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Design and electrochemical characteristics of single-layer cathode for flexible tubular type zinc-air fuel cells

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ABSTRACT

A cathode of zinc-air fuel cells (ZAFCs) comprises a catalyst layer and a diffusion layer. We propose a new type of cathode, which overcomes the disadvantages of a double-layer cathode used in ZAFCs. To improve the performance of the single-layer cathode, dispersing the particles and reducing their size in the cathode mixture were conducted. The single-layer cathode had the same hydrophobicity as with the diffusion layer of the double-layer cathode and showed better electrochemical properties than the catalyst layer of the double-layer cathode. The single-layer cathode had a dense microstructure and a flat surface. The electrochemical performance and mechanical strength of the single-layer cathode were superior to those of a double-layer cathode. We showed single-layer cathode cell had better electrochemical performance than the double-layer cathode cell through a newly designed flexible-tubular-type ZAFC.

1. Introduction

In the field of eco-friendly energy, which is being actively developed due to global warming, metal-air fuel cells are considered promising alternatives to fossil fuels because of their high energy density, chemical stability, and low cost [1–5]. The zinc-air fuel cell (ZAFC) is the latest in metal-air fuel cell technology [6]. ZAFCs are economical because the materials required are abundant. They have zinc as an anode and a water-based electrolyte, so there is a low risk of explosion of the battery due to an active reaction and there is no pollution. The energy density per unit mass of ZAFCs is high because they have a large anode and a thin cathode [7]. In addition, the zinc oxide generated can be reused as a fuel through a reduction process or as a raw material in cosmetics, sensors, and film [8–10].

Despite the many advantages of ZAFCs, problems with their components result in low performance and hamper commercialization [11]. The cathode is the most important component of ZAFCs. The voltage drop due to high overvoltage reduces energy efficiency and output. Therefore, it is necessary to develop new cathode for oxygen-reduction reactions and conductivity and to improve the catalyst dispersibility, structure, porosity, and hydrophobicity of the cathode [12]. Recently, many studies have been carried out to improve cathode performance. The specific surface area was increased by using a 3D structure of catalyst support [13]. Hydrophobic binders were substituted to prevent chain breaking of polymer binders during discharge at high current densities [14]. Development of complex catalysts and new structures of cathode improved the performance [15,16]. However, most of the developed cathodes were based on double-layer structure.

The cathode of ZAFCs comprises a catalyst layer and a diffusion layer, and each layer has different functions [17–19]. Polytetrafluoroethylene (PTFE) is used as a hydrophobic binder in both layers. However, unlike the diffusion layer, a small amount of PTFE is added to the catalyst layer for active the oxygen-reduction reaction. The catalyst layer is immersed rapidly in electrolyte solution due to its low hydrophobicity, and the diffusion layer, which lacks a catalyst, does not help the active oxygen-reduction reaction [20–22]. For this reason, it is necessary to develop a functional cathode capable of overcoming the disadvantages of the diffusion and catalyst layers.

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In this study, we have proposed the new type of cathode structure that is different from the conventional cathode structure. This cathode is fabricated in single layer structure through the shorter process than the previous one and functions as both a catalyst and a diffusion layer. To improving the performance of the new type cathode, the influences of PTFE content, cathode mixture particle size, and cathode thickness were investigated. In addition, the single-layer cathode was applied to a flexible-tubular-type ZAFC and its characteristics were analyzed.

2. Experimental

2.1. Materials

The cathode mixture consisted of activated carbon (Darco-G 60, -100 mesh, Aldrich), super P (Cobat Corp.), and manganese dioxide (MnO_2) (particle size < 5 μm, purity 92.15%; Aldrich). The cathode mixture was used after drying at 120 °C for 12 h. A polytetrafluoroethylene (PTFE) dispersion (solid content 60.3%, particle size 0.05–0.5 μm; Dupont) was used as a hydrophobic binder and 8.5 M KOH was used as the electrolyte.

2.2. Fabrication of single-layer cathode

Before mixing, the cathode mixture was pulverized using a ball mill (BML-6) for 2 days. The single layer was composed of super P (5 wt%), MnO_2 (5 wt%), Darco-g 60 (40 wt%), and PTFE (50 wt%). To manufacture the cathode, the PTFE dispersion was mixed with distilled water/ethyl alcohol (300/100 ml) for 30 min at 2000 rpm using a stirrer. Next, the cathode mixture was added to the PTFE solution, stirred at 2000 rpm for 1 h, poured into a tray, and the solvent was evaporated in an oven at 120 °C for 12 h. The dried slurry and isopropyl alcohol (IPA) were mixed to making the paste. The paste was made from a 0.4-mm-thick cathode using a roll press. The finished cathode was dried at room temperature for 6 h and cut to the desired size. The parameters for improving the cathode performance in the above single-layer cathode are the PTFE content of the cathode, the ball milling time of the carbon mixture, and the final thickness of the single-layer cathode. Range of parameters; PTFE content (10, 20, 30, 40, 50 wt%), ball milling time (2 days, 5 days), cathode thickness (0.2, 0.4, 0.6, 0.8, 1.0 mm).

