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Short communication

Development of a passive direct methanol fuel cell stack for high methanol concentration

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ABSTRACT

In order to develop a vertically arranged passive DMFC with a porous carbon plate, PCP, the effect of the head height of the methanol solution in contact with the porous carbon plate on the power generation was investigated for a 55 mm height using a single cell. The single cell was operated at several methanol concentrations greater than 70 wt%. By filling the reservoir with 90 and 100 wt% methanol solutions, power densities greater than 30 mW cm^{-2} for over 10 h were demonstrated. Based on the result of the single cell study, a passive DMFC stack consisting of 8 unit cells with the PCP was designed and fabricated. The power generation characteristics were then experimentally measured. The maximum power output of 1.8 W, which was almost 10% lower than that expected from the single cell performance, was obtained with 100% methanol. At the same time, a nonuniform cell voltage among the 8 unit cells was found as a reason for the decreasing power output with the increasing current.

1. Introduction

Direct methanol fuel cells (DMFCs) have received considerable attention as a new power source for electric portable devices because of their high theoretical energy densities. The volumetric or gravimetric theoretical energy density of methanol is about 10 times higher than that of the currently used Li-ion battery. On the other hand, the DMFC usually shows a maximum power at a methanol low concentration such as 1–3 M [1–4] under active conditions and about 5 M [5–8] under passive conditions due to the methanol crossover (MCO). Therefore, when a methanol solution with a high concentration such as 100% is used in the DMFC, it must be diluted with water produced by the cathode reaction or supplied from the outside, before the methanol reaches to the anode. As a remedy for the dilution of methanol, a system using additional devices, like a methanol sensor, mixers and pumps, can be considered. However, it is disadvantageous for the DMFC because of the decreased power output due to the internal power consumption for the dilution subsystem, and also, because of the increased system volume by adding the subsystem. On the other hand, it is known that water required for the anode reaction can be supplied from the cathode through the electrolyte membrane by the vapor feeding of methanol to the anode [8–10]. Recently, it was clarified, by using mass spectrometry, that the actual methanol activity on the anode was similar to that of the usual liquid feed DMFC even when a very high concentration of methanol was in the reservoir [11].

We have proposed a novel electrode structure with a porous carbon plate, PCP, for the DMFC [8,12–16] and we have demonstrated that the DMFC with PCP can be operated at very high methanol concentrations, even 100%, because the DMFC with PCP efficiently uses a high concentration of methanol with a significantly reduced MCO, and the system does not require any additional devices such as pumps and sensors. In this novel electrode structure, methanol was supplied to the anode through the PCP as a vapor in a CO_2 gas layer formed between the anode surface and PCP. At this time, water produced from the cathode reaction was supplied to the anode through the membrane by back diffusion. This system is quite simple and an effective remedy for using a high concentration of methanol in the DMFC and increases the energy density of the DMFC. It is expected that a unit cell of the DMFC with PCP can be stacked with other unit cells in order to increase the power output for actual use.

Referring to the DMFC supplying methanol as a vapor to the anode, this has been reported by several groups [9,10,17,18]. Kim obtained a power density of 20–25 mW cm^{-2} for 360 h with the vapor feed passive DMFC with using a humidified MEA [17]. Guo and his group presented a vapor feed DMFC that reached a power

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density of 16.5 mW cm^{-2} with 100% methanol, and they also fabricated 0.5 W DMFC prototypes [9,10]. Eccarius et al. obtained 15 mW cm^{-2} with using pure methanol [18]. These power densities of the passive DMFC with 100% methanol are still low; therefore, a higher power density and also a higher energy density were required for practical applications.

