These Sn-rich zones originally formed the only second phase in the Mg-Sn alloy. Still, the Mg2Sn was not formed due to the large solid solubility of Sn in the Mg matrix, which reduces the precipitation of the Mg2Sn phase [30]. EDS images are tested to determine the distribution of Sn in Mg-Sn alloys, as shown in figures 2(d)–(i), corresponding to the inserted images in figure 2(a)–(c), respectively. In the elemental distribution maps, uniformity of elements in the Mg-1Sn alloy are revealed, aggregation and non-uniformity of elements in the Mg-9Sn alloy are displayed clearly. For Mg-Sn alloys, the increase in Sn content will decrease the distance between the liquidus line and the final eutectic temperature (i.e., the solidification interval). Compared with Mg-1Sn alloy, Mg-9Sn alloy has a lower total solid fraction at the end of solidification but a higher residual liquid phase or eutectic phase [31]. Due to the increase of the eutectic phase, the alloys with high Sn contents show evident element segregation in the eutectic region.

3.2. Electrochemical analysis

Figure 3(a) shows the open circuit potential (OCP) curves of Mg-Sn alloys in 3.5 wt% NaCl solution for 3600s. In the early stage of immersion, the OCP curves of Mg-Sn alloys all have a similar tendency. The potential first increases rapidly to a certain peak and then drops quickly. This rapid increase is due to the zero charge potential of Mg is more negative than its equilibrium potential, contributing to the accumulation of cation on the electrode surface, which causes the apparent potential to move in the inert direction [32]. Then the OCPs gradually shift in a positive direction. As the immersion time increases, the Mg-9Sn alloy is almost at a constant open circuit potential. Because there is a dynamic balance between the progress of the corrosion reaction and the deposition of corrosion products on the surface during the subsequent immersion for Mg-9Sn alloy [33]. The average OCP measured in the last 1600 s is set to EoCP, as shown in table 2. Mg-1Sn alloy has the most negative EoCP value of −1.883 V (versus SCE). With the increase of Sn content, the potential continuously turns into a more positive value, which suggests that the content of Sn in the Mg matrix plays a vital role in the electrochemical behavior of the Mg-Sn alloys [34].

Figure 3(b) reflects the polarization curves of the investigated alloys. It can be seen that with the increase of Sn content, the corrosion potential (Ecorr) gradually shifts towards positive potential, consistent with the OCP results. It proves once again that Mg-1Sn alloy has the strongest electrochemical activity. According to the literature, the polarization curve is comprised of two parts: the cathodic polarization curve indicates the water reduction (2H₂O + 2e⁻ → H₂ + 2OH⁻), while the anodic polarization curve represents the dissolution of magnesium (Mg → Mg²⁺ + 2e⁻) [21, 35]. In figure 3(b), with the increase of Sn content, the cathodic
polarization curve continuously shifts to the direction of a large current, which indicates that the cathodic reaction kinetics of the investigated alloy follow the sequence: Mg-9Sn > Mg-5Sn > Mg-1Sn [36]. As reported, Sn has a high hydrogen evolution overpotential, and when adding minor Sn to Mg can effectively inhibit the HER of the Mg matrix [8, 37]. The related electrochemical parameters obtained from the polarization curve are summarized in table 2. The corrosion current density (Jcorr) value of Mg-1Sn alloy is 19.73 μA cm⁻², which increases to 25.75 and 29.44 μA cm⁻² for Mg-5Sn and Mg-9Sn alloys. The Jcorr could reflect the initiate of corrosion because each polarization curve is tested only after 10 min immersion [38]. Although the Jcorr hardly gives many Mg alloys accurate corrosion rates, it is still receivable to make a qualitative reference [39]. According to literature research, a smaller Jcorr value shows better corrosion resistance [40, 41]. Therefore, the order of corrosion resistance of the alloy is Mg-1Sn > Mg-5Sn > Mg-9Sn.

Figure 4(a) displays the electrochemical impedance spectroscopy (EIS) in Nyquist plots of Mg-Sn alloys at OCP in 3.5 wt% NaCl solution. According to the Nyquist curves, two obvious capacitor semicircles are observed in Mg-1Sn alloy and Mg-5Sn alloy. For Mg-9Sn alloy, the middle capacitive semicircle becomes less evident and the inductive loop appears at low frequencies frequency. The EIS of Mg-1Sn and Mg-5Sn alloys are fitted using the equivalent circuit shown in figure 4(b), and the Mg-9Sn alloy is fitted using the equivalent circuit shown in figure 4(c). Among them, R_s represents the solution resistance, R_c represents the charge transfer resistance, R_f and CPE_f represent the resistance and capacitance of the oxide film, respectively. A constant phase element (CPE) is used to describe the non-ideal capacitive behavior. The element includes two parameters, namely Y and n. Y is like the capacitance of a corrosion system, and n changes from 0 to 1, which is a unitless index [7]. If n is equal to 1, then CPE is equivalent to pure capacitance. At last, CPE_dl represents double-layer capacitors.

