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A High Catalyst-Utilization Electrode for Direct Methanol Fuel Cells

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ABSTRACT

In this study, a simple method is devised to investigate the local current distribution of the anode of a direct methanol fuel cell (DMFC). It is shown that the local current decreases along the methanol flow direction as a result of the decreased methanol concentration along the same direction during discharge. This finding suggests that the catalyst loading along the flow direction needs to be distributed by following the same trend as the distribution of methanol concentration to achieve high catalyst utilization. In line with this idea, we propose and fabricate a novel anode structure that enables the catalyst loading to be reduced along the methanol flow direction. The fuel cell performance characterization demonstrates that the new anode with uneven catalyst loading matches the performance of the conventional anode involving an evenly distributed catalyst, but the total amount of catalyst loaded in the new anode is substantially reduced.

1. Introduction

In recent years, direct methanol fuel cells (DMFCs) have attracted significant attention due to their high energy densities; however, the high cost of DMFCs hinders their widespread commercialization [1–4]. This high cost is the result of DMFCs' expensive components, such as Nafion membranes, catalysts for anodes and cathodes, carbon paper and bipolar plates, etc. Among these materials, the largest portion of the cost is attributed to the catalysts.

In DMFCs, noble metals of Pt and PtRu are conventionally used as catalysts for cathodes and anodes, due to the sluggish kinetics of oxygen reduction reaction and methanol oxidation reaction. Although the literature shows that non-noble metal compounds such as ferric, cobalt, nickel, and carbonaceous materials can potentially act as substitutes for Pt [5–7], much more research needs to be done to completely replace noble metals by non-noble metal compounds as catalysts. Thus, noble metals currently remain as the most dominant materials for DMFCs' catalysts.

Hence, a promising way to cut down the cost is to improve the utilization of the noble metal catalyst. There are two methods to achieve this: the first method is to develop advanced supporting materials such as carbon nanotubes [8–11], carbon nanofibers [12–14], mesoporous carbon [15–18] and other types of materials [19–22]; the second method is to optimize the electrode structure to improve the utilization of the catalyst. For example, Liu [23] prepared novel anode catalyst layer by ultrasonic-spray process which combines directly spray method and catalyst-coated membrane switchover method. Results show that the anode outer catalyst with pores and mesh work structure has increased the electrochemical active surface area and retained the transfer of protons and electrons, and the anode inner catalyst layer with compact structure has prevented methanol crossover. The peak power density increased from 116.8 mW cm^{-1} of traditional MEA to 202.6 mW cm^{-1} of novel MEA. Suo [24] also proposed a novel anode structure composed of a hydrophilic inner catalyst layer with PtRu black and an outer catalyst layer with PtRu/C. In the double-layer structured anode, there existed a catalyst concentration gradient and porosity gradient, resulting in good mass transfer, proton and electron conducting. Therefore, the performance got enhanced. Nakashima [25] designed the multi-layer anode with localized catalyst loading prepared by the sputtering method. The designed multi-layer electrode showed a high cell performance and mass activity because of the good contact at the interface between the catalyst and the electrolyte membrane and low mass transfer resistance. The ultra-low catalyst loading electrode preparing by the sputtering method was a very effective method for reducing the catalyst amount and enhancing the mass activity.

The above researchers mainly focused on the optimization of electrode in the through-plane direction, while few papers were published about the optimization of electrode in the in-plane

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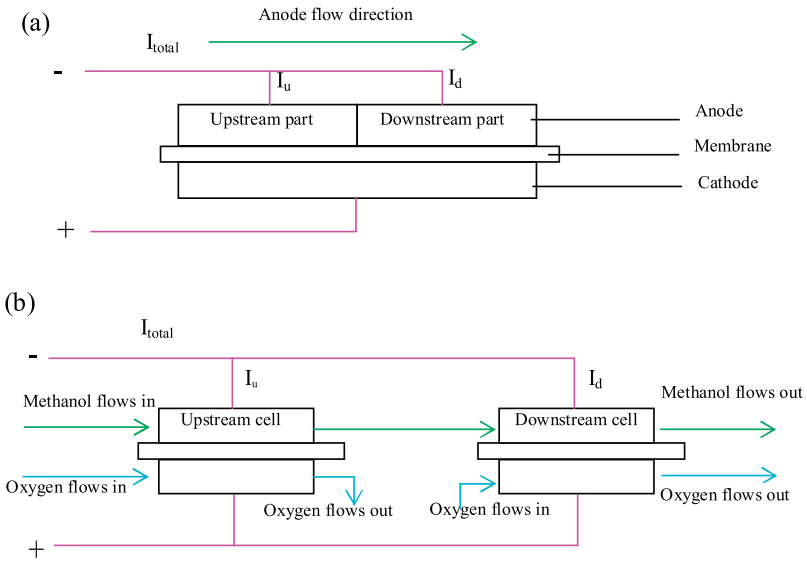

