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Electrochemical Properties Evaluation of a Novel Mg Alloy Anode on Mg Air Batteries

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Magnesium alloy is considered an environmentally friendly material that contains none of mercury, lead and chromate. This study aims to evaluate the performance of the new magnesium (Mg-Zn-In-Sn) alloy by adding elements Zn-In-Sn in AZ91 which are established by orthogonal design and manufactured by two roll continue casting methods, in order to improve the electrochemical properties of magnesium alloy, and then determine the application of Mg-Zn-In-Sn alloy on the air batteries. The electrochemical properties of magnesium air battery are measured to investigate the practical use of Mg-Zn-In-Sn alloy anode. Magnesium and zinc mixed button battery, as a kind of magnesium air battery is developed to measure the continuous discharge curves. And the discharge voltage is calculated by the concentrations of magnesium ion, which are measured via inductively coupled plasma (ICP) analysis and FACSIMILE software simulation. The comparison of pure magnesium, AZ31, AZ91 and Mg-Zn-In-Sn alloy anodes used in the magnesium fuel cell vehicle model were performed. The results show that Mg-Zn-In-Sn alloy anode has the most negative and stable open circuit potential used on the air battery. The stable discharge of magnesium and zinc mixed button battery is more than 60 hours. And the mechanism of corrosion reactions in magnesium and zinc mixed button battery is certificated by electrochemical calculation. Furthermore the speed of magnesium fuel cell vehicle model with Mg-Zn-In-Sn alloy anode is higher than the one with other alloy anodes. It is investigated that Mg-Zn-In-Sn alloy anode is suitable to use on the air batteries by this paper.

Keywords: Magnesium alloy anode; Magnesium air battery; Magnesium button battery; Magnesium fuel cell vehicle

1. INTRODUCTION

Advanced energy storage systems such as batteries are required for use in electric vehicle and other applications. The vast majority of current electrochemical studies are directed toward the promising lead-acid, nickel-cadmium and lithium-ion systems. But magnesium (Mg) alloy possesses a number of characteristics which make it be an attractive material with the properties of relatively low equivalent weight, high melting point, low cost, relative abundance, high safety and ease of handling which was allowed for urban waste disposal. It has been considered a suitable anode material for high energy density batteries [1]. The thermodynamic properties of Mg batteries allow for lighter and safer than common lead-acid and nickel-cadmium batteries. Firstly, lead-acid battery is quite heavy and as a heavy metal is unfriendly to the environment. It is the shortcoming for Nickel-cadmium batteries that the cathode could grow the needle-like crystals of cadmium under charge and discharge, Sometimes, which may penetrate separated substrate to cause a short circuit of internal dendrites crystal. Since cadmium is toxic, it must be recycled Comparing with lithium-ion batteries, Mg is considerably cheaper and safer to handle than lithium, as well as having a higher theoretical charge to volume ratio [2, 3]. Lithium battery has a higher production costs and may cause an explosion when it is being impacted during operation.

Additionally, Mg alloy has been proven to cycle with high efficiency in laboratory-scale cells.

Mg alloy anodes can achieve high cycle life and efficiency. The high energy density of Mg batteries will also lead to lower cost. The predominant cost components of today's lithium cells are manufacturing and materials, including electrolytes, separators, current collectors and active material. Mg batteries are expected to use similar, and in many cases identical, materials and methods [4-8]. Therefore we developed a new Mg alloy to improving the electrochemical properties of Mg alloy and manufactured Mg air battery using the new Mg alloy anode. And Mg and Zn mixed button battery with Mg-Zn-In-Sn alloy powder and Zn powder was trial manufactured to evaluate the life of battery. Electrochemical calculation value proved the mechanism of Mg, Zn and O_2 reactions. Furthermore, fuel cell vehicle (FCV) speed measurements were operated for comparing the electrochemical properties of Mg alloy anodes. The anticipation of battery mass reuses important step forward FCV light weight.

