

Short communication

Suppression of the methanol crossover by hydrogels in passively operated flat-pack type DMFCs and its application for the power source of cellular phone

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Received 22 August 2005; received in revised form 8 May 2006; accepted 27 May 2006

Available online 17 July 2006

Abstract

In this study, a unique fuel-supplying method, which adopted hydrogels as fuel-diffusion-rate-controlling agents, was introduced and its influence on the methanol (MeOH) crossover behavior in passively operated flat-pack type direct methanol fuel cells (DMFCs) was investigated. When the MeOH fuel is supplied soaked in hydrogels rather than as a liquid itself, the power density was abruptly increased from 16 to 22 mW cm⁻² as well as the optimum fuel concentration. Analyses of fuel diffusion rates at various fuel-supply types revealed that this enhanced performance of DMFCs originated from the remarkable reduction of MeOH crossover by using hydrogels. That is, hydrogels suppress the excess fuel supply from the fuel reservoir to the anode electrode even at high fuel concentrations by reducing the fuel diffusion rate, so that, the unconverted MeOH, which crosses over to the cathode electrode, is minimized. The improvement of the cell performance by the reduction of MeOH crossover in hydrogels-adopted systems was also investigated by three-electrode tests. Using this novel DMFC system, we successfully operated the cellular phone for about 40 min at a maximum power consuming condition with 18 cm³ of 6 M MeOH fuel.

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Keywords: Hydrogels; Fuel diffusion rate; Methanol crossover; Flat-pack; DMFCs

1. Introduction

A passively operated flat-pack type DMFC is one of the most promising power sources for portable electronics, because it can be constructed in a small size without any ancillary device and operated at ambient environments. However, low catalytic activity at the anode electrode and the ensuing MeOH crossover problems must be solved for the flat-pack type DMFC to be commercialized [1–4].

Recently, we reported a novel fuel-supplying method, which utilized hydrogels as fuel-diffusion-rate-controlling agents, and its influence on the performance of passively operated flat-pack type DMFCs [5]. When the fuel is supplied as soaked in hydrogels, the cell performance increased and the open cell voltage

(OCV) did not drastically decrease even at high fuel concentrations. We attributed the enhanced performance of the DMFCs equipped with hydrogels to the reduction of MeOH crossover by using hydrogels.

This study reports the results of our continued work on the performance of flat-pack type DMFCs equipped with hydrogels, particularly on the influence of hydrogels on the MeOH crossover behavior. The MeOH crossover flux according to the fuel-supply type was compared and its influence on the performance of anode and cathode electrode was also investigated. Finally, we have operated a cellular phone using this novel DMFCs system.

2. Experimental

Pt–Ru and Pt black was used as an anode and cathode catalyst, respectively, and sprayed on carbon papers (Toray) coated

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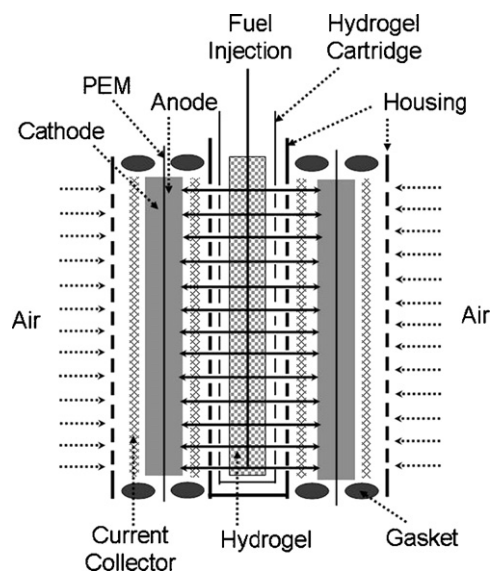


Fig. 1. The schematic structure of the flat-pack type direct methanol fuel cell.

with carbon black (Vulcan-XC). The loaded amount of catalyst was 5 mg cm^{-2} for both anode and cathode electrode. Nafion[®]-115 (Dupont) was used as a proton-exchange membrane and was pre-treated to enhance its proton-exchange capability prior to the insertion into a membrane electrode assembly (MEA). Two MEAs with a size of $30 \text{ mm} \times 50 \text{ mm}$ were attached on both sides of the fuel reservoir. The detail procedure of MEA fabrication was presented in our previous paper [6].

Epoxy carbon with a thickness of 1 mm was used as an end plate and epoxy glass with a thickness of 5 mm was used as a material for the fuel reservoir. Ni mesh coated with Pt was used as a current collector and placed between the electrodes and epoxy carbon end plates.

