Microstructure and electrochemical corrosion behavior of extruded Mg–Al–Pb–La alloy as anode for seawater-activated battery

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HIGHLIGHTS

- Extrusion improves the discharge activity of Mg–Al–Pb–La alloy.
- The relation between grain orientation and electrochemical corrosion behavior is clarified.
- The extruded Mg–Al–Pb–La alloy is an appropriate anode for seawater-activated battery.

GRAPHICAL ABSTRACT

The anisotropy of corrosion resistance in the extruded Mg–Al–Pb–La alloy is associated with grain orientation. The longitudinal section along extrusion direction (ED) has a high proportion of low-energy (0001) planes and exhibits better corrosion resistance than the transversal section along radial direction (RD).

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ABSTRACT

A seawater-activated battery is a disposable reserve battery that is specifically designed to pollute less due to the absence or relatively less use of heavy metals. Mg–Al–Pb–La alloy is a typical anode material that is used in high-power seawater-activated batteries. In this study, we use microstructure characterization to demonstrate that hot extrusion refines the grains of the alloy and leads to the formation of banded structures composed of the lamellar β -Al₁₁La₃ and lump Al–Mn phases. Our electrochemical measurements reveal that the extruded Mg–Al–Pb–La alloy is a promising anode material that exhibits excellent discharge activity and high anodic efficiency at a large current density. Moreover, we also examine the correlation between the grain orientation induced by extrusion and the electrochemical corrosion behavior of Mg–Al–Pb–La alloy. We believe that our results can significantly contribute to the development of seawater-activated batteries.

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1. Introduction

Magnesium alloys with high energy density, negative standard electrode potential, and large capacity can serve as anodes for seawater-

activated batteries, magnesium-air batteries, dissolved-oxygen batteries, etc. [1–5]. In this backdrop, magnesium-based anodes such as Mg–Hg–Ga, Mg–Al–Pb, and Mg–Al–Ti with high cell voltages have recently been developed [6]. Mg–Al–Pb alloy has been widely used in high-power seawater-activated batteries, particularly the AP65 alloy that has a negative corrosion potential and a nominal composition of Mg-6%Al-5%Pb (wt%) [6].

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A seawater-activated battery is composed of two indispensable parts: a metal anode and a metal chloride cathode made of compounds such as AgCl and CuCl, and such batteries can be used as potential power sources for undersea devices including sonobuoys and electric torpedoes [7,8]. However, magnesium alloys are susceptible to self-corrosion, and the alloy surface is often covered with corrosion products after discharge, which undermines their discharge performance [8–12]. Thus, there is a trade-off between activation and passivation for magnesium. The choice of a suitable magnesium anode significantly impacts the properties of seawater-activated batteries [3,8]. The commonly utilized methods to further improve the properties of magnesium are alloying, plastic deformation, and heat treatment [5,10,12,13].

Rare earth elements (REs) have been found to be suitable candidate elements for alloying with magnesium, since they offer the functionalities of melt purification, lattice distortion, and cathode passivation [12,14,15]. In this regard, Hu et al. [16] reported that the addition of cerium to AP65 alloy led to the refinement of β ($\text{Mg}_{17}\text{Al}_{12}$) phases and the formation of Al–Ce phases, which significantly enhanced the electrochemical properties of AP65 alloy. Further, Mg–Al–Pb–Ce–Y alloy was found exhibit improved corrosion resistance and discharge performance over those of pure magnesium, AZ31, and Mg–Al–Pb alloys because of the modified microstructures induced by the REs [4]. In addition, lanthanum-containing magnesium alloys such as AE21 and AE42 have been developed as commercial alloys [17]. In this regard, Feng et al. [6] determined that the discharge activity and corrosion resistance of AP65 alloy were enhanced by the addition of lanthanum, which can be mainly attributed to the refined grains and the increasing amount of weak cathodic rare earth phases. Meanwhile, it has been reported that plastic deformation, such as hot extrusion, can significantly change the microstructure of magnesium, exerting an obvious effect on its properties [8,18]. Generally, hot extrusion leads to a deterioration in the corrosion resistance because of the rearranged β ($\text{Mg}_{17}\text{Al}_{12}$) phases, deformed grains, and increased density of crystal defects, which are strongly supported by many reports [18–20]. However, Jeong et al. [21] found that the corrosion resistance of a Mg–Ca alloy with $\text{Ca} \geq 1\%$ was enhanced by extrusion, which was closely related to the effective break-up of Mg_2Ca phases. A similar effect was found by Minárik et al. [17] for an equal channel angular pressed (ECAPed) AZ42 alloy. Moreover, the discharge activity and anodic efficiency of AP65 alloy can be improved via hot extrusion due to the refined grains and uniform grain size according to Wang et al. [8]. It is noting that plastic deformation often gives rise to variations in grain orientation, which in turn has an obvious effect on the electrochemical corrosion behavior of magnesium [7,22,23]. Until recently, however, most reports focused on crystal defects and second phases, and grain orientation has rarely been taken into consideration. It has been reported that grains with basal orientation exhibited better corrosion resistance than those with non-basal orientation for polycrystalline pure magnesium [24]. The rolling surfaces of the rolled AZ31 and AP65 alloys have a much higher proportion of basal crystal planes, and thus, they usually exhibit relatively better corrosion resistance than a cross-sectional surface, owing to the lower surface energy of the basal planes [7,22,24].

