

Research progress of magnesium anodes and their applications in chemical power sources



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Abstract: Magnesium is a promising metal used as anodes for chemical power sources. This metal could theoretically provide negative discharge potential and exhibit large capacity during the discharge process. However, when the magnesium anode is adopted for practical applications, several issues, such as the discharge products adhered to the electrode surface, the self-discharge occurring on the anode material, and the detachment of metallic particles, adversely affect its inherently good discharge performance. In this work, the types of chemical power sources using magnesium as anodes were elaborated, and the approaches to enhance its anode performance were analyzed.

Key words: magnesium anode; discharge activity; anodic efficiency; activation mechanism; electrolyte

1 Introduction

It is well known that chemical power source normally adopts active metal as anode to deliver electrons for current generation. During the discharge process, the anode loses electrons and dissolves into the electrolyte in the form of metallic ions. Meanwhile, the electrons are sent through external circuit to produce current for energy supply. Thus, the performance of the power source is mainly affected by the metal anode, which plays a vital role in determining the cell voltage, energy density and battery capacity [1,2]. Magnesium is promising anode material due to its inherently good discharge performance.

Firstly, magnesium has negative standard electrode potential of -2.37 V (vs SHE) [3], which is more negative than those of aluminum (-2.31 V (vs SHE)) and zinc (-1.25 V (vs SHE)) [4,5]. Thus, magnesium anode could theoretically exhibit high discharge activity and possess strong ability to deliver electrons for power generation.

Secondly, magnesium has high Faradic capacity of 2.205 A·h/g [3,4], which is lower than those of lithium (3.862 A·h/g) and aluminum (2.980 A·h/g) [4], but

significantly higher than that of zinc (0.820 A·h/g) [5]. As a consequence, magnesium anode could theoretically offer a large number of electrons per unit mass to produce electric current.

Thirdly, magnesium has low density of 1.74 g/cm³, which is lower than those of aluminum (2.70 g/cm³) and zinc (7.14 g/cm³). The low density of the anode favors mass reduction of the battery system, thus leading to an achievement of high output energy density.

Based on the above three advantages, magnesium has been widely employed as ideal anode materials for many chemical power sources. The types of these power sources are summarized below and the aim of this work is to clarify the property of magnesium employed as anodes and present the approaches to enhance its discharge performance.

2 Applications of magnesium anodes in chemical power sources

As prospective anode material used in chemical power sources, magnesium possesses many excellent properties such as high discharge activity, wide voltage range, high energy density, large current capacity, and less environmental contamination [6–8]. Accordingly,

this metal has been successfully used as anodes for a wide range of power sources, such as seawater activated battery, dissolved-oxygen seawater battery, air battery, hydrogen peroxide semi-fuel battery, primary battery, and secondary battery [9–13]. When these batteries are put into use, the magnesium anode is normally discharged in neutral electrolytes containing aggressive ions (e.g., Cl^- and ClO_4^-) [14,15], which exert important effect on dissolving the discharge products, i.e., $\text{Mg}(\text{OH})_2$ film, adhered to the electrode surface. Thus, the anode material can be quickly activated and the lagging voltage effect for the battery system is effectively inhibited. The types of chemical power sources adopting magnesium as anodes are summarized as follows.

2.1 Seawater activated battery

Seawater activated battery was first developed in 1940s to meet the requirement of military applications [8,9]. This battery system normally includes two indispensable parts, i.e., active metal anode (e.g., magnesium) and metal chloride cathode (e.g., AgCl , CuCl , Cu_2I_2 , and PbCl_2). Since the battery is constructed in dry and stored in the dry condition, it usually has a long shelf life. The structure of the basic seawater activated battery is shown in Fig. 1 [9]. In the course of discharge, seawater acting as the electrolyte is poured into the battery system and the magnesium anode is activated to deliver electrons for power generation. At the cathode, the metal chloride receives the circulating electrons in the form of reduction reaction and the overall cell reaction is established. Seawater activated battery can be used in a wide range of short-term high-power undersea devices, e.g., detection devices, electric torpedoes, ocean buoys, air-sea rescue equipment, and sonobuoys [8,9,15,16].

The sorts of seawater activated batteries include Mg/AgCl battery, Mg/CuCl battery, $\text{Mg}/\text{Cu}_2\text{I}_2$ battery,

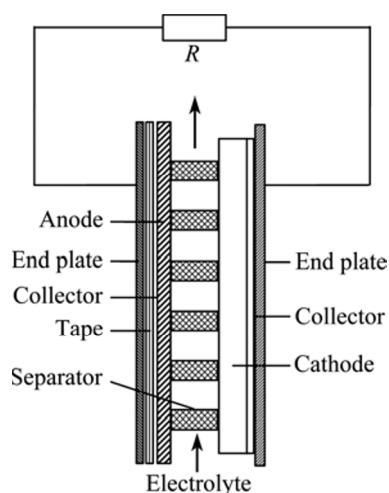
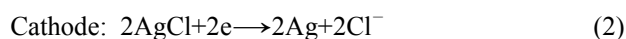


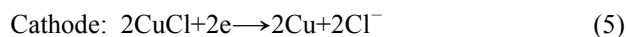
Fig. 1 Structure of basic seawater activated battery [9]

and Mg/PbCl_2 battery. Among these batteries, Mg/AgCl battery was developed by Bell Telephone Laboratories as the power source for electric torpedoes. The design of this battery promotes the development of other small high-energy density batteries, which is also adaptable for serving as the power sources for undersea devices [9]. The current-producing and principal overall reactions for Mg/AgCl battery are as follows:

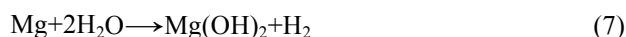


Mg/AgCl battery is able to operate at large current density and provide high energy density of $88 \text{ W}\cdot\text{h}/\text{kg}$ [17,18]. Moreover, this battery can be used in a wide temperature range and stored in the dry condition for more than 5 years. However, Mg/AgCl battery is costly due to the use of AgCl .

Mg/CuCl battery was developed by the former Soviet Union and became commercially available in 1949 [9]. In contrast with Mg/AgCl battery, this battery is significantly less expensive because the costly cathode material (i.e., AgCl) is replaced by the relatively cheap CuCl cathode. However, Mg/CuCl battery exhibits lower energy density and smaller capability in comparison with Mg/AgCl battery. In addition, Mg/CuCl battery cannot be stored at high humidity, and SnCl_2 or argon are needed to avoid the oxidation of CuCl cathode. The major application of Mg/CuCl battery is in airborne meteorological equipment, in which the use of the more expensive Mg/AgCl system is not warranted. The current-producing and principal overall reactions for Mg/CuCl battery are as follows:



Except for the electrochemical reactions listed above, the magnesium anode used for seawater activated battery also suffers severe self-discharge occurring at the electrode/electrolyte interface. This self-discharge is side reaction, which promotes the evolution of hydrogen and leads to heat release during the discharge process. It can be expressed as follows:



The self-discharge reduces the anodic efficiency and actual capacity of magnesium anode, thus the metal cannot be completely used to generate current. However, the evolved hydrogen caused by self-discharge stirs the electrolyte near the electrode surface, thus accelerating the self-peeling of the discharge products and sustaining relatively large active electrode area. Moreover, the heat released in the course of self-discharge plays an

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