The schematic structure of a flat-pack type fuel cell used in this study is illustrated in Fig. 1. Hydrogels, which act as fuel-diffusion-rate-controlling agents, are positioned at the center of the fuel cell. The MeOH/H₂O fuel is injected directly into the hydrogels and through which, the fuel is supplied to the anode catalyst by natural diffusion. Hydrogels are selected as fuel-diffusion-controlling agents due to their hydrophilic characters. The structure of hydrogels used in this study is represented in Fig. 2. They are crosslinked polymers with low crosslinking density, and mainly composed of polyvinyl alcohol and polyacrylic acid.

MeOH diffusion rates at various fuel-supply types were measured using a refractive index detector (Young Lin Instrument, Acme HPLC). Nafion[®]-115 was placed between the two fuel tanks. MeOH solution with various fuel concentrations was poured into one of the fuel tank and pure deionized water was poured into the other fuel tank. Increase in the MeOH concentration at the fuel tank filled with deionized water was measured using a refractive index detector. MeOH diffusion rate was calculated from the increase in the MeOH concentration per unit area of the membrane and unit time. Three-electrode tests were also performed to measure the voltage of anode and cathode electrode, respectively. As a reference electrode, the 0.5 M H₂SO₄ solution was used.

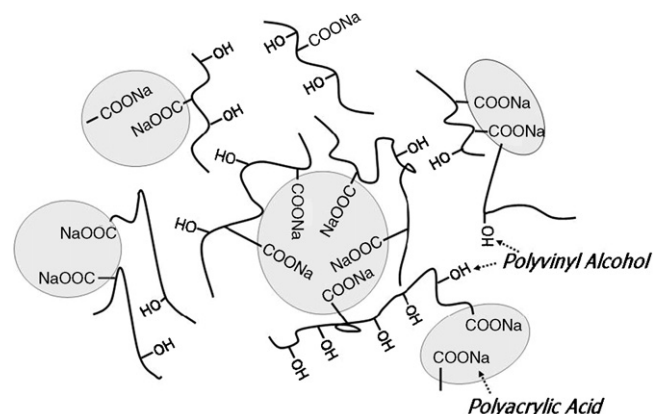


Fig. 2. The structure of hydrogels.

A cellular phone was operated using the novel DMFCs. Three sets of flat-pack type DMFCs were used to adjust the power required to operate the cellular phone (Samsung electronics, SPH-X7000). A dc/dc converter with an efficiency of 70–80% was used to convert the voltage and the current of the fuel cells to those required by the cellular phone.

3. Results and discussion

3.1. Performance of flat-pack type DMFCs equipped with hydrogels

Fig. 3 shows the cell performance at various fuel concentrations and fuel-supply types. The power density was always higher when the fuel was supplied through hydrogels (Fig. 3B) than as a liquid itself (Fig. 3A) at all fuel concentrations. The maximum power density was 22 mW cm^{-2} at 6 M MeOH for the hydrogel-cartridge type and 16 mW cm^{-2} at 4 M MeOH for the liquid-cartridge type. The power density for both cases decreased above the optimum concentration, e.g., 6 M for the hydrogel-cartridge type and 4 M for the liquid-cartridge type, certainly due to the MeOH crossover [7]. However, the power density decreased more abruptly in the liquid-cartridge type (6 mW cm^{-2} at 8 M MeOH) than in the hydrogel-cartridge type (18 mW cm^{-2} at 10 M MeOH).

All the above findings indicate that the hydrogels influence the MeOH crossover behavior, since all the other experimental conditions except the fuel-supply method were the same. The MeOH crossover, which strongly influences the cell performance, is directly related to the MeOH diffusion rate due to the low catalytic activity of the anode electrode [4]. To further investigate the influence of hydrogels on the MeOH diffusion rate, we studied the MeOH crossover behavior at various fuel-supply types.

3.2. Influence of hydrogels on the methanol crossover behavior

We investigated the influence of hydrogels on the MeOH crossover behavior. MeOH fuel was placed in one vessel either soaked in hydrogels or as a liquid itself, and pure deionized

