International Journal of ELECTROCHEMICAL SCIENCE www.electrochemsci.org

# Electrochemical performance of Mg-Al-Zn and Mg-Al-Zn-Ce alloys as anodes for Mg-air battery

Hualong Zhu<sup>1,2</sup>, Hui Liu<sup>1,2</sup>, Hongjie Fang<sup>1,2</sup>, Yilong Dai<sup>2</sup>, Li Li<sup>2</sup>, Xiangchun Xu<sup>2</sup>, Yang Yan<sup>1,2</sup>, Kun Yu<sup>1,2,\*</sup>

<sup>1</sup> Department of Materials Science and Engineering, Yantai Nanshan University, Yantai 265713, China <sup>2</sup> School of Materials Science and Engineering, Central South University, Changsha 410083, China \*E-mail: <u>yukun2010@csu.edu.cn</u>

Received: 22 July 2018 / Accepted: 5 September 2018 / Published: 1 October 2018

The microstructure of rolled annealed Mg-6%Al-1%Zn (AZ61) and Mg-6%Al-1%Zn-0.5%Ce (AZ61Ce) alloys (wt.%) was investigated by optical microscope (OM), scanning electron microscopy (SEM) and X-ray diffraction (XRD). The electrochemical and corrosion behaviors were studied by potentiodynamic polarization curve, electrochemical impedance spectroscopy (EIS) and hydrogen evolution test. The results show that the addition of Ce refines the grains of AZ61 alloy and promotes formation of Al<sub>11</sub>Ce<sub>3</sub> phase. In addition, the AZ61Ce alloy exhibits better corrosion resistance than the AZ61 alloy, probably because the Ce can reduce the content of impurities (such as iron and nickel) and refine the grain of AZ61 alloy. When the two alloys were assembled into Mg-air battery, the AZ61Ce alloy exhibits significantly improved performance than the AZ61 alloy. This improvement in performance may due to the changes in alloy structure and composition. The refined grain and reduced impurities lower its self-corrosion and enhance its anode efficiency during discharge, the refined grains also lead to more grain boundaries, which provide more channels for the anode reaction, the refined grains and the existence of Al<sub>11</sub>Ce<sub>3</sub> phase may together make the products film thinner and more porous during discharge, which result in easier contact of the electrolyte with the metal and a larger area of the anode reaction. This study shows that AZ61Ce alloy is an ideal anode material for Mg-air battery.

**Keywords:** Magnesium alloy; Microstructure characteristic; Corrosion behavior; Mg-air battery discharge performance

# **1. INTRODUCTION**

Mg-air batteries have attracted increasing attention as promising electrochemical energy storage and conversion equipment because they have the advantages of having high theoretical voltage (3.09V) and high specific capacity density  $(2230Ah\cdot kg^{-1})$ , being safe to use, using abundant materials,

and being low cost [1-3]. However, some issues still limit the application of Mg-air batteries, and these issues include low anode efficiency and the actual discharge voltage being far less than the theoretical value. The former results from high self-corrosion of the magnesium alloy, and the latter results because discharge products (e.g.,  $Mg(OH)_2$ ) adhere to the magnesium anode surface. Thus, the magnesium anode, which has a high corrosion resistance and high discharge performance, tends to be used in the research of Mg-air batteries.

One way to improve the corrosion resistance and discharge properties of Mg alloys is to alloy Mg with other elements, such as Al, Zn, Sn, Pb, In, Ga, and RE [4-9]. AZ series (Mg-Al-Zn) magnesium alloys have been widely used and studied as anode materials [10-12]. In particular, the AZ61 alloy has a lower self-corrosion rate and a more negative discharge potential than those of the AZ31 alloy [12, 13]. It has been reported that Ce is used in magnesium alloys to improve the corrosion resistance of magnesium alloys [14, 15] and also to enhance the discharge performance of the magnesium anode [16-18]. However, there are few reports on the application of Ce in the AZ series of magnesium anodes.