2. EXPERIMENTAL

2.1 Electrochemical model

The composition of AZ31 is Al 3.0％， Zn1.0％and the others is Mg. The composition of AZ91 is Al 9.0％， Zn1.0％and the others is Mg. The AZ31 and AZ91 due to have only the three elements Mg and Al, and lack of In and Sn which can improve the grain refinement and electrochemical properties.

Firstly, the study used the continuous casting method to manufacture the new magnesium alloy (Mg-Zn-In-Sn) plate. Continuous casting method is method which makes the Mg board thinner and the grain can be refined. Element In and Sn are added to the alloy can refine the grain and improve the electrochemical performance of the alloy. Then, the magnesium plate was cut into powder. The powder was as the anode of the button battery. Zn that in form of powder was selected and applied to the experiment.

The Mg and Zn mixed button battery had the electrolyte versatility of using 40% KOH (Alkaline) solution. The anodic active materials are Mg alloy powder and Zn powder, and the cathodic active material is oxygen in the air. Mg-Zn-In-Sn alloy and Zn melt in the electrolytic solution, and emits Mg ions, Zn ions and electrons, as shown in Eq. 1 and 2.

(i) Anode

$$Mg \rightarrow Mg^{2+} + 2e^- \quad (1)$$

$$Zn \rightarrow Zn^{2+} + 2e^- \quad (2)$$

On the other hand, the oxygen and water in the cathode receive electrons to become the hydroxide ion, as shown in Eq. 3.

(ii) Cathode

$$O_2 + 2H_2O + 4e^- \rightarrow 4OH^- \quad \text{(Dissolved-oxygen battery)} \quad (3)$$

Overall, magnesium hydroxide (Mg $(OH)_2$) and zinc hydroxide (Zn $(OH)_2$) are produced from Mg, Zn, oxygen and water [9-13]. The electrochemical reactions for Mg and Zn mixed button battery can be written in Eq. 4 and 5 form:

