

Electrochemical properties of magnesium alloy anodes discharged in seawater

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Abstract: Magnesium alloys can be developed as anode materials for seawater activated batteries. The electrochemical properties of AZ31, AP65 and Mg–3%Ga–2%Hg alloy anodes discharged in seawater were studied. The potentiodynamic polarization shows that the Mg–3%Ga–2%Hg alloy provides more negative corrosion potentials than AZ31 or AP65 alloy. The galvanostatic discharge results show that the Mg–3%Ga–2%Hg alloy exhibits good electrochemical properties as anodes in seawater. And the EIS studies reveal that the magnesium alloy anode/seawater interfacial process is determined by an activation controlled reaction. The Mg₃Hg and Mg₂₁Ga₅Hg₃ phases in Mg–3%Ga–2%Hg alloy improve its electrochemical properties better than the Mg₁₇(Al,Zn)₁₂ phase in AZ31 and Mg(Pb) solid solution phase in AP65 alloys.

Key words: magnesium alloy; Mg–Ga–Hg alloy; electrochemical properties; seawater activated battery; anode

1 Introduction

Magnesium alloys can be used as anode materials in seawater activated batteries which are power sources for under water instruments [1,2]. The battery with magnesium alloy anode makes the seawater electrolyte, so it obtains more practicability and lower cost advantages than other lithium ion or alkaline batteries [2,3]. The seawater activated batteries rely on the corrosion of metal anode in seawater to provide the cell voltages [3]. Hence, magnesium can be applied as the key anode material because it offers an appropriate corrosion rate and provides a high electrode potential of –2.73 V vs. normal hydrogen electrode (NHE) [4]. Recently, some seawater activated magnesium alloy anodes have been developed for applications, such as AZ31 (Mg–3%Al–1%Zn) and AP65 (Mg–6%Al–5%Pb) alloys. The previous investigations show that the AZ31 alloy cannot provide suitable electrochemical properties as AP65 alloy does when they used as anode in seawater with cuprous chloride (CuCl) or silver chloride (AgCl) as cathode [5,6]. The Mg–Ga–Hg alloy is a new developed anode because it can provide a high specific energy of about 150 W·h/kg in the seawater activated battery. Mercury can improve the corrosion voltage of battery and gallium can control the corrosion rates of anode [7].

Thus, in order to achieve good performance of magnesium alloy anode, it is necessary to obtain a thorough understanding of the associated electrochemical properties of AZ31, AP65 and Mg–Ga–Hg alloy in seawater with different discharge parameters and performance. Accordingly, the present study examines and compares the discharge properties of such three magnesium alloys in the artificial seawater.

2 Experimental

The AZ31, AP65 and Mg–3%Ga–2%Hg (mass fraction) alloys were prepared by melting high purity magnesium (>99.9%), aluminum (>99.9%), zinc (>99.9%), lead (>99.9%), gallium (>99.99%) and mercury (>99.99%), respectively. The analyzed chemical compositions of the experimental alloys are shown in Table 1.

Table 1 Analyzed chemical compositions of three experimental alloys

Alloy	w(Al)/ %	w(Zn)/ %	w(Pb)/ %	w(Ga)/ %	w(Hg)/ %	w(Mg)/ %
AZ31	2.94	0.93	–	–	–	Bal.
AP65	6.11	–	5.08	–	–	Bal.
Mg–Ga–Hg	–	–	–	3.13	2.21	Bal.

