Journal of Power Sources 249 (2014) 13–20

Contents lists available at ScienceDirect

Journal of Power Sources

journal homepage: www.elsevier.com/locate/jpowsour

High performance zinc air fuel cell stack

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HIGHLIGHTS

- A ZAFC system with MnO_2 as catalyst and KOH electrolyte was developed.
- The peak power density of ZAFC can be as high as 435 mW cm^{-2}.
- The influence factors on cell performance and uniformity are studied.
- The dynamic response time of ZAFC is in milliseconds.

ARTICLE INFO

Article history:
Received 17 July 2013
Received in revised form
15 October 2013
Accepted 17 October 2013
Available online 29 October 2013

Keywords:
Zinc air fuel cell
Electrolyte circulation
Uniformity
Dynamic response

ABSTRACT

A zinc air fuel cell (ZAFC) stack with inexpensive manganese dioxide (MnO_2) as the catalyst is designed, in which the circulation flowing potassium hydroxide (KOH) electrolyte carries the reaction product away and acts as a coolant. Experiments are carried out to investigate the characteristics of polarization, constant current discharge and dynamic response, as well as the factors affecting the performance and uniformity of individual cells in the stack. The results reveal that the peak power density can be as high as 435 mW cm^{-2} according to the area of the air cathode sheet, and the influence factors on cell performance and uniformity are cell locations, filled state of zinc pellets, contact resistance, flow rates of electrolyte and air. It is also shown that the time needed for voltages to reach steady state and that for current step-up or current step-down are both in milliseconds, indicating the ZAFC can be excellently applied to vehicles with rapid dynamic response demands.

1. Introduction

Environmental pollution and shortage of fossil fuels have made it a popular trend to develop electrical vehicles (EVs) and use renewable energy. Many efforts are focused on batteries and fuel cells, which can be used for EVs propulsion and large-scale energy storage. However, the existing batteries and hydrogen fuel cells cannot meet all the market needs; for example: low price, high safety, longer lifetime, and zero pollution. For electrochemical power sources, it is worth noting that zinc possesses a unique set of characteristics as anode material, including low equilibrium potential, electrochemical reversibility, stability in aqueous electrolytes, good conductivity, low equivalent weight, high specific energy, and high volumetric energy density [1–4]. Moreover, zinc also has other merits, such as, abundant resources, low cost, low toxicity, easy storage and safe handling. Up to now various types of zinc air batteries and fuel cells have been developed, such as primary battery [5], electrically rechargeable battery [6–8] and fuel cell (or called mechanically rechargeable battery) [9–12]. However, the primary battery is not applicable to EVs and energy storage, and the electrically rechargeable battery has a relatively short lifetime [13]. Compared to the hydrogen proton exchange membrane fuel cell (PEMFC) [14], the catalysts of zinc air fuel cell (ZAFC) are made by non-precious metals and also the zinc fuel is convenient for storage and transportation [11,15,16]. Additionally, the high stability of zinc in aqueous electrolytes makes the ZAFC more superior to the high energy lithium ion battery in safety. Overall, the ZAFC has great potential for EVs propulsion and large-scale energy storage, and is also attractive for portable, stationary, and military purposes.

Currently, the performance of ZAFC still cannot meet the commercialization requirement. The power densities of ZAFC with manganese dioxide (MnO_2) catalyst reported in previous researches are quite low, mostly in the range of 50–100 mW cm^{-2} [17–19]. This falls far behind the PEMFC. MnO_2 is one of the typical oxygen reduction catalysts, and has a reasonably high catalytic activity for oxygen reduction in alkaline electrolyte. In this study, a ZAFC stack with inexpensive MnO_2 catalyst was developed to study the factors affecting the stack performance and maximize power density.

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http://dx.doi.org/10.1016/j.jpowsour.2013.10.073

2. Experimental

2.1. Stack design and assembly

The development of a zinc air fuel cell with a configuration of bipolar plates in series is shown in Fig. 1. The bipolar design allowed current to flow from the anode to the adjacent cathode with minimal electrical resistance. The anode plate, cathode plate, and bipolar plates were fabricated from graphite material, and each fuel cell had an active surface area of 215 cm^2. The air cathode was constructed of three layers: an active layer, a current collector layer, and a hydrophobic layer (as shown in Fig. 1). The active layer was produced from a mixture of active carbon powder with manganese oxide catalyst powder and PTFE binder. The current collector layer was a woven nickel mesh. The hydrophobic layer was a porous Teflon film. The configurations of the anode chamber are shown in Fig. 2. At the bottom of the zinc pellet beds was a gap or mesh layer that allows potassium hydroxide (KOH) electrolyte and the extremely small particles to fall out of the pellets bed.