In our study, we prepared Mg–Al–Pb–La alloy to analyze the effects of hot extrusion on the alloy's microstructure and electrochemical corrosion behavior. In addition, we especially examined the effects of crystal orientation, grain defect, and second phase in detail.

2. Experimental detail

2.1. Materials preparation

Mg–6Al–5Pb–1La (wt%) alloy (referred to as AP65–La) was prepared by melting and casting using an induction furnace under the protection of an argon atmosphere at 750 °C. The alloying elements (Al, Zn, and Pb) were added in the form of pure metals (99.99 wt%), while other elements such as Mn and La were added via intermediate alloys, i.e., Al–

Table 1
Chemical composition of the as-quenched AP65–La alloy (wt%).

Element	Al	Pb	La	Zn	Mn	Fe	S	P	Mg
Content	5.600	4.760	0.910	0.540	0.089	0.006	0.003	0.001	Bal.

15%Mn and Mg–30%La (wt%). Next, the molten metal was poured into an iron mold with a diameter of 120 mm under the protection of sulfur powder. Table 1 lists the chemical composition of AP65–La alloy as analyzed with inductively coupled plasma atomic emission spectrometry. Next, progressive solution treatments at 330 °C for 16 h and then 420 °C for 2 h were performed for the as-cast AP65–La alloy followed by water quenching. The as-quenched AP65–La alloy was preheated at 450 °C for 18 h. Subsequently, it was extruded into a rod with a diameter of 40 mm at an extrusion speed of 3 m min^{−1} and an extrusion ratio of 9:1. Thereafter, the extruded alloy was air cooled.

2.2. Microstructure characterization

Optical microscopy, scanning electron microscopy (SEM), electron probe microanalyses (EPMA), and electron backscatter diffraction (EBSD) were employed to characterize the microstructures of AP65–La alloys before and after extrusion. The longitudinal section along the extrusion direction (ED) and the transversal section along the radial direction (RD) of the extruded alloy are shown in Fig. 1.

The specimens used for metallographic observations were ground with SiC abrasive paper followed by diamond polishing, and then etched in a solution consisting of 3 g picric acid, 2.5 mL acetic acid, 50 mL ethanol, and 5 mL distilled water. The average grain sizes of the alloys were evaluated by means of the linear intercept method using Nano Measurer 1.2 software. The number of grains taken into account was 200 before and after extrusion, respectively. The EBSD was carried out under SEM condition, and the thin foils used for EBSD observation were pared down to 500 μm with an electron discharge cutter, and then ground to a thickness of 70 μm with SiC abrasive paper. Finally, the thin foils were ion-milled with ion incident angle of 3° using an ion beam thinner to remove the surface stress layer. The corrosion morphologies after cleaning of the corrosion products were monitored after 72 h of immersion in 3.5 wt% NaCl aqueous solution. The 3.5 wt% NaCl solution was prepared with analytical grade chemicals and distilled water to simulate seawater [7,8].

2.3. Weight loss measurements

The specimens used for weight loss measurements were ground and weighed using a digital balance with the precision of 0.1 mg to obtain the original weight. Next, the specimens were immersed in 3.5 wt% NaCl solution for 72 h at (25 ± 1) °C. Finally, the specimens were cleaned with chromic acid, dried by hot air flow, and reweighed to obtain the weight loss and weight loss rate.

2.4. Electrochemical measurements

The corrosion behavior at the open-circuit potential (OCP) and the discharge performance of AP65–La alloys before and after extrusion

Fig. 1. Sampling directions in the extruded AP65–La alloy. The ED is extrusion direction and the RD is radial direction, respectively.

were investigated by polarization, impedance, OCP, and galvanostatic measurements. The specimens used for electrochemical measurements were prepared with an exposed area of $10 \text{ mm} \times 10 \text{ mm}$, and the other surfaces were mounted using epoxy resin. Subsequently, the working surface was ground with 1200-grit SiC abrasive paper. The galvanostatic measurements were conducted in a CHI660D workstation, while other tests were performed with a Zahner workstation. All measurements were carried out in 3.5 wt% NaCl solution at $(25 \pm 1)^\circ\text{C}$ using a three-electrode configuration, i.e., a platinum foil as the counter electrode, a saturated calomel electrode (SCE) as the reference electrode, and the specimen as the working electrode.

