



Template-directed fabrication of porous gas diffusion layer for magnesium air batteries



Yejian Xue, He Miao^{**}, Shanshan Sun, Qin Wang, Shihua Li, Zhaoping Liu^{*}

Ningbo Institute of Materials Technology and Engineering, Chinese Academy of Sciences, No. 519, Zhuangshi Road, Zhenhai District, Zhejiang 315201, PR China

HIGHLIGHTS

- Preparation of the interconnected regular pores in the GDL.
- Gas permeability of the GDL with the regular pores was improved.
- $P_{\max}$ of the Mg air batteries with the regular porous GDL was elevated.
- The porous GDL exhibited the improved the long term stability.

ARTICLE INFO

Article history:

Received 6 May 2015
Received in revised form
16 June 2015
Accepted 25 June 2015
Available online xxx

Keywords:

Porous gas diffusion layer
Mg air battery
Fuel cell
Silica template
Carbon fiber felt

ABSTRACT

The uniform micropore distribution in the gas diffusion layers (GDLs) of the air-breathing cathode is very important for the metal air batteries. In this work, the super-hydrophobic GDL with the interconnected regular pores is prepared by a facile silica template method, and then the electrochemical properties of the Mg air batteries containing these GDLs are investigated. The results indicate that the interconnected and uniform pore structure, the available water-breakout pressure and the high gas permeability coefficient of the GDL can be obtained by the application of 30% silica template. The maximum power density of the Mg air battery containing the GDL with 30% regular pores reaches 88.9 mW cm^{-2} which is about 1.2 times that containing the pristine GDL. Furthermore, the GDL with 30% regular pores exhibits the improved the long term hydrophobic stability.

© 2015 Elsevier B.V. All rights reserved.

1. Introduction

Recently, there has been a strong global incentive to develop electric vehicles (EVs) to reduce petroleum oil dependence and mitigate greenhouse gas emission [1,2]. But there is a great obstacle to develop the EVs because of the high cost and insufficient energy density of the state-of-art lithium ion batteries. In the past few years, metal air batteries have received revived interest due to their high energy density, low cost and friendly environment [3,4].

Metal air batteries feature with the electrochemical coupling of a metal negative electrode to an air-breathing positive electrode through an aqueous solution electrolyte [5]. The cathode structure

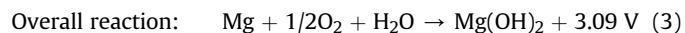
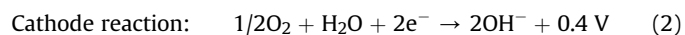
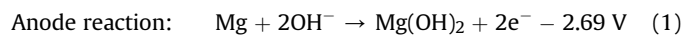
of the metal air batteries which includes the current collecting layer, the gas diffusion layer and catalyst layer are similar with that of the low temperature fuel cells [6,7]. Among them, the gas diffusion layer (GDL) admits continuous and inexhaustible oxygen from the surrounding air to reach the three-phase boundary (TPB) between air, liquid electrolyte and solid electrode catalyst to occur the oxygen reduction reaction. Thus, an ideal GDL is expected to possess the properties with the waterproof structure to avoid the water flooding, high electronic conductivity to transfer the electron, and high oxygen permeation rate to reduce the concentration polarization.

The electrochemical reactions of the Mg-air batteries can be described by the Equations (1)–(3) [13]. As can be seen in the equations, the theoretical open cell voltage of the Mg-air batteries was 3.09 V, but the as-measured values are usually smaller than 2 V due to the large polarization caused by the sluggish cathode reaction and the self-corrosion of Mg anode [28].

^{*} Corresponding author.

^{**} Corresponding author.

E-mail addresses: miaohe@nimte.ac.cn (H. Miao), liuzp@nimte.ac.cn (Z. Liu).



It was reported that the energy consumption for each kilogram of Mg produced by the traditional Pidgeon process was 280 MJ [29,30]. Whereas, the theoretical and as-measured electrochemical energy of the Mg with the same weight were 24.5 MJ and 1.8 MJ with the assumption of the theoretical and as-measured power density of Mg-air batteries was 6800 Wh kg⁻¹ and 500 Wh kg⁻¹, respectively. The energy loss from the Mg production to the Mg air batteries is serious. Therefore, decreasing the energy consumption of Mg production and improving the electrochemical properties of the Mg-air batteries are two important factors to enhance the energy utilization of the Mg anode. In general, the performances of the Mg-air batteries can be related to many factors, such as the compositions of the Mg-based anode, the ORR catalysts, the electrolyte additives, and the GDLs.

A traditional GDL is usually composed of carbon materials (such as carbon powder [8,9], carbon nano-fibers (CNF) [10], carbon nanotubes (CNT) [11,12] and carbon fiber felt (CFF) [13]) as the electronic conduction support and the polytetrafluoroethylene (PTFE) binder as the water proof material to avoid flooding the pores by the electrolyte. Among them, the GDL made by CFF/PTFE has been extensively used in the metal air batteries. The pores in the GDL with the proper quantity and dimension are very important for the properties of the metal air batteries. It will be very hard for the gas diffusion, and subsequently increase the concentration polarization of the metal air batteries containing the GDL with a few or small pores. Whereas, the electrolyte will be flooded the GDL and block the transport of oxygen to the TBP as the GDL contains too many or large pores. In addition, the gas diffusion coefficient of the GDL always decreases during long-term operation because the pore channels are readily to be clogged by the particles in air. It is well known that the uniform micropore regulation and distribution in the GDL can effectively alleviate its geometry variation, and then keep the diffusion coefficient of oxygen unchanged after long term operation [14,15].