$$2Mg + O_2 + 2H_2O = 2Mg(OH)_2 \quad (4)$$

$$2Zn + O_2 + 2H_2O = 2Zn(OH)_2 \quad (5)$$

2.2 Development of Mg air battery and button battery

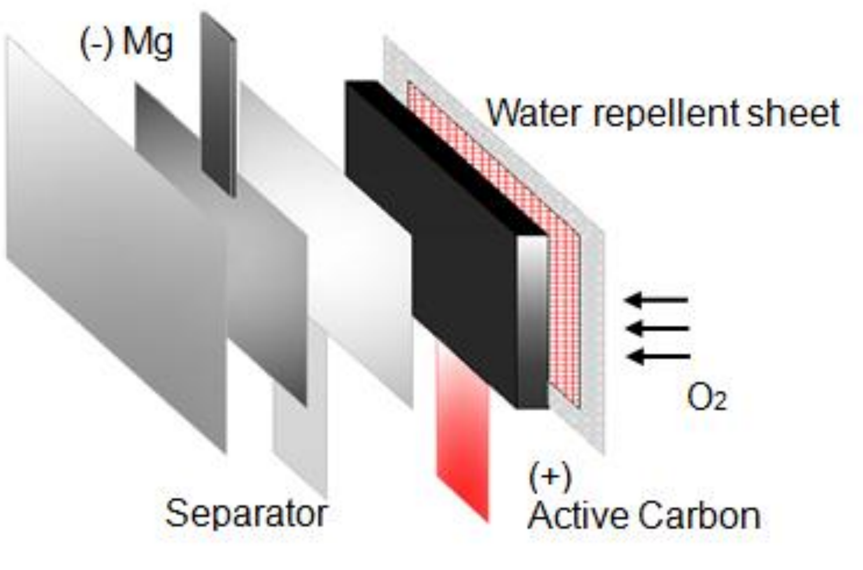

Figure 1. Schematic diagram of Mg air battery

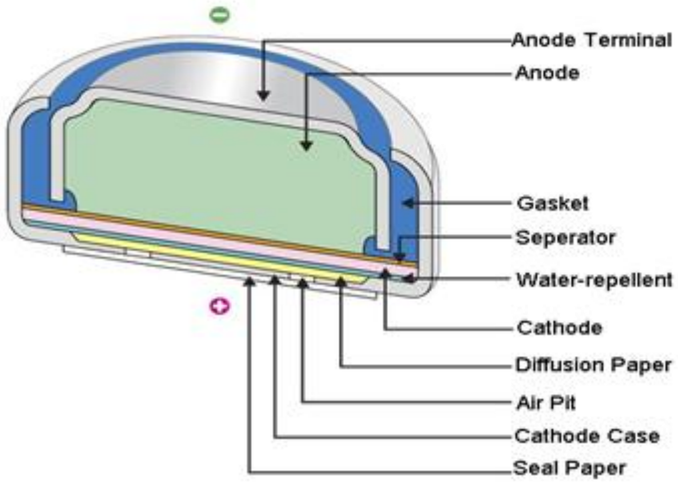

Figure 2. Schematic diagram of Mg and Zn mixed button battery

The schematic diagram of Mg air battery is shown in Fig. 1. The anodic material is Mg-Zn-In-Sn alloy, which is developed by our previous research. And the cathodic material is the active carbon absorbing the oxygen in the air. The saline solution is fixed on the separator (nonwoven fabric) of battery to transfer electrons of the electrochemical reaction. On the both sides, the water repellent sheet is used to prevent from losing the activity of electrode before getting start of the air battery [14-17]. As the application of Mg air battery, Mg and Zn mixed button battery is developed with the Mg-Zn-In-Sn alloy powder. Figure 2 shows the schematic diagram of Mg and Zn mixed button battery, and the continuous discharge curve is measured to evaluate the potential of this battery.

2.3 Electrochemical calculation of Mg and Zn mixed button battery

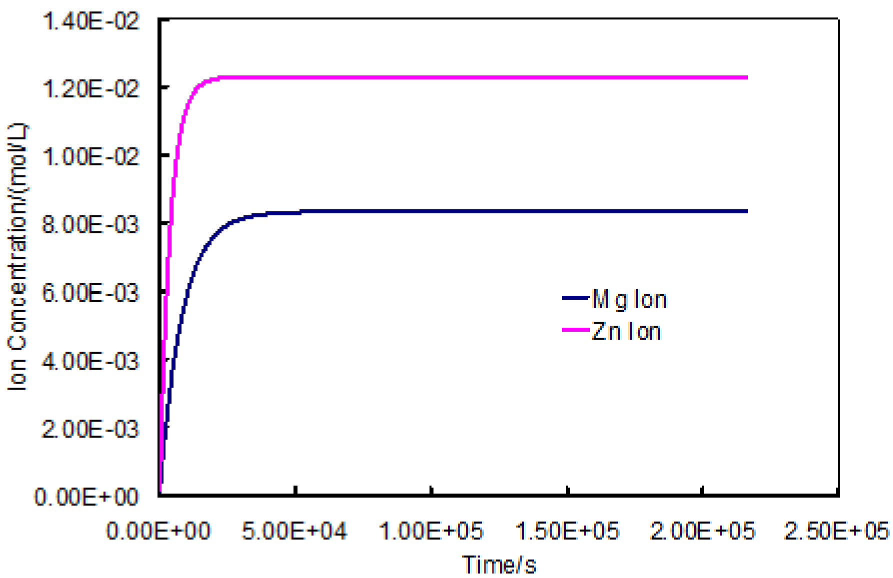

Figure 3. Ion concentration simulated curves of Mg and Zn mixed button battery

The electrochemical corrosion experiments of Mg and Zn mixed button battery are carried out in 40 wt.% KOH solution for 1 h at room temperature. Concentrations measurements of Mg^{2+} and Zn^{2+} in the corrosion solution are performed by ICP (ICPS-7000, SHIMADSU). The standard curve of Mg^{2+} and Zn^{2+} concentration is drawn via standard concentration of 0, 1, 2, 5 and 10 mg/L. Based on the standard curve, Mg^{2+} and Zn^{2+} concentrations are measured before and after corrosion reaction of the battery. As shown in Fig. 3, the variations of Mg^{2+} and Zn^{2+} concentration are simulated by FACSIMILE software during 1 h with the reaction rate calculated by ion concentration measurements.

