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A new direct methanol fuel cell with a zigzag-folded membrane electrode assembly

Mamoru Shibasaki [a,*], Toshiaki Yachi [a], Tatsuo Tani [b]

[a] *Yachi Laboratory, Department of Electrical Engineering, Graduate School of Engineering, Tokyo University of Science, 1-3 Kagurazaka, Shinjyuku-ku, Tokyo 162-8601, Japan*
[b] *Tokyo University of Science, Suwa, 5000-1 Toyohira, Chino-shi, Nagano 391-0292, Japan*

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Abstract

We propose a new direct methanol fuel cell with a zigzag-folded membrane electrode assembly. This fuel cell is formed by a membrane, which is made up of anode and cathode electrodes on a zigzag-folded sheet, separated by insulation film and current collectors. Individual anodes, cathodes and membranes form a unit cell, which is connected to the adjacent unit cell. The fuel cell can achieve high output voltage through easy in-series connection. Since it is not necessary to connect electrodes, as in the manner of conventional bipolar plates, there is no increase in fabrication cost and no degradation in reliability. The fuel feeds for the anode and cathode are achieved through methanol and air feeds on each electrode, which do not require electricity to run a pump or blower. The experimental cells were formed with an active area of 16 cm × 2 cm on membrane-folded cells. Filter papers with slits were inserted between anodes to improve their methanol supply. A power density of 3 mW cm^{-2} was obtained at a methanol concentration of 2 M at ambient temperature. The cell power was affected by the slit area on cathode.

Keywords: Zigzag structure; Series connection; Fuel feed; Slits

1. Introduction

Recently, the rapid advancement of wireless data communication and electronic circuit design technologies has resulted in a great diversity of function for personal portable electronic devices. Correspondingly, the electricity requirements for these devices have also increased. However, the performance capabilities of conventional lithium-ion batteries are unlikely to keep pace with the increasing power requirements. As such, new high-energy power generation systems are desired.

Fuel cells have attracted world-wide attention because of their potential application in clean and efficient electric power generating systems [1]. Most notably, the liquid feed direct methanol fuel cell (DMFC) was expected to be applied as a power source for portable applications because of the theoretical potential of the DMFC and its simplicity [2]. The electrochemical reactions of the DMFC are described as follows:

$$CH_3OH + H_2O \rightarrow CO_2 + 6H^+ + 6e^- \quad \text{(anode reaction)}$$

and

$$6H^+ + 6e^- + (3/2)O_2 \rightarrow 3H_2O \quad \text{(cathode reaction)}$$

The total reaction is

$$CH_3OH + (3/2)O_2 \rightarrow CO_2 + 2H_2O \quad \text{(overall reaction)}$$

When total reaction occurs, the Gibbs free energy of formation and enthalpy of formation are

$$\Delta g_f = -702.4\,\text{kJ mol}^{-1}$$

* Corresponding author. Tel.: +81 3 3260 4272; fax: +81 3 5261 4805.
E-mail address: j4304627@ed.kagu.tus.ac.jp (M. Shibasaki).

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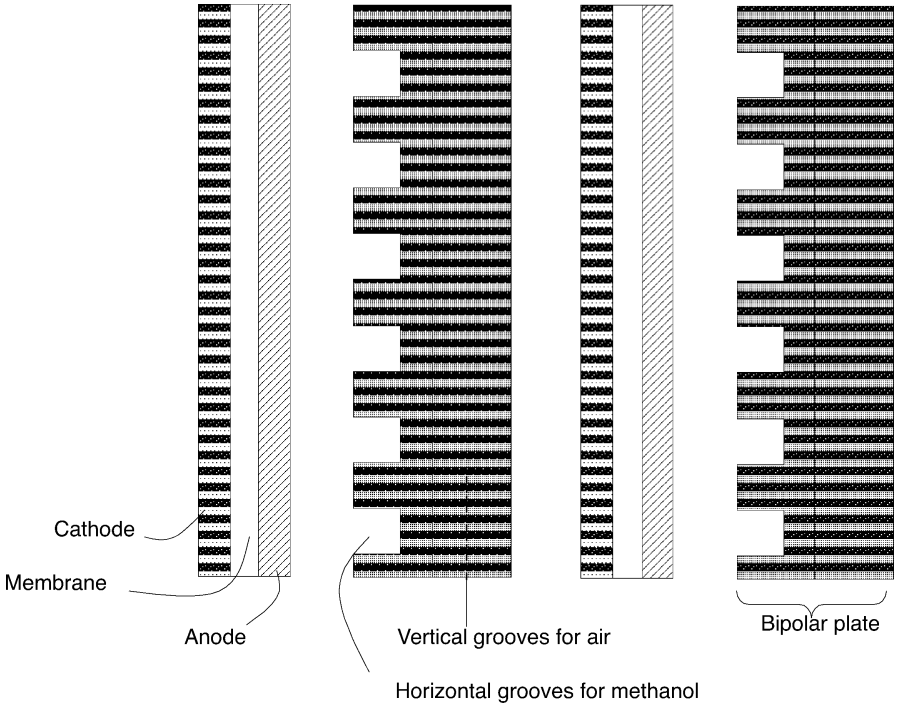

Fig. 1. Conventional cell stack.

and

$$\Delta h_f = -726.5\,\text{kJ mol}^{-1}$$

respectively.

