

Short communication

Hydrogels in methanol fuel cartridge used as a diffusion-rate-controlling agent suppressing the methanol crossover in passively operated flat-pack type DMFCs

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Abstract

Hydrogels are used in methanol fuel cartridges to control fuel diffusion from the fuel reservoir to the anode electrode. This ability to control fuel diffusion rates enables the reduction of excess fuel supply that causes fuel crossover through the proton-exchange membrane. Cell performance was increased drastically from 14 to 21.5 mW cm⁻² with higher methanol concentrations using hydrogel fuel cartridges that fulfill the role of a diffusion-rate-controlling agent. This result implies that the hydrogel retards fuel diffusion, even at higher concentrations and suppresses the methanol crossover.

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1. Introduction

Direct methanol fuel cells (DMFCs) have been highlighted as potential power sources for portable devices, such as cellular phones, PDA and laptop computers, due to the simplicity of their systems, convenience in fuel replacement and an operational environment suited to ambient conditions. To commercialize the small DMFC system, however, many researches are currently underway to solve some key problems involved in DMFCs, such as low catalytic activity and methanol (MeOH) crossover [1–4].

This study was particularly focused on developing a novel fuel-supplying method, which can suppress methanol crossover in passively operated flat-pack type DMFC systems. Methanol crossover from the anode electrode to the

cathode electrode through the conventional proton-exchange membrane, lowers fuel efficiency and decreases the cell potential, because both oxidizing and reducing agents are undergoing redox reactions simultaneously at the cathode electrode [1]. The following introduces the recent results obtained in this study on passively operated flat-pack type DMFC systems in which this unique fuel cartridge had been adopted. The hydrogels were used in the methanol fuel cartridge to control the rate of fuel diffusion from the fuel reservoir to the anode electrode.

2. Experimental

In these experiments, Pt-Ru and Pt black were used as anode and cathode catalysts, respectively, and were loaded on carbon paper (Toray) with a thickness of 275 μm, on which carbon black (Vulcan-XC) had been pre-coated using

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a spraying method. The loaded amount of catalyst was adjusted to be 3 mg cm^{-2} . Nafion[®]-115 (thickness: $100 \mu\text{m}$, equivalent weight: 1100 g mol^{-1} , water content: 34%, conductivity: $0.059 \Omega^{-1} \text{ cm}^{-1}$) from DuPont was used as a proton-exchange membrane. The membrane was pretreated to enhance its proton exchange capability using the following procedures. It was cleaned in 3 wt.% H_2O_2 solution, rinsed in boiling deionized (DI) water to remove any organic compounds, boiled in 0.5 M H_2SO_4 to both remove metal compounds and replace Na^+ ions with H^+ ions in the membrane pores, and then finally rinsed in boiling de-ionized water. Each step was performed at 80°C and lasted for 2 h [5].

3. Results and discussion

The schematic diagram of the structure of the passive-type DMFC is illustrated in Fig. 1. Methanol is supplied to the anode side of the MEA by natural diffusion while the cathode is breathing the air. Epoxy carbon was used as a housing material. Fig. 2 shows the photographs of the flat-pack type DMFC system used in these experiments, in which two MEAs with a size of $30 \text{ mm} \times 60 \text{ mm}$ were attached to both sides of the fuel reservoir. Methanol fuel was supplied either as a liquid itself or soaked in hydrogels. The total dimensions of

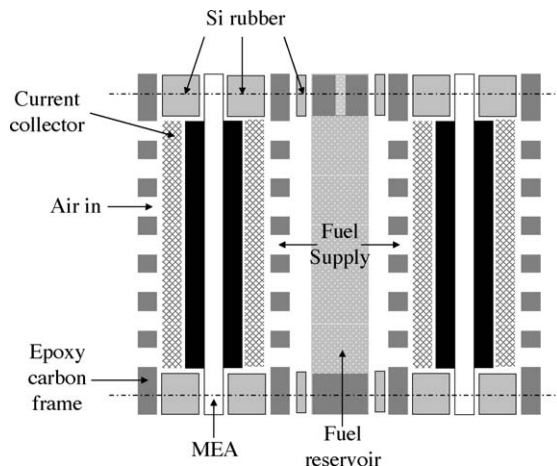


Fig. 1. The schematic diagram of small passive-type direct methanol fuel cells.

the fabricated DMFC including the fuel reservoir (18 cm^3) were $81 \text{ mm} \times 74 \text{ mm} \times 10 \text{ mm}$, which contains four MEA units.