Hence, in this work, a trace amount of Ce was added to the AZ61 alloy to extend its storage life and improve its discharge performance. The electrochemical and corrosion behaviors of the Mg-Al-Zn and Mg-Al-Zn-Ce alloys were investigated using potentiodynamic polarization curves, hydrogen evolution measurements, and electrochemical impedance spectroscopy. The performances of the Mgair battery using Mg-Al-Zn and Mg-Al-Zn-Ce alloys as anodes were evaluated. The mechanisms of how Ce improves the electrochemical performance of the Mg-Al-Zn alloy were also analyzed in combination with microstructure characterization.

### **2. EXPERIMENTAL**

Pure Mg (99.95 wt%), Al (99.99 wt%), Zn ( 99.999 wt%), and Mg-Ce master alloy (30 wt% cerium) were melted in a resistance furnace at 1023 K under the protection of an argon atmosphere to prepare Mg-6 wt% Al-1 wt% Zn (AZ61) and Mg-6 wt% Al-1 wt% Zn-0.5 wt% Ce (AZ61Ce). The actual chemical composition of the alloys was determined using inductively coupled plasma atomic emission spectrometry (ICP-AES). The results are shown in Table 1. The as-cast alloys were homogenized and hot rolled at 673 K, then the rolled alloys were annealed at 473 K for 2 h.

The surface morphologies of the experimental alloys were observed using optical microscopy (OM) and a Quanta-200 scanning electron microscope (SEM). The crystalline phases were identified using an X-ray diffractometer (XRD, D/Max 2550) with Cu K<sub> $\alpha$ </sub> X-ray radiation from 15° to 75° and a scan speed of 4(°)/min.

Immersion tests and electrochemical measurements were carried out in 3.5 wt% NaCl solution at 298  $\pm$  0.5 K. A three-electrode system with platinum as the counter electrode, a saturated calomel electrode (SCE) as the reference electrode, and the sample as the working electrode were used in all of the electrochemical experiments. After the sample was soaked in electrolyte for 15 min to achieve a steady open circuit potential (OCP), potentiodynamic polarization curve measurements with a scan rate of 1 mV/s were taken for the different alloys. Pure magnesium and commercial Mg-3 wt% Al-1 wt%

Zn (AZ31) alloy were considered here for comparison. Electrochemical impedance spectra (EIS) were recorded using perturbation amplitude of 5 mV and a scan frequency ranging from 100 kHz to 10 mHz; the spectra were recorded at OCP after 15 min of immersion in electrolyte, and then the EIS data were fitted using ZSimpWin software.

For hydrogen collection, the area of a specimen was  $1 \text{ cm}^2$ . The sample was placed in a glass beaker, and then an upturned filter funnel was set over the sample to channel the evolved hydrogen into a burette filled with 3.5 wt% NaCl solution.

After assembling different alloys in the Mg-air battery, the voltage-time curves of the experimental alloys at current densities of 10 mA•cm<sup>-2</sup>, 15mA•cm<sup>-2</sup>, and 20mA•cm<sup>-2</sup> for 5h were obtained. Boiled 15 wt% chromic acid was used to clean the discharge product.

The anode efficiency  $(\eta)$  was calculated using the following formula:

 $\eta = M_t / M_a$ 

where  $\eta$  is the anode efficiency (%);  $M_t$  is the theoretical mass loss (g) that corresponds to the impressed current;  $M_a$  is the actual mass loss (g) during the discharge. Also, the theoretical mass loss was calculated using the following equation [19]:

 $M_t = (i \times A \times t)/(F \times \sum (x_i \times n_i/m_i))$ 

where *i* is the current density (A cm<sup>-2</sup>); *A* is the surface area (cm<sup>-2</sup>); *t* is the discharge time (s); *F* is the Faraday constant (96485C mol<sup>-1</sup>);  $x_i$ ,  $n_i$ , and  $m_i$  are respectively the mass fraction, ionic valence, and molar mass (g mol<sup>-1</sup>) of an alloying element.