The maximum electrical energy available is equal to the change in the Gibbs free energy, so the maximum possible efficiency is:

$$\Delta g_f/\Delta h_f \times 100\% = 96.7\%$$

Six electrons are passed around the circuit, and so the equation for the open circuit voltage is

$$E = -\Delta g_f/6F = 1.21\,\text{V}$$

where F is Faraday's constant. The voltage of a single cell is fixed by its particular electrochemical reaction, so it is necessary to connect several cells in series to obtain higher voltages.

The design of the conventional cell stack is shown in Fig. 1. With the conventional stack structure of direct methanol fuel cells, in which the film-like membrane electrode assembly is laminated through board-like separators, and alignment and attachment processes are required. These processes increase manufacturing costs and cause degradation in reliability. Moreover, air blowers and pumps may be required to feed the units, in order to supply air and methanol fuel through the narrow grooves formed by the separators. Decreased output due to the power consumption of feed units has been a problem. To avoid this problem, a natural-drive-type DMFC, which can supply air and methanol by natural diffusion or natural convection, is ideal. In-series connection has also been investigated. Although a flat-type DMFC, which provides natural driving, has already been proposed, an electric wire penetrates the membrane to connect the adjacent cell, or the anode is placed in-plane with the cathode [3,4], both of which increase the fabrication cost and make fuel feed difficult. Therefore, we propose herein a natural-drive-type DMFC that allows in-series connections to be constructed easily. It is expected that it will be possible to enlarge the per-product active area, and that the output density per volume can be enlarged according to the structure.

In the present study, as a basic experiment to examine the possibility of the natural-drive-type DMFC, an experimental cell was created and investigated with respect to power generation performance and operating characteristics.

2. New DMFC structure

In order to increase the output voltage of the DMFC, a new DMFC structure, the zigzag DMFC, which can easily be made into a stack structure and is a natural-drive-type DMFC, is proposed. The method of manufacturing this structure is described below and is shown in Fig. 2:

(a) Separate anode and cathode electrodes are attached to a membrane. Current collectors are then placed as shown in Fig. 2(a), and the sheet is then folded.
(b) An insulation film having the same area as one cathode is then placed over the first cathode. The current collectors are then folded back over the insulation film.

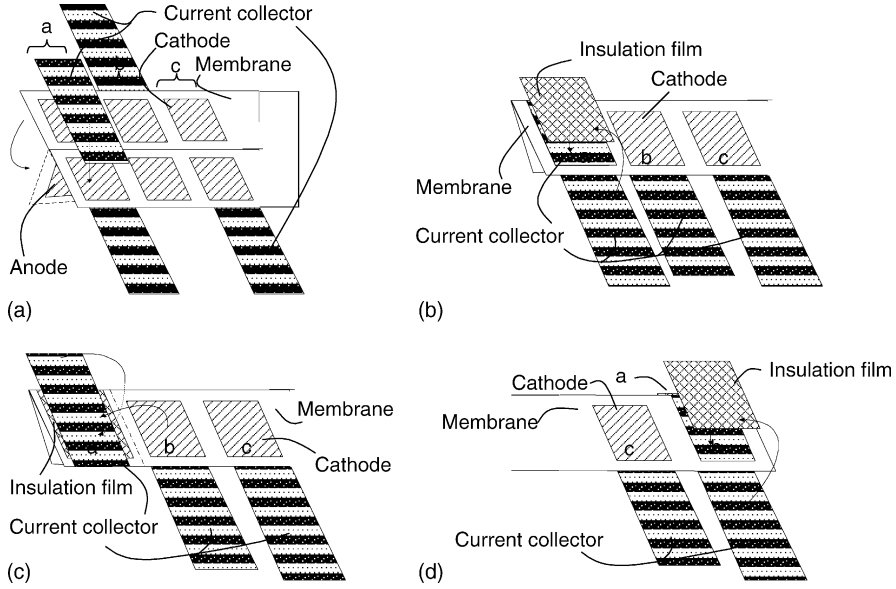

Fig. 2. New DMFC structure formation method.

(c) The sheet is then folded back over the current collector, and the current collector is folded back over the sheet.
(d) Steps (b) and (c) are repeated as necessary.