The polarization curves were measured from -1.9 V to -1.1 V at a scanning rate of 1 mV s^{-1} after the OCPs stabilized. The measuring time for OCP curves was 1200 s. The impedance spectra with perturbation amplitude of 20 mV were recorded at OCPs over a frequency range from 100 kHz to 0.5 Hz after 600 s of immersion in electrolyte. Next, the spectra were fitted using Zview software. The galvanostatic curves were recorded during discharge at the current densities of 180 and 300 mA cm^{-2} , which were selected in order to test the discharge performance of the anodes for high-power seawater-activated battery [8]. Finally, the average discharge potential and anodic efficiency were obtained after discharge for 600 s and 1 h, respectively. The discharge morphologies of AP65-La alloys discharged at 180 mA cm^{-2} were monitored before and after extrusion. The anode efficiency was calculated by dividing the theoretical weight loss by the actual weight loss according to Eq. (1) [25]. Meanwhile, the theoretical weight loss caused by electron transfer can be calculated by Eq. (2), in which I is the discharge current; t is time in seconds; F is the Faraday constant ($96,500 \text{ C mole}^{-1}$); f_i , n_i and a_i are the mass fraction, the number of electrons exchanged and the atomic weight, respectively, of the i th alloying element [25].

$$\text{Efficiency}(\%) = \left(\frac{W_{\text{theoretical}}}{W_{\text{actual}}} \right) \times 100\% \quad (1)$$

$$W_{\text{theoretical}} = \frac{I \times t}{F \times \sum \left(\frac{f_i \times n_i}{a_i} \right)} \quad (2)$$

To obtain good reproducibility and accuracy of data, some measurements were conducted in triplicate under identical conditions.

3. Results and discussion

3.1. Microstructure

The optical micrographs and backscattered images of AP65-La alloys before and after extrusion are shown in Fig. 2, while the calculated grain sizes and recrystallization diagrams are depicted in Fig. 3. The grain sizes and the corresponding errors represent the average values and the standard deviations, respectively. The confidence bands in Fig. 3(a) represent the standard deviations of these sizes. The various colors in the recrystallization diagram represent the different states of grains, i.e., blue denotes recrystallized grains, red deformed grains, and yellow the intermediate state.

It is visible that the lamellar, lump, and granular phases distribute homogeneously in the as-quenched AP65-La alloy, whose grain size is $167.5 \mu\text{m}$. In contrast, the extruded AP65-La alloy exhibits finer grains, whose sizes are $35.6 \mu\text{m}$ and $44.9 \mu\text{m}$ along the RD and ED directions, respectively. Thus, the extruded AP65-La alloy had more grain boundaries than the as-quenched one for the same area. In addition, it can be observed from confidence bands in Fig. 3(a) that the distribution of grain sizes in the extruded alloy is more uniform than before extrusion. In addition, the lamellar and lump phases appear “crushed”, and banded structures parallel to the ED direction can be observed; however, the transversal section (along RD) only exhibits evenly distributed phases. Recrystallization is assumed to have occurred after extrusion because no obvious distorted grains can be found in the extruded alloy, which assumption is also supported by the recrystallization diagrams in which most of the grains exhibit recrystallization. A large amount of deformation energy is accumulated during hot extrusion at a large extrusion ratio of 9:1 and the high extrusion temperature of 450°C , thereby leading to the recrystallization.

The identification of the second phases and their compositions using EPMA are shown in Fig. 4 and listed in Table 2, respectively. According to Fig. 4, the sizes of second phases 1, 2, and 4 are small ($< 5 \mu\text{m}$). The

Fig. 2. Optical micrographs and backscattered images of AP65-La alloys: ((a) and (d)) as-quenched, ((b) and (e)) as-extruded (along RD), and ((c) and (f)) as-extruded (along ED).

Fig. 3. Grain sizes (a) of AP65-Li alloys before and after extrusion, and recrystallization diagrams of the extruded AP65-Li alloy along RD (b) and ED (c) directions, respectively. The confidence bands in Fig. 3(a) represent the standard deviations of grain sizes.

Fig. 4. β - $\text{Al}_{11}\text{La}_3$ (a) and $\text{Mg}_{17}\text{Al}_{12}$ (b) phases in the as-quenched AP65-Li alloy, and β - $\text{Al}_{11}\text{La}_3$ (c), $\text{Al}_{10}\text{Mn}_3$ (d), and $\text{Al}_{11}\text{Mn}_4$ (e) phases in the extruded one identified with EPMA.

Table 2
Element contents of different phases in AP65-La alloys identified by EPMA (at.%).