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The experimental alloy was melted from 943 K to 973 K under a protection of Ar_2+SF_6 gas mixture to impede the inflammation of magnesium at high temperature. The molten alloy was cast in the water-cooled copper mold. Then the as-cast experimental alloy ingots were homogenized at 698 K for 16 h and hot rolled to sheets with (0.5 ± 0.1) mm in thickness with several rolling passes. During every hot rolling pass, the experimental alloy plates were reheated to 673 K for 0.5 h to improve the deformability. At last, the rolled experimental alloy sheets were annealed at 533 K for 2 h and produced as the specimens for electrochemical measurement. All these specimens were performed in a Solartron SI 1287 potentiostat/galvanostatic system with a three-electrode configuration for electrochemical testing. The working electrode was the experimental alloy and the counter electrode was a platinum plate. A saturated calomel electrode (SCE) was served as the reference electrode. The potentials in this study were reported with respect to such reference electrode except for special illustration. The polarization, galvanostatic

test and electrochemical impedance spectroscopy (EIS) of the experimental alloy anode were measured and the data were acquired and processed by the Zplot/Zview software version 2.6. The electrolyte in this study was artificial seawater with a pH 7.02. Its composition was 26.5 g/L NaCl + 24 g/L MgCl_2 + 0.73 g/L KCl + 3.3 g/L MgSO_4 + 0.2 g/L NaHCO_3 + 1.1 g/L CaCl_2 + 0.28 g/L NaBr [8]. The temperature of the artificial seawater in this study was (286 ± 1) K.

The microstructures of the experimental alloys were observed by using a Polyvar-MET metallographic microscope, a JSM-5600Lv scanning electron microscope (SEM) with energy-dispersive X-ray spectroscopy (EDS).

3 Results and discussion

3.1 Microstructure of three alloys

The morphologies of the three experimental alloys in as-cast and rolling-annealed states are shown in Fig. 1. The phases in as-cast and rolling-annealed states can be