By repeating steps (b) and (c), in-series cells may be composed. A natural-drive-type DMFC having in-series connection matched to the voltage of the load can be created. The basic concept of the zigzag-folded DMFC is shown in Fig. 3. Unlike the conventional stack type structure, complicated separators are not required, and manufacturing costs can therefore be lowered. Moreover, like the conventional flat-type, no external wiring is needed to connect the cells.

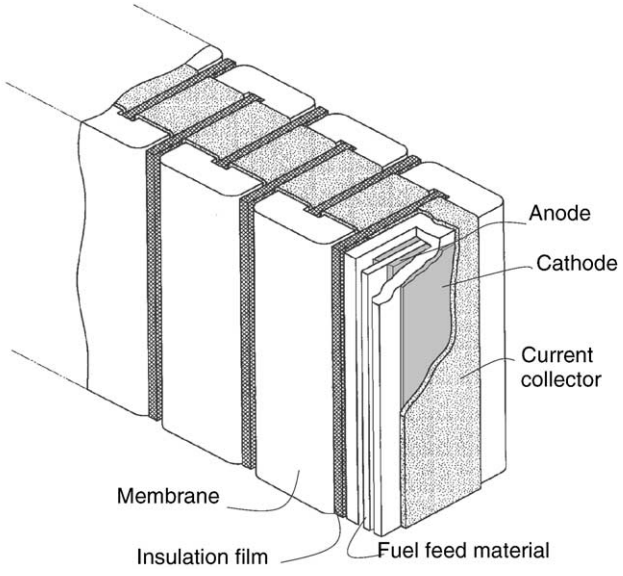

Fig. 3. Schematic diagram of zigzag-folded type DMFC.

The new structure reduces surface area more effectively than the conventional flat-type structure. It is believed that the temperature of a cell can be raised for exothermic reaction without the need for heat units, such as heaters. For the DMFC, low output density is a problem even though the energy density is high. Since the output density can be increased by raising the cell temperature, this new structure may increase the output density of the DMFC.

3. Experimental

For the zigzag-folded DMFC, the fuel-feed methods for anodes and cathodes differ from those of conventional cells. Fuel feed material between anodes is soaked up and fed to the anodes, and air is fed to the cathodes through spaces in the insulation film, as shown in Fig. 4. Multiple prototype units were constructed in order to verify the basic performance of the zigzag-folded DMFC and to explore issues related to the micro-fabrication approach. The simplest case of a zigzag-folded DMFC was produced.

The prototype cell had two electrodes on the membrane. The areas of the electrodes and the membrane were 16 and 50 cm^2, respectively. Nafion117 was used as the membrane, and aluminum was used as the current collector. Electrochemical catalysts for the anode of the DMFC were made from platinum and ruthenium. Electrochemical catalysts for the cathode of the DMFC were made from platinum. The amount of catalyst in each anode and cathode was 3 mg cm^{-2}. A photograph of the cell is shown in Fig. 5.

For a non-folded cell, i.e. a basic cell, the cathode was exposed to ambient air and the anode was exposed to 2 M methanol solution, for comparison with the prototype cell, as

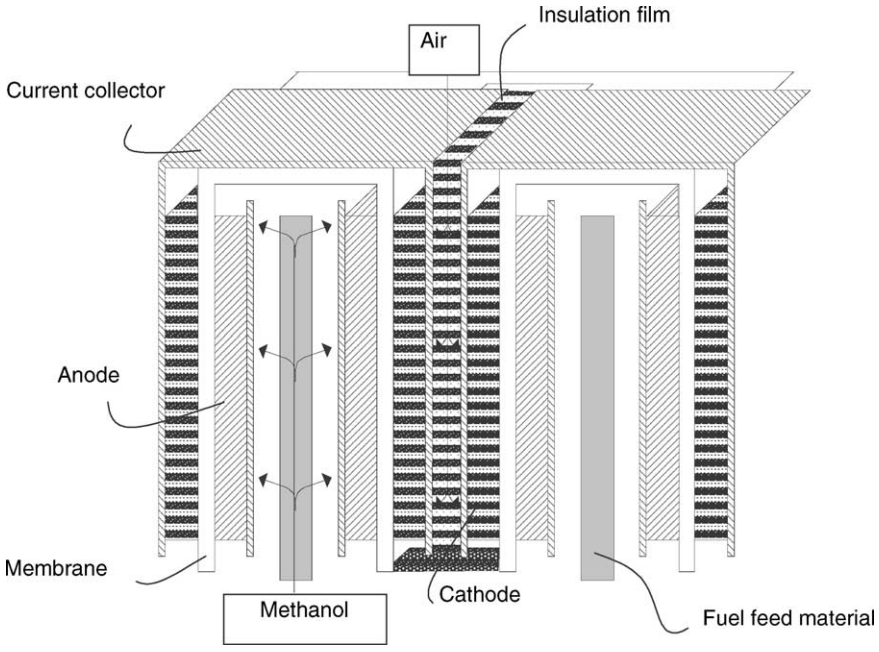

Fig. 4. Fuel feed method of zigzag-folded type DMFC.

shown in Fig. 6. The cell voltage and current were measured using a data logger (Yokogawa Co., HR1300).

