Synthesis and characterization of carbon black/manganese oxide air cathodes for zinc-air batteries

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HIGHLIGHTS

- The average electron transfer number of the ORR on α-MnO$_2$ is close to 4.
- Transformation from α-MnO$_2$ to MnOOH is significant with XC72 content larger than 50 wt%.
- The composite with the XC72/α-MnO$_2$ weight ratio equal to 1 shows the highest ORR activity.
- A discharge peak power density, 67.51 mW cm^{-2}, is obtained for a Zn-air battery.
- A power density of 23.0 mW cm^{-2} and specific capacity of 798 ± 20 mAh g^{-1} are obtained at 20 mA cm^{-2}.

ARTICLE INFO

ABSTRACT

Due to the poor electric conductivity but the excellent catalytic ability for the oxygen reduction reaction (ORR), manganese dioxide in the α phase (denoted as α-MnO$_2$) anchored onto carbon black powders (XC72) has been synthesized by the reflux method. The specific surface area and electric conductivity of the composites are generally enhanced by increasing the XC72 content while the high XC72 content will induce the formation of MnOOH which shows a worse ORR catalytic ability than α-MnO$_2$. The ORR activity of such air cathodes have been optimized at the XC72/α-MnO$_2$ ratio equal to 1 determined by the thermogravimetric analysis. By using this optimized cathode under the air atmosphere, the quasi-steady-state full-cell discharge voltages are equal to 1.353 and 1.178 V at 2 and 20 mA cm^{-2}, respectively. Due to the usage of ambient air rather than pure oxygen, this Zn-air battery shows a modestly high discharge peak power density (67.51 mW cm^{-2}) meanwhile the power density is equal to 47.22 mW cm^{-2} and the specific capacity is more than 750 mAh g^{-1} when this cell is operated at 1 V.

1. Introduction

Metal-air batteries [1—5] have attracted great attention in recent years because they have been demonstrated to meet the required energy density (>400 mAh g^{-1}) of electric vehicles (EVs). Metal-air batteries generally show the great advantages of high theoretical energy density (e.g., 1312 Wh kg^{-1} for Zn-air batteries, excluding oxygen) and specific capacity (820 mAh g^{-1}) [3] because they are considered to be a hybrid cell of batteries and fuel cells. Similar to fuel cells, the air cathode employs a gas diffusion layer to obtain the unlimited and free supply of oxygen from ambient air which is not stored in the device, resulting in the high energy density. On the other side, many kinds of metals, such as zinc [1,3—5], aluminum [5—8], lithium [2,4,5,9], and magnesium [5] have been widely employed as the anode of the metal-air batteries. Among these high energy-density power sources, Zn-air batteries are the most developed devices for both the small cells (e.g., for mobile phones and laptops) and the large module (for EVs). However, there are, at least, three challenges to be overcome or circumvented in order to meet the application demands of the modern society: (1) Zn dendrites during the charging process [10]; (2) the loss in the hydrophobic property of the air cathode due to accumulation of carbonate salts; and (3) the electrocatalytic and rechargeable properties of the air cathode [1,11].

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Since the air cathode is one of the key factors influencing the overall performances of Zn-air batteries [12], developing a suitable ORR catalyst on the cathode is very important in improving the performances of Zn-air batteries. Furthermore, the ORR on the cathode is a complicated reaction with slow kinetics at room temperature either in acidic or alkaline solutions. Until now, the best and most frequently used catalysts for the ORR are Pt-based materials [13], while its high price and scarcity make the Pt-based catalysts be practically inapplicable. Accordingly, it is desirable to use cost-effective catalysts, e.g. Co-based catalysts [14,15], Fe-based catalysts [16], Mn-based catalysts [17,18], and certain perovskite catalysts [1,19] to replace the expensive Pt-based catalysts.

Manganese dioxide [20–23] has been considered to be an attractive catalyst material for the cathode of metal-air batteries because of its low toxicity, low cost, environmental friendliness, and considerable activity toward the ORR. Manganese dioxide can be operated effectively in aqueous [21,24] and non-aqueous [25,26] systems, and generally exhibits a better efficiency in the alkaline electrolytes [3,27]. Meanwhile the ultimate performance and application of MnO_2 have been found to be affected by its microstructures (e.g., particle shape, size, and crystalline phases, etc.). For instance, the catalytic performance of MnO_2 has been reported to follow the sequences: $\alpha > \beta > \gamma$ phases of MnO_2 [28] or $\alpha \sim \delta > \gamma > \lambda > \beta$ phases of MnO_2 [29]. Fortunately, both reports were in agreement with that α-MnO_2 possesses the highest catalytic activity for the ORR in the Zn-air batteries. According to the literature [20], α-MnO_2 possesses a large tunnel structure (2×2) which makes ion transfer easily in the lattice framework, further promoting the ORR rate. Furthermore, there are more defects and hydroxyl groups on α-MnO_2 surface, which are favorable for the adsorption/desorption of oxygen molecules and the dissociation of the oxygen double bond [28,30]. Although α-MnO_2 shows a better ORR catalytic activity, its electric conductivity is very poor. In order to solve this issue, adding carbon black into MnO_2 is usually employed to increase the electric conductivity and surface area of the resultant composites [21,24,31,32].