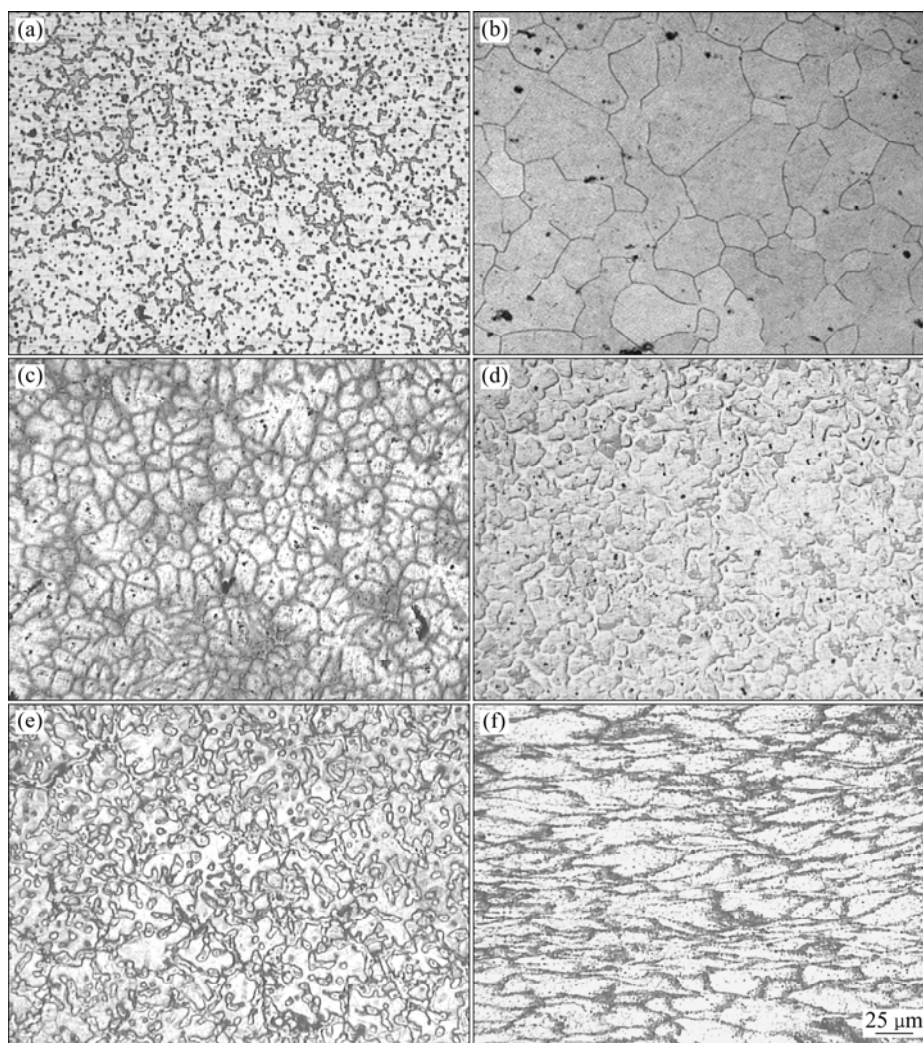


Fig. 1 Microstructures of three experimental alloys in as-cast and rolling-annealed states: (a) AZ31 alloy in as-cast state; (b) AZ31 alloy in rolling-annealed state; (c) AP65 alloy in as-cast state; (d) AP65 alloy in rolling-annealed state; (e) Mg-3%Ga-2%Hg alloy in as-cast state; (f) Mg-3%Ga-2%Hg alloy in rolling-annealed state

identified through X-ray spectroscopy. The result show that the typical phase in AZ31 alloy is $\text{Mg}_{17}(\text{Al,Zn})_{12}$. The Pb forms the solid solution in Mg matrix in AP65 alloy and the phases in Mg–Ga–Hg alloy are $\text{Mg}_{21}\text{Ga}_5\text{Hg}_3$ and Mg_3Hg [9].

3.2 Self-corrosion behaviors of three alloys

The self-corrosion behaviors of the three magnesium alloy specimens immersed in seawater are shown in Fig. 2. The results obviously show that the Mg–3%Ga–2%Hg alloy obtains the highest self corrosion in seawater but the AZ31 alloy gets the lowest. The corrosion products on the surface of Mg–3%Ga–2%Hg alloy is the greatest among the three experimental alloys but only a little on the AZ31 alloy (Fig. 3). Such phenomenon matches with the mass loss curves of the three alloys.

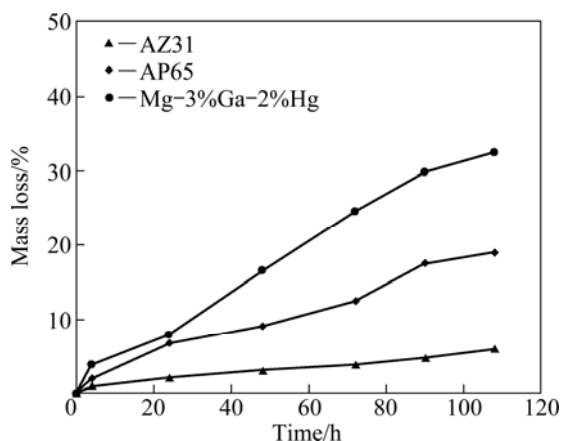


Fig. 2 Self-corrosion behavior of three experimental alloys

3.3 Potentiodynamic polarization of three alloys

The potentiodynamic polarization curves of the three alloys are shown in Fig. 4. The polarization parameters measured from the polarization curves are given in Table 2. The results show apparent variations in the corrosion potential and the corrosion current density for the three alloys in seawater. The corrosion potential of Mg–3%Ga–2%Hg alloy is more negative than that of AP65 or AZ31 alloy. Compared the Mg–3%Ga–2%Hg alloy with AZ31 alloy, the corrosion potential shifts negatively by 0.077 V, meanwhile, the corrosion current increases by 0.80 mA/cm^2 . And for AP65 alloy, such two measured parameters are 0.045 V and 0.28 mA/cm^2 respectively. As it well known that the standard potential of the magnesium electrode is -2.73 V (vs NHE), but the steady-state working potential is generally about -1.50 V (vs NHE). This deviation in potential is due to the formation of a magnesium hydroxide film on the metal surface. Therefore, the result that Mg–Ga–Hg alloy obtains the most negative corrosion potential with a higher corrosion current shows the utilization of