Fig. 3 shows the performance of the passively operated flat-pack type DMFCs used in these experiments, with various methods of fuel supply and fuel concentrations. All the experiments were performed under room temperature con-

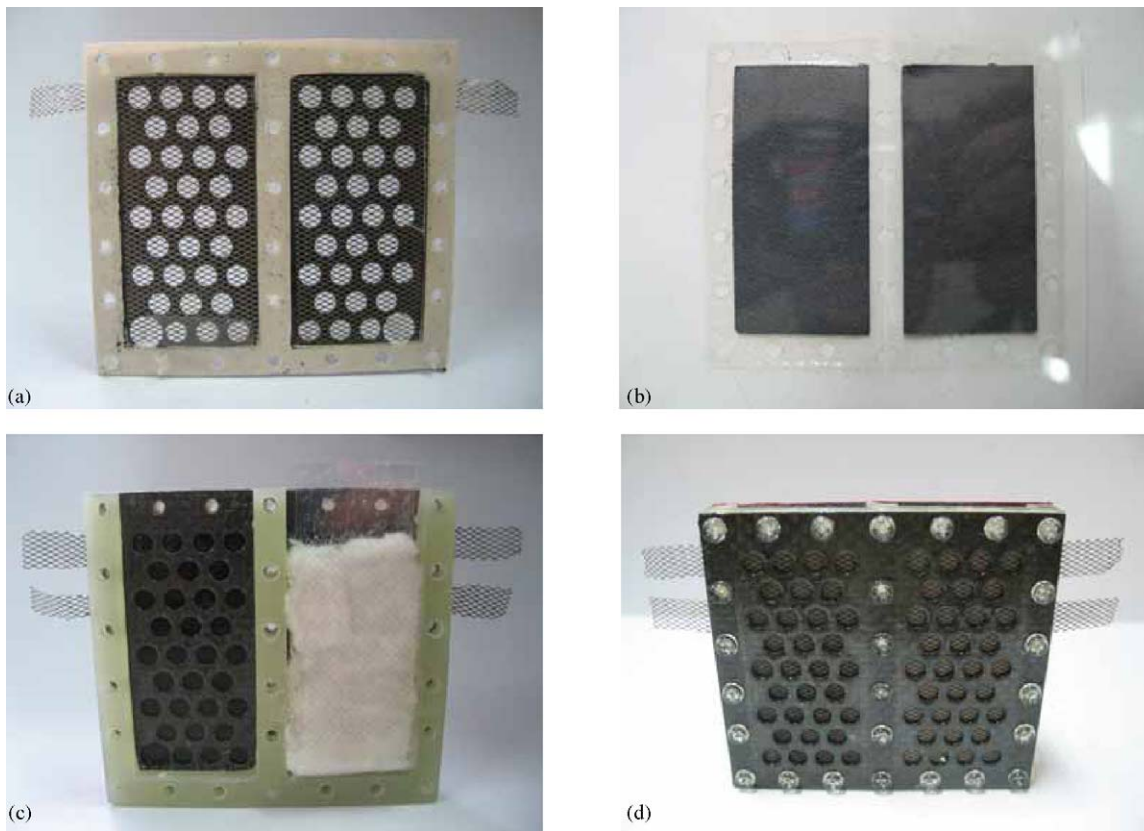


Fig. 2. Photographs of (a) the current collector with gasket, (b) membrane–electrode assembly, (c) fuel reservoir equipped with a hydrogel fuel cartridge and (d) an assembled flat-pack of DMFCs (the size of the entire system including the fuel reservoir is $81 \text{ mm} \times 74 \text{ mm} \times 10 \text{ mm}$).