In this paper, we report an approach for the prototype development of a passive DMFC based on our electrode structure for the practical applications. In our previous report [16], we demonstrated that a DMFC single cell with a PCP having the appropriate property, i.e., a high bubble-point pressure and a high resistance to fluid flow, can generate a stable and equivalent power output both in the horizontal and vertical arrangement. This suggested that the DMFC with PCP having the appropriate properties can be applied for a practical use in which the cell orientation significantly varied. However, the cell area used in the previous study was small, 4.84 cm^2, and its height was 22 mm in the vertical arrangement. For a practical application, enlargement of the electrode area by increasing its height to over 50 mm is required for the unit cell. Moreover, stacking of some unit cells is necessary to increase the voltage and the power output. For these reasons, by using a single cell with a 55 mm height in the vertical arrangement, we investigated the cell performance at a constant voltage of 0.25 V, and investigated the effect of the methanol concentration and head height of the methanol solution in contact with the PCP on the power density. Based on the results of the vertically arranged single cell, the DMFC stack consisted of 8 unit cells with a 55 mm height was designed and fabricated. The power generation characteristics of the DMFC stack with 100% methanol was measured and discussed based on a comparison with that of the single cell.

2. Experimental of the single cell

2.1. MEA preparation

A membrane electrode assembly (MEA) with an 8.25 cm^2 active cell area (15 mm width and 55 mm height) was prepared and fabricated in the same manner as described in our previous report [8]. Pt black (HiSPEC1000, Johnson Matthey Fuel Cells Co., Ltd.) and Pt–Ru black (HiSPEC6000, Johnson Matthey Fuel Cells Co., Ltd.) were used as the catalyst for the cathode and anode, respectively. The catalyst ink was prepared by dispersing an appropriate amount of the catalyst in a solution of deionized water, isopropylalcohol, and 5 wt% Nafion (Wako, Inc.). The ink was then coated on carbon cloth (35% Teflonized, Electrochem, Inc.). The catalyst loading was 10–12 mg cm^{-2} in each electrode, and the ionomer loading of the catalyst was 10 wt% for the cathode and 15 wt% for the anode. Nafion 112 was used as the electrolyte membrane. The MEA was fabricated by sandwiching the membrane between the anode and cathode and hot pressing them at 408 K and 5 MPa for 3 min.

2.2. Porous carbon plate (PCP)

Based on our previous study of the PCP property suitable for vertical operation of the DMFC, PCP with the appropriate pore structure, i.e., having a high bubble-point pressure and a high resistance to fluid flow, was prepared by Mitsubishi Pencil Co., Ltd. The PCP was made of graphitic carbon and amorphous carbon and it had a 0.5 mm thickness, 55 mm height and 15 mm width.

2.3. Structure of the single cell vertically arranged

Fig. 1 is a cross-sectional view of the vertically arranged single cell structure with a PCP used in this experiment. A methanol reservoir with a 12 cm^3 capacity and 55 mm height was prepared in the anode compartment. The MEA was sandwiched between two current collectors, which were made of stainless steel with open holes, a 74% open ratio, for the transport of the fuel and oxidant. The thickness of the current collector was 2 mm for the cathode and 1 mm for the anode.

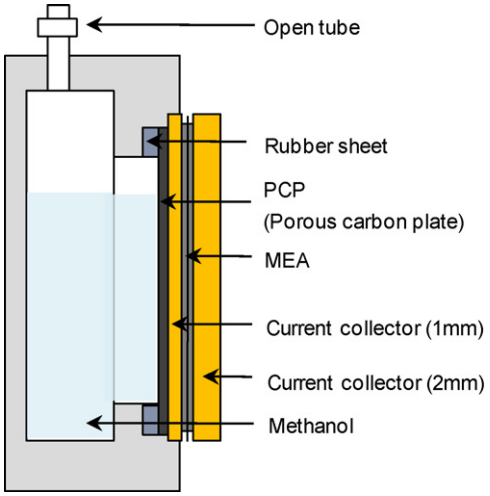

Fig. 1. Schematic diagram of a vertically arranged single cell of a DMFC with a PCP.

PCP was placed between the anode current collector and the methanol reservoir. As a result of this configuration, methanol had to be transported to the anode through the PCP and the open holes of the anode current collector. Under a closed circuit condition, the open holes of anode current collector were filled with CO_2 gas produced by the anode reaction, and a layer of CO_2 was formed between the PCP and the anode of the MEA. Therefore, in the electrode structure with the PCP, the methanol was supplied as a vapor to the anode through the CO_2 gas layer.