AP65-La alloy		Mg	Al	Mn	La	Pb	Zn	Phase
As-quenched	1	62.63	29.14	–	7.06	0.15	0.99	β -Al ₁₁ La ₃
	2	50.02	37.25	9.12	3.36	0.12	0.13	Mg ₁₇ Al ₁₂
As-extruded	3	8.82	69.16	0.09	19.69	0.01	2.23	β -Al ₁₁ La ₃
	4	27.06	52.58	15.33	4.91	0.04	0.08	Al ₁₀ Mn ₃
	5	3.86	62.47	24.61	9.04	–	0.02	Al ₁₁ Mn ₄

compositions of phases as identified by EPMA are influenced by the size and depth of electron generation area Z_m , especially in small phase size ($<5 \mu\text{m}$). The Z_m is associated with electron acceleration voltage (V_0), excitation energy (V_k), atomic mass (A), metal density (ρ), and atomic number (Z), i.e., $Z_m = 0.033(V_0^{1.7} - V_k^{1.7})A/\rho z$. We control the test parameters, such as electron acceleration voltage, excitation energy, to reduce the effective electron generation area Z_m . The results are considered to be credible. Therefore, the dominant second phases in the as-quenched AP65-La are identified as lamellar β -Al₁₁La₃ and lump Mg₁₇Al₁₂; however, the main phases in the extruded one are fragmented β -Al₁₁La₃, polygonal Al₁₁Mn₄ and Al₁₀Mn₃. La preferentially combines with Al to form high-melting-point β -Al₁₁La₃, thereby leading to reduction in the amount of Al that combines with Mn to form Al–Mn [15]. The Al–Mn phases possess several stoichiometric compounds including Al₂Mn, Al₈Mn₅, Al₁₀Mn₃, Al₁₁Mn₄, and Al₁₉Mn₄ [26]. Therefore, the stoichiometric ratios of the Al–Mn phases vary with change in the Al and Mn content. The amount of Mg₁₇Al₁₂ phase in the as-quenched alloy is small because of its poor thermal stability and the suppression induced by β -Al₁₁La₃ [26]. The Mg₁₇Al₁₂ phase dissolves into the α -Mg matrix after hot extrusion, as can be inferred from Table 2. In comparison, Al–Mn phases such as Al₁₀Mn₃ and Al₁₁Mn₄ still exist in the extruded AP65-La alloy because of their high thermal stability [7].

The grain orientation maps of the extruded AP65-La alloy are shown in Fig. 5. The colors of different grains correspond to different crystal orientations as defined in the inverse pole figures (IPFs) [8]. The grains along the RD direction have their less densely packed prismatic crystallographic planes, i.e. (10 $\bar{1}0$) and (11 $\bar{2}0$), preferentially exposed; however, those along the ED direction showed a high proportion of the most closely packed basal (0001) planes. This proves the existence of anisotropy in grain orientation between the RD and ED directions for the extruded alloy. Normally, the surface energies of (0001), (11 $\bar{2}0$), and (10 $\bar{1}0$) planes are 1.808, 2.156 and 1.868 eV nm^{−2}, respectively [22]; and a crystal plane with high surface energy is prone to corrosion.

Fig. 6. Polarization curves of AP65-La alloys before and after extrusion at OCPs in 3.5 wt% NaCl solution at $(25 \pm 1)^\circ\text{C}$.

3.2. Polarization and weight loss measurements

The polarization curves of the AP65-La alloys before and after extrusion are shown in Fig. 6. The polarization curves are composed of two branches, i.e., the cathodic branch associated with the hydrogen evolution reaction and the anodic branch related to the oxidation of the electrode [13,21]. It can be observed that the two alloys do not passivate but remain active over the whole potential range. Meanwhile, the anodic and cathodic branches are not symmetrical, which result is in good agreement with previous reports [7,8]. The cathodic branches of AP65-La alloys are close to each other, and they exhibit good linearity. The corrosion current densities and the cathodic Tafel slopes are obtained by Tafel extrapolation over a potential range from 120 to 250 mV more negative than the corrosion potential [4,5]. The Tafel slope is defined according to Eq. (3), in which η represents the corrosion-potential-subtracted cathodic potential, a_c the intercept, b_c the cathodic Tafel slope, and J the corresponding corrosion current density [8].

$$\eta = a_c + b_c \log(|J|) \quad (3)$$

The corrosion potential (E_{corr}), cathodic Tafel slope (b_c), corrosion current density (J_{corr}), and weight loss rate (ΔW) of the specimens are

Fig. 5. Inverse pole figures of the extruded AP65-La alloy along RD (a) and ED (b) directions, respectively.

Table 3

Corrosion parameters of AP65–La alloys before and after extrusion at OCPs obtained from polarization and weight loss measurements. The confidence bands represent the standard deviations of these parameters.