The high-frequency capacitance semicircle is caused by the oxide film at the electrode/solution interface on the alloy surface. Its diameter corresponds to the R_c [39]. The fitting results are exhibited in table 3. The R_c value of the Mg-9Sn alloy is 444 Ω cm², which increases to 779 and 760 Ω cm² for Mg-1Sn and Mg-5Sn alloys, respectively. It indicates that the order of corrosion resistance is Mg-1Sn > Mg-5Sn > Mg-9Sn. The intermediate frequency capacitance semicircle is related to the interface between the passivation layer and the solution [42, 43]. The semicircle diameter shows the oxide film resistance (R_s) corresponding to the working electrode [44]. Since the Mg anode immersed in the NaCl solution will spontaneously dissolve and produce Mg²⁺, when the concentration of Mg²⁺ near the surface of the Mg anode reaches saturation, it will be deposited in the form of Mg(OH)₂ [45]. If the semicircle in the intermediate frequency range is not obvious, it means that the Mg(OH)₂ film could not be easily formed on the surface of the alloy [7], as shown in Mg-9Sn alloy in figure 4(a). Hence, the increasing Sn content consecutively increases the self-corrosion in Mg-Sn alloys. This is in keeping with the results obtaining from the polarization curves.

### Table 3. Impedance parameters of the investigated alloys by fitting the EIS.

| Electrolyte | R_s (Ω cm²) | R_c (Ω cm²) | Y_dl (Ω⁻¹ cm² s⁻¹) | n_dl | R_f (Ω cm²) | L(H) |
|-------------|-------------|-------------|---------------------|------|-------------|------|
| Mg-1Sn      | 7.61        | 779         | 2.91 × 10⁻³         | 0.530| 735         | —    |
| Mg-5Sn      | 8.72        | 760         | 1.78 × 10⁻³         | 0.444| 694         | —    |
| Mg-9Sn      | 8.26        | 444         | 1.68 × 10⁻³         | 0.948| 297         | 700  |

Figure 4. (a) Electrochemical impedance spectra (EIS) of Mg-Sn alloys in 3.5 wt% NaCl solution; the EIS of Mg-1Sn and Mg-5Sn alloy at OCP is fitted by the equivalent circuit (b), and the Mg-9Sn alloy fitted by (c).
3.3. Performance of Mg-air batteries

Figure 5 shows the voltage-time discharge curves of Mg-air batteries assembled with Mg-xSn anodes at current densities of 2.5 mA cm$^{-2}$, 5 mA cm$^{-2}$, 10 mA cm$^{-2}$ and 20 mA cm$^{-2}$ in 3.5 wt% NaCl solution for 10 h. At the early stage of the discharge process, due to the rapid accumulation of discharge products especially at the low current density (2.5 mA cm$^{-2}$), the surface area between anode and electrolyte greatly reduced, resulting in a significant decrease of battery voltage. Then three anodes maintain relatively stable discharge voltage during the whole discharge tests at 2.5 mA cm$^{-2}$. However, with the increase of current density, this stability decreases to varying degrees. Table 4 lists the average discharge voltage of the Mg-air batteries discharged for 10 h with different anodes. It can be seen that the Mg-1Sn anode has the highest discharge voltage in all tested alloys at each current density. Materials with a more negative potential in OCP may provide higher voltages when used as anodes in fully assembled batteries, results of this work are consistent with the rule. The results of anode potentiostatic polarization by Yang et al. show that the breakdown resistance of the surface films could be arranged in the following order: pure Mg < Mg-2Sn < Mg-5Sn, indicating that the corrosion resistance of the surface films to localized breakdown increased with the increase in the Sn content. Thus, at 2.5 mA cm$^{-2}$, the discharge product film on the surface of the Mg-9Sn anode is relatively complete, resulting in a lower discharge voltage than the Mg-5Sn anode. Because the dissolution rate of the anode gradually increases with the increased current density. When the current density is greater than 2.5 mA cm$^{-2}$, the average discharge voltage