2.4. Measurement of the power generation characteristics for the single cell

The single cell operations were conducted in the completely passive mode with surrounding air under ambient conditions (303 K, 1 atm). During the single cell operations, the current–voltage, *i*–*V*, characteristics were measured from the open circuit voltage to zero voltage using an electrochemical measurement system (HAG-5010, Hokuto Denko, Co., Ltd.). The current density, i.e., *i*–*t*, at the cell voltage of 0.25 V from 8 to 85 h was also measured. The cell temperature was measured using a thermocouple placed on the cathode current collector. The measurement was started within several minutes after injecting the methanol into the reservoir in order to avoid direct contact of the methanol solution with the MEA, and was conducted for different amounts of injected methanol from 1.1 cm^3 (5 mm in height) to 12 cm^3 (55 mm in height) depending on the operation.

3. Results and discussion

3.1. Performance of the vertically arranged single cell

3.1.1. Influence of the methanol concentrations on the single cell performance

Fig. 2 shows the changes in the power density at 0.25 V for several methanol concentrations that ranged from 70 to 100 wt%. At the start of the measurement, the fuel reservoir was completely filled with a 12 cm^3 methanol solution, i.e., so that the whole PCP area, from the bottom to the top, was in contact with the methanol solution. The power densities initially increased and became sta-

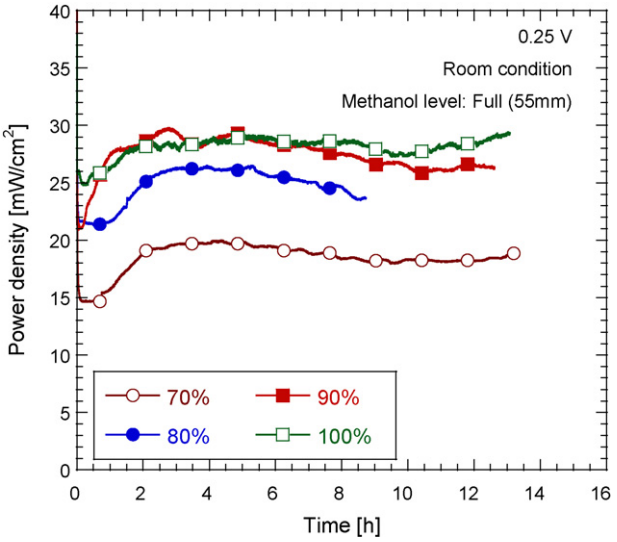

Fig. 2. Power density profile during continuous operation of vertically arranged single cell with 55 mm methanol level at cell voltage of 0.25 V.

ble within a few hours regardless of the methanol concentrations. In the electrode structure with PCP, methanol is supplied to the anode as a vapor through the CO_2 layer formed between the anode surface and the PCP under closed circuit conditions. At the beginning of the power generation, the power density was low due to the low methanol vapor pressure in the CO_2 gas layer [11]. It takes a few minutes for nitrogen, originating from the initial air in the gas layer, to be replaced with methanol and CO_2 [11] until the current density becomes stable. The stable power densities increased with the increasing methanol concentration, and they were about 30 mW cm^{-2} for 90 and 100 wt%, 25 mW cm^{-2} for 80 wt% and 20 mW cm^{-2} for 70 wt%. It was found that the PCP used in this study could strictly control the methanol transport resulting in the use of a high concentration of methanol up to 100%. Moreover, it was demonstrated that the vertically arranged DMFC with a height increased to 55 mm was successfully operated with the PCP having the appropriate property.

3.1.2. Long time operation

Fig. 3 shows the long-term variations in the power density and the cell temperature measured at 0.25 V after injecting 12 cm^3 (55 mm in height) of 100% methanol. At 25 h, a power density of 28–30 mW cm^{-2} was obtained, and then the power density gradually decreased with the increasing time. "The decrease in the power density during this period may be due to the decreasing methanol concentration by the back diffusion of the water from the cathode to the anode [8]. Moreover, the decrease of the head height of the methanol in the reservoir may also cause the decrease of the power density after 25 hours operation."

