Study on electrolyte additives of water-based magnesium batteries

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Abstract. The effects of different inorganic salt additives on the corrosion resistance, hysteretic behavior and activation potential of magnesium anode in MgSO4-Mg(NO3)2 composite electrolyte (1.86 mol·L⁻¹ Mg(NO3)2 + 0.14 mol·L⁻¹ MgSO4) were compared by electrochemical method. The electrochemical test results showed that in the solution containing 0.02 mol/L NaHCO3, the activation potential of magnesium anode was the most positive, the passivation range was expanded, and the polarization current was reduced. The impedance of magnesium alloy with 0.02 mol/L NaHCO3 has the highest corrosion resistance, which is consistent with the conclusion that the corrosion current density of Tafel polarization curve is the lowest. Under the additive concentration, the magnesium anode has the shortest lag time, the most negative discharge potential and the least potential drop, which greatly improve the discharge performance of magnesium anode.

1. Introduction

With the development of the times, the continuous advancement of science and technology also brings many ecological problems that cannot be ignored. In the face of environmental pollution, resource shortages, population expansion and many other problems, the most effective solution is to vigorously develop green and environmentally friendly renewable energy such as solar, wind, and tidal energy. However, these renewable energy sources have practical problems such as difficulty in conversion and low energy utilization. Therefore, the current energy supply structure is still dominated by fossil energy such as coal, oil, and natural gas. This makes the current environmental problems and resource depletion problems still not well resolved. Electricity has the advantages of cleanliness, safety, and convenience. Therefore, in energy development, vigorously develop new green and clean energy sources and convert the energy into electric energy for storage. This is undoubtedly a clean and effective way. Now in the information age, the demand for electrical energy is increasing. Therefore, the development of a low-cost, clean and safe battery is of vital importance.
In the current market battery system, Zn-Mn dry battery has low capacity, high cost, is not suitable for long time large current discharge, and the Hg contained in the battery is serious pollution to the environment; Although lead-acid batteries and nickel-cadmium batteries are ideal secondary batteries, they contain heavy metal elements Pb and Cd, which will cause certain harm to the environment. In the development of battery lithium ion battery research has made great progress, and has been widely used in the market, but the metal Li is very active, in the high current charge and discharge, easy to precipitate metal Li in the negative electrode, resulting in safety accidents. Therefore, there is an urgent need to develop a class of low-cost, safe and environmentally friendly high-performance batteries [1]. As a light metal, Mg has the advantages of low relative density, good thermal and electrical conductivity, and Mg and Li are in the diagonal position of the periodic table of elements, so they have many similar chemical properties and have great development potential. Magnesium batteries have low pollution, large capacity, and are suitable for long-term discharge. Compared with zinc-manganese dry batteries, the cost of Mg is lower than that of Zn. Moreover, magnesium batteries do not contain heavy metals Pb and Cd which are harmful to the environment like lead-acid batteries and nickel-cadmium batteries. China is a country with abundant reserves of magnesium in the world, so the development of magnesium batteries has unique advantages. At present, magnesium has become the third largest metal engineering material after steel and aluminum, and is honored as "the green engineering material with the most development and application potential in the 21st century", and its application is expected to achieve considerable development [2-5].

The reason why magnesium batteries have not been put into the market on a large scale is because they still have some unresolved problems, such as the storage capacity of the battery after discharge, the unique "voltage hysteresis" phenomenon of magnesium electrode materials, and serious electrode self-corrosion. And problems such as low current efficiency. Therefore, the research of magnesium batteries has important guiding significance for the future development of the battery industry [6]. The essence of "voltage hysteresis" is that the magnesium electrode is passivated in the electrolyte, and a dense passivation film composed of magnesium oxide is formed on the surface of the magnesium alloy. When the battery starts to discharge, the existence of the passivation film hinders the reaction the reaction can proceed smoothly only after the passivation film is broken down. Therefore, after the battery is loaded, it will take a period of time before the normal output voltage can be achieved [11-12]. The "hysteresis" phenomenon produced in magnesium batteries is mainly related to factors such as the coverage of the surface passivation film, the rate of film destruction, and the relaxation time of film breakdown. Some researchers have found that choosing the appropriate electrolyte or magnesium anode material can change the structure of the magnesium surface film, thereby reducing the voltage hysteresis effect [7-9]. This dissertation mainly studies the influence of additives on the electrochemical behavior of AZ31B magnesium alloy anode, looking for the optimal concentration of electrolyte additives to maximize the discharge activity of the electrode while ensuring the corrosion resistance of the electrode.