All of the above electrochemical and battery experiments were tested at least three times to assess the repeatability of the experiment.

# **3. RESULTS AND DISCUSSION**

#### 3.1 Microstructures

XRD patterns of the AZ61 and AZ61Ce alloys are shown in Fig. 1, and the results indicate that only the  $Al_{11}Ce_3$  phase appears in the AZ61Ce alloy, which means that this new secondary phase has a relatively higher melting point than the  $Mg_{17}Al_{12}$  phase. The  $Mg_{17}Al_{12}$  phase, which is a major secondary phase in the Mg-Al series of alloys [20], was not detected in either the AZ61 or AZ61Ce alloys; it might be dissolved in the magnesium matrix after heat treatment and processing.

Table 1 shows the chemical composition of both experimental alloys. The contents of impurities such as iron and nickel are significantly reduced because of the addition of cerium. Also, there is no obvious difference in the copper content of the two alloys. Iron, nickel, and copper are generally considered to be harmful to the corrosion resistance of magnesium alloys [21]; thus, the addition of cerium may be beneficial to the corrosion resistance of the AZ61 alloy. This result is consistent with that reported by Mert et al. [22].



Figure 1. XRD patterns of the AZ61 and AZ61Ce alloys.

 Table 1. Chemical composition of the AZ61 and AZ61Ce alloys (wt%)

Alloy	Mg	Al	Zn	Ce	Fe	Cu	Ni	Mn
AZ61	Bal.	5.85	0.94	-	0.0041	0.0037	0.0012	0.075
AZ61Ce	Bal.	5.76	0.92	0.46	0.0008	0.0045	0.0005	0.061

Fig. 2a and b show secondary electron images of the AZ61 and AZ61Ce alloys, respectively. The region in Fig. 2a is labeled as c, and the point in Fig. 2b is labeled as d. Combing with the XRD pattern of the AZ61Ce alloy, the white particle in the AZ61Ce alloy (Fig. 2b) is identified as the  $Al_{11}Ce_3$  phase. Differences between the content of impurity elements (such as iron, nickel, and copper) in the  $Al_{11}Ce_3$  phase and that in the magnesium matrix were not detected, and this is quite different from what Mert et al. reported [22]. This may be due to the limited detection accuracy of the instrument.





Figure 2. Secondary electron images of AZ61(a) and AZ61Ce(b) and the energy spectra of the c-region(c) and the d point(d).

Fig. 3a and b show the optical metallographic microstructures of the AZ61 and AZ61Ce alloys, respectively. It can be seen that the addition of Ce effectively refines the grains of the AZ61 alloy. This may be because the  $Al_{11}Ce_3$  phase hinders the growth of recrystallized grains, and this is different from the effect of Ce on the as-cast AM50 alloy grains [22]. The differences between the two experimental results may be related to the states of the alloys and to different effects of the added elements (i.e., zinc versus manganese).



Figure 3. Optical metallographic microstructures of AZ61(a) and AZ61Ce(b).

#### 3.2 Polarization behavior and hydrogen evolution

Fig. 4a shows the potentiodynamic polarization curves of the four experimental alloys in 3.5 wt% NaCl solution. Both the anodic and cathodic current densities of the AZ61Ce alloy are lower than those of the AZ61 alloy, which means that the addition of Ce restrains both the anodic and cathodic processes. Fig. 4b gives the corresponding hydrogen evolution-time curves. The corrosion data is given in Table 2. The corrosion current densities are the average values, and the corresponding errors are the standard deviations of three parallel tests. The corrosion current density (I<sub>corr</sub>) of the experimental alloys, which is obtained by extrapolating the cathodic Tafel area back to the corrosion potential [23],