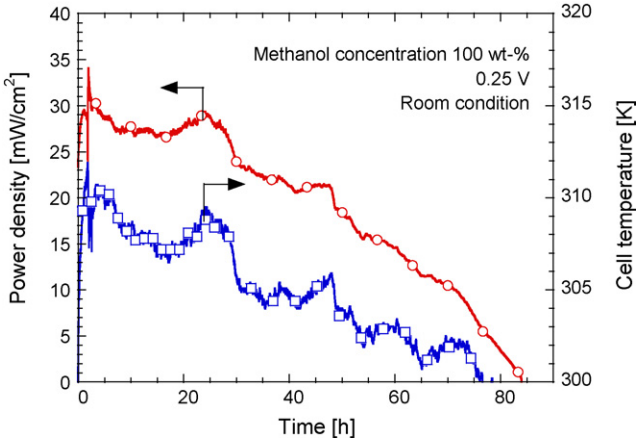

Fig. 3. Power density and temperature profiles for long time operation with 100% methanol at a voltage of 0.25 V.

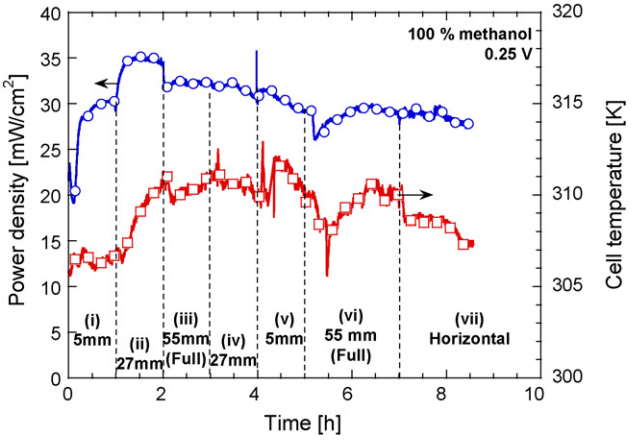

Fig. 4. Influence of the methanol head height methanol and orientation of the cell on the power density and cell temperature with 100% methanol at the voltage of 0.25 V.

Power generation was continued for 85 h until the methanol was completely consumed. During this operation, the volumetric energy density, based on the injected methanol volume (12 cm^3), was calculated to be about 800 Wh L^{-1}. This was higher than that obtained from other passive DMFCs of 600 Wh L^{-1} [8], 95 Wh L^{-1} [17] and 480 Wh L^{-1} [7]. In the vertically arranged single cell with a 55 mm height, an efficient operation was demonstrated. Hence, it is expected that a DMFC stack with the same electrode structure using PCP also provides an efficient operation.

3.1.3. Influence of the head height of methanol on the performance

To reveal the effect of the head height of methanol in contact with the vertically arranged PCP on the power generation characteristics, *i–t* measurements for the various methanol head heights were conducted. Fig. 4 shows the influence of the methanol head height and orientation, i.e., vertical and horizontal, on the power density and cell temperature at 0.25 V with 100% methanol. At the beginning of the operation, the head height of the methanol was started at 5 mm. The height was kept for 1 h and then it was increased to 27 mm by adding more methanol. After a 1-h operation, it was further increased to 55 mm in height at which the fuel reservoir was fully filled with methanol. The head height was decreased to 27 mm and then to 5 mm by removing a certain amount of methanol from the reservoir. As shown in the figure, the power output was about 30 mW cm^{-2} for the 7 h of operation regardless of the head height of the methanol solution. This means that the PCP used in this experiment had the proper pore structure for sucking methanol to the top of the PCP. However, it should be pointed out that the power density sharply increased to 35 mW cm^{-2} for 1 h, when the methanol level was changed from 5 mm (span (i)) to 27 mm (span (ii)). This would be due to the increase in temperature caused by an increase in the MCO during this period (span (ii)). The gradual increase in the power density and the cell temperature at span (ii) would be related to the slow sucking rate of the methanol solution into the PCP due to its very small pore diameter [16].

After the methanol reservoir was completely filled to 55 mm with the methanol solution in span (ii), the power density stabilized

Fig. 5. Pictures of the fabricated passive DMFC stack.

