Investigation of Sodium Phosphate and Sodium Dodecylbenzenesulfonate as Electrolyte Additives for AZ91 Magnesium-Air Battery

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This paper reports on the improvement of discharge performances of magnesium-air batteries by adding sodium phosphate and sodium dodecylbenzenesulfonate to sodium chloride aqueous solution. Four different electrolytes are tested. Results obtained show that the discharge potential and anode utilization of magnesium-air battery increase significantly with addition of the additives. With an electrolyte of 3.5 wt% sodium chloride +0.5 g·L⁻¹ sodium phosphate, the discharge potential increases from 1.120 V to 1.150 V and the anode utilization increases from 44.1% to 49.1%. The self-corrosion rate of anode has a tendency to decrease with addition of the additives. In solution of 3.5 wt% sodium chloride +0.5 g·L⁻¹ sodium dodecylbenzenesulfonate +0.5g·L⁻¹ sodium phosphate, the self-corrosion is low and the inhibition efficiency can reach 95.2%.

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Magnesium-air (Mg-air) battery plays an increasingly significant role in power source energy and storage devices. There are lots of advantages of Mg-air battery, such as high theoretical potential (3.09 V), high specific energy density (6.8 kWh·kg⁻¹), neutral electrolyte, environmental friendliness, and low cost. Although Mg-air battery has a promising future, there are still some problems remarkably limiting its development and delaying its application in daily life. One of the major problems is anodic polarization during battery discharge. As the total reaction of Mg-air battery (Eq. 1) shows:

\[ 2Mg + 2H_2O + O_2 \rightarrow 2MgO + 2H_2O \]  

The discharge product is magnesium hydroxide which has a tendency to attach to the surface of anode. It can reduce the reaction surface area leading to a decrease of discharge potential when battery discharges in a constant-current mode. As we all know, the potential of Mg is −2.37 V (vs. SHE) and it can react spontaneously with aqueous solution according to the following equation:

\[ Mg + 2H_2O \rightarrow Mg(OH)_2 + H_2 \]  

This wasteful self-corrosion leads to low utilization efficiency during discharge process. There are numerous efforts to reduce self-corrosion of magnesium, focusing either on how to improve anode behaviors or how to optimize electrolyte composition. Compared to studies for anode improvement, there are few studies aimed at electrolyte optimization. Furthermore, adding additives to the electrolyte is known to be a convenient and effective method. For example, the self-discharge capacity is significantly increased by adding water soluble graphite to NaCl solution. Jing et al. found that when NaF and Na₃PO₄ were used as additives to electrolyte Mg-MnO₂ cell demonstrated an excellent discharge performance. And sodium dodecylbenzenesulfonate (SDBS) as a good organic inhibitor can work together with the Na₂SiO₃ on the AZ31 magnesium alloy in 1% NaCl. Although electrolyte is one of the most crucial factors, additive research is few comparing the anode materials. Up to now, Mg-air batteries with NaFPO₄ and SDBS as additives have never been studied. It is known that sodium chloride aqueous solution (3.5% NaCl) is the most suitable electrolyte for Mg-air battery. And the AZ91 is the most commonly used magnesium alloy which is more suitable as anode compared to pure Mg in our previous studies. Therefore, discharge performances of AZ91 Mg-air batteries are studied with four electrolytes in this paper. The electrochemical performances of AZ91 in different electrolytes are also investigated by potentiodynamic polarization measurement, electrochemical impedance spectroscopy and self-corrosion experiment.

Experimental

Material preparation.—In this work, AZ91 magnesium alloy is supplied by Hunan Yueyang aerospace New Materials Co.LTD. Its chemical composition is as follows: 9.35% Al, 0.62% Zn, 0.25% Mn, 0.009% Si, 0.004% Fe, 0.008% Cu, 0.001Ni and the rest is Mg. Samples are cut at 40mm × 10mm × 3mm for battery discharge tests and 10mm × 10mm × 8mm for electrochemical and self-corrosion experiments. Chemical composition of different electrolytes is summarized in Table I. All of reagents are analytical pure. Electrolytes were prepared with distilled water.