The chemical reactions taking place in the ZAFC stack and the transportation of electrons in a bipolar plate can be summarized as Fig. 1. During the power generation process, Zinc lost electrons to the graphite plate turning to a Zn^{2+} cation. The electrons generated on the anode traveled via the bipolar plate to an air cathode where the reduction of oxygen took place forming hydroxyl ions (OH^-). The hydroxyl ions traveled towards the anode side via the electrolyte and combined with zinc cations to form zinc oxides. Because the hydrophobic layer was insulated, the electrons, generated in the anodes and traveling via the bipolar plates, could only be transported from the air cathode margins into the active layer and the current collector layer, as shown in Fig. 1. In order to connect the circuit between the bipolar plates and air cathodes, nickel foils (0.08 mm thick) were used to edge-clad the air cathode sheets (see Fig. 3).

Fig. 4 shows a schematic design of the zinc air fuel cell system. Zinc pellets with an average size of 1 mm stored in the fuel tank, were fed to each anode chamber uniformly and intermittently by a mechanical device above the fuel cell stack. Potassium hydroxide (KOH) electrolyte (40 wt.%) was contained in a separate storage tank, and the electrolyte was driven by a magnetic pump to make circulation flow. Under the action of gravity, the zinc pellets automatically entered the anode chamber trough from the upper slit with the flowing electrolyte. The discharge products (potassium zincate) were carried out by the flowing electrolyte. Meanwhile, the ambient air was fed through the stack inlet and distributed in parallel amongst the unit cells by an electric fan. The outflow from the unit cells were combined in the outlet header and exited through the stack outlet. Similar to the traditional hydrogen fuel cell system, the fuel tank or the energy reservoir can be scaled up independently of the power.

2.2. Stack testing

At first, a 5-cell stack with anode chamber of type V was assembled and the polarization characteristics of each cell were tested, and the cells located from the positive electrode (near to the blower) to negative electrode were numbered #1, #2, #3, #4, and #5 in turn. Then several 2-cell stacks were assembled, and series of control tests were carried out to study the effects of different cases on performance differences between cells in the 2-cell stack. The cases are shown in Table 1. In the 2-cell stack, the cell located close to the blower was numbered #1, and the other cell was numbered #2. All of the air cathode sheets used in 5-cell and 2-cell stacks were cut from a large one. Only the air cathode A and B were used twice in Case I and Case II. The edge-cladding material for air cathode was nickel foil. The corroded nickel foils were exposed to room air for more than a month, while the cleaned nickel foils were treated ultrasonically with 1 mol L^{-1} HNO_3 and 1 mol L^{-1} HCl, and then washed with deionized water. In order to eliminate the effect of the changes of zinc pellets size and electrolyte concentration after the tests on the performance of ZAFC, the zinc pellets and the KOH electrolyte used in the 5-cell stack and 2-cell stack tests were changed with fresh ones before each tests. Besides, in all of the tests, the amounts of KOH electrolyte were the same, and the flow rates of electrolyte and air were kept constant.

In addition, the dynamic response characteristics of ZAFC were tested with the 2-cell stack used in Case IV. In order to investigate the step-up characteristics, the current of the stack was firstly stabilized at 10 A, then followed by loading the current to 20 A, 30 A, 40 A, 50 A, respectively, with stack voltage monitored and recorded. Also, current step-down cases were performed, in which the stack was firstly stabilized at 20 A, 30 A, 40 A, 50 A, then stepped down to 10 A, respectively.

All of the experiments were implemented at room temperature, and the change of relative humidity of ambient air was negligible. An electronic load (Hoecherl & Hackl GmbH ZLSV1502) was used for the performance tests, and a NI PXI-1033 data acquisition instrument was used to measure each cell voltage.

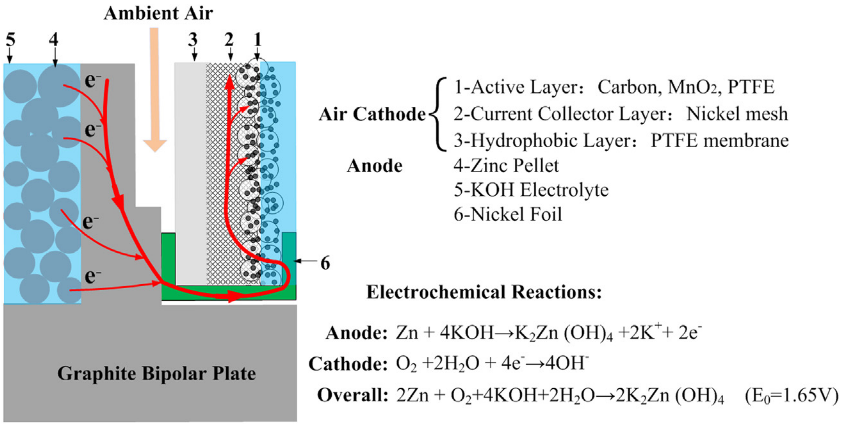

Fig. 1. Basic principle of ZAFC.