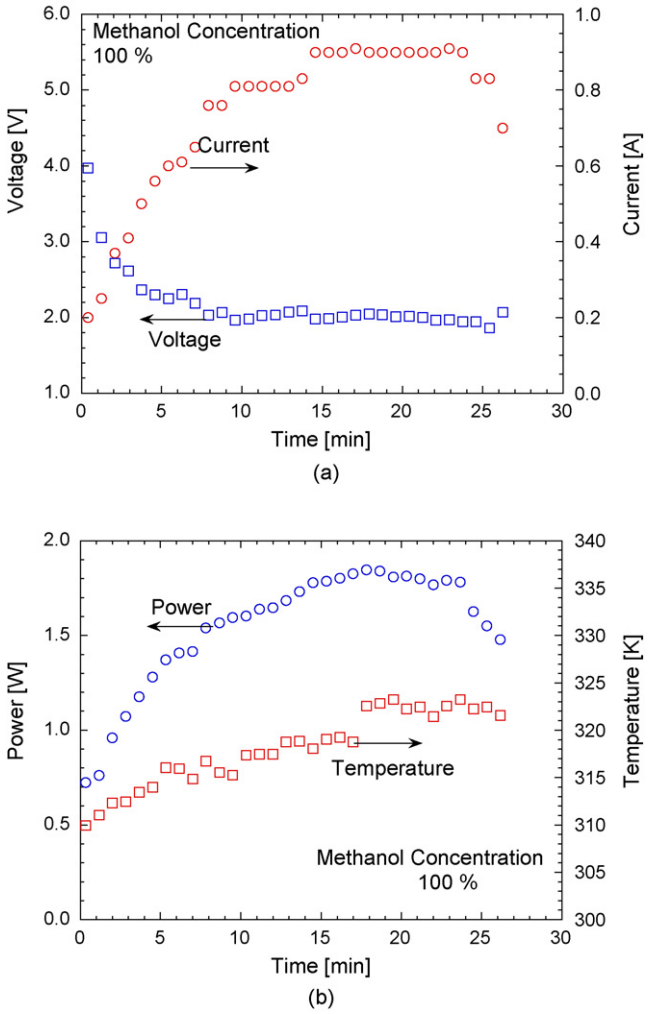

Fig. 6. Power generation characteristics and temperature profile of a passive DMFC stack with 100% methanol. (a) Current and voltage profiles, (b) power and temperature profile.

at 30 mW cm^{-2} regardless of the head height of methanol although slight variation of the temperature was seen after methanol reservoir was completely filled to 55 mm with the methanol solution in span (iii). At 7 h (from span (vi) to span (vii)), we changed the cell orientation from vertical to horizontal while keeping the reservoir full. One can see that the power density was stayed at 30 mW cm^{-2} for span (vi) and span (vii) as well as for spans (iii)–(vi). Therefore, it was confirmed that a nearly stable power density was obtained irrespective of the cell arrangement and the head height of methanol in the case of the vertically arranged single cell even when the height of the electrode was expanded to 55 mm by selecting the PCP with the appropriate characteristics.

3.2. Fabrication of a passive DMFC stack

Based on the single cell structure with PCP, a passive DMFC stack was designed and fabricated as shown in Fig. 5. It consisted of 8 unit cells, which had the same configuration of the vertically arranged single cell, and a fuel reservoir, which was shared by each unit cell. It was octagonal with a total volume of 430 mL, and was designed as a completely passive type.

3.3. Power generation characteristics of a passive DMFC stack

All the experiments for the DMFC stack were conducted in air at ambient conditions (303 K, 1 atm). First, to verify the power generation characteristics with 100% methanol, the voltage–time characteristics were measured using a multifunctional DC electronic load system (PLZ164WA, Kikusui Electronic Corp.).