2.4 Application in Mg FCV

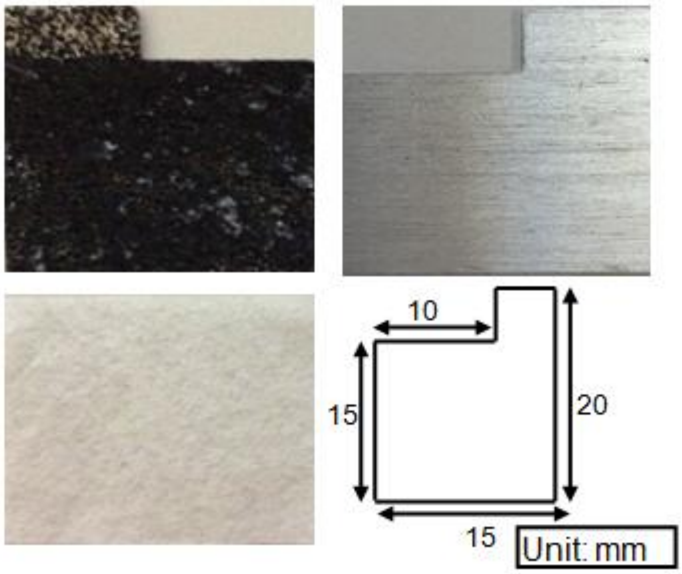

Figure 4. Mg FCV model battery

And then the Mg alloy anodes are applied on the marketing Mg FCV model to measure the speed. Figure 4 shows photo of dimension of the Mg air battery. The end of active carbon as cathode is coated by metal to improve the conductivity. And the saline solution is input drops on the separator as the electrolyte solution. In this experiment, pure Mg and various Mg alloys are used as the anode to compare the speed of Mg FCV.

3. RESULTS AND DISCUSSIONS

3.1 Open circuit potential and loop current′s measurements of Mg air battery

Figure 5 shows the open circuit potential and loop current of Mg air battery using Mg-Zn-In-Sn alloy anode. The results show that negatively stable voltage is obtained for a long time. However, the current is low and decreases rapidly in this experiment due to the resistance of air battery. The current is large when the internal resistance is small under the same voltage according to Ohm's law; the current becomes small with increasing the internal resistance. The increase of internal resistance was caused due to the influence factors from electrolyte ion concentration ' s change during the reacted process and the formation of the metal oxide was further confirmed.

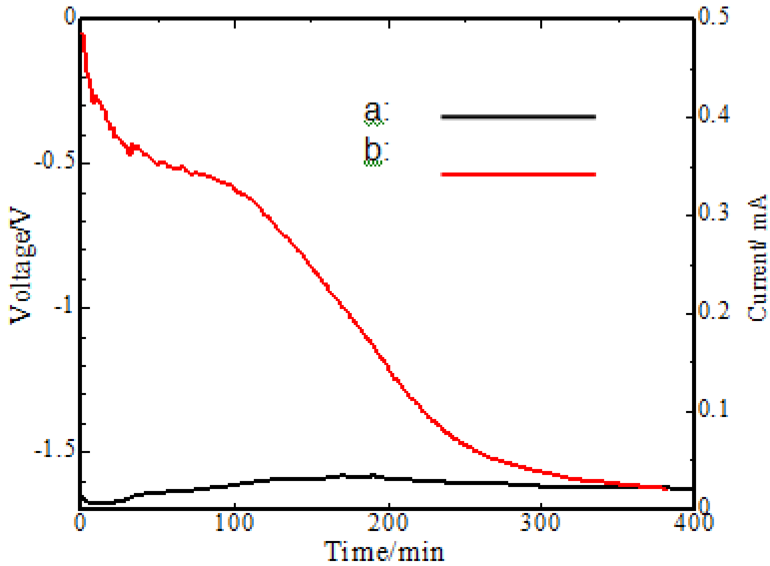

Figure 5. Electrochemical properties of Mg air battery (a: Open circuit potential; b: Loop current)

