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# Composition optimization and electrochemical properties of Mg-Al-Sn-Mn alloy anode for Mg-air batteries

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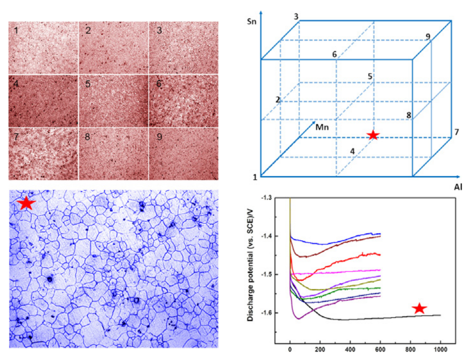
## HIGHLIGHTS

- Systematic study of the effect of alloy elements on the magnesium alloy anode's electrochemical properties.
- The effect of Al, Sn, Mn on the electrochemical performance of magnesium alloy anode ranks in the order of Al, Sn and Mn.
- Optimized Mg-6Al-1Sn-0.4Mn alloy shows the best electrochemical performance as magnesium anode.

## GRAPHICAL ABSTRACT

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## ABSTRACT

The effect of Al, Sn and Mn on the electrochemical properties of extruded magnesium alloy anode was systematically investigated by orthogonal design. The optimal combination, Mg-6Al-1Sn-0.4Mn alloy anode, was obtained through comprehensive analysis. The combination was further verified by the characterization of microstructure, composition and electrochemical performance. The average discharge potential reaches −1.602 V (vs. SCE), showing obvious discharge superiority against the trial samples. The research result is also of value to the development of low cost, non-toxic and well-performance magnesium alloy anode.



## 1. Introduction

Magnesium is usually studied as structural metal material [1–4]. Recently, with its high chemical activity, high theoretical specific energy and abundant resources, the use of magnesium in the field of meta-air battery has also aroused a lot of interest [5–8]. The theoretical voltage of the Mg–air battery is 3.1 V, and the specific energy density reach 6.8 kWh $kg^{-1}$, through replacing the spent Mg anode and electrolyte, the general primary battery could also be "second battery" [5]. Compared with Al–air and Zn–air batteries, the use of magnesium-air battery faces more problems [9]. The main problem of magnesium-air battery is caused by the characteristics of magnesium anode [10]. Magnesium anode is easily covered by discharge product during the discharge process, this issue weakens the discharge performance [11]. Another core issue that counteract the merit of magnesium is the self-corrosion in both the storage and discharge state [12]. Moreover, this self-corrosion leads to low coulombic efficiency due to the negative difference effect of Mg which causes greater Mg dissolution during the discharge process than predicted from the applied current [5,8,9].

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Modifying the performance of magnesium anode is of great importance for the overall performance of magnesium-air battery.

Alloying is the common method to modify the magnesium anode performance, adding appropriate alloying elements into magnesium can suppress the hydrogen evolution reaction of magnesium and can improve the Coulomb efficiency of the anode. On the other hand, it can also accelerate the spalling of discharge product from the surface of the magnesium anode, maintaining the discharge activity of the electrode [13–16]. Some researches have been conducted on the effect of Pb, Ga, Hg and so on [12,13,15–17]. Though promotion is obvious, these alloying elements are not environmentally friendly and economical, excessive these elements are even unsafe to human health [18]. In the time facing the pressure of energy and environmental problem, it is necessary to develop green magnesium alloy anode. In addition, systematic study of the effect of other commonly used alloy elements on the electrochemical properties of magnesium anode is needed. As a candidate of green magnesium alloy anode, the study of electrochemical performance of Mg-Al-Sn-Mn alloy is limited, the systematic effect of Al, Sn, Mn on the electrochemical behavior of magnesium anode is also insufficient.

For magnesium alloys, the stability of the surface film can be improved when Al element solves into magnesium matrix [19]. At the same time, Al and Mg will form β-$Mg_{17}Al_{12}$ phase, which is the main second phase of the Mg-Al system. β phase has a dual effect on the corrosion resistance of magnesium alloys. On the one hand, the dissolving of α-phase, namely the corrosion of magnesium matrix, can be hindered when the volume fraction is large. On the other hand, β phase can accelerate micro galvanic corrosion when its volume fraction is small enough to form a network structure [20,21]. The Sn element with low melting can form second phase with Mg. It can promote the destruction of the passivation film, promote the dissolution of the magnesium anode as an activation point [22]. At the same time, with high hydrogen overpotential, it can effectively inhibit the self-corrosion of magnesium matrix [23,24]. The element Mn can effectively remove the impurity of the magnesium alloy, refine the grain size of the magnesium alloy and improve the self-corrosion behavior of the magnesium alloy [25,26]. Furthermore, hot extrusion is also an effective means to modify the performance of magnesium anode [27–29].