Fig. 6 shows the power generation characteristics of the passive DMFC stack in this study. In this experiment, the current was slowly increased to 0.9 A, and then it was maintained for a certain period as shown in Fig. 6(a). In Fig. 6(b), the power output, obtained from Fig. 6(a), increased with the current increasing. When the current was set at 0.9 A, the power reached about 1.8 W. The maximum power output, 1.8 W, was calculated to be 27 mW cm^{-2}. The cell temperature increased with the increasing current as shown in Fig. 6(b). The cell temperature increased to 320 K, which was higher than that obtained from the single cell operations shown in Figs. 3 and 4. This could be related to the low heat dissipation due to the compact stack design, i.e., high electrode area to volume, and/or the increase of the MCO of each unit cell in comparison to that in the single cell structure. Therefore, the polymer electrolyte membrane at the stack operation tended to be dehydrated at the higher temperature comparing to that at the single cell operation, and then the power density of the stack was lower than that of the single cell. Another reason of the lower power density, 27 mW cm^{-2}, of the stack comparing to the single cell, 30 mW cm^{-2}, would be explained by the uneven performance among the 8 unit cells as shown in the next figure. Fig. 7 shows the cell voltages of the unit cells, cell 1 to cell 8, during the operation shown in Fig. 6. One can see the difference in the cell voltage among the 8 unit cells. The difference was relatively small, about 80 mV at 1 min, and gradually increased with time, to about 0.125 V at 25 min. It is important to make the unit

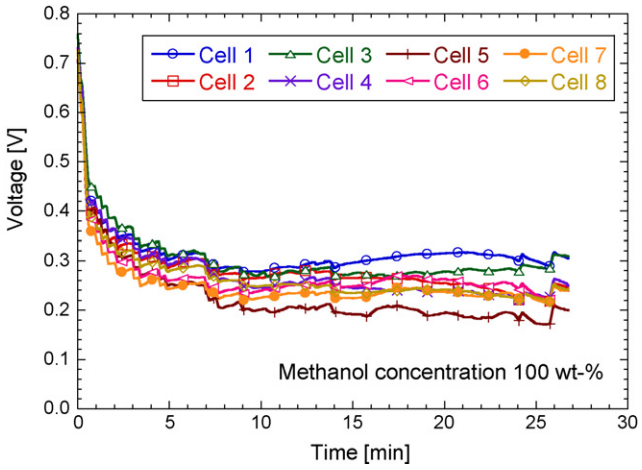

Fig. 7. Voltage profiles of each unit cell shown in Fig. 6.

cell performance uniform in a DMFC stack operation [19–22] for a higher power output. The voltage distribution among the unit cells would be caused by many factors such as a small difference in characteristics of the PCP and hydration of the membrane. Although this DMFC stack is fabricated using the same type of PCP, there may be a small difference in the pore structure and/or its distribution over the plate among the 8 unit cells. The difference would affect the methanol transport, and then the unit cell performance and MCO amount. Therefore, an increase in the temperature was observed in the stack operation as shown in Fig. 6(b). In order to achieve a higher power output for the DMFC stack, it is necessary to make each unit cells, especially the PCP, performance uniform.

Due to the increase in the stack temperature, the operation was stopped after about a half hour. We are now considering the way to better control the MCO in the stack design whether using uniform PCPs or with other alternative ways. This result will be published elsewhere in the near future.

4. Conclusions

Using a single cell with a 55 mm height in a vertically arranged passive DMFC with a PCP, the effect of the methanol head height in contact with the porous carbon plate on the power generation, and the long time operation for over 80 h were investigated. Based on the result of the single cell study, a passive DMFC stack consisting of 8 cells with the PCP was designed and fabricated. The power generation characteristics were then experimentally measured. Based on the above investigations, the following conclusions were obtained:It was demonstrated that the PCP used in this study with the appropriate characteristics could strictly control the methanol transport, and a high concentration of methanol, up to 100%, could be used, and it enabled the vertically arranged DMFC to operate with up to a 55 mm height. We could obtain a power density of 30 mW cm^{-2} and energy density of 800 Wh L^{-1} using a vertically arranged single cell with the PCP.DMFC stack consisted of 8 vertically arranged unit cells was designed and fabricated. The maximum power output of 1.8 W was obtained with 100% methanol for the fabricated DMFC stack.It was suggested that the structure of unit cell and/or stack make the performance of each unit cell uniform and the operating instructions to keep the cell condition uniform are required for a DMFC stack with the PCP to obtain a higher performance.

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