represents the rate of reaction on the electrode surface at the corrosion potential ( $E_{corr}$ ). The corrosion potential represents the magnitude of the reaction driving force at the electrode surface. The AZ61Ce alloy has the smallest value of  $I_{corr}$  among the four experimental alloys, and the values of  $E_{corr}$  for the four alloys have the following order: AZ61Ce (-1.544 V) > AZ61 (-1.548 V) > AZ31 (-1.574 V) > Pure Mg (-1.679 V). These observations mean that in the natural state, AZ61Ce is more corrosion resistant than the other experimental alloys. In the natural state, the RE-containing phase (Al<sub>11</sub>Ce<sub>3</sub>) is a weak cathode phase compared with the Mg matrix [24]. The addition of Ce weakens the adverse effects that impurities have on corrosion resistance [12], and the refined grains contribute to improving the corrosion resistance of the alloy [25, 26].



**Figure 4.** Potentiodynamic polarization curves of different alloys in 3.5 wt% NaCl solution (a) and the corresponding hydrogen evolution in 3.5 wt% NaCl solution (b).

Table 2.	Corrosion	parameters of differen	t magnesium	alloys in	3.5 wt%	NaCl solution.
				2		

Alloy	E <sub>corr</sub> /(V vs SCE)	$I_{corr}/\mu A \cdot cm^{-2}$	E <sub>b</sub> /(V vs SCE)	$R_p(\Omega)$
AZ61	-1.548	$43.2\pm4.2$	-1.471	693
AZ61Ce	-1.544	$18.4\pm3.1$	-1.411	2178
Pure Mg	-1.679	$68.4\pm5.6$	-	240
AZ31	-1.574	$45.8\pm3.6$	-	341

In the anode region, only the AZ61 and AZ61Ce alloy curves show obvious inflection points, which are called  $E_b$  and represent the breakdown potential of the product film [27]. Also, the  $E_b$  of the AZ61Ce alloy is more positive than that of the AZ61 alloy. This result indicates that the addition of Ce makes the surface product film of the AZ61 alloy in the anode region more protective. The AZ61Ce alloy also has the highest polarization resistance ( $R_p$ ) of the four experimental alloys, and this also indicates that the added Ce improves the corrosion resistance of the AZ61 alloy.

Although the corrosion data from polarization curves deviate from the actual corrosion rate of magnesium alloys [28], the polarization curve is still an important method for evaluating the corrosion behavior of magnesium alloys at the corrosion potential.

To further describe the corrosion behavior of the four experimental alloy anodes, the hydrogen evolution curves of the two alloys are given in Fig. 4b. Of the rates and volumes of evolved hydrogen for the four alloys, these rate and volume are lowest for AZ61Ce, which means that AZ61Ce has a lower rate of self-corrosion than the other experimental alloys in 3.5 wt% NaCl solution. These results are consistent with results of the polarization curves.

#### 3.3 Mg-air battery discharge performance

Fig. 5 shows a schematic diagram of a Mg-air battery. The battery uses a positive electrode with  $MnO_2$  as the active material, 3.5 wt% NaCl solution as the electrolyte, nickel mesh as the current collector, and a test alloy as the negative electrode material. Fig. 6 gives the voltage-time curves of Mg-air batteries using anodes made of different alloys at current densities of 10, 15, and 20 mA•cm<sup>-2</sup>. All of the voltage-time curves are similar. At the beginning of discharge, the voltage decreased rapidly, and this was caused by the formation of discharge products on the anode surface [17, 30]; the voltage then slightly increased because the product film was shed from the anode surface. As the discharge product film on the anode surface.