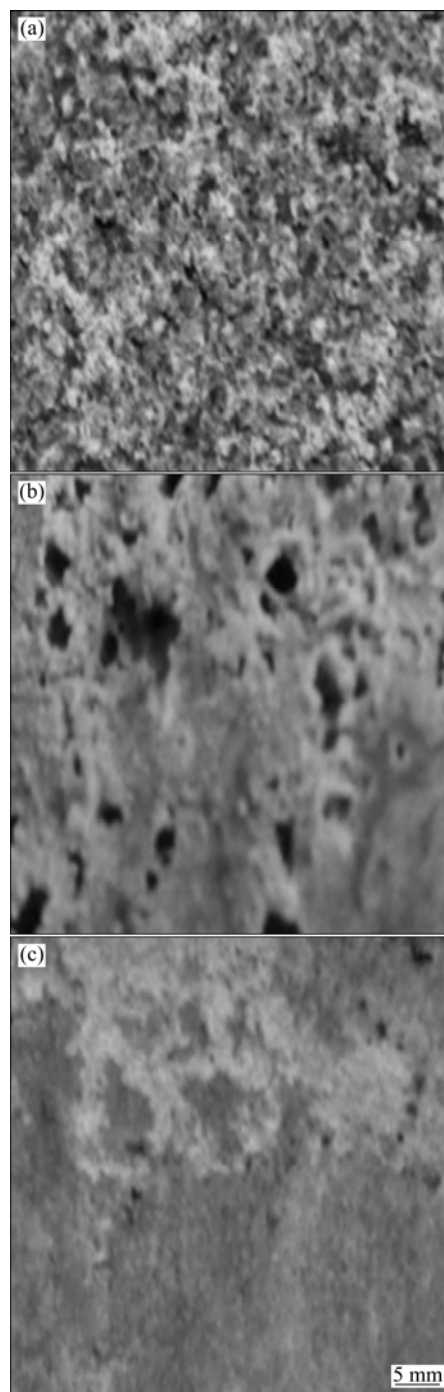


Fig. 3 Surface corrosion morphologies of three experimental alloys: (a) Mg–3%Ga–2%Hg alloy; (b) AP65 alloy; (c) AZ31 alloy

Mg–3%Ga–2%Hg alloy as anode in the seawater activated battery is more suitable than other two alloys.

The electrochemical reactions for Mg alloy in seawater can be minimized by the corrosion product $\text{Mg}(\text{OH})_2$ which pastes on the surface of magnesium alloy and results in reducing anode reacting area [10]. The firm adhesion of $\text{Mg}(\text{OH})_2$ on the surface of AZ31 alloy impedes the corrosion reaction process.

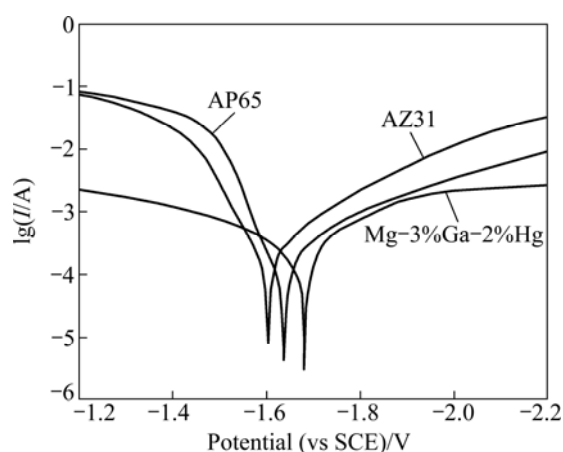


Fig. 4 Potentiodynamic polarization curves of three alloys in seawater

Table 2 Parameters of three alloys obtained from polarization curves

Alloy	Corrosion potential (vs SCE)/V	Corrosion current/(A·cm ⁻²)
AZ31	-1.602	1.61×10^{-3}
AP65	-1.634	2.13×10^{-3}
Mg-3%Ga-2%Hg	-1.679	2.41×10^{-3}