3.2 Life evaluation and electrochemical calculation of Mg and Zn mixed button battery

And the continuous discharge curve is measured to evaluate the potential of Mg and Zn mixed button battery as shown in Fig. 6. In order to measure the time and the continuous of the new Mg anode .The meter can be used to measure the changes in open circuit potential and loop current. This sentence has out into the 3.2 section.

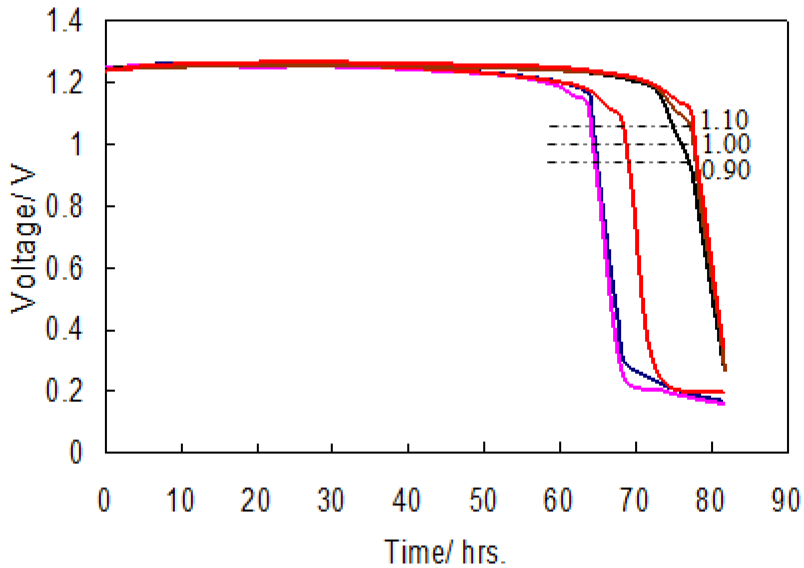

Figure 6. Continuous discharge curves of Mg and Zn mixed button batteries

As a result, the stable discharge of Mg and Zn mixed button battery is more than 60 hours. According to the different ratios of magnesium and zinc in the air batteries, the study used different colors to represent the measured result of the continuous discharge voltage. All of the results are more than 60 hours, in which the ideal value was obtained. The life of trial manufactured battery still does not meet the requirements of product, but the potential of battery is evaluated as a basic experimental date. The simulated Mg^{2+} and Zn^{2+} concentrations values are used to calculate discharge voltage values of Mg and Zn mixed button battery by the Nernst equation, as following:

$$E = E_0 + \frac{RT}{nF}\ln\frac{[O_x]}{[R_{ed}]} \qquad (6)$$

where E_0, F and R are the equilibrium potential for this reaction, Faraday constant and gas constant, respectively. [Ox] and [Red] are the concentration of oxidant and concentration of reluctant. The Nernst equations are transformed to Eq. 7 and 8 according to electrochemical corrosion reactions.

$$E_{Mg} = E_{Mg_0} + \frac{RT}{nF}\ln[Mg^{2+}] \qquad (7)$$

$$E_{Zn} = E_{Zn_0} + \frac{RT}{nF}\ln[Zn^{2+}] \qquad (8)$$

And the discharge voltage value of Mg and Zn mixed button battery is calculated by introducing surface factors a and b to adjust voltage ratio of Mg and Zn. Therefore, discharge voltage is expressed:

$$E = aE_{Mg} + bE_{Zn} \qquad (9)$$

Equation 9 is developed empirically and provides a reasonable representation of experimental results. Comparisons of the discharge voltage curves between experimental and calculated values are shown in Fig. 7.