Unfortunately, it is difficult to make the uniform porous PTFE by a typical polymer melt foaming process because its high molecular weight and melt viscosity [16]. Even if the template method is popular for the porous material fabrication, the templates are very hard to remove from the PTFE bulk due to its low melting point (327 °C) and superbly hydrophobic property. Up to now, the porous PTFE have still been prepared by the traditional method of extrusion, rolling, and stretching.

In this work, a facile method with the silica as the hard template to create the regular and uniform pores in the PTFE/CFF GDL was applied, and then the electrochemical properties of the magnesium air batteries containing this GDL were investigated. To the best of our knowledge, it is almost the first report about the porous PTFE fabricated by the traditional template method. This template method to create the regular and uniform pores in the PTFE can also be used in the other areas, such as the fabrication of the porous PTFE air cathode for microbial fuel cells, the porous PTFE substrate for redox flow battery, the PTFE membrane with highly ordered pores distribution for the desalination, the gas diffusion layer (GDL) of proton exchange membrane (PEM) with the desired mono-disperse pores for water management and the hierarchical porous materials for the sieving membrane or the catalyst support [17–25], besides the fabrication of the GDL for the metal air batteries in this work.

2. Experimental

2.1. Fabrication of GDL and cathode

A facile fabrication approach of the PTFE/CFF GDL with regular pores was illustrated in Fig. 1. The 60 wt.% PTFE suspension (Shanghai 3F New Material Co. Ltd. of China) was diluted from 10 to 40 wt.% by the deionized water. The commercial silica spheres (Sinopharm Chemical Reagent Co. Ltd. of China) with a relatively uniform particle size of 2 μm were added into the diluted PTFE solution and dispersed uniformly. The carbon fiber felts (CFFs) (Haoshi Carbon Fiber Material Co. Ltd. of China) were immersed into the mixture of the diluted PTFE suspension and the silica spheres, and then dried at the temperature of 50 and 80 °C for 8 and 24 h, respectively. Then, the immersed CFFs were sintered at 350 °C for 1 h. After sintering, the prepared GDLs were pressed for 2 min under a pressure of 10 MPa at the temperature of 200 °C, and then etched by the mixture solution of 50 wt.% ethanol, 20 wt.% HF and 30 wt.% H₂O to remove the silica templates. In this work, the GDL samples before and after the pore creation are denoted as PTFE-x and PTFE-x/CFF-y, where x and y represent the concentration of the PTFE suspension and the percent of SiO₂ in the mixture of PTFE and SiO₂, respectively.

The cathodes with the as-prepared GDLs were made by the following procedure. The homemade MnO₂/C catalyst was uniformly dispersed in the mixture of the PTFE suspension and the terpineol solvent to prepare the catalyst slurry. The catalyst slurry was coated on the surface of the GDLs with the loading of 3 mg cm⁻² by the screen-printing method. The cathodes were dried at 80 °C for 2 h, and then sintered at 350 °C for 1 h. The as-prepared cathode was finally pressed with Ni foam as current collector for 1 min under a pressure of 2 MPa at the temperature of 200 °C.

2.2. Characterizations and test

The morphologies of the GDLs and SiO₂ powders were examined by the scanning electron microscope (SEM, FEI Quanta FEG 250). The contact angles of the electrolyte and ethanol on the GDLs were determined by the contact angle measurement system (Dataphysics, OCA20, Germany) at 25 °C. The bulk porosity of the samples was tested by an analog Archimedes measurement in the decane solution which could flood both the hydrophilic and hydrophobic pores [26]. The hydrophilic porosity of the GDLs was measured by a homemade apparatus. The sample was placed horizontally in the quartz tube at room temperature. Water vapour carried by the air flowed through the sample. In this process, the capillary condensation occurred in the hydrophilic pores and the liquid water accumulated with time till it filled the hydrophilic pores. By weighing the sample before and after the measurement, the hydrophilic porosity could be calculated. Hydrophobic porosity was obtained by subtracting the hydrophilic porosity from the bulk porosity. For testing the electrochemical properties of the Mg air batteries containing the GDLs mentioned above, the 10 wt. % sodium chloride solution, as-prepared cathode and magnesium alloy of AZ61 were used as the electrolyte, cathode and anode, respectively. And then the Mg air battery was tested in the homemade testing house at the room temperature. The active area of the cathode of the Mg air battery was 2 × 2 cm². And the I–V and I–P curves of the Mg air batteries containing the different GDLs were obtained by the cell testing system (LAND CT2001A, China). The morphologies and elemental compositions of the aged cathodes were detected by scanning electron microscope (SEM, FEI Quanta FEG 250) with Energy-dispersive X-ray Spectroscopy (EDS).

Download English Version:

<https://daneshyari.com/en/article/7730284>

Download Persian Version:

<https://daneshyari.com/article/7730284>

[Daneshyari.com](https://daneshyari.com)