Furthermore, the second phase of $\text{Mg}_{17}(\text{Al,Zn})_{12}$ also improves the corrosion resistance of AZ31 alloy [11]. Hence, the corrosion potential and current of AZ31 alloy are the lowest and hard to meet the requirement as an anode for seawater activated battery. But the solid solution of Pb in Mg matrix in AP65 alloy and the intermetallic $\text{Mg}_{21}\text{Ga}_5\text{Hg}_3$ and Mg_3Hg phases in Mg-3%Ga-2%Hg alloy make the electrochemical reaction more uniform and increase the corrosion rate. This phenomenon can be observed on the corrosion surface of the specimens after discharging, as shown in Fig. 5. Figure 5(a) shows that the corrosion products around the $\text{Mg}_{21}\text{Ga}_5\text{Hg}_3$ phase break off and result in the corrosion reaction penetrating into the interior of Mg-3%Ga-2%Hg alloy matrix. Same situation occurs on the surface of AP65 alloy where the solubility of Pb in Mg matrix is higher (Fig. 5(b)). But the main solid corrosion product $\text{Mg}(\text{OH})_2$ impedes the corrosion penetrating into the Mg matrix on the surface of AZ31 alloy specimen.

3.4 Galvanostatic measurements of three alloys

In order to further understand the discharge behaviors of Mg-3%Ga-2%Hg alloy and compare with AZ31 and AP65 alloys, the discharge relation between the current density and time for three experimental alloy sheets on a steady discharge voltage of 1.5 V is shown in Fig. 6. And the galvanostatic measurements are

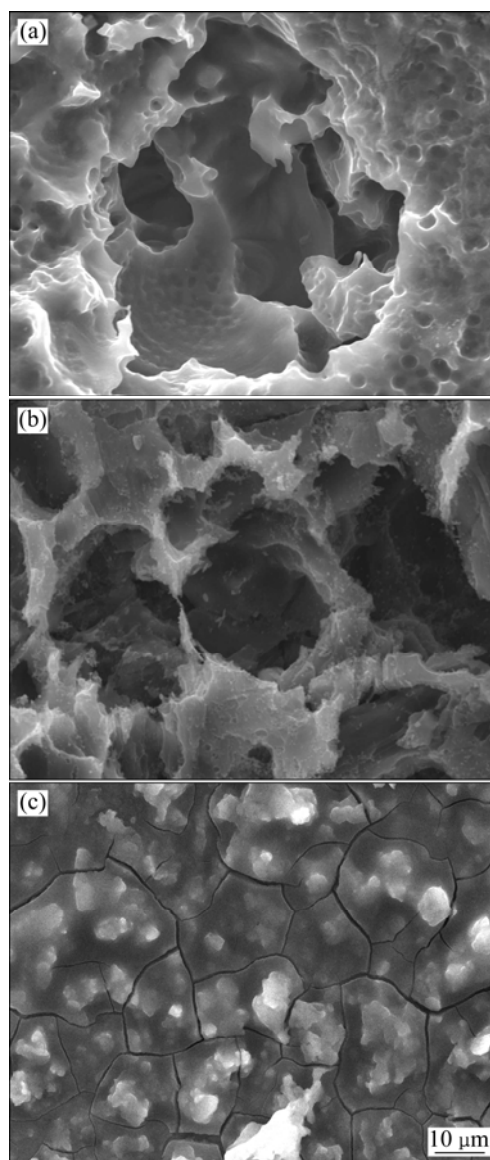


Fig. 5 SEM images showing corrosion surface of three specimens after potentiodynamic polarization test: (a) Mg-3%Ga-2%Hg alloy; (b) AP65 alloy; (c) AZ31 alloy

performed with different current densities, 100 and 300 mA/cm², respectively, in Fig. 7. The low current density of 100 mA/cm² aims to evaluating the discharge behavior of power source anode material for low-power applications. And the high current density of 300 mA/cm² is used to measure the discharge behavior of anode for high-power applications.