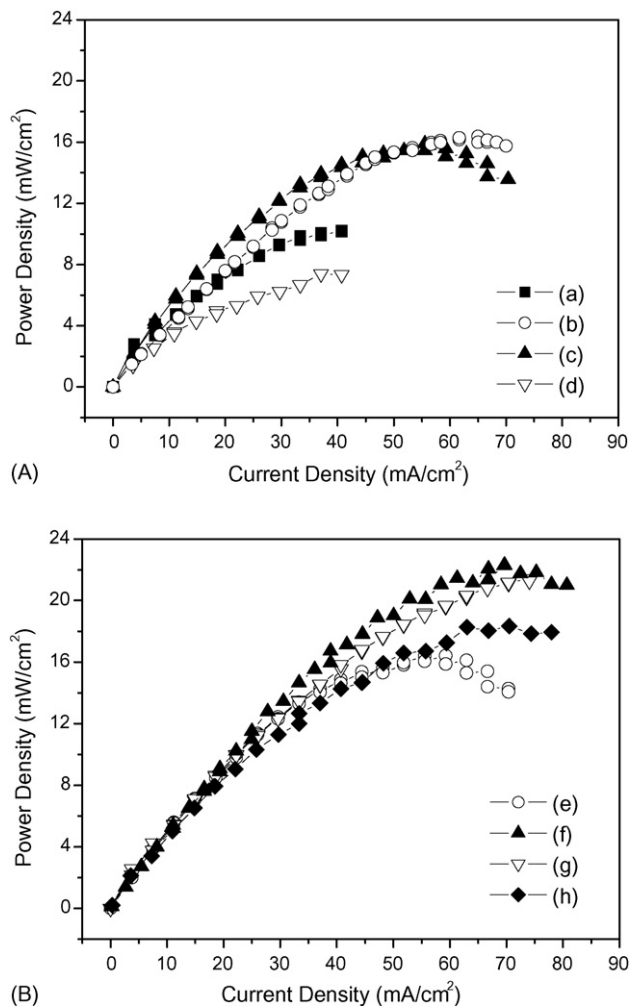


Fig. 3. The performance of flat-pack type DMFCs at various fuel concentrations and fuel-supply types. (A) Liquid-cartridge type, and (B) hydrogel-cartridge type. (A)—(a) 2 M MeOH, (b) 4 M MeOH, (c) 6 M MeOH, and (d) 8 M MeOH. (B)—(e) 4 M MeOH, (f) 6 M MeOH, (g) 8 M MeOH, and (h) 10 M MeOH.

water was placed in the other vessel, at which the increase of MeOH concentration was measured. MeOH was transferred from the tank filled with MeOH fuel to the tank filled with deionized water, due to the MeOH concentration gradient. The MeOH diffusion rate through the proton-exchange membrane (PEM), was calculated based on the increase of MeOH concentration in the deionized water. It was expressed as the moles of MeOH transferred per unit time (s) and unit area (cm²) of the PEM.

The MeOH diffusion rates, measured at various fuel concentrations and fuel-supply types, were shown in Fig. 4. The MeOH diffusion rate increased as the fuel concentration was raised, for both fuel-supply types. However, it was much slower for the hydrogel-cartridge type than for the liquid-cartridge type at all fuel concentrations.

The power density of liquid-cartridge type decreased slightly when the fuel concentration was increased from 4 to 6 M MeOH (Fig. 3A), at which the MeOH diffusion rate increased from 4.2 to 6.8 mol cm⁻² s⁻¹ (Fig. 4), and it decreased abruptly

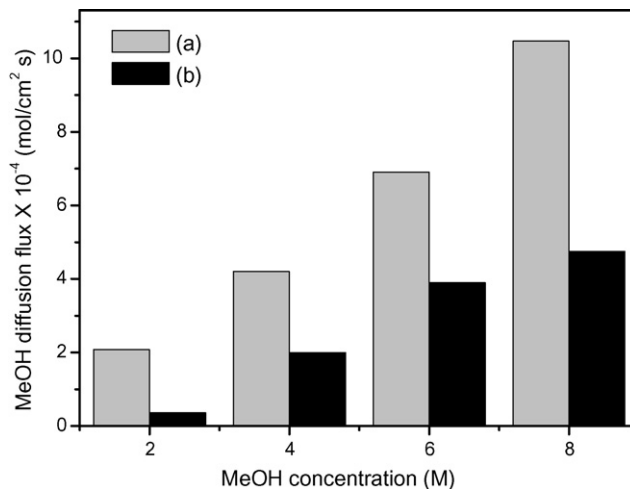


Fig. 4. MeOH diffusion rates at various fuel concentrations and fuel-supply types. (a) Liquid-cartridge type, and (b) hydrogel-cartridge type.