![Figure 5. Discharge curves of investigated anodes in 3.5 wt % NaCl solution at current density of: (a) 2.5 mA cm$^{-2}$, (b) 5 mA cm$^{-2}$, (c) 10 mA cm$^{-2}$ and (d) 20 mA cm$^{-2}$.](image)

| Anode   | 2.5 mA cm$^{-2}$ | 5 mA cm$^{-2}$ | 10 mA cm$^{-2}$ | 20 mA cm$^{-2}$ |
|---------|------------------|----------------|-----------------|-----------------|
| Mg-1Sn  | 1.418 ± 0.026    | 1.335 ± 0.005  | 1.245 ± 0.007   | 0.999 ± 0.050   |
| Mg-5Sn  | 1.346 ± 0.010    | 1.258 ± 0.018  | 1.119 ± 0.011   | 0.910 ± 0.018   |
| Mg-9Sn  | 1.342 ± 0.007    | 1.256 ± 0.006  | 1.222 ± 0.006   | 0.983 ± 0.023   |
of the Mg-9Sn anode exceeds the Mg-5Sn anode due to the cracks in the discharge product film, which ensures the contact between the electrolyte and the anode surface [9]. In addition, with the increase of Sn content, the volume fraction of the Mg$_2$Sn phase increases, which accelerates the dissolution of the Mg anode and significantly improves the discharge performance of the Mg-air battery [47].

The average voltage of Mg-1Sn anode at 10 mA cm$^{-2}$ reaches 1.245 ± 0.007 V, which is higher than pure Mg, Mg-Al-Zn, Mg-Al-Pb and Mg-Sn-Mn-Ca anodes [7, 19]. In the early stage of Mg-air battery discharge, the discharge product Mg(OH)$_2$ film can provide temporary protection for the Mg alloy and reduce the active area of the anode reaction. However, with the extension of the discharge time, the Mg(OH)$_2$ film will be partially removed from the surface of the Mg anode through the self-peeling effect and the activity will be restored [42]. Some saw-toothed peaks with larger fluctuation can be seen in Mg-1Sn and Mg-5Sn anodes at 20 mA cm$^{-2}$. In contrast, the Mg-9Sn anode remains some tiny cell voltage fluctuation during the whole discharge process. This indicates a relative dynamic balance between the dissolution of the Mg-9Sn matrix and the peeling of the oxidation products. Figure 6 displays the anodic efficiencies, specific capacity and specific energy of Mg-Sn anodes at different current densities. From figure 6(a), Mg-1Sn anodes have the highest anode efficiency at each current density. When the current density is 20 mA cm$^{-2}$, its average anode efficiency is 54.11%, 7.38% and 22.69% higher than Mg-5Sn and Mg-9Sn anode, respectively. According to the work of Baek et al [48], the potential of the Mg$_2$Sn phase seems to be about 350 mV higher than that of the α-Mg matrix, and the corrosion driving force generated by this potential difference leads to micro-galvanic corrosion, which accelerates the

Figure 6. Discharge properties of assembled Mg-air batteries with different anodes: (a) anodic efficiency, (b) specific capacity and specific energy.

Figure 7. Surface morphologies of investigated anodes after discharge 10 min (a)–(c) and 10 h (d–f) in 3.5 wt% NaCl solution at 2.5 mA cm$^{-2}$ with removing of discharge products: (a), (d) Mg-1Sn, (b), (e) Mg-5Sn, (c), (f) Mg-9Sn.
dissolution of the Mg matrix. Combined with the results of this work, Mg-Sn alloys with high Sn content (5 wt% and 9 wt%) are obviously not as suitable as the Mg-1Sn alloy as the anode of the Mg-air battery. In the Mg-1Sn alloy, the minor micron-sized Mg₂Sn phase in the Mg matrix with relative dispersed distribution favors its uniform dissolution during the discharge process. Additionally, the polarization curve and EIS reveal that the Mg-1Sn anode possesses a slight self-corrosion reaction. Therefore, it is not surprising that the Mg-1Sn alloy has the highest specific capacity and specific energy at each current density, as shown in figure 6(b). For example, at 20 mA cm⁻², its average discharge specific capacity and specific energy are 1180.68 mA h g⁻¹ and 1180.00 mW h g⁻¹ respectively, which are 8.49% and 19.22% higher than Mg-5Sn anode, and 26.87% and 29.06% higher than Mg-9Sn anode. As a consequence, it can be seen from the above results that among the three alloys prepared, the Mg-1Sn anode has the best discharge performance at each current density tested.