Orthogonal experimental design is an effective mathematical analysis method for reasonable arrangement of experiment, and the scientific analysis of experimental factors. To explore the best combination of factors, some representative test conditions are selected from a large number of test conditions, then the overall design, comprehensive comparison, statistical analysis are carried out using orthogonal tables. Optimal conditions can be found through a small number of experiments through the orthogonal experimental design, so it's been used widely for scientific research in various fields [30–33].

In present work, we choose environmentally friendly Al, Sn, Mn as alloying element, the specific effect of the Al, Sn, Mn on the electrochemical performance of magnesium alloy anode was systematically studied, and the chemical composition of the experimental Mg-Al-Sn-Mn alloys is optimized by orthogonal test. Optimized alloy presents good electrochemical performance and is meaningful to the application extension of magnesium anode.

**Table 1**
Factors and levels of the experiment.

| Level | Factor | | |
|---|---|---|---|
| | A (Al) | B (Sn) | C (Mn) |
| 1 | 5 wt% | 1 wt% | 0 |
| 2 | 6 wt% | 2 wt% | 0.2 wt% |
| 3 | 7 wt% | 3 wt% | 0.4 wt% |

**Table 2**
Actual composition of the cast alloys (wt%).

| Number | Alloy | Actual composition | | | |
|---|---|---|---|---|---|
| | | Al | Sn | Mn | Mg |
| 1 | AT51 | 4.60 | 1.05 | 0 | Bal |
| 2 | AT52-0.2Mn | 5.22 | 2.25 | 0.25 | Bal |
| 3 | AT53-0.4Mn | 5.04 | 3.35 | 0.45 | Bal |
| 4 | AT61-0.2Mn | 5.77 | 1.14 | 0.23 | Bal |
| 5 | AT62-0.4Mn | 6.20 | 2.23 | 0.43 | Bal |
| 6 | AT63 | 5.99 | 3.33 | 0 | Bal |
| 7 | AT71-0.4Mn | 7.49 | 1.17 | 0.47 | Bal |
| 8 | AT72 | 7.36 | 2.24 | 0 | Bal |
| 9 | AT73-0.2Mn | 7.38 | 3.33 | 0.23 | Bal |

## 2. Experimental

### 2.1. Orthogonal experimental design

According to previous studies [8,12,14,17,30], the main indexes to evaluate the performance difference of magnesium anode are self-corrosion behavior, the dissolution rate and discharge performance of magnesium anode in the electrochemical reaction, and the activation and dissolution of magnesium anode at open circuit potential. And the alloying elements Al, Sn and Mn as factor A, B and C respectively with three levels each are presented in Table 1.

### 2.2. Alloys preparation

The alloys were prepared by melting pure magnesium (99.98 wt%), pure aluminum (99.95 wt%), pure tin (99.9 wt%) and Mg-4.02 wt% Mn in a resistance furnace at 740 °C. In order to make the alloying elements distributed evenly, the refining agent hexachloroethane was added and then the melts were stirred, afterwards, the slag was removed. A mixture of $CO_2$ and $SF_6$ was used as the shielding gas during the melting process. The melts were poured into a metal mold preheated at 300 °C, a cylindrical ingot with a diameter of 90 mm was obtained after cooling. Homogenization was then conducted at 360 °C for 12 h, then 420 °C for 8 h. Then, alloys were extruded at 350 °C, extruded bars with a diameter of 16 mm were obtained.

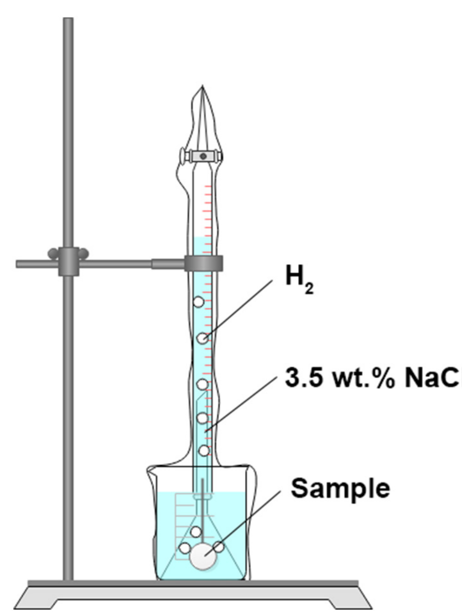


**Fig. 1.** Schematic illustration of hydrogen evolution apparatus.