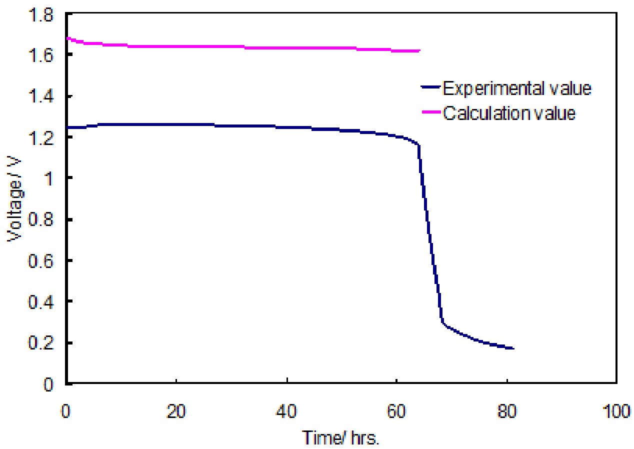

Figure 7. Comparison of discharge curves for Mg and Zn mixed button battery

However, the experimental value of Mg and Zn mixed button battery has obvious deterioration, which is not consistent with the calculation value of battery. This finding can be attributed to the interference of environmental factors, such as the forming of corrosion product film and pH value of solution [18].

3.4 Speed measurements and comparison of cell mass

Table 1. Speed measurement of Mg FCV model

Anode of battery	Speed (km/h)
Pure Mg	1.440
AZ31	1.350
AZ91	1.584
Mg-Zn-Sn-In	1.728

Using the anode of pure Mg, AZ31, AZ91 and Mg-Zn-Sn-In alloy operates the speed measurements of Mg FCV model. As shown in Table 1, Mg FCV model with Mg-Zn-Sn-In alloy anode has the highest speed of 1.728km/h. As only one set of battery powered FCV model, the speed of model is considerably high for the application of Mg air battery. Nissan has released a new type of FCV for the mass media recently. The heart of Nissan FCV is the Lithium-ion battery, which is manufactured by business enterprise of Nissan and NEC Group, Automotive Energy Supply Corporation (AESC). However, the total mass of the battery packs is about 300kg. Among them, the mass of the electrodes is over 100kg. However, by using the mass ratio of Mg air battery and Mg fuel cell model car, the mass of electrodes of battery can be calculated as only 24.52kg for Mg FCV with the same mass of Nissan FCV. Table 2 shows the mass of electrodes of battery comparison of FCVs. The mass of mass of electrodes of battery will be considerably lighter than Lithium-ion batteries using on FCV.

Table 2. The battery mass comparison of FCVs

	Mass of cell	Mass of vehicle
Mg FCV model	0.293g	14.337g
Mg FCV	24.52kg	1200kg
Nissan FCV	>100kg	1200kg

4 CONCLUSIONS

This paper discussed the developing of a new Mg alloy anode material by adding the elements Zn, In and Sn. And the new Mg alloy anode is applied on the Mg air battery. Furthermore, electrochemical property measurements were operated by themb speed comparison of Mg FCV and the anticipatation of battery mass utilize the lightweighting of FCV.

1. The negatively stable open circuit potential is obtained for a long time by Mg air battery, but the current is low and decreases rapidly in this experiment due to the resistance of air battery.

2. The stable discharge of Mg and Zn mixed button battery is more than 60 hours. The life of trial manufactured battery still does not meet the requirements of product, but the potential of battery is evaluated as a basic experimental date.

3. The mechanism of corrosion reactions for Mg and Zn mixed button battery is certificated by electrochemical calculation. The experimental value of Mg and Zn mixed button battery had obvious deterioration, which is not consistent with the calculation value of battery. This finding is attributed to the forming of corrosion coating and the changing of pH value in the solution.

4. Mg FCV model with Mg-Zn-Sn-In alloy anode has the highest speed of 1.728km/h. And the mass of Mg air battery will be considerably lighter than Lithium-ion batteries using on FCV.

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