The results show that the discharge current density of Mg-3%Ga-2%Hg alloy is the highest among the three alloys and about twice that of AZ31 alloy as shown in Fig. 6. Figure 7 shows that the Mg-3%Ga-2%Hg alloy provides the most negative voltage values and maintains a stable corrosion potential value during the whole discharge process. The AP65 alloy can be used as battery anode material due to its high corrosion potential

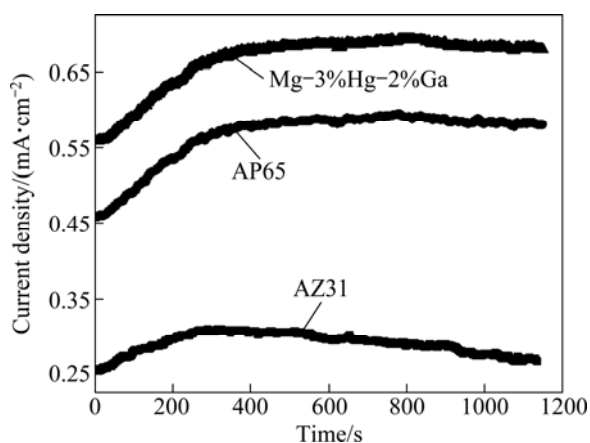


Fig. 6 Discharge relationship between current density and time at steady voltage of 1.5 V

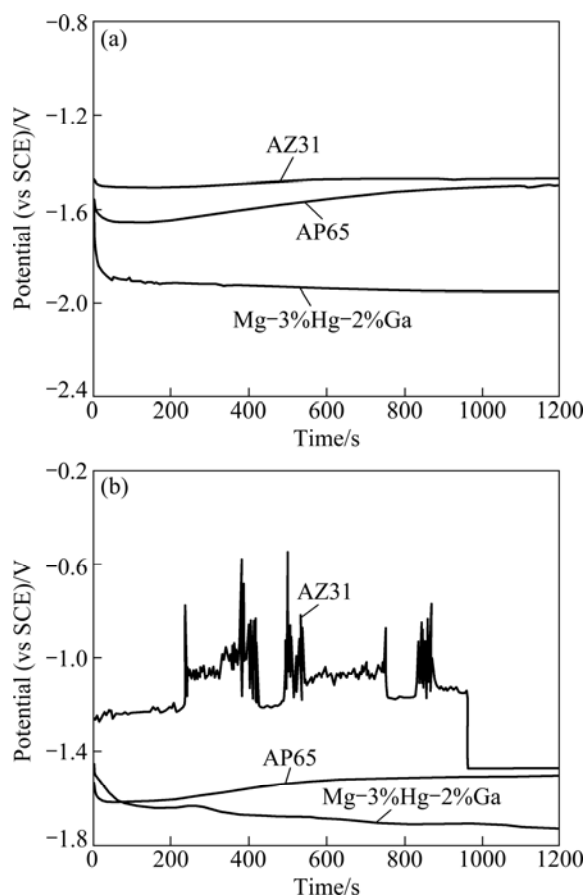


Fig. 7 Discharge potential vs time curves at current density of 100 (a) and 300 (b) mA/cm²

value during the discharge process. And the corrosion potential value of AP65 alloy will first move to negative and then move to positive because of the polarization effect which is due to the heterogeneous distribution of the Pb solid solution in Mg matrix. And the discharge behavior of AZ31 alloy is unstable with the current density of 300 mA/cm². This difference is due to the