AP65–La alloy	Tafel slope, b_c (mV dec ^{−1})	Corrosion potential, E_{corr} (V) (vs. SCE)	Corrosion current density, j_{corr} ($\mu\text{A cm}^{-2}$)	Weight loss rate, ΔW (mg cm ^{−2} d ^{−1})
As-quenched	−161.2	−1.297	11.9 ± 0.3	6.86 ± 0.53
As-extruded (along ED)	−153.4	−1.292	12.4 ± 0.2	8.10 ± 0.42
As-extruded (along RD)	−180.4	−1.292	20.7 ± 1.3	9.93 ± 0.32

listed in Table 3. The corrosion current densities and the weight loss rates together with their errors are the average values and standard deviations of three parallel measurements, respectively. The as-quenched and extruded AP65–La alloys exhibit different cathodic Tafel slopes. The corrosion potentials of the two alloys are close to -1.29 V (vs. SCE); however, the corrosion current densities show different values. The corrosion current density of the as-quenched AP65–La alloy is $11.9 \mu\text{A cm}^{-2}$, which is close to that of the extruded one along the ED direction; however, it slightly increases to $20.7 \mu\text{A cm}^{-2}$ along the RD direction. In general, there exists no predictable relationship between the corrosion potential and corrosion current density [5,27]. The corrosion potential as evaluated from the polarization curve does not reflect the corrosion kinetic of magnesium; however, magnesium with a more negative corrosion potential usually exhibits a larger tendency to corrode [5,27]. Further, magnesium with a larger corrosion current density usually exhibits poorer corrosion resistance [8,10,28]. However, it is strongly recommended that other methods such as weight loss measurement should be utilized to complement the above results, which has been explained elsewhere [28]. According to Table 3, the weight loss rates increase from $6.86 \text{ mg cm}^{-2} \text{ d}^{-1}$ to 9.93 and $8.10 \text{ mg cm}^{-2} \text{ d}^{-1}$ along the RD and ED directions after extrusion, respectively. Considering the reliability and stability of the two different experimental methods, we speculate that the corrosion resistance of AP65–La alloy at OCP deteriorates after hot extrusion, which is strongly supported by the electrochemical impedance measurements considered in the following discussion.

The corrosion behavior of magnesium is related to the microstructure features. Firstly, micro-galvanic corrosion is a kind of corrosion mechanism for magnesium, and it is caused by micro-galvanic cells formed by the coupling of the α -Mg matrix and the second phases due to their potential differences [26,29]. The phase with higher potential acts as the cathode, and the α -Mg matrix serves as the anode and is oxidized [30]. The amounts and distribution of phases, as well as their potentials, have decisive influences on micro-galvanic corrosion, and the cell with higher corrosion driving force could further accelerate the corrosion [15,30]. The $\text{Mg}_{17}\text{Al}_{12}$ phase with a potential of about 60 mV more positive than the α -Mg matrix has negligible effect on the corrosion of AP65–La alloy because of its small amount [19]; however, the β - $\text{Al}_{11}\text{La}_3$ and Al–Mn phases exert significant effect on corrosion

[19,21]. The lamellar β - $\text{Al}_{11}\text{La}_3$ phase is a type of weak cathode [15]. Unlike β - $\text{Al}_{11}\text{La}_3$, the Al–Mn phase behaves as a type of strong cathode with a potential of about 300 mV more positive than the α -Mg matrix [22,26]. It is visible from Fig. 7(a) that the α -Mg matrix adjacent to the banded structures composed of β - $\text{Al}_{11}\text{La}_3$, $\text{Al}_{11}\text{Mn}_4$, and $\text{Al}_{10}\text{Mn}_3$ phases is severely corroded. Hence, the corrosion morphology of the extruded magnesium alloy exist band features, with exposure of second phases. It can be deduced that the banded structures accelerate the micro-galvanic corrosion of AP65–La alloy, and the corrosion is indeed related with second phases. Thus, the corrosion resistance at OCP deteriorates after hot extrusion because of the increase in the amount of the second phases.

Secondly, as a kind type of crystal defect, grain boundary is prone to corrosion [22], as shown in Fig. 7(b) where the grain boundaries in the extruded AP65–La alloy are severely corroded. Thus, the extruded AP65–La alloy exhibits poor corrosion resistance at OCP because of more grain boundaries [31]. We next note that the anisotropy in the corrosion resistance of the extruded AP65–La alloy is associated with grain orientation. The grains along the ED direction exhibit a high proportion of low-energy (0001) planes, and they are more stable, and they exhibit a lower corrosion rate than those along the RD direction.

3.3. Electrochemical impedance spectroscopy (EIS)

The EIS at OCPs, and the corresponding OCP curves of AP65–La alloys before and after extrusion are shown in Fig. 8. It can be seen that the Nyquist plots of the two alloys exhibit two capacitive loops. The first major loop in high-frequency region is associated with the double layer capacitance at the metal/solution interface, and the diameter of the loop is the charge transfer resistance (R_c) of the working electrode [3,31]. The second smaller loop in low-frequency region is associated with $\text{Mg}(\text{OH})_2$ film on the electrode surface [3,4]. Hence, the electrode processes of AP65–La alloy before and after extrusion are mainly activation-controlled combined with the discharge products covered on the electrode surface in the course of discharge [3,7,8]. The as-quenched alloy exhibits considerably larger loops than the extruded one in both the high- and low-frequency regions, as does the impedance modulus in the Bode plot. In addition, all the log (f) vs. phase angle curves exhibit two peaks corresponding to the two capacitive loops.