2. Experiment reagents and instruments

2.1. Experimental reagent
The main components of the AZ31B magnesium alloy anode used in this experiment are shown in Table 1. The test solutions used in the experiment are all prepared with deionized water.

| Element | Al   | Zn   | Si   | Fe   | Mn   | Cu   | Ni   | Margin |
|---------|------|------|------|------|------|------|------|--------|
| Wt%     | 2.90-3.90 | 0.70-1.0 | ≤0.25 | ≤0.05 | 0.15-0.2 | ≤0.03 | ≤0.005 | Mg     |

2.2. Preparation of working electrode
Cut the AZ31B magnesium alloy into a square with a width and height of 1cm × 1cm × 0.5cm, and polish the six sections with 400#, 600#, 800#, 1000#, 1200# metallographic sandpaper until the metal surface is smooth and smooth. The smooth side of the alloy with a cross-sectional area of 1cm² is used
as the working surface, and the opposite side of the alloy is slotted, and the prepared copper wire is embedded in the slot and fixed; the mass ratio of epoxy resin and ethylenediamine is weighed as 1:0.25 is configured as a curing agent. After mixing and stirring, let it stand for 15~20min. After the curing agent has no fluidity, pour it into a PVC cylinder sealed with transparent glue at one end, and then try to make the alloy in the middle and horizontal position of the cylinder. The curing agent is completely cured after 12h. Before use, polish the electrode working surface with metallographic sandpaper until it is completely exposed, and then use 400#, 600#, 800#, 1000#, 1200# metallographic sandpaper to polish step by step until the metal surface is smooth.

2.3. Experimental method

The electrochemical test system used in this experiment all adopts a three-electrode system, which are working electrode (magnesium alloy), reference electrode (saturated calomel) and auxiliary electrode (carbon rod). The three-electrode system can be divided into two parts: a polarization loop composed of a working electrode and an auxiliary electrode, and a potential measurement loop composed of a working electrode and a reference electrode. The potentiodynamic polarization curve is carried out at a scan rate of 0.5 mV/s. The current density used for constant current discharge is 2.5 mA/cm². The electrochemical impedance spectroscopy is measured under the open circuit potential. The frequency range of the test is 10⁵-10⁻² Hz, and the sinusoidal signal disturbance is 5mV.

3. Results and discussion

3.1. Polarization characteristics

Figure 3.1 shows the Tafel curves of AZ31B magnesium alloy with 0, 0.01, 0.02 and 0.03 mol/L NaHCO₃ added in the MgSO₄-Mg(NO₃)₂ molar ratio of 0.7:9.3. The scanning speed was 0.5mV/s, and the corrosion current density and corrosion potential parameters corresponding to the Tafel polarization curves were shown in Table 2. According to Fig.3.1 and the fitting data, the corrosion potential increased with the increase of NaHCO₃ concentration. When the NaHCO₃ concentration was 0.02mol/L, the corrosion potential was the most positive (-1.20V), and when the concentration increased, the corrosion potential shifted negatively. The addition of NaHCO₃ made the anode corrosion current density of the polarization curve shift negatively, and when the concentration of NaHCO₃ was 0.02mol/L, the corrosion current density was the minimum, and Icorr=0.47×10⁻⁵·A·cm⁻². Compared with the absence of NaHCO₃, the corrosion current density was reduced by 5 times.