different compounds which influence the corrosion behaviors in different alloys. The typical compounds, such as Mg₁₇(Al,Zn)₁₂ phase in AZ31 alloy, will hinder the corrosion process during the discharge process and result in the unstable discharge behavior. But the Mg₃Hg and Mg₂₁Ga₅Hg₃ phases in Mg-3%Ga-2%Hg alloy obtain a greater electrode potential difference compared with the α -Mg matrix. Such two compounds in Mg-3%Ga-2%Hg alloy will accelerate the corrosion of α -Mg matrix and induce the corrosion penetrating into the internal of alloy. The dissolving of α -Mg matrix with Mg₃Hg and Mg₂₁Ga₅Hg₃ will produce Hg and Ga ions, which combine with Mg to produce amalgam that reacts severely with water and maintains the activation reaction circle. Furthermore, the corrosion products on the surface of Mg-3%Ga-2%Hg alloy fall off easily and can not paste sturdy enough to prevent the continue corrosion of the α -Mg matrix in the Cl⁻ environment. All these will result in a persistent corrosion and steady discharge potential of Mg-3%Ga-2%Hg alloy.

3.5 Electrochemical impedance spectroscopy of three alloys

The electrochemical impedance spectroscopy (EIS) was used to study the corrosion mechanism of the three experimental alloys in seawater. The impedance locus diagrams of Mg-3%Ga-2%Hg, AP65 and AZ31 alloys were obtained by applying a frequency range of 0.01–100 kHz with an AC amplitude of 10 mV. Typical Nyquist plots for the three magnesium alloys are shown in Fig. 8(a). The Nyquist plot shows that the curves of the three alloys have a single capacitive loop at all frequencies. The semicircles of the three alloys indicate that the Mg alloy/seawater interface in this investigation is controlled predominantly by activation-controlled processes [12]. The diameter of the semicircle gives the charge-transfer resistance (R_{ct}) at the Mg alloy/seawater interface which is related to the corrosion rate. The intercept on the x-axis at the higher frequencies gives the solution resistance (R_s). The equivalent circuit model of the impedance diagram is provided in Fig. 8(b). And the EIS spectra of the three alloys are similar except in diameter, which shows that the corrosion mechanism is same but the corrosion rate is different. Since the corrosion rate is inversely related to R_{ct} , the higher the R_{ct} value is, the lower the corrosion rate is. The least diameter is obtained for Mg-3%Ga-2%Hg alloy, indicating that the corrosion resistance of such alloy is the lowest. And the order of the R_{ct} values with respect to the three experimental alloys is: AZ31>AP65>Mg-3%Ga-2%Hg. This reflects that the corrosion rate of Mg-3%Ga-2%Hg alloy is the highest. Furthermore, the calculated C_{dl} values of the three alloys are 1.29×10^{-3} F for Mg-3%Ga-2%Hg alloy, 8.48×10^{-4} F for AP65

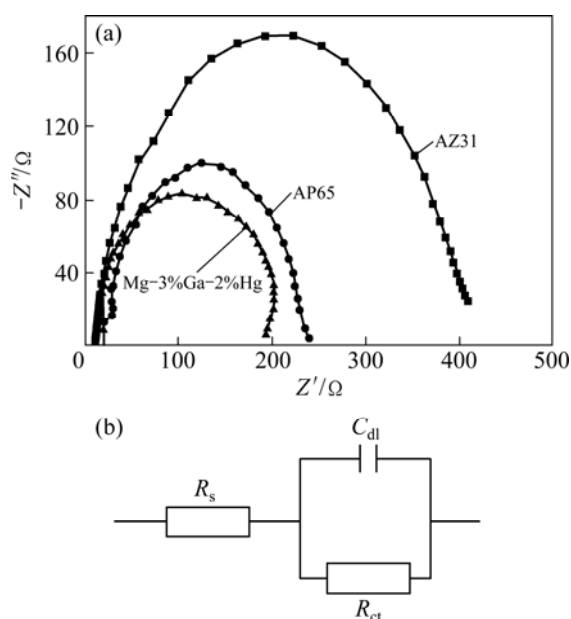


Fig. 8 Nyquist plots and equivalent circuit model of three experimental alloys in seawater: (a) Nyquist plots; (b) Equivalent circuit model

