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Full Length Article

Effect of grain size on the electrochemical behavior of pure magnesium anode

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Abstract

Three kinds of pure magnesium anode materials with different grain sizes were prepared by extrusion at different temperatures. The grain size of each sample was calculated, then the effect of grain size on the electrochemical properties of pure magnesium anode was investigated by chemical immersion hydrogen test, potentiodynamic polarization scanning, constant current discharge and electrochemical impedance spectroscopy. As the extrusion temperature increases from 180 °C to 250 °C, the average grain size of pure magnesium increases from 20 μm to 30 μm, and the pure magnesium extruded at 250 °C has the best electrochemical performance as magnesium anode, with the discharge potential of −1.571 V (vs. SCE). Plastic deformation process is a convenient method that can change the microstructure and improve the electrochemical behavior of magnesium anode.

Keywords: Pure magnesium; Anode; Electrochemical behavior

1. Introduction

Energy is the basis for the development of the society, fossil fuels are main energy sources and have promoted the social development greatly. However, the enormous amount use of fossil fuels has caused the problems like air pollution and climate change, and fossil fuels are non-renewable resources which will face exhaustion one day. Confronting environmental pollution energy crisis, there is far demand and some measured advancement in the research and application of clean power. One of the key problems for the present power sources is the low theoretical specific energy compared with fossil fuels [1,2]. The metal−air battery is a possible candidate due to its high specific energy, and lighter metals are in favor of increasing the theoretical specific energy [3–7].

Magnesium is the lightest structural metal material with high chemical activity, high theoretical specific energy and abundant resources. With these advantages, the use of magnesium in the field of battery has aroused a lot of interest [8–10]. Some research into the electrochemical behavior of magnesium alloys as the anode of metal air-battery have been conducted [11–15]. The most common method to promote the performance of magnesium anode is alloying. Wang et al. reported the influence of Al and Pb on activation of magnesium as anode and synergistic effect of Al and Pb is propitious to the anode behavior [16]. Basing on this research, the effect of In on the Mg-Al-Pb anode properties was also conducted by Wang et al. [17]. Feng et al. also demonstrated that Ga and Hg can promote the electrochemical activity of the alloy [18]. Though evident promotion in the magnesium anode performance can be seen through alloying method, the alloying elements like Pb and Hg are not environmental friendly, which may cause secondary pollution during the operation process, the high cost of these alloy elements also limits the wide application. On the contrary, pure magnesium without the addition of other heavy metals is environmental friendly. And pure magnesium also shows price superiority over the magnesium alloy doping with Pb, Hg or other rare earth elements. However, casting defects such as shrinkage hole, porosity, inclusions and so on are not in favor of the electrochemical performance of magnesium anode, the self-corrosion tendency is more serious, current efficiency decreases, and service life shortens. Studies have shown that

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increasing the purity of magnesium can reduce the self-corrosion behavior of pure magnesium anode and improve the electrochemical properties of magnesium anode [8,19], but this will counteract the price superiority and make production more difficult.

Plastic deformation is common method to modify the microstructure and properties of magnesium alloys. Changing the grain size of the magnesium alloy by plastic deformation will lead to a change in the grain boundary area, which in turn affects the electrochemical behavior of the magnesium alloys [20,21]. Furthermore, cast defect can be eliminated. But there is limited report about the effect of grain size on the electrochemical properties of hot extruded pure magnesium anode. Herein we conduct hot extrusion to get pure magnesium with different grain sizes, and the effect of grain size on the electrochemical performance of pure magnesium anode is studied. We show that hot extrusion can change the grain size of pure magnesium and improve the performance of pure magnesium anode. Further systematic investigation into the effect of grain size should be conducted to understand the electrochemical behavior of pure magnesium anode.

2. Experiment

2.1. Materials

The pure magnesium (99.95 wt.%) ingots were purchased. The ingots were held at the corresponding temperature for 1 h before the extrusion, the extrusion temperatures were 180 °C, 200 °C, and 250 °C, respectively. The extrusion was carried out with an extrusion ratio of 26 at an extrusion speed of 1 m/min. After air cooling to room temperature, pure magnesium bars with a diameter of 16 mm were obtained.