Figure 7 displays the surface morphologies of Mg-xSn anodes after discharging in 3.5 wt% NaCl solution at 2.5 mA cm⁻² for 10 min and 10 h after removing the oxidation products. After 10 min of discharging, the surface morphology of the Mg-1Sn anode is mainly composed of dispersed holes and shallow grooves, as shown in figure 7(a). When the discharge time increased to 10 h, the discharge morphology also shows relatively uniform dissolution like 10-minutes-discharge. Strip-like morphology composed of small discharge pits and strips is similar to the metallographic structure of figure 2(a), as shown by the yellow arrow in the inset of figure 7(d). This can be preliminarily judged that the Mg₂Sn phase and the Sn-enriched area promote the dissolution of the Mg anode. The Mg-5Sn anode also shows that the Mg₂Sn phase plays an essential role in Mg-Sn alloys dissolution. The most Mg₂Sn phase segregates at the dendrite boundary resulting in obvious grain boundary shedding. Some Mg₂Sn phase and Sn-rich zones disperse in the matrix resulting in irregular discharge pits with different sizes and depths at 2.5 mA cm⁻². After 10 h of discharge, the lamellar eutectic Mg₂Sn phase can be observed, as shown by the yellow arrow in figure 7(e). Although the Mg-9Sn alloy has an equiaxed dendritic structure, uneven discharge morphology is found in the initial discharge process of the Mg-9Sn anode. And some areas are not dissolved in the discharge process, marked by the orange circle in figure 7(c). After 10 h of discharge, apparent petal-like intergranular morphologies were found. Such deep discharge morphology exists in Mg-5Sn and Mg-9Sn alloys cause the metal blocks on the anode surface to fall off and cannot be used for effective battery discharge. When calculating the efficiency of the anode, the loss of weight due to the falling off of the metal block causes the efficiency to decrease [14]. This is another reason why the Mg-1Sn anode has a higher anode efficiency than Mg-5Sn and Mg-9Sn anodes when the current density is 2.5 mA cm⁻².

Figure 8 exhibits the surface morphologies of Mg-Sn anodes discharged at 20 mA cm⁻² for 10 h after removing the oxidation products. With the increase of Sn content, the discharge pits significantly deepen. As the Sn composition increases, the segregation of the Sn elements becomes more prominent and the dendrite size becomes larger, as shown in figures 2(g)–(i). In Mg-Sn alloys, this segregation is dominated by Mg₂Sn accompanied by some Sn-rich regions. And they can form a micro-galvanic couple with the α-Mg matrix to accelerate the dissolution of the Mg anode. Therefore, retiform and deep discharge holes are observed in Mg-9Sn anode at a discharge current density of 20 mA cm⁻². In the Mg-1Sn anode, relative even and shallow corrosion holes can be seen in figure 8(a). The results also show that when Sn is added with a mass fraction of 1 wt%, Mg-Sn anode has better discharge performance. As the above discussion, the volume fraction, distribution, size and morphology of the Mg₂Sn phase and Sn-rich region are the main factors that affect the discharge performance of the Mg-Sn binary anodes.

4. Conclusions

In this work, the electrochemical behaviors and discharge performance with different Sn content as the anode for Mg-air batteries in 3.5 wt% NaCl solution is studied. The main conclusions are as follows:...
(1) In the Mg-1Sn alloy, the micron-sized Mg$_2$Sn phase is dispersed in the matrix. As the Sn content increases, the volume fraction of the Mg$_2$Sn phase increases, promoting dendrite refining. In the elemental distribution maps, the segregation of Sn elements becomes more obvious with the increase of Sn content.

(2) The polarization curve and electrochemical impedance spectra show that the order of corrosion resistance is Mg-1Sn $>$ Mg-5Sn $>$ Mg-9Sn. From the cathodic polarization curve, Mg-9Sn alloy exhibits better reaction kinetics. Because the Mg$_2$Sn phase can form a micro-galvanic couple with the $\alpha$-Mg matrix, it accelerates the corrosion of the Mg anode. In addition, the more Mg$_2$Sn phase in the Mg-9Sn alloy accelerates the micro-galvanic corrosion between it and the Mg matrix, resulting in more significant reaction kinetics.

(3) In the discharge measurement, the Mg-1Sn anode achieves the best average discharge voltage, anode efficiency, specific capacity, and energy under all current densities tested. When the current density is 10 mA cm$^{-2}$, the average discharge voltage and specific energy of the Mg-1Sn anode are 1.245V and 1239.621 mWh g$^{-1}$, respectively, which are 10.120% and 37.163% higher than the Mg-5Sn anode, 1.847% and 24.795% higher than the Mg-9Sn anode. And the Mg-1Sn anode shows a more uniform dissolution due to the dispersed micron Mg$_2$Sn phase and slight Sn-rich areas around it. However, compared with the Mg-1Sn alloy, the large-scale Mg$_2$Sn phase in the Mg-5Sn and Mg-9Sn alloys causes local and deep discharge pits on the surface of the Mg anode after discharge.

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Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).

ORCID iDs

Gaofeng Quan @ https://orcid.org/0000-0001-5928-3082

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