Electrochemical measurements.—Three electrode system is used for electrochemical testing with a CHI660C Electrochemical Workstation. The working electrode is AZ91 magnesium alloy which was inlaid by epoxy resin, and the exposed area is about 1 cm². They are soaked in corresponding electrolytes, and the test was conducted after the system was stable. The auxiliary electrode is a graphite electrode. The reference electrode is the saturated calomel electrode (SCE). The Electrochemical impedance spectroscopy’s frequency range was from 100 kHz to 0.1 Hz and the peak of the ac excitation signal was 5 mV. The scan rate of the Potentiodynamic polarization curve was 1mV·s⁻¹ and the scanning range was from −1.9 V to −1.2 V.

Self-corrosion.—Weight of samples was measured with a 10⁻⁴ g accuracy. The corrosion products were cleaned by chromat solution (200 g·L⁻¹ CrO₃ + 10 g·L⁻¹ AgNO₃). The corrosion rate (V) and inhibition efficiency (IE) were then determined using the following equation:

\[ V = \frac{W}{t} \]  

\[ IE = \left(1 - \frac{V_{inhibitor}}{V_{control}}\right) \times 100\% \]  

where W is the weight of the sample, t is the time of corrosion, V_inhibitor and V_control are the corrosion rates with and without inhibitors, respectively.

Table I. Chemical composition of different solutions.

| Different solutions | NaCl (wt%) | Na₃PO₄ (g·L⁻¹) | SDBS (g·L⁻¹) |
|---------------------|------------|----------------|--------------|
| A                   | 3.5        | –              | –            |
| B                   | 3.5        | 0.05           | –            |
| C                   | 3.5        | –              | 0.05         |
| D                   | 3.5        | 0.05           | 0.05         |
Table II. Corrosion rate and inhibition efficiency of AZ91 in different solutions.

| Different solutions | A   | B   | C   | D   |
|---------------------|-----|-----|-----|-----|
| $V_{g}$ ($g \cdot cm^{-2} \cdot h^{-1}$) | 0.063 | 0.022 | 0.023 | 0.003 |
| $IE/$% | – | 65.1 | 63.5 | 95.2 |

equations:

\[
V = \frac{W_0 - W_1}{At}
\]

\[
IE = \frac{V - V_0}{V} \times 100\% \tag{4}
\]

$W_0$ and $W_1$ are the weight of samples before and after soaking in electrolyte (mg), $t$ is soaking time (h), and $A$ is the sample surface area ($cm^2$).

$V$ is the corrosion rate ($g \cdot cm^{-2} \cdot h^{-1}$) of samples soaked in electrolyte without additive, and $V_0$ is the corrosion rate of samples soaked in electrolyte with different additives.

**Battery test.—** In this part, cathode is a air electrode composed of a waterproof layer, nickel net and catalytic layer which used the MnO$_2$ as catalyst. Electrolytes are the solution A, B, C and D; anode is AZ91 Magnesium air battery is discharged 300 min at a current of 20 mA $\cdot cm^{-2}$. The test system is blue power discharge test system (CT2001ALAND). The anode utilization ($\eta$) is defined as the following equation:

\[
\eta = \frac{i \times t \times M_a}{2F(W_i - W_f)} \times 100\%
\]

$i$ is current density ($A \cdot cm^{-2}$), $M_a$ is atomic mass of the specimens, $F$ is Faraday constant, $t$ is discharge time (s), $W_i$ and $W_f$ are weight (g) of samples before and after the test.

**Results and Discussion**

**Self-corrosion.—** According to formula (3) and (4), the corrosion rate and inhibition efficiency of AZ91 magnesium alloy in different solutions are determined and summarized in Table II. Comparing with solution A, corrosion rate of AZ91 in solution B, C and D is clearly decreased. Although inhibition efficiency in solution B and C are not ideal, it works well in solution D which can be up to 95.2%.

It is known that Cl$^-$ is the main cause of the corrosion of magnesium alloys.\cite{18,19} Because Cl$^-$ is so small that it can easy pass the magnesium hydroxide film which is porous and thus not very protective. When the erosion area is exposed in electrolyte, it will form a primary cell with the surrounding film, which can accelerate the corrosion rate of magnesium matrix. When Na$_3$PO$_4$ is added, it can react with mg$^{2+}$ generating Mg$_3$(PO$_4$)$_2$ in electrolyte,\cite{20,21} as the following equation shows:

\[
3Mg^{2+} + 2(PO_4)^{3-} \rightarrow Mg_3(PO_4)_2
\]