when the fuel concentration was increased from 6 to 8 M MeOH, at which the MeOH diffusion rate increased from 6.8 to 10.5 mol cm⁻² s⁻¹. However, the power density of hydrogel-cartridge type only slightly decreased when the fuel concentration was increased from 6 to 8 M MeOH (Fig. 3B), at which the MeOH diffusion rates were also similar to each other (3.9 mol cm⁻² s⁻¹ at 6 M MeOH and 4.5 mol cm⁻² s⁻¹ at 8 M MeOH), as shown in Fig. 4. These results indicate that the decrease in the cell performance is directly related to the MeOH diffusion rate. That is, the cell performance begins to decrease when the MeOH diffusion rate exceeds certain value, which is between 4.2 and 6.8 mol cm⁻² s⁻¹ in this study, regardless of the fuel-supply type. The fact that the fuel diffusion rate, at which the liquid-cartridge type DMFCs showed its maximum performance, was about 4.2 mol cm⁻² s⁻¹ (4 M MeOH), which is similar to that of the hydrogel-cartridge type DMFCs, e.g., 3.9 mol cm⁻² s⁻¹ (6 M MeOH) at its maximum performance, further support the above findings. In conclusion, the fuel diffusion rates were maintained at very low values and consequently MeOH crossover was also suppressed, even at high fuel concentrations by using hydrogels.

Three-electrode tests were performed to investigate the influence of hydrogels on the performance of the anode and cathode electrode, respectively, and the results were shown in Fig. 5. Three-electrode tests were performed at 6 M MeOH solution, which was the optimum fuel concentration in the cell performance experiments (Fig. 3). The MeOH crossover is known to decrease the potential of the cathode electrode rather than that of the anode electrode due to the MeOH oxidation at the cathode catalyst caused by the crossovered MeOH [8–10]. However, when the hydrogels were utilized as fuel-diffusion-controlling agents, the potential of the cathode electrode was not lowered even at high fuel concentrations, as observed in Fig. 5, further indicating the MeOH crossover was suppressed by using hydrogels, since MeOH crossover affects only the cathode potential. Consequently, the overall cell performance increased

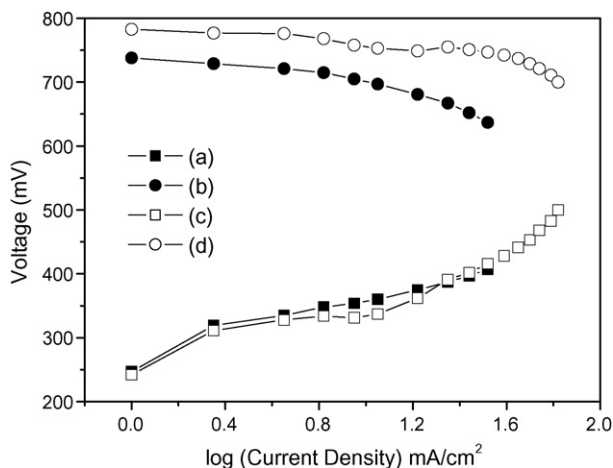


Fig. 5. Influence of hydrogels on the anode and cathode electrode, respectively. (a) Anode voltage of liquid-cartridge type, (b) cathode voltage of liquid-cartridge type, (c) anode voltage of hydrogel-cartridge type, and (d) cathode voltage of hydrogel-cartridge type.

about 37.5% compared to the liquid fuel-supplying system (cf. Fig. 3).

3.3. Role of hydrogels

When excess amount of MeOH is supplied to the anode electrode, and the MeOH, which cannot react on the anode catalyst due to its low activity, crosses over to the cathode electrode, as illustrated in Fig. 6. The decrease of the cell performance due to the MeOH crossover becomes significant as the fuel concentration is increased, as can be observed in the liquid-cartridge type DMFCs (cf. Fig. 3). However, if the fuel diffusion rate can be retarded even at the same fuel concentration, most of the fuel can be reacted on the anode catalyst, thus the MeOH crossover will be suppressed and the catalytic activity will be increased, as illustrated in Fig. 6.

Hydrogels are hydrophilic networked polymers and absorb water and MeOH to form gel structure. Therefore, the MeOH/H₂O fuel is supplied to the anode electrode at much slower rate through hydrogels than as a liquid itself. This diffusion-rate-controlling character of hydrogels prevents excess fuel supply, which eventually induces the MeOH crossover, even at high fuel concentrations.

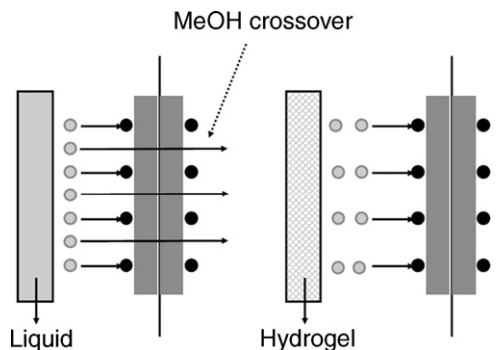


Fig. 6. MeOH crossover suppression mechanism of hydrogels.

