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A micro-porous current collector enabling passive direct methanol fuel cells to operate with highly concentrated fuel

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ABSTRACT

Operating direct methanol fuel cells (DMFCs) with concentrated fuel is desired to increase the energy density of the power pack. In this paper, we propose and fabricate a micro-porous anode current collector, which enables a passive DMFC to operate with methanol solutions as concentrated as 22.0 M without sacrificing the performance generated with diluted methanol. It is found that the micro-porous current collector allows an accumulation of CO_2 gas in the porous structure, forming a barrier to resist the transport of methanol to the catalyst layer. The reduced methanol concentration level in the anode catalyst layer tends to reduce the rate of methanol crossover and hence, improve the performance.

1. Introduction

Passive direct methanol fuel cells have garnered much attention as one of the most promising power supply systems for portable electronic devices [1–11]. This type of fuel cell offers a compact, simple and reliable system structure and has a high theoretical energy density. The commercialization of passive DMFCs has been postponed due to several technical issues, among which methanol crossover is most critical [12–15]. Methanol crossover not only lowers the cell voltage, but also reduces the fuel utilization. For this reason, conventional DMFCs have to operate with diluted methanol (2.0 M - 6.0 M), which unfortunately sacrifices the energy density.

Extensive efforts have been made to increase the operation concentration and in turn, to increase the energy density of the power packs [16–21]. Chen et al. [16] prepared a Nafion/Zeolite nanocomposite membrane to achieve low methanol permeability by the in-situ hydrothermal crystallization method. With this membrane, the performance was better at higher concentration (5.0 M) than that with Nafion membranes. Lu et al. [17] inserted a compact microporous layer in the anode as a methanol barrier, which could reduce the rate of methanol crossover; they showed that the DMFC could yield reasonable performance even at 8.0 M. Zhang and Hsing [18] designed a flexible-graphite based anode that serves both as the anode diffusion layer and the anode flow filed. The mass transfer rate was much lower due to the denser anode, and the performance significantly increased at high concentration scenarios (12.0 M and above) compared with the conventional design. Nakagawa [19,20] proposed another kind of barrier layer, a porous carbon plate, which was located between the fuel reservoir and the current collector. This system could operate with 22.0 M methanol. Kim et al. [21] used hydrogels in methanol fuel cartridges to control the fuel diffusion rate from the fuel cartridge to the anode electrode; by this design, the feed concentration could reach 8.0 M.

The literature review shows there are three main approaches to achieving high concentration operation: (1) modifying electrolyte membranes to reduce methanol permeability; (2) modifying the anode diffusion layer to increase the methanol transport resistance; and (3) adding a barrier layer to control the methanol transport rate. For Option 1, modified membranes do have lower methanol permeability, but the conductivity decreases at the same time. Option 2 is limited by the material, carbon paper/cloth, to form the anode diffusion layer; both carbon papers and cloth, however, have relatively high permeability. The disadvantage of Option 3 is that the added layer will increase the volume and complexity of fuel cells. In this work, we propose and fabricate a new type of current collector, a micro-porous anode current collector (denoted as MPCC hereafter), retaining the conventional DMFC structure. The results show that the passive DMFC employing the MPCC can yield good performance with methanol solution as concentrated as 22.0 M.

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2. Experimental

2.1. Membrane electrode assembly

A pretreated Nafion 115 membrane was employed in this work. The details about the pretreatment procedures can be found elsewhere [6]. Two commercial electrodes from Johnson Matthey® were used as anode and cathode. A SGL® carbon paper with 5 wt.% Polyterafluoroethylene (PTFE) treatment and a MPL was used as GDLs for both electrodes. The catalyst layers of anode and cathode consist of carbon supported PtRu (50% Pt, 25% Ru) with a loading of 4.0 mg cm^{-2} and carbon supported Pt (60% Pt) with a loading of 2.0 mg cm^{-2} respectively. The anode, the Nafion 115 membrane, and the cathode were sandwiched by hot-pressing at 135 °C under 4.0 MPa for 3 min to form the MEA with an active area of 4.0 cm^2.

2.2. Single cell fixture

The MEA was sandwiched between an anode and a cathode current collector, with the entire setup held together by both anode and cathode fixtures. A 5.0 ml fuel tank was built at the anode and a thermocouple was fixed at the out surface of anode diffusion layer to measure cell temperature. The cathode current collector was made of a perforated 316L stainless steel plate with a thickness of 1.5 mm. Two different types of anode current collectors were fabricated, shown in Fig. 1. One was the conventional perforated type made of 316L stainless steel with open ratio of 47.8%, while the other was the MPCC fabricated by porous metal supplied by SINTO Co. Ltd. Japan with a thickness of 1.0 mm. The pore diameter of MPCC ranges from 3-7 μm and its porosity is 25%.