Fig. 7. Corrosion morphologies of the extruded AP65–La alloy after immersion in 3.5 wt% NaCl solution for 72 h.

Fig. 8. Electrochemical impedance spectra at the OCPs and the OCP curves of AP65-La alloys before and after extrusion in 3.5 wt% NaCl solution at $(25 \pm 1)^\circ\text{C}$: (a) Nyquist plots after 600 s immersion, (b) Bode plots after 600 s immersion, and (c) OCP curves.

For the extruded alloy, the capacitive loops and the curves of $\log(|Z|)$ vs. $\log(f)$ are relatively close to each other both along the ED and RD directions. It can be observed that the OCPs of AP65-La alloys shift along the negative direction in the early stage, and then shift towards the positive direction with further increase in time. After about 10 min of immersion in the electrolyte, all the OCPs essentially stabilize.

An equivalent circuit model, as shown in Fig. 9, is employed to figure out the EIS parameters, including the solution resistance (R_s), the charge transfer resistance (R_t), the constant phase angle element (CPE_{dl}) for the double layer, the $\text{Mg}(\text{OH})_2$ film resistance (R_f), and the $\text{Mg}(\text{OH})_2$ film capacitance (C_f) [3,8]. The main EIS parameters are listed in Table 4. The high-frequency loop is described via the parallel connection of charge transfer resistance (R_t) and constant phase angle element for the double layer (CPE_{dl}) [3,31]. The film resistance (R_f) in parallel with

Fig. 9. Equivalent circuit for fitting the EIS of AP65-La alloys before and after extrusion at the OCPs.

film capacitance (C_f) is utilized to illustrate the low-frequency loop [3, 4]. The constant phase angle element (CPE) is adopted to describe the non-ideal capacitive behavior, and to compensate the non-homogeneity in the system [3–5,32]. The presence of CPE is caused by microscopic roughness of electrode surface [33], and the CPE_{dl} can be calculated via the two parameters, Y_{dl} and n , with the use of Eq. (4), in which ω_m represents the angular frequency when the imaginary part reaches the maximum value.

$$C = Y \cdot (\omega_m)^{n-1} \quad (4)$$

In addition, the time constant can be calculated according to Eq. (5), in which C and R represent the values of the capacitance and resistance connected in parallel with each other, respectively [8].

$$\tau = C \cdot R \quad (5)$$

We determined that the as-quenched AP65-La alloy had a charge transfer resistance of $456 \Omega \text{ cm}^2$, while the extruded one had resistances of $275 \Omega \text{ cm}^2$ and $336 \Omega \text{ cm}^2$ along the ED and RD directions, respectively. The extruded alloy has a smaller charge transfer resistance, indicating that the electrons can pass the double layer more easily [5,34]. Thus, the extruded AP65-La alloy exhibits enhanced anodic dissolution rates and discharge activity than the as-quenched one, which can be obviously reflected by the shrinkage of the high-frequency loops [4,7]. In addition, the polarization resistance (R_p) of the AP65-La alloys before and after extrusion can be calculated via Eq. (6). The reciprocal of polarization resistance (R_p) is proportional to the corrosion rate [18]. Thus, the as-quenched alloy with larger polarization resistance (R_p) had better corrosion resistance than the extruded one at OCP, which is consistent with the result of weight loss measurements.

$$R_p = R_s + R_f + R_t \quad (6)$$

The as-quenched alloy has a $\text{Mg}(\text{OH})_2$ film resistance of $103 \Omega \text{ cm}^2$, which is nearly thrice those of the extruded one. This film can provide magnesium with temporary protection [5,8,35,36]. Therefore, the $\text{Mg}(\text{OH})_2$ film on the electrode surface of the extruded AP65-La alloy only weakly inhibits continuous corrosion in the α -Mg matrix than the as-quenched one [3]. The reason why the $\text{Mg}(\text{OH})_2$ film resistance is lower than charge transfer resistance (R_t) is that the $\text{Mg}(\text{OH})_2$ film is not stable in a solution of $\text{pH} < 11.5$ [34]. Moreover, the aggressive

Table 4

Electrochemical parameters of AP65-La alloys before and after extrusion at the OCPs obtained by fitting the EIS.