2.2. Microstructure

The extruded pure magnesium bars were cut into small cylinders, the small cylinders were ground with a series of sandpaper (up to 1000 grit) and cleaned with ethanol, and then the samples were conducted with electrolytic polishing in AC2 polishing solution. Finally, the microstructure was examined using a JSM-7800F SEM with an Oxford Instruments-HKL Technology Nordlys EBSD system. The grain size was calculated using the Nano Measurer software by truncation method.

2.3. Hydrogen evolution testing

The hydrogen evolution tests were carried out in the 3.5 wt.% NaCl solution at room temperature. Before the experiment, the pure magnesium samples extruded at different temperatures were cut into 10 × 10 × 5 mm samples, then sealed with resin to expose 1 cm^2 working surface to the electrolyte. Afterwards, working surfaces were ground with a series of sandpaper (up to 1000 grit), rinsed with alcohol and dried with cold air. Finally, as shown in Fig. 1, the samples were put into 250 mL 3.5 wt.% NaCl solution for 30 h. The samples were suspended with strings so that the samples' working surface is perpendicular to the bottom of the beaker. By collecting the hydrogen during the test, the volume of the hydrogen evolved was measured.

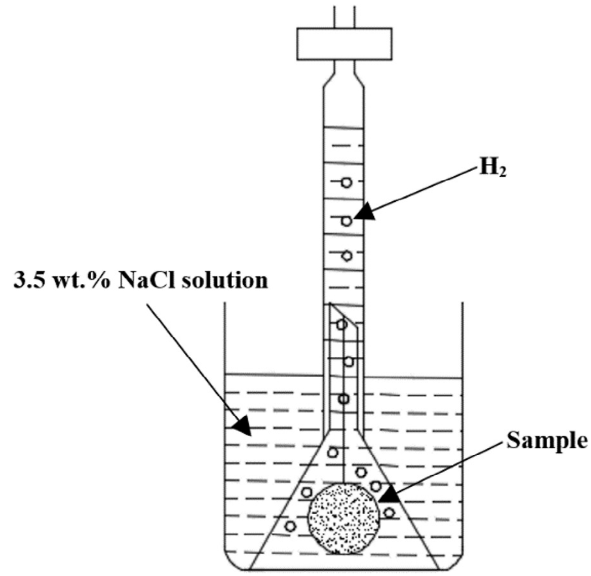

Fig. 1. Schematic illustration of hydrogen evolution apparatus.

2.4. Electrochemical test

The electrochemical tests, excluding electrochemical impedance spectroscopy test, were carried out using CHI660D electrochemical workstation, the EIS test was conducted using Zennium E electrochemical workstation. All electrochemical tests were performed in a traditional three electrode system at room temperature, the electrolyte used was 3.5 wt.% NaCl solution composed of analytical-reagent grade sodium chloride and distilled water. The working electrode was the as-prepared magnesium samples with an exposed area of 1 cm^2. The auxiliary electrode was platinum foil electrode (15 × 15 mm) and the reference electrode was supersaturated calomel electrode (SCE).

Before the test, the pure magnesium sample was put in the electrolyte for about 5 min to establish a stable open circuit potential The polarization curves of the pure magnesium samples were determined by the dynamic potential scanning method. The scan was performed at a scan rate of 10 mV/s from negative direction to positive direction at a scan range of −2.0 to −1.0 V (vs. SCE). The constant current discharge curves of the extruded pure magnesium samples in the 3.5 wt.% NaCl solution were measured by means of galvanostat. The discharge current densities were 50 mA cm^{-2} and 100 mA cm^{-2}, respectively. Electrochemical impedance spectroscopy test was conducted at the frequency ranges of 10^{-1} Hz to 10^5 Hz with the potential amplitude of 5 mV. To explain the discharge behavior and corrosion mechanism of the extruded pure magnesium anode, the equivalent circuit model for the electrochemical reaction process was established by fitting the EIS diagram using Zview software.

3. Results and discussion

3.1. Microstructural characterization

Fig. 2 shows the cross-sectional microstructures of the pure magnesium extruded at different temperatures. It is obvious that

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