Figure 5. Schematic diagram of Mg-air battery

The discharge properties of Mg-air batteries with four experimental alloys as anodes at various current densities are summarized in Table 3. From Table 3 and Fig. 6, it can be seen that the average voltage, anode efficiency, and specific capacity of the AZ61Ce alloy are higher than those of the other

three alloys. With an increase in the current density, the AZ61Ce alloy exhibits increased anode efficiency and more stable specific capacity. This may be for the following reasons: first, large grains (AZ61 alloy) fall off when they are not fully reacted while small grains (AZ61Ce alloy), and this is favorable for the full reaction of the Mg anode during discharge; second, the AZ61Ce alloy (small grains), which has more grain boundaries, provides more channels for the anode reaction [30,31] than the AZ61 alloy (larger grains); third, the reduction of impurity elements reduces the self-corrosion of the anode alloy during discharge, which allows more metal to be supplied to the external circuit, thereby increasing the anode efficiency.

At a current density of 10 mA•cm<sup>-2</sup>, the AZ61Ce alloy has a higher discharge voltage (0.896V) and specific capacity (1377mAh•g<sup>-1</sup>) than the Mg-Al-Mn-Ca alloy (discharge voltage: 0.651V, specific capacity: 1331mAh•g<sup>-1</sup>). The AZ61Ce and Mg-Al-Mn-Ca alloys have comparable anode efficiencies of 55.09% and 60.4%, respectively [32]. This suggests that the AZ61Ce alloy is a promising candidate anode for the Mg-air battery.



**Figure 6.** Voltage-time curves using different alloys as anodes of a Mg-air battery at current densities of 10 mA•cm<sup>-2</sup> (a), 15mA•cm<sup>-2</sup> (b), and 20mA•cm<sup>-2</sup> (c).

Table 3. Discharge prop	perties when differe	nt alloys are use	ed as the anode of	a Mg-air batte	ry at current
densities of 10 n	$hA \cdot cm^{-2}$ , 15mA \cdot cm	$^{-2}$ , and 20mA•cm	$n^{-2}$ .	C	-

Current	Material	Average	Anodic	Specific
density(mA•cm <sup>-2</sup> )		voltage(mV)	efficiency (%)	capacity(mAh•g <sup>-1</sup> )
10	AZ61	833	52.3	1184
	AZ61Ce	896	55.1	1377
	Pure Mg	806	54.3	1204
	AZ31	819	53.6	1194
15	AZ61	507	53.7	1172
	AZ61Ce	670	56.6	1349
	Pure Mg	482	55.6	1160
	AZ31	502	55.4	1176
20	AZ61	418	60.4	1094
	AZ61Ce	608	62.6	1376
	Pure Mg	387	58.9	984
	AZ31	410	60.2	1071

#### 3.4. Electrochemical impedance spectroscopy (EIS)

Electrochemical impedance spectroscopy was measured after the two experimental alloys were discharged at 10 mA•cm<sup>-2</sup> for 5 h. Nyquist plots are shown in Fig. 7. Each plot consists of two capacitive loops. The large capacitive loop in the high frequency region is related to the double electric layer formed at the electrode/electrolyte interface [33], and the small capacitive loop in the low frequency region is caused by the product film attached to the electrode surface [18,34]. The Nyquist plot of the AZ61Ce alloy exhibits one inductive loop in the low frequency region. The inductive loop may be related to the intermediate product  $Mg^+$  or to the nucleation of pores in the product film [35, 36].

EIS plots of the AZ61 and AZ61Ce alloys are equivalent to the circuits shown in Fig. 8, and the EIS fitting results are listed in Table 4.  $R_s$ ,  $R_t$ , and  $R_f$  are the solution resistance, charge transfer resistance, and product film resistance, respectively. The constant phase element (CPE) is adopted to evaluate the double electric layer at the electrode/electrolyte interface [37], and CPE consists of Y and n. Y represents the capacitance of the double electric layer, and n describes how close the actual system is to the pure capacitance; the value of n varies from 0 to 1. If n equals 1, then CPE is equivalent to pure capacitance.