AP65-La alloy	$R_s(\Omega \text{ cm}^2)$	$R_t/(\Omega \text{ cm}^2)$	$Y_{dl}/(\Omega^{-1} \text{ cm}^{-2} \text{ s}^n)$	n_{dl}
As-quenched	1	456	5.90×10^{-6}	0.99
As-extruded (along ED)	1	275	5.54×10^{-6}	0.97
As-extruded (along RD)	1	336	4.22×10^{-6}	0.93
AP65-La alloy	$R_f/(\Omega \text{ cm}^2)$	$C_f/(\Omega^{-1} \text{ cm}^{-2} \text{ s})$	τ_{dl}/s	τ_f/s
As-quenched	103	1.01×10^{-3}	2.25×10^{-3}	1.035×10^{-1}
As-extruded (along ED)	30	7.01×10^{-3}	1.25×10^{-3}	2.032×10^{-1}
As-extruded (along RD)	31	6.49×10^{-3}	8.60×10^{-4}	2.005×10^{-1}

Fig. 10. Galvanostatic discharge curves of AP65-La alloys before and after extrusion at current densities of 180 (a) and 300 (b) mA cm^{-2} in 3.5 wt% NaCl solution at $(25 \pm 1)^\circ\text{C}$.

chloride ions in NaCl solution can cause the dissolution of $\text{Mg}(\text{OH})_2$ film when adsorbed at the electrode surface [29,30,37–39].

3.4. Galvanostatic discharge

The galvanostatic discharge curves of AP65-La alloys before and after extrusion at current densities of 180 and 300 mA cm^{-2} are shown in Fig. 10. The average discharge potentials, theoretical mass losses after 1 h discharge, and anodic efficiencies are listed in Table 5. The confidence bands in Table 5 represent the standard deviations of these anodic efficiencies. Hot extrusion leads to a negative shift of the average discharge potential, i.e., from -1.704 V to -1.761 V and -1.756 V along the ED and RD directions discharged at 180 mA cm^{-2} , and from

-1.152 V to -1.199 V and -1.210 V along the ED and RD directions discharged at 300 mA cm^{-2} , respectively. In comparison, the average discharge potential of the extruded AP65-La at 180 mA cm^{-2} is more negative than those of the as-rolled AP65 (-1.641 V) and Mg–Li–Al–Ce–Y–Zn (-1.604 V) alloys, and close to that of the extruded AP65 (-1.701 V) when discharged at 180 mA cm^{-2} [5, 7, 8]. In addition, the anodic efficiency of AP65-La alloy increases from 79.9% to 86.1% and 81.8% along the ED and RD directions discharged at 180 mA cm^{-2} , and increases from 78.7% to 83.4% and 81.9% along the ED and RD directions discharged at 300 mA cm^{-2} , respectively. The anodic efficiency of the extruded AP65-La alloy is higher than that of the Mg–Li–Al–Ce–Y–Zn alloy [5]. We found that the AP65-La alloy exhibits better discharge properties when discharged at 180 mA cm^{-2} than that discharged at 300 mA cm^{-2} . The discharge activities of the extruded AP65-La alloy during discharge both at 180 and 300 mA cm^{-2} are similar along different directions; however, the anodic efficiencies exhibit obvious anisotropies. Meanwhile, the anisotropy of anodic efficiencies of the extruded AP65-La alloy during discharge at 300 mA cm^{-2} is less obvious than that during discharge at 180 mA cm^{-2} . The occurrence of these negligible anisotropies is that the difference in grain orientation is offset by strong anodic polarization when discharged at 180 and 300 mA cm^{-2} .

The enhanced discharge performance of the extruded AP65-La alloy can be explained by its modified microstructure. Firstly, the more negative discharge potential and higher anodic efficiency of the alloy signify better discharge performance [3,8]. Further, magnesium with fine grains and uniform grain boundaries usually exhibits stronger discharge activity [3,8,40]. In this context, Song et al. [40] reported that a large activated current in AZ31B alloy was caused by the presence of fine grains and uniform grain boundaries. Further, Wang et al. [8] suggested that the discharge activity of the extruded AP65 alloy is boosted by the presence of fine grains and uniform grain size induced by hot extrusion. Hot extrusion significantly refines the grains of the as-quenched alloy, and this leads to enhanced discharge activity. Secondly, $\text{Mg}_{17}\text{Al}_{12}$ in magnesium mainly serves as a corrosion barrier, and it can hinder the discharge process and undermine the discharge activity [4]. Therefore, the stronger discharge activity of the extruded AP65-La is more or less associated with the disappearance of the $\text{Mg}_{17}\text{Al}_{12}$ phase. Thirdly, the discharge performance of AP65-La alloys can also be deduced from the discharge morphologies. For instance, it can be observed from Fig. 11 that the discharge products in the extruded alloy at 180 mA cm^{-2} exhibit considerably more number of micro-cracks than the as-quenched one, thereby indicating that the electrolyte can penetrate the surface easily to contact with the α -Mg matrix [2,7,8]. Thus, the extruded alloy has a larger reaction area, which contributes to the enhanced discharge activity. This hypothesis is in good agreement with the conclusions inferred from impedance measurements.