![Figure 1. Tafel curves of magnesium alloy anode in different concentrations of NaHCO₃ composite electrolyte](image-url)
Table 2. Corrosion current density and corrosion potential of AZ31B in different concentrations of NaHCO₃ composite electrolyte.

| NaHCO₃ concentration/mol/L | Icorr/10⁻⁵·A·cm⁻² | Ecorr/V |
|---------------------------|-------------------|--------|
| 0                         | 2.52              | -1.39  |
| 0.01                      | 1.34              | -1.34  |
| 0.02                      | 0.47              | -1.20  |
| 0.03                      | 1.69              | -1.34  |

3.2. Discharge characteristics

Figure 3.2 shows the discharge curve of AZ31B magnesium anode in MgSO₄-Mg(NO₃)₂ composite electrolyte with NaHCO₃ concentration of 0.01, 0.02 and 0.03mol/L, respectively. The lag time of magnesium anode decreases first and then increases with the increase of NaHCO₃ concentration, and the lag time is the shortest when CNaHCO₃ =0.02mol/L, and the discharge potential is the most negative. By comparing CP curves without NaHCO₃, it can be seen that the lag time of AZ31B magnesium electrode in Figure 3.2 is controlled within 2s after soaking for 1d, while the lag time of AZ31B magnesium electrode in the composite electrolyte is about 3s. This phenomenon indicates that the corrosion film formed by HCO₃⁻ and SO₄²⁻ and NO₃⁻ ions can significantly improve the hysteretic effect of AZ31B magnesium electrode.

3.3. AC impedance characteristics

Figure 3.3 shows the AC impedance spectra of magnesium anode in MgSO₄-Mg(NO₃)₂ composite electrolyte with different concentrations of NaHCO₃, and the equivalent circuit matching is shown in the upper left illustration of Figure 3.3. The electrode was left standing in the electrolyte for 1h before the test. R and L of the inductive parts appear in the equivalent circuit diagram, which is caused by the intermediate products between the electrode surface and the film layer due to the short immersion time. Can see clearly from the table to join the capacitive reactance arc has increased obviously after the NaHCO₃, R value increase, film resistance increases, the patience, the better, and when the concentration of NaHCO₃ additive is 0.02 mol/L when maximum value of the impedance, the strongest corrosion resistance, and Tafel polarization curve of the corrosion current density of least one conclusion, so 0.02 mol/L NaHCO₃ in composite electrolyte corrosion effect more apparent.
3.4. Surface topography

The AZ31B magnesium alloy electrode was immersed in the composite electrolyte with NaHCO\textsubscript{3} concentration of 0.02mol/L and MgSO\textsubscript{4}-Mg(NO\textsubscript{3})\textsubscript{2} molar ratio of 0.7:9.3. After the immersion time of 2h and 5d, the surface morphology of the alloy was shown in Figure 3.4. As can be seen from the SEM figure, the film layers of (a) and (b) in Figure 3.4 are composed of numerous lumps, all of which are grayish black. The reason why the film layer is slightly white in Figure (b) is that the film layer becomes thicker after a long time of immersion, and the electrical conductivity is weakened, which makes it difficult for the electron beam to penetrate the film layer. It is not caused by the alloy itself. In Figure (a), the surface is more complete, smooth and compact, while in Figure (b), the crack increases, with a width of about 3 m. The film layer composed of each block is sparse, but it is still much denser than the surface morphology of the alloy without any additives. Therefore, the addition of NaHCO\textsubscript{3} reduces the corrosion rate of AZ31B magnesium electrode in the electrolyte, thus extending the storage time of magnesium battery.

Figure 3. EIS curves of AZ31B alloy with different concentration of NaHCO\textsubscript{3} in composite electrolyte

4. Conclusion

The effect of different concentrations of NaHCO\textsubscript{3} on the electrochemical performance of AZ31B in MgSO\textsubscript{4}-Mg(NO\textsubscript{3})\textsubscript{2} composite electrolyte with mole ratio of 0.7:9.3 was studied. The results show that the corrosion inhibition effect of NaHCO\textsubscript{3} additive in the composite electrolyte is significantly improved, and the corrosion current density is the least when the concentration is 0.02 mol/L, which is reduced by
5 times to $0.47 \times 10^{-5} \text{A} \cdot \text{cm}^{-2}$. The discharge performance of magnesium anode is significantly improved, and the discharge potential is negatively shifted, and the lag time is shortened to 0.7s.

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