Fig. 1. Scheme diagram of the local current measurement. (a) Local current measurement of a single cell; (b) the setup with two cells simulated as a cell.

direction. It is well known that the catalyst is evenly distributed in the in-plane direction for the conventional electrodes. However, when a DMFC discharges, the concentration of reactants decrease and the concentration of products increase along the flow direction from inlet to outlet. As a result, this concentration disparity will lead to an uneven local current distribution in the in-plane direction, despite the even catalyst distribution. The part with large local current definitely contributes more to the total performance than that with small local current contributes. Therefore, catalyst utilization may not be consistent, varying according to the position along the flow direction and consequently causing the total utilization of the catalyst to be lowered.

To investigate the local current distribution of a DMFC to figure out the contributions of different parts, we divided the anode into upstream and downstream two parts along the flow direction. This anode structure can be simulated by applying two single cells with anodes connected by series. By measuring the currents of these two single cells, we are able to determine the local currents at the upstream and the downstream parts, as well as their contributions to the total performance. Based on the results of the local current distribution, we propose and fabricate a novel anode structure, in which the catalyst is unequally loaded at the upstream and downstream parts. With this new anode structure, the total amount of catalyst loaded at the anode decreases significantly, while the performance is barely influenced. Hence, the catalyst utilization remarkably increases.

2. Experimental

2.1. Preparation of the membrane electrode assembly (MEA) for DMFCs

The MEA studied in this work was fabricated according to the following method [26,27]. For the anode, a diffusion layer comprising of Vulcan XC-72 carbon powder and PTFE was brushed onto a PTFE-treated carbon paper (Toray), followed by the catalyst layer consisting of PtRu/black (Johnson Matthey) and Nafion ionomer. The cathode was fabricated by using a similar method as that of the anode with Vulcan XC-72 carbon powder, 60% Pt/carbon (Johnson Matthey), PTFE, and Nafion ionomer. The amount of cathode catalyst loaded was 2 mg cm^{-2}.

In the conventional anode structure, the loadings of catalyst at the upstream part and the downstream part were the same (6 mg cm^{-2}), denoted as A6 + 6. While in the new anode structure, the catalyst was unevenly distributed: 6 mg cm^{-2} was loaded at the upstream part and 4 mg cm^{-2} and 2 mg cm^{-2}, denoted as A6 + 4, and A6 + 2, respectively, was loaded at the downstream part.

The MEA was obtained by hot-pressing the anode and cathode on each side of a pretreated Nafion 115 membrane. This pretreatment included boiling the membrane for 1 hour in 5 vol.% H_2O_2 at 80 °C and another 1 hour in 0.5 M H_2SO_4 at 80 °C before washing it in boiling DI water.

2.2. Single cell test

The MEA was sandwiched between two stainless steel plates with a single serpentine flow field on each plate. It was noted that when assembling the new structured MEA, the upstream portion should be installed close to the inlet, and the downstream portion

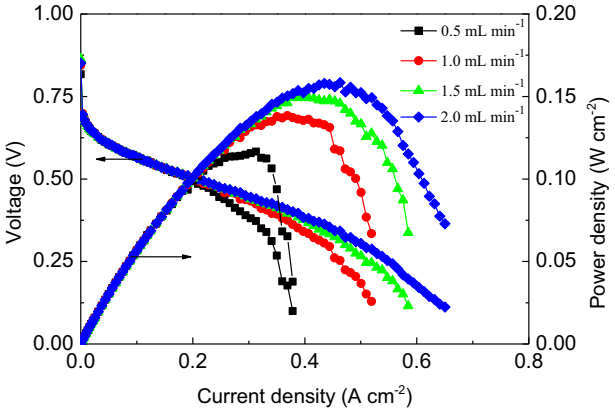

Fig. 2. I-V performance of the anode with evenly distributed catalyst at the anode flow rates of 0.5 mL min^{-1}, 1.0 mL min^{-1}, 1.5 mL min^{-1}, and 2.0 mL min^{-1}.