The difference in anodic efficiency can be explained via the discharge morphology without discharge products. The as-quenched AP65-La

Table 5

Average discharge potential and anodic efficiency of AP65-La alloys before and after extrusion at current densities of 180 and 300 mA cm^{-2} in 3.5 wt% NaCl solution at $(25 \pm 1)^\circ\text{C}$. The confidence bands represent the standard deviations of anodic efficiencies.

AP65-La	180 mA cm^{-2}		
	Average discharge potential (V) (vs. SCE)	Theoretical mass loss, (g cm^{-2}) (1 h discharge)	Anodic efficiency, (%)
As-quenched	-1.704	0.089	79.9 ± 0.13
As-extruded (along ED)	-1.761	0.089	86.1 ± 0.58
As-extruded (along RD)	-1.756	0.089	81.8 ± 0.16
AP65-La	300 mA cm^{-2}		
	Average discharge potential (V) (vs. SCE)	Theoretical mass loss, (g cm^{-2}) (1 h discharge)	Anodic efficiency, (%)
As-quenched	-1.152	0.148	78.7 ± 0.11
As-extruded (along ED)	-1.199	0.148	83.4 ± 0.32
As-extruded (along RD)	-1.210	0.148	81.9 ± 0.24

Fig. 11. Discharge morphologies of AP65-La alloys before and after extrusion at 180 mA cm^{-2} with (600 s) and without (1 h) discharge products: ((a), (d), and (g)) as-quenched, ((b), (e), and (h)) as-extruded (along RD), and ((c), (f), and (i)) as-extruded (along ED).

alloy exhibits the roughest surface and many corrosion pits, some of which result from the detachment of small metallic pieces during discharge, similar to the cases of Mg–Al–Mn–Ca and AP65 alloys [2,8]. These detached metallic pieces cannot be used to generate current through electrolytic dissolution, which leads to a reduction in the anodic efficiency [2,4,8]. In comparison, the extruded alloy exhibits the smoothest surface with zonally distributed phases along the ED direction, followed by the smoothness of the surface along the RD direction. There also exist fewer corrosion pits in the extruded alloy, signifying reduced detachment of metal pieces and higher anodic efficiencies. Thus, the longitudinal section along the ED direction exhibits the highest anodic efficiency of 86.1%.

It is worth noting that the composition of seawater is $26.5 \text{ g L}^{-1} \text{ NaCl} + 24 \text{ g L}^{-1} \text{ MgCl}_2$, wherein the chloride ions mainly corrode magnesium [3,26,37]. The presence of “aggressive” chloride ions leads to the initiation and development of pitting corrosion, and this also causes the dissolution of $\text{Mg}(\text{OH})_2$ film when adsorbed at the electrode surface [29, 30,36–39]. Therefore, 3.5 wt% NaCl solution has been extensively used to simulate seawater in many researches [7,8]. Magnesium with high anodic efficiency can provide more electrons per unit mass to generate current when used as the anode [1]. Considering the excellent discharge performance of the extruded AP65-La alloy in 3.5 wt% NaCl solution, we believe that this alloy is a good candidate for the anodic material in high-power seawater-activated batteries.

4. Conclusions

In conclusion, the effect of hot extrusion on the microstructure and electrochemical corrosion behavior of Mg–Al–Pb–La alloy can be summarized as follows.

- (1) Hot extrusion refines the grains of Mg–Al–Pb–La alloy and triggers crystallization. The $\text{Mg}_{17}\text{Al}_{12}$ phase dissolves into the α -Mg matrix after hot extrusion. Further, the Al–Mn and β - $\text{Al}_{11}\text{La}_3$ phases are crushed and stretched, thus leading to the formation of banded structures. More second phases including β - $\text{Al}_{11}\text{La}_3$, $\text{Al}_{11}\text{Mn}_4$, and $\text{Al}_{10}\text{Mn}_3$, and grain boundaries degrade the corrosion resistance of the extruded Mg–Al–Pb–La alloy at OCP.
- (2) The corrosion resistance at OCP is anisotropic for the extruded Mg–Al–Pb–La alloy, and this anisotropy is mainly associated with grain orientation. The grains along the RD direction have (10 $\bar{1}$ 0) and (11 $\bar{2}$ 0) planes preferentially exposed, signifying poorer corrosion resistance at OCP; however, the grains along the ED direction exhibit a large proportion of low-energy (0001) basal planes, thereby indicating better corrosion resistance at OCP.
- (3) The average discharge activity and anodic efficiency of Mg–Al–Pb–La alloy at current densities of 180 and 300 mA cm^{-2} is improved by hot extrusion. The extruded alloy along the ED

direction exhibits the highest anodic efficiency during discharged at 180 mA cm^{-2} because of the least weight loss. Thus, we conclude that the extruded Mg–Al–Pb–La alloy is a promising anodic material in high-power seawater-activated batteries.

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