The AZ61Ce alloy exhibits a smaller Rt (30.92  $\Omega \cdot \text{cm}^2$ ) and a bigger capacitance (4.798×10<sup>-4</sup> F•cm<sup>-2</sup>) than the AZ61 alloy (R<sub>t</sub> = 273.6  $\Omega \cdot \text{cm}^2$ , C<sub>1</sub> = 1.067×10-4 F•cm<sup>-2</sup>), and this means that the AZ61Ce alloy has a higher surface reactivity than the AZ61 alloy. R<sub>f</sub> of AZ61Ce is smaller than that of the AZ61 alloy, and C<sub>2</sub> of AZ61Ce is larger than that of the AZ61 alloy; these observations indicate that AZ61Ce may have a more porous and thin product film [38] than the AZ61 alloy. According to Fig. 7 and Fig. 8b, in the low frequency region, only the AZ61Ce alloy exhibits inductive reactance. This is probably because of the nucleation of pores in the product film of the AZ61Ce alloy surface, which indicates that the product film on the surface of the AZ61Ce alloy is more susceptible to

damage.

The time constant  $(\tau)$  for a capacitive loop is calculated as:

 $\tau = CR$ 

where C and R represent the capacitor and resistor connected in parallel. C and Y have the following relation:

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

where  $\omega_m$  is the characteristic frequency of the capacitor and the value of  $\omega_m$  is the frequency at which the imaginary part of the impedance is at a maximum.  $\tau$  is an important parameter for evaluating the relaxation process of the state variables on the electrode surface; when the value of  $\tau$  is smaller, the corresponding relaxation process is faster [35]. The charge transfer process of the double electric layer ( $\tau_c$ ) and the formation of the product film ( $\tau_f$ ) of the two experimental alloys are listed in Table 3. It is clear that the AZ61Ce alloy shows smaller values of  $\tau_c$  and  $\tau_f$  than the AZ61 alloy, which explains why the time for the AZ61Ce alloy to reach a stable voltage is shorter than that for the AZ61 alloy (Fig. 6a).



**Figure 7.** Electrochemical impedance spectra (EIS) of AZ61 and AZ61Ce in 3.5wt% NaCl solution after discharge at a current density of 15mA•cm<sup>-2</sup>.



Figure 8. Equivalent circuits of AZ61(a) and AZ61Ce(b)

Mg alloy	$R_s(\Omega \cdot cm^2)$	$R_t(\Omega \bullet cm^2)$	$C_1(F \bullet cm^{-2})$	$Y_{dl}(\Omega^{-1} \circ cm^{-1})$	n <sub>dl</sub>
AZ61	4.719	273.6	1.067×10 <sup>-4</sup>	-	-
AZ61Ce	5.464	30.92	-	$8.134 \times 10^{-4}$	0.8979
Mg alloy	$C_2(F \cdot cm^{-2})$	$R_{f}(\Omega \cdot cm^{2})$	$L(H \cdot cm^2)$	$\tau_{c}(s)$	$\tau_{\rm f}({\rm s})$
AZ61	4.289×10 <sup>-4</sup>	203.8	_	2.919×10 <sup>-2</sup>	8.741×10 <sup>-2</sup>
AZ61Ce	5.815×10 <sup>-4</sup>	50.85	6275	1.483×10 <sup>-2</sup>	2.957×10 <sup>-2</sup>

**Table 4.** Electrochemical parameters of the AZ61 and AZ61Ce alloys obtained from fitting theelectrochemical impedance spectra in Fig. 7 using the equivalent circuits in Fig. 8a and b.

# 3.5. Surface analysis after discharge

Surface morphologies of the AZ61 and AZ61Ce alloys after discharge at 10 mA•cm<sup>-2</sup> for 5 h in 3.5 wt% NaCl solution were obtained using scanning electron microscopy, and the results are shown in Fig. 9. A large amount of dense discharge products accumulate on the surface of the AZ61 alloy (Fig. 9a and b), whereas many cracks appear on the surface of the AZ61Ce alloy (Fig. 9c and d). Also, the residual product of the AZ61Ce alloy is less than that of the AZ61 alloy, which means that the product film on the surface of the AZ61Ce alloy falls off more easily than that of the AZ61 alloy. These results are consistent with EIS analysis.