2.3. Fabrication of double-layer cathode

The manufacturing process of the double-layer cathode was similar to that of the single-layer cathode. The catalyst layer was composed of super P (5 wt%), MnO_2 (5 wt%), Darco-g 60 (70 wt%), and PTFE (20 wt%). The diffusion layer consisted of super P (5 wt%), Darco-g (45 wt%), and PTFE (50 wt %). The cathode mixture was not ball-milled. Mixing, drying, kneading, and rolling were carried out as described above. During the final rolling, the thicknesses of the catalyst and diffusion layers were 0.30 and 0.50 mm, respectively. The layers were dried at room temperature for 6 h. Finally, a roll press with 0.4 mm spacing was used to bond the catalyst layer physically to the diffusion layer to produce a 0.6-mm-thick double-layer cathode.

2.4. Characterization of the cathode

The particle size of the powder was measured using a particle size analyzer (Malvern Mastersizer 2000E). Cathode microstructure was visualized by field-emission scanning electron microscopy (FE-SEM) (S-4800). The mechanical properties of cathodes were evaluated using a universal testing machine (AG-X plus). The values of properties were obtained by measuring and averaging four samples. The electrochemical characteristics were determined in a three-electrode half-cell with potentio/galvanostat (VMP3, Biologic Inc.) (Fig. 1). A standard oxidized mercury electrode (Koslow Scientific Co. USA), a Pt mesh, and the cathode in 8.5 M KOH were used as a reference electrode, counter electrode, and working electrode, respectively [23]. Linear-sweep voltammetry (LSV) was performed to evaluate the electrochemical characteristics of the cathodes at a scan rate of 2 mVs^{-1} and a cut-off voltage of −0.4 V.

2.5. Assembly and characterization of a tubular cell

The cathode can be used in several types of ZAFCs. Among them, the tubular-type cell can be variously designed because its shape and the capacity can be changed [24]. In addition, tubular-type cells can be used in several applications by eliminating the installation restriction due to the shape. A flexible tubular ZAFC was produced by rolling the cell components in turn onto the surface of a spring-shaped anode collector. The structure of the cell is shown in Fig. 2(b). The separator, cathode, and current collector of the cathode were arranged in the order the outside of the current collector of the anode. The area of the cathode was 17 × 4 cm^2. A Maccor battery test system (Maccor MC-4, USA) was used for fuel-cell tests. A diagram of a fuel-cell test is shown in Fig. 2(a). The zinc gel used as fuel was mixed with 8.5 M KOH (39.48 wt%), a gelling agent (0.52 wt%), and zinc powder (60 wt%) [25]. Zinc gel was poured into the zinc fuel tank and circulated with a flow rate of 100 ml min^{-1}. The fuel-cell discharge current density was 50 mA cm^{-2}.

3. Results and discussions

3.1. Effect of PTFE content

A single-layer cathode should have hydrophobicity and durability higher than those of a double-layer cathode [26]. This was achieved by increasing the PTFE content. Cathodes with PTFE contents of 10–50 wt% were fabricated and their electrochemical properties were evaluated. Fig. 3(a) shows the electrochemical characteristics of the cathode as determined by LSV. Cathode conductivity decreased with increasing PTFE content. Fig. 3(b) shows the IR loss of the cathode determined using the current-

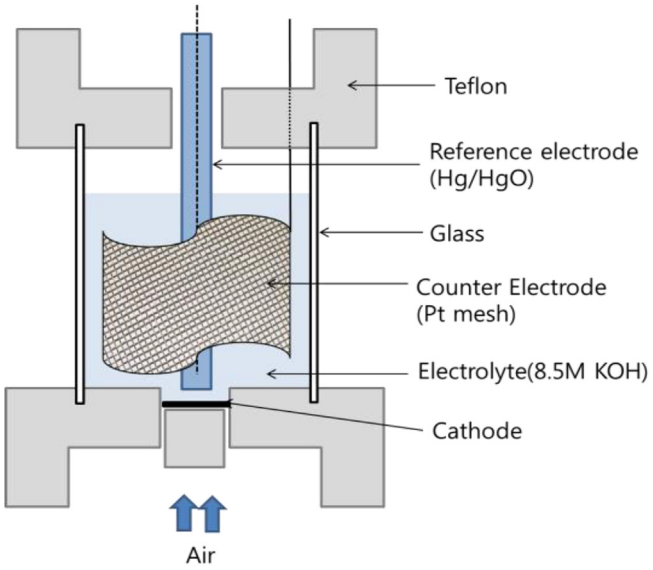

Fig. 1. Structure of the three-electrode half cell.