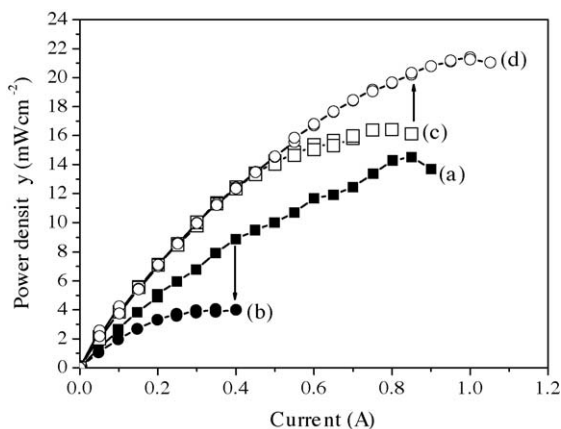


Fig. 3. The DMFC performance differences between the systems with and without hydrogel fuel cartridges. The systems were operated passively under ambient conditions. Each cell performance was obtained with (a) liquid 4 M methanol fuel, (b) liquid 8 M methanol fuel, (c) 4 M methanol in a hydrogel fuel cartridge and (d) 8 M methanol in a hydrogel fuel cartridge.

Table 1

The open cell voltage (OCV) measurements of DMFCs with various methods of fuel supply and fuel concentrations

Fuel concentration (M)	Open cell voltage (V)	
	Liquid type	Hydrogel cartridge type
4	0.58	0.60
8	0.49	0.61

ditions without any ancillary devices. The maximum power density of the liquid-type fuel was 14 mW cm^{-2} when using 4 M MeOH. As the fuel concentration was raised to 8 M MeOH, the performance abruptly decreased, obviously due to methanol crossover [6]. In contrast, the power density of the cell equipped with the hydrogel fuel cartridge increased from 16.5 to 21.5 mW cm^{-2} when the MeOH concentration was changed from 4 into 8 M. Similar trends were also observed in open cell voltage (OCV) measurements, listed in Table 1. When using 4 M MeOH, the OCVs of both cells with liquid-type and hydrogel-cartridge-type fuel feedings were close to 0.6 V. These results appeared reasonable, because, when using 4 M MeOH, methanol crossover was not significant, even when the fuel was supplied as a liquid itself [7].

However, when the concentration of MeOH solution was increased from 4 to 8 M, notable changes in OCV were observed depending on the fuel-supply type. When the fuel was supplied as a liquid, the OCV abruptly decreased from 0.58 to 0.49 V, due to methanol crossover, as in the cell performance measurements. In contrast, however, when the fuel was supplied via soaked hydrogels, the OCV did not change significantly. The above results imply that the hydrogel suppresses methanol crossover, even at higher fuel con-

centrations, which is caused by the suppression of the rate of methanol diffusion.

Due to the slow reaction kinetics of methanol oxidation at room temperature, the surface reaction usually becomes a rate determining step at high fuel concentrations in passively operated DMFCs [4], so that the excess fuel, which cannot react on the anode catalysts, crosses over through the proton-exchange membrane and thus lowers the overall cell potential as observed in the conventional liquid-type fuel supplying systems. However, when the fuel is supplied to the anode electrode within hydrogels, the hydrogels play a role as controlling agents for the rate of diffusion and reduce the amount of excess fuel even at high fuel concentrations by retarding fuel diffusion, thus suppressing methanol crossover. Therefore, the DMFCs equipped with hydrogel fuel cartridges exhibit high performance even at high fuel concentrations, as shown in Fig. 3.

4. Conclusions

To summarize, we have developed a new-concept fuel cartridge for passive-type DMFC systems using hydrogels, which function as fuel diffusion-rate-controlling agents for the rate of fuel diffusion. This advanced fuel-supplying system enables adoption of higher concentrations of methanol into the passively operated DMFCs, which increases the cell performance while reducing methanol crossover within the system.

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