The solubility-product constant of Mg$_3$(PO$_4$)$_2$ ($1.04 \times 10^{-24}$) is smaller than Mg(OH)$_2$ ($1.2 \times 10^{-11}$) in electrolyte so that it can be more easily deposited. The film on the anode surface becomes relatively compact and dense. So its protective effect is significantly improved. SDBS is an adsorbent inhibitor.\cite{21} The molecular structural formula of SDBS in different solutions is shown in Fig. 1. It is mainly composed of hydrophobic groups which can be adsorbed on the surface of magnesium matrix and Mg(OH)$_2$ film and polar bases which are directionally arranged forming an effective hydrophobic layer to prevent the erosion of Cl$^-$. A good synergy is shown when Na$_3$PO$_4$ and SDBS are used simultaneously because, comparing with the Mg(OH)$_2$ film, SDBS is more easily adsorbed on the surface of Mg$_3$(PO$_4$)$_2$ film.\cite{22} The inhibition mechanism of AZ91 alloy in different solutions is presented in Fig. 2. It is visible that, the inhibition efficiency of AZ91 in solution D is the highest.

Corrosion morphologies are shown in Fig. 3 after removing corrosion production of AZ91 magnesium alloy in different solutions. AZ91 is very serious corroded in solution A and presents many corrosion pits in Fig. 3a. However, corrosion morphologies in solution B, C and D are significantly different compared with solution A. The
from charge transfer, whereas the inductive loop may be attributed to mass transport relaxation in solid phase on alloy surface.24–26 As shown in Fig. 4, a proverbial equivalent circuit was chosen by ZView software, involving elements $R_s$, $R_t$, $R_p$, L and CPE. Relative fitting parameters are shown in Table IV. Generally, $R_t$ is the control step for this reaction of corrosion, so a higher $R_t$ represents a lower corrosion rate. $R_p$ decreases in the following order: solution $D$ > solution $B$ > solution $C$ > solution $A$. This result is consistent with the $i_{corr}$ values listed in Table III.

**Mg-Air battery discharge performance.**—Discharge curves at 20 mA·cm$^{-2}$ for 300 min are shown in Fig. 7. Obviously, potential-time curves for AZ91 anode are similar in all solutions. The potential reduces rapidly at the beginning of discharging and then it reaches a more stable value. This is mainly caused by passive film on the anode surface. Moreover, the battery with the solution $A$ has the longest time when the potential reaches stability and it is bad for the battery discharge. The batteries with solution $B$, $C$ and $D$, especially solution $B$, exhibit higher potentials compared with solution $A$. $Na_3PO_4$ and SDBS have a good inhibition effect in 3.5 wt% NaCl solution for AZ91 magnesium alloy and their inhibition mechanism has been discussed before. Comparing with solution $A$, the corrosion rates of AZ91 in solution $B$, $C$ and $D$ are obviously decreased. The potentials of Mg-air batteries increase with addition of the additives and they mainly attribute to suppression of the self-corrosion.27,28 There is a competition between the self-corrosion reaction (Eq. 2) that consumes electrons to generate hydrogen and the battery reaction (Eq. 1) that releases electrons to the external circuit. We concluded that additives have a good corrosion inhibition effect on AZ91 magnesium alloy in NaCl solution. The self-corrosion rates decreased significantly after adding additives to NaCl solution. So there is smaller competition with the battery discharge reaction. More electrons are used for the battery discharge reaction. Therefore, the potentials of batteries are improved with addition of the additives.

It is obvious that $Na_3PO_4$ perform better than SDBS in Mg-air battery. On the one hand, Mg anode has a lower self-corrosion rate.

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**Table III. Fitting data of polarization curves in different solutions.**

| Different solutions | $i_{corr}/10^{-4}$A·cm$^{-2}$ | $E_{corr}$/V | $R_p$/Ω·cm$^{-2}$ |
|---------------------|-------------------------------|--------------|------------------|
| A                   | 2.887                         | −1.483       | 83.9             |
| B                   | 1.130                         | −1.567       | 234.6            |
| C                   | 2.085                         | −1.535       | 128.6            |
| D                   | 0.187                         | −1.574       | 888.0            |

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**Table IV. Fitting data of AC impedance of AZ91 magnesium alloy in different solutions.**

| Different solutions | $R_s$/Ω·cm$^2$ | $CPE$/10$^{-5}$μF·cm$^{-2}$ | $n$  | $R_t$/Ω·cm$^2$ | $R_p$/Ω·cm$^2$ | $L/H$·cm$^2$ |
|---------------------|----------------|-----------------------------|------|----------------|----------------|---------------|
| A                   | 5.512          | 1.354                       | 0.9150 | 626            | 100.1          | 16.65         |
| B                   | 10.530         | 4.656                       | 0.8758 | 1820           | 203.6          | 20.20         |
| C                   | 8.638          | 1.115                       | 0.9150 | 991            | 135.5          | 21.60         |
| D                   | 5.091          | 1.629                       | 0.9028 | 2861           | 869.4          | 122.20        |

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**Figure 5.** Nyquist diagrams and AC impedance’s fitting result of AZ91 magnesium alloy in different solutions.