alloy and 1.33×10^{-5} F for AZ31 alloy. The low C_{dl} value for the magnesium alloy implies the formation of relatively thick and compact protective film on the alloy surface. As expected, the Mg-3%Ga-2%Hg alloy obtains the highest C_{dl} value and AZ31 alloy obtains the lowest value. It is also seen that the increase in R_{ct} is accomplished by the reduction in C_{dl} due to the total difference corrosion behaviors among these three alloys. During the corrosion process, the $Mg_{17}(Al,Zn)_{12}$ phase in AZ31 alloy acts as effective barrier. Hence, the corrosion product film on such phase is continuous so that the dissolution of α -Mg is inhibited. The discharge process of AZ31 alloy will be impeded so that it can not be used as the seawater-activated anode. On the contrary, the Mg_3Hg and $Mg_{21}Ga_5Hg_3$ phases in Mg-3%Ga-2%Hg alloy are activated more easily and accelerate the corrosion of α -Mg matrix. So it is hard for such alloy to form effective protective film in chloride environment, indicating that such alloy can be used as anode in seawater. The addition of Ga and Hg in the alloy promotes the electrochemical activity and lets the anode react persistently. The Mg_3Hg phase and the amalgam produced during the electrochemical reactions provide enough negative potential for the application of battery. The solid solution of Ga in α -Mg and the dispersed distribution of $Mg_{21}Ga_5Hg_3$ phase which precipitates from the solid solution of α -Mg matrix produce a little charge transfer resistance in the faradaic reaction, which leads to a good electrochemical performance such as a fast activity time and negative corrosion potential. This leads to a controllable corrosion driving force and lets

the alloy exhibit an appropriate corrosion rate during the discharge process [13–15].

4 Conclusions

1) The electrochemical properties of Mg-3%Ga-2%Hg alloy show that it provides more negative corrosion potential and higher discharge current density than AZ31 or AP65 alloy.

2) EIS studies reveal that the Mg alloy/seawater interfacial process is determined by an activation controlled reaction. The formation of protective film on the Mg alloy surface follows the following sequence: Mg-3%Ga-2%Hg < AP65 < AZ31. Hence, the corrosion rate of Mg-3%Ga-2%Hg alloy is the highest.

3) The different phases in different alloys play important roles on the electrochemical properties. The Mg_3Hg and $Mg_{21}Ga_5Hg_3$ phases in Mg-3%Ga-2%Hg alloy provide enough negative potential and accelerate the dissolution of α -Mg in the seawater during the electrochemical reactions. It means that the Mg-Ga-Hg alloy can be used as a candidate for seawater activated battery anode.

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镁合金阳极材料在海水中放电的电化学性能

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摘 要: 镁合金可以作为海水激活电池阳极材料来使用。研究了 AZ31、AP65 和 Mg–3%Ga–2%Hg 3 种镁合金在海水中放电的电化学性能。Mg–3%Ga–2%Hg 合金的阳极极化曲线表明, 该合金具有比 AZ31 和 AP65 合金更负的腐蚀电位。恒电流放电实验结果表明, Mg–3%Ga–2%Hg 合金在海水中表现出更好的阳极放电性能。交流阻抗测试表明, 镁合金阳极和海水接触表面的电化学反应决定反应的活性, Mg–3%Ga–2%Hg 合金中的 Mg₃Hg 和 Mg₂₁Ga₅Hg₃ 化合物比 AZ31 合金中的 Mg₁₇(Al,Zn)₁₂ 相以及 AP65 合金中的铅在镁中形成的固溶体具有更好的电化学活性。

关键词: 镁合金; Mg–Ga–Hg 合金; 电化学性能; 海水激活电池; 阳极

(Edited by YANG Hua)