This work aims to use the reflux method with three precursors (i.e., potassium permanganate, manganese sulfate, and XC72 carbon black) to prepare α-MnO_2/XC72 composite samples. The electrocatalytic activity of α-MnO_2/XC72 composites was optimized by varying the amount of XC72 carbon black meanwhile the effect of the α-MnO_2/XC72 ratio on the average electron transfer of the ORR was systematically investigated. Finally, the full cell performances of a Zn-air battery with various α-MnO_2/XC72 electrocatalysts were characterized in this work.

2. Experimental details

2.1. Preparation of α-MnO$_2$/XC72 electrocatalysts

XC72 carbon black (Vulcan XC-72, Cabot Corp., USA), $KMnO_4$ (Showa Chemical Industry Co., Ltd.), $MnSO_4 \cdot H_2O$ (Showa Chemical Industry Co., Ltd.), and Nafion® perfluorinated resin solution (5 wt% in a mixture of water and lower aliphatic alcohols with 45% water), ethylene glycol (Hayashi Pure Chemical Industry Co., Ltd.), KOH (Showa Chemical Industry Co., Ltd.) were all analytical grade and used without any further purification. Carbon paper (SGL carbon paper 10AA, 4 cm × 4 cm) was used as the substrate of the air cathode. A zinc foil (Alfa Aesar, 0.25 mm thick) was employed as the anode in the Zn-air battery.

Alpha-MnO_2/XC72 electrocatalysts were prepared from a mixture consisting of XC72 powders (in various amounts: 0, 1, 2, 3, 4, 5, 6 g) and 4.056 g $MnSO_4 \cdot H_2O$ powders into a three-necked round bottom flask. Then, 3.792 g $KMnO_4$ powders were dissolved and stirred in a 60-ml de-ionized (DI) water to form a 0.4 M $KMnO_4$ solution. This $KMnO_4$ solution was added slowly into the three-necked round flask containing the well-mixed XC72 and $MnSO_4 \cdot H_2O$ powders. Finally, the above mixtures were stirrer at 100 °C for 20 h. After the above steps, the solution was filtered and washed with DI water several times by a high-speed centrifuge (at 11,000 rpm, 10 min) to remove the excess K^+. The final products were obtained by drying in an oven at 85 °C overnight. The α-MnO_2/XC72 electrocatalysts prepared from the solutions containing 0, 1, 2, 3, 4, 5, 6 g of XC72 were labeled as a0, a1, a2, a3, a4, a5, and a6, respectively.

2.2. Materials characterization

The morphologies and microstructures of α-MnO_2 and composites were examined using a field-emission scanning electron microscope (FE-SEM, Hitachi S-4200) and a transmission electron microscope (TEM, JEOL JEM-2010). The powder X-ray diffraction patterns were measured from an X-ray diffractometer (Cu K$_\alpha$, Ultima IV, Rigaku) at an angular speed of (2θ) 1°min^{-1}. The Brunauer-Emmett- Teller (BET) method was utilized to calculate the specific surface areas (S_{BET}) using the adsorption data from the N_2 adsorption/desorption isotherms in a relative pressure range from 0.02 to 0.2 (Quantachrome Instruments NOVA 1200e). Prior to running N_2 adsorption/desorption isotherms, all samples have been degassed at 85 °C for 6 h. By the Barrett-Joyner-Halenda (BJH) model, the pore volumes and pore size distributions in the mesopore range (>2 nm) were derived from the adsorption branches of the isotherms, and the total pore volumes (V_t) were estimated from the adsorbed amount at a relative pressure, P/P_0, equal to 0.995. The carbon content of composites was determined by thermogravimetric analysis (TGA, TA Instruments SDT Q600), which was performed in an air flow at 10 °C min^{-1} from room temperature to 800 °C. Note that all sample powders employed for the TGA analysis did not contain any ethylene glycol because this compound was only added in the step of air cathode preparation.

2.3. Preparation of α-MnO$_2$/XC72 air cathodes

An air cathode includes a catalyst layer (on the electrolyte side) and a gas-diffusion layer (on the air side; i.e., the 10AA carbon paper). The paste of the electrocatalyst powders was a homogeneous mixture containing 0.1 g α-MnO_2/XC72 powders, 0.035 g Nafion, and 0.25 g ethylene glycol. This paste was coated onto the 4 cm × 4 cm 10AA carbon paper to form an air cathode sheet with an exposed surface area of 2 cm × 2 cm for the electrocatalysts by means of the doctor-blade method. Finally, the air electrodes were dried in an oven at 85 °C for 24 h.

2.4. Electrochemical measurements

Electrochemical analyses (e.g., polarization curves and rotating ring-disk electrode (RRDE) voltammetry) were measured by electrochemical system modules (CH Instruments 660C or CH Instruments 730D) at a scan rate of 5 mV s^{-1}. The exposed area of all air cathodes to the 0.1 M KOH electrolyte was 4 cm^2 for polarization and 0.247 cm^2 for the RRDE. An Ag/AgCl electrode (Argenthal, 3 M KCl, 0.207 V vs. SHE at 25 °C) in a Luggin capillary was used as the reference and a large piece of platinum gauze was employed as the counter electrode. The Luggin capillary was used to minimize errors due to *iR* drop in the electrolytes. For the RRDE voltammetric measurements, the RRDE was polished with Al_2O_3 slurry and cleaned in ultrasonic bath with ethanol and de-ionized water before coating the electrocatalyst. Suspensions of α-MnO_2 or α-MnO_2/XC72 powders were prepared by adding 1.32 mg of sample