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**Figure 4.** Polarization curves of AZ91 magnesium alloy in different solutions.
in solution B than solution C from self-corrosion and electrochemical experiments. The competition between self-corrosion reaction (Eq. 2) and the battery reaction (Eq. 1) is reduced. So a larger proportion of Mg anode is used to release electrons to the external circuit. On the other hand, (PO₄)₃⁻ can reduce the concentration of Mg²⁺ around Mg anode according to Eq. 6. So the addition of (PO₄)₃⁻ can accelerate the battery discharge reaction (Eq. 1). In conclusion, the Na₃PO₄ solution performs better than SDSB in Mg-air battery. Although Mg anode has the lowest self-corrosion rate in solution D, it is not as good as solution B and C. The discharge activity of magnesium anode decreased significantly with the decrease of self-corrosion rate in solution D. Therefore, it is very important to find the balance between activation and passivation of Mg anode.

Table V lists discharge parameters of all batteries at a current density of 20 mA · cm⁻². As it is shown Mg-air batteries with solution B, solution C and solution D have higher anodic efficiency and potential than solution A. Among all the solutions, the best discharge performances is obtained with solution B with a working potential of 1.150 V and an anodic efficiency of 49.1%.

**Discharge morphology of AZ91.—** In order to further study the effect of additives on discharge performances, discharge morphologies of AZ91 anode in different solutions are shown in Fig. 8. It is obvious that solutions B, C and D possess different discharge morphologies compared to solution A. It seems that bulk discharge products adhere to the surface of AZ91 anode in solution A (Fig. 8a) and a small quantity of discharge products are also observed in solution C and solution D (Figs. 8c, 8d). However, they are not observed in solution B (Fig. 8b). It is known that lots of products can enhance the internal resistance of batteries resulting in a decrease of the potential.²⁹ So the battery with solution A as electrolyte exhibits a lower potential comparing with those of solution B, C and D, especially solution B. Furthermore, there are some cracks on the surface of AZ91 anodes in all solutions which allow an effective contact of magnesium matrix with electrolyte to ensure a continuous discharge of Mg-air batteries.²⁸,³⁰ Therefore, the discharge performance of Mg-air battery is closely related to the crack density on the anode surface. It is clear that the crack density on the anode surface in solution A is lower than in other solutions. This explains why the battery with solution A has the lowest potential.

**Conclusions**

The electrochemical performances of AZ91 in different solutions are investigated by self-corrosion test, electrochemical method and SEM. It has shown that the corrosion rate of AZ91 in 3.5 wt% NaCl can be reduced by adding 0.5 g · L⁻¹ Na₃PO₄ and 0.5 g · L⁻¹ SDSB. When anodes are soaked in the solution of 3.5 wt% NaCl+0.5 g · L⁻¹ Na₃PO₄+0.5 g · L⁻¹ SDSB, the inhibition efficiency can reach 95.2%.

The discharge performances of Mg-air batteries with different electrolytes are investigated by galvanostatic discharge test at 20 mA · cm⁻² for 300 min. The results demonstrate that batteries with 3.5 wt% NaCl+0.5 g · L⁻¹ Na₃PO₄, 3.5 wt% NaCl +0.5 g · L⁻¹ SDSB and 3.5 wt% NaCl+0.5 g · L⁻¹ SDSB +0.5 g · L⁻¹ Na₃PO₄ as electrolyte exhibits a higher potential and anode utilization than those with 3.5 wt% NaCl. The improvement of potential is mainly attributed to the decrease of the accumulation of discharge products and more cracks on the surface of discharge product. A higher anode utilization is mainly due to the decrease of self-corrosion rate. In particular, the Mg-air battery with solution of 3.5 wt% NaCl+0.5 g · L⁻¹ Na₃PO₄ can sustain 1.150 V average potential at an applied current density of 20 mA · cm². And its anode utilization can reach 49.1%.
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