Figure 9. Corrosion morphologies of AZ61((a) and (b)) and AZ61Ce((c) and (d)) after discharge at 15mA•cm<sup>-2</sup> in 3.5wt.%NaCl solution.

The thin and porous product film allows the electrolyte to penetrate, and this maintains a large reaction surface during discharge. Changes in the product film should be attributed to the refined grains and to the presence of  $Al_{11}Ce_3$  phases in the AZ61Ce alloy.

# 4. CONCLUSIONS

Electrochemical behaviors of the Mg-6% Al-1% Zn (AZ61) and Mg-6% Al-1% Zn-0.5% Ce (AZ61Ce) alloys are studied using potentiodynamic polarization curves and electrochemical impedance spectroscopy. Also, the performances of Mg-air batteries with the two experimental alloys as anodes are also measured. Microstructures are obtained using OM, SEM, and XRD. The main conclusions are as follows:

(1) The addition of Ce reduces the content of harmful impurities such as iron and nickel, and this is beneficial to the corrosion resistance of the AZ61 alloy.

(2) The addition of Ce refines the grains of the AZ61 alloy and forms a high-melting phase  $Al_{11}Ce_3$ .

(3) In the natural state, the addition of Ce to the AZ61 alloy increases corrosion resistance, and this may be because of the reduced impurities and refined grains.

(4) When Ce is present, the discharge product film becomes thinner and more porous, and this enhances the discharge performance of the AZ61 alloy.

(5) The addition of Ce improves the anode efficiency and specific capacity of the AZ61 alloy, and thus, the AZ61 alloy 0.5 wt% added Ce is a promising anode material for the Mg-air battery.

# ACKNOWLEDGEMENTS

This work was financially supported by the Fundamental Research Funds for the Central Universities of Central South University Project (2017zzts425), China, the Natural Science Foundation of Hunan Province of China (2018JJ2506), the 2015 Shangdong Province Project of Outstanding Subject Talent Group, the Key Research and Development Program of Hunan Province, and the Natural Science Foundation of Shandong Province of China (ZR2017MEM005).

# References

- 1. T.B. Reddy and D. Linden, Linden's handbook of batteries, McGraw-Hill, (2010) New York, USA.
- 2. M.A. Rahman, X. Wang and C. Wen, J. Electrochem. Soc., 160 (2013) 1759.
- 3. F. Cheng and J. Chen, Chem. Soc. Rev., 41 (2012) 2172.
- 4. L. Wen, K. Yu, H.Q. Xiong, Y.L. Dai, S.H. Yang, X.Y. Qiao, F. Teng and S.F. Fan, *Electrochim. Acta*, 194 (2016) 40.
- 5. H.Q. Xiong, H.L. Zhu, J. Luo, K. Yu, C.L. Shi, H.J. Fang and Y. Zhang, *J. Mater. Eng. Perform.*, 26 (2017) 1.
- 6. M.C. Lin, C.Y. Tsai and J.Y. Uan, Corros. Sci., 51 (2009) 2463.
- 7. J. Li, K. Wan and N. Wang, Int. J. Electrochem. Sci., 12 (2017) 3030.
- 8. Q. Jiang, Int. J. Electrochem. Sci., 12 (2017) 10199.
- 9. Z. Yu, G. Shi and D. Ju, Int. J. Electrochem. Sci., 9 (2014) 6668.
- 10. N.G. Wang, R.C. Wang, C.Q. Peng, C.W. Hu, Y. Feng and B. Peng, Trans. Nonferrous Met. Soc.China, 24 (2014) 2427.