2.3. Measurement instrumentation and test conditions

An Arbin BT2000 electrical load interfaced to a computer was employed to control the condition of discharging and record the voltage-current curves. For each discharging current point, one minute was needed to obtain the stable voltage. The temperature of the cell was measured by an Arbin BT2000 built-in function. Prior to each experiment, the MEA was installed into an active fixture and activated for 12 h at 60 °C. During this process, 1.0 M methanol was fed at 1.0 mL min^{-1}, while dry air was supplied under atmospheric pressure at a flow rate of 100 mL min^{-1}.

2.4. Measurement of the methanol-crossover flux

The methanol-crossover flux was measured by the voltammetric method. To finish this test, the cathode was changed to an active mode from the air breathing mode. The anode was still maintained as the passive mode. DI water was fed into cathode at a flow rate of 1.0 mL min^{-1} to create an inert atmosphere. A positive voltage of 0.85 V was applied to the cathode to ensure that the penetrated methanol was oxidized completely.

3. Results and discussion

3.1. Cell performance at different concentrations

Fig. 2 shows the cell performance of the passive DMFC with the conventional perforated current collector at various methanol concentrations from 2.0 M to 8.0 M. It is evident that the cell performance improved as the concentrations increased from 2.0 M to 5.0 M. A further increase to 7.0 M, however, led to a decline in performance. The optimal performance occurred at both 5.0 M and 6.0 M, and the corresponding peak power density is 30 mW cm^{-2}. The improved cell performance with methanol concentration increasing from 2.0 M to 5.0 M can be attributed to two reasons.

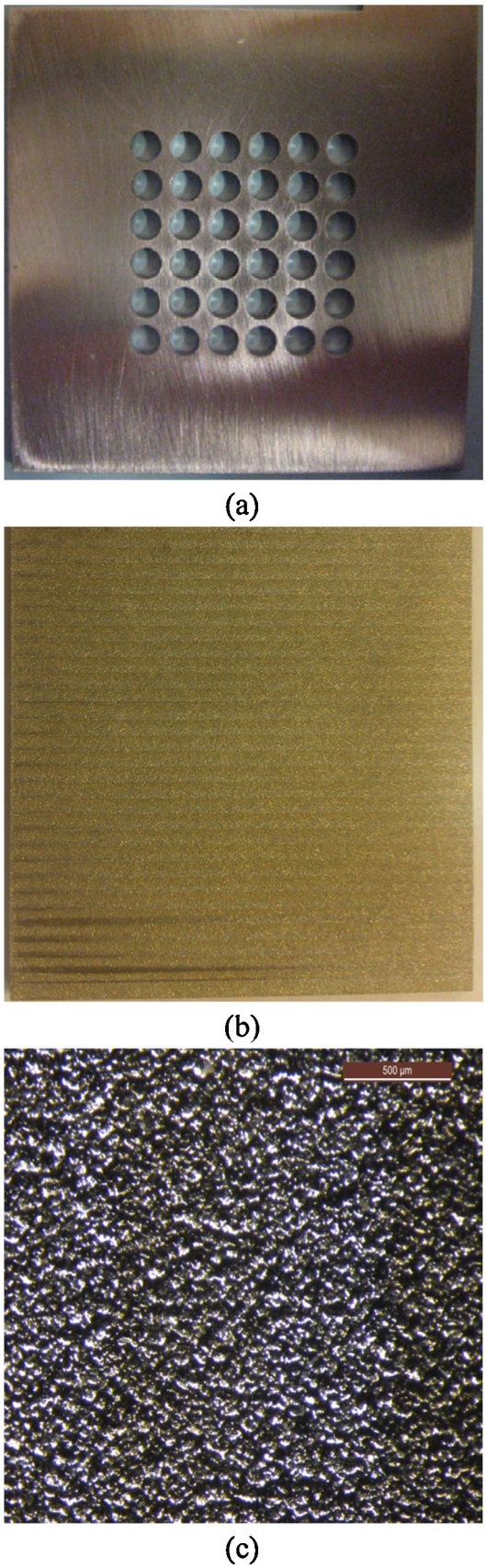

Fig. 1. Schematic of the current collector. (a) Perforated-plate current collector; (b) Micro-porous current collector and (c) Microstructure of the micro-porous current collector.