Air Batteries Discharge Behavior of Mg-Al-Zn and Mg-Li-Al-Zn Alloys

Liang Wu[1,2,*], Huabao Yang[1], Yuantai He[1], Wenhui Yao[1,2], Jingfeng Wang[1,2], Bin Jiang[1,2], Fusheng Pan[1,2]
1. College of Materials Science and Engineering, Chongqing University, Chongqing, China
2. National Engineering Research Center for Magnesium Alloys, Chongqing University, Chongqing, China
*Corresponding address: e-mail: wuliang@cqu.edu.cn

Mg-air batteries have attracted increasing attention as promising electrochemical energy storage and conversion equipment because they have the advantages of having high theoretical voltage (3.09V) and high specific capacity density (2230Ah kg^{-1}), being safe to use, using abundant materials. However, some issues still limit the application of Mg-air batteries, and these issues include low anode efficiency and the actual discharge voltage being far less than the theoretical value. The former results from high self-corrosion of the magnesium alloy, and the latter results because discharge products (e.g., $Mg(OH)_2$) adhere to the magnesium anode surface. Thus, the magnesium anode, which has a high corrosion resistance and high discharge performance, tends to be used in the research of Mg-air batteries. One way to improve the corrosion resistance and discharge properties of Mg alloys is to alloy Mg with other elements.

AZ series (Mg-Al-Zn) magnesium alloys have been widely used and studied as anode materials. The Mg-Al-Zn and Mg-Li-Al-Zn alloys were used as the anode materials for magnesium-air batteries. The effects of texture, second phase, grain size, twins, and discharge products on the discharge performance of Mg-Al-Zn and Mg-Li-Al-Zn alloys were investigated by controlling the microstructure of the above alloys. Firstly, four representative Mg-3Al-1Zn anodes with different texture characteristics, i.e., ET0°, ET30°, ET60°, and ET90°, are assembled as the anodes for Mg-air batteries, and the correlation between texture and discharge products and the influences of texture and discharge products on the discharge performance are studied. The results show that the discharge performance of the four anodes follows the order: ET90° > ET60° > ET30° > ET0°. The discharge performance of AZ31 anode for Mg-air battery is affected by the texture and discharge products. It can be seen that the discharge products formed on the ET90° anode surface are more easily to fall off than those formed on the ET0° anode surface. The prismatic oriented grains such as the (10-10) and (11-20) oriented grains have higher discharge activities than the basal oriented (0002) grains. The ET90° anode provides higher and steadier discharge voltage and higher anodic efficiency than the ET0° anode. Although the ET90° anode discharged at 40 mA cm^{-2} still suffers a more severe self-corrosion. However, the ET90° anode exhibits more uniform dissolution without the existence of large pits, resulting in its higher anodic efficiency. Considering the influences of chunk effect and self-corrosion on the anodic efficiency, the ET90° anode still has higher anodic efficiency than the ET0° anode. Therefore, the ET90° anode possesses highest and steadiest discharge voltages of 1.46 V at 2.5 mA cm^{-2} and 0.71 V at 40 mA cm^{-2}. The corrosion behavior at open circuit potential and discharge properties under applied anodic currents of Mg-1Li-3Al-1Zn (LAZ131) and Mg-5Li-3Al-1Zn (LAZ531) alloys are investigated to analyze the effect of microstructural features for primary Mg-air batteries. The results show that the grain boundaries contribute equally to the corrosion and discharge processes, which are attacked preferentially than the grain interiors and accelerate the dissolution processes of α-Mg based Mg-Li alloys. The (10−10)/ (11–20) orientated grains are attacked preferentially than the (0002) orientated grains on the corrosion and discharge processes. The increased corrosion rate and improved discharge properties of α-Mg based Mg-Li alloys are attributed to the refinement of grain size, the decreased content of (0002) orientated grains and the increased content of (10−10)/ (11–20) orientated grains. The LAZ531 alloy possesses high and steady discharge voltage at small discharge current density for long time, with the values of 1.4801 V at 2.5 mA cm^{-2} and 1.3742 V at 10 mA cm^{-2}. Additionally, its anodic efficiency is higher than the LAZ131 alloy. Further, in order to improve their anodic efficiencies of the LAZ alloys, the Mg–5Li–3Al–1Zn (LAZ531) alloy sheets with different rolling reductions are investigated using hydrogen evolution, potentiodynamic polarization, electrochemical impedance spectroscopy, and galvanostatic discharge measurements. The results show that rolling changes the microstructure of LAZ531, such as the texture (grain orientation) and the presence of twins, and rolling increases the corrosion resistance and strengthens the discharge ability of LAZ531 alloy, which is attributed to the increased density of twins and the change of grain orientation. The grain boundaries and twins play the same roles on the corrosion and discharge processes. After application of the discharge current, the grain boundaries dissolve preferentially, meanwhile the twins are attacked. With increasing discharge time, more grain boundaries and twins are attacked. With the discharge time further increasing, the grain interiors are attacked. The uniform distribution of twins is helpful to the uniform dissolution of the anode material during the discharge process. Eventually, the LAZ531%-20% alloy has high and steady discharge voltage at small discharge current density for long time, with the values of 1.490 V at 2.5 mA cm^{-2} and 1.411 V at10 mA cm^{-2}. Besides, the LAZ531%-20% alloy has the highest anodic efficiency at each discharge current density, with the values of 36.9% at 2.5 mA cm^{-2} and 45.2% at 10 mA cm^{-2}.

In conclusion, the corrosion and discharge behavior of AZ alloy (LAZ131 and LAZ531) is studied. Based on the Li elemental content, extrusion and rolling, the different microstructure characteristics of alloys is prepared and the suitable microstructure characteristics of Mg alloys for the anodes of magnesium-air batteries were summarized as follows: fine grain size, a high content of (11-20)/ (10-10) orientated grains, introduction of twins and uniform distribution of fine second phases. These microstructure characteristics can effectively improve Mg-air battery anode performance.

Keywords: Magnesium alloys, Microstructure, Mg-air batteries, Discharge properties