- 11. H.Q. Xiong, K. Yu, X. Yin, Y.L. Dai, Y. Yan and H.L. Zhu, J. Alloys Compd., 708 (2016) 652.
- 12. Z.P. Xiong, Y.J. Si, X.S. Feng, and M.J. Li, Adv. Mater. Res., 1051 (2014) 211.
- 13. R.P. Hamlen, E.C. Jerabek, J.C. Ruzzo and E.G. Siwek, J. Electrochem. Soc., 116 (1969) 1588.
- 14. W. Liu, F. Cao, L. Chang, Z. Zhang and J. Zhang, Corros. Sci., 51 (2009) 1334.
- 15. F. Mert, C. Blawert, K.U. Kainer and N. Hort, Corros. Sci., 65 (2012) 145.
- 16. Y. Feng, W.H Xiong, J.C Zhang, R.C. Wang and N.G. Wang, J. Mater. Chem. A, 4 (2016) 8658.
- 17. Y.B. Ma, N. Li, D.Y. Li, M.L. Zhang and X.M. Huang, J. Power Sources, 196 (2011) 2346.
- 18. D.X. Cao, L. Wu, Y. Sun, G.L. Wang and Y.Z. Lv, J. Power Sources, 177 (2008) 624.
- 19. D. Cao, L. Wu, G. Wang and Y. Lv, J. Power Sources, 183 (2008) 799.
- 20. M. Yuasa, X. Huang, K. Suzuki, M. Mabuchi and Y. Chino, Mater. Trans., 55 (2014) 1202.
- 21. G.L. Song, A. Atrens, Adv. Eng. Mater., 1 (1999) 11.
- 22. F. Mert, C. Blawert, K. U. Kainer and N. Hort, Corros. Sci., 65 (2012) 145.
- 23. M.C. Zhao, M. Liu, G.L. Song and A. Atrens, Corros. Sci., 50 (2008) 3168.
- 24. W.J. Liu, F.H. Cao, A. Chen, L.R. Chang, J.Q. Zhang and C.N. Cao, Corros. Sci., 52 (2010) 627.
- 25. N.N. Aung and W. Zhou, Corros. Sci., 52 (2010) 589.
- 26. K.D. Ralston, D. Fabijanic and N. Birbilis, *Electrochim. Acta*, 56 (2011) 1729.
- 27. W. Liu, F. Cao, A. Chen, L. Chang, J. Zhang and C.Cao, Corrosion -Houston Tx- 68 (2012) 14.
- 28. Z.M. Shi, M. Liu and A. Atrens, Corros. Sci., 52 (2010) 579.
- 29. J. Zhao, K. Yu, Y.N. Hu, S.J. Li, X. Tan, F.W. Chen and Z.M. Yu, *Electrochim. Acta*, 56 (2011) 8224.
- 30. L. Fan and H. Lu, J. Power Sources, 284 (2015) 409.
- 31. X. Yin, K. Yu, T. Zhang, H. Fang, H. Dai, H.Q. Xiong and Y.L. Dai, *Int. J. Electrochem. Sci.*,12 (2017) 4150.
- 32. M. Yuasa, X. Huang, K. Suzuki, M. Mabuchi and Y. Chino, J. Power Sources, 297 (2015) 449.
- 33. R. Udhayan and D.P. Bhatt, J. Power Sources, 63 (1996) 103.
- 34. Y.W. Song, D.Y. Shan, R.S. Chen and E.H. Han, Corros. Sci., 51 (2009) 1087.
- 35. C.N. Cao and J.Q. Zhang. An introduction to electrochemical impedance spectroscopy, Science Press, (2002) Beijing, China.
- 36. G.L. Song, Corrosion and protection of magnesium alloy, Science Press, (2006) Beijing, China.
- 37. C.H. Hsu and F. Mansfeld, Corrosion -Houston Tx- 57 (2012) 747.
- 38. G.L. Song and K.A. Unocic, Corros. Sci., 98 (2015) 758.

© 2018 The Authors. Published by ESG (<u>www.electrochemsci.org</u>). This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution license (http://creativecommons.org/licenses/by/4.0/).