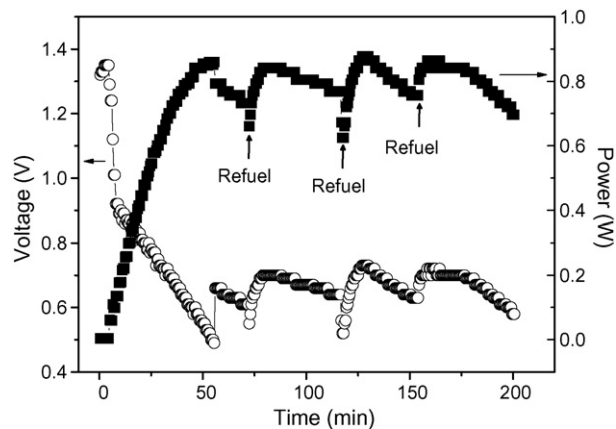


Fig. 7. The cell performance of one flat-pack type DMFC, which adopted hydrogels, at a constant current of 1.2 A.

3.4. Application of the novel flat-pack type DMFCs to a cellular phone

We operated the flat-pack type DMFCs using 6 M MeOH, at which the maximum power density of the cell was about 22 mW cm^{-2} . The power needed to operate the cellular phone is 240 mW at stand-by mode, 1.23 W at calling mode, and 2.4 W at maximum power consuming condition. Considering that the efficiency of a dc/dc converter is about 70–80% and the total MEA area of one flat-pack type DMFC is 60 cm^2 , three sets of flat-pack type DMFCs were used to operate the cellular phone.

We measured the lifetime of the DMFCs equipped with hydrogels at the maximum power consuming condition of the cellular phone, e.g., 2.4 W. Fig. 7 shows the performance of one flat-pack type DMFC at a constant current of 1.2 A, at which the cell power was 2.4 W in the case of three sets of flat-pack type DMFC system.

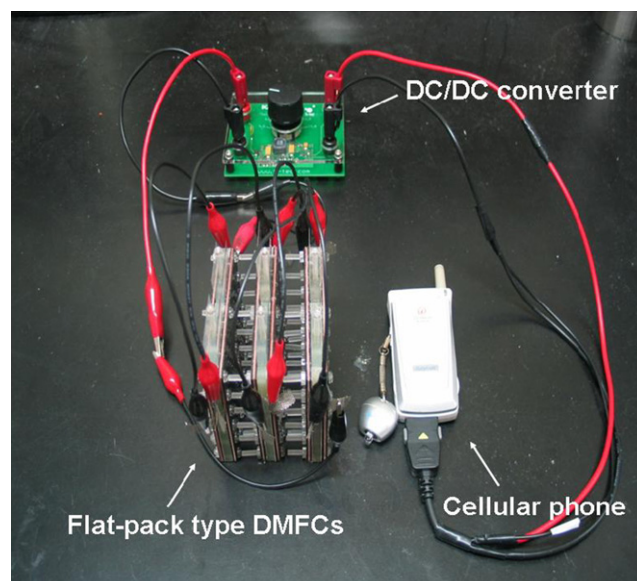


Fig. 8. Operation of cellular phone using the novel flat-pack type DMFCs.

The cell maintained a power of 800 mW for about 40 min using 18 cm³ of MeOH fuel. The power gradually decreased as the fuel was depleted, but it increased again when the additional fuel was supplied.

Based on these results, we operated the cellular phone as illustrated in Fig. 8. We successfully operated the cellular phone for about 40 min at a maximum power consuming condition (2.4 W) with 18 cm³ of 6 M MeOH.

4. Conclusions

Hydrogels were used as fuel-diffusion-rate-controlling agents in passively operated flat-pack type DMFCs, and its influence on the MeOH crossover behavior was investigated. Hydrogels remarkably retard the fuel diffusion rate, thus suppressed the MeOH crossover even at high fuel concentrations. Therefore, the DMFCs, which adopted this novel fuel-supplying system, showed enhanced cell performance and this enabled the successful operation of the cellular phone using only three sets of the flat-pack type DMFCs.

Acknowledgement

This work was supported by research fund (Grant No. 10022760-2005-12) from the Ministry of Commerce, Industry and Energy of Korea.

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