3.1. Anode folded cell

The cell was combined with current collectors on both sides of the electrodes to form the unit cell, and was folded in half (anodes inside) over two sheets of filter paper, which was used as a fuel feed material. Each sheet of filter paper was 0.2 mm thick. The folded cell was sandwiched between two acrylic plates. The fuel was 2 M methanol solution and was stored in a small container below the anode. The cathode was exposed to ambient air so that natural convection of the ambient air supplied oxygen to the cell. The feed solution

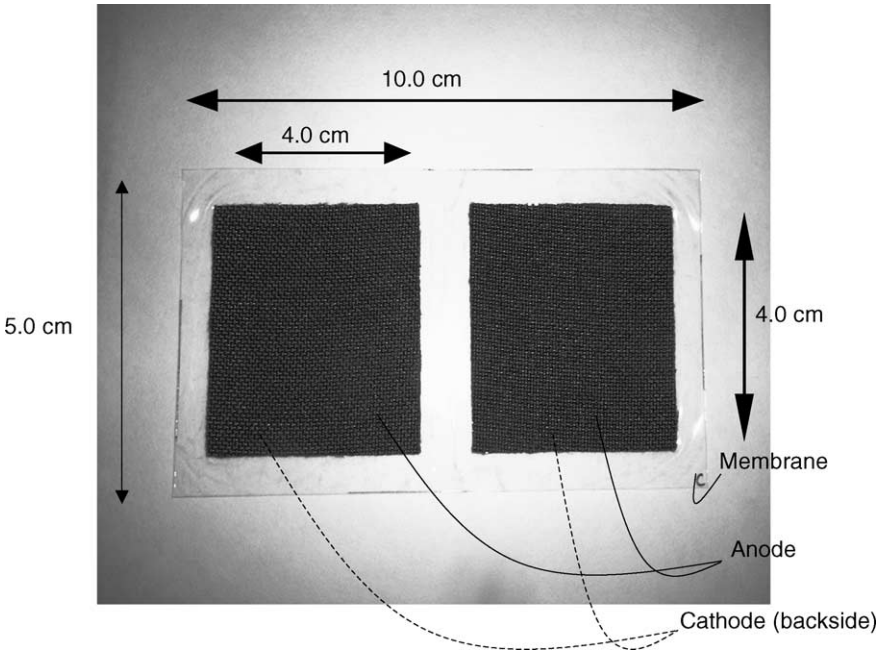

Fig. 5. Experimental cell.

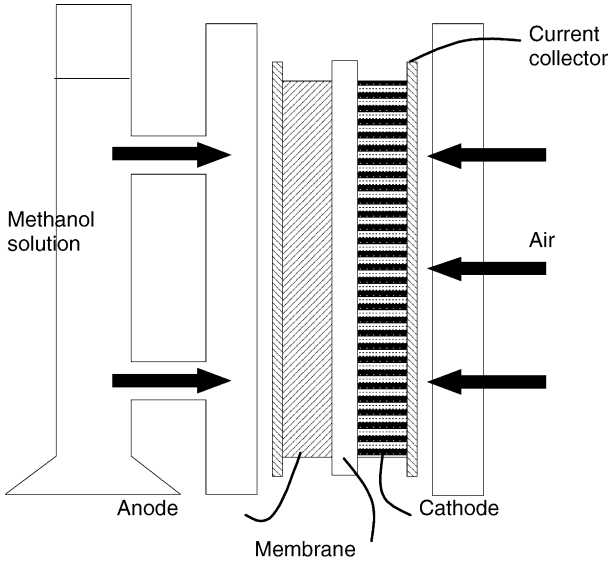

Fig. 6. Experimental set-up for the basic cell.

was replenished through the filter papers. A cross-sectional view of the folded cell is shown in Fig. 7. Three 2-mm-wide slits were introduced in the fuel feed material. The positions of the slits are shown in Fig. 8.

3.2. Cathode folded cell

The cell was combined with current collectors on both sides of the electrodes to form the unit cell, and the cell was folded in half (cathodes inside) over several sheets of filter paper. In order to feed air to the cathode, slits were made in the filter paper. These slits did not block the holes in the current collector. The folded cell was sandwiched between two acrylic plates. The anode was exposed to 2 M methanol solution that was stored in small containers connected to the anodes. A cross-sectional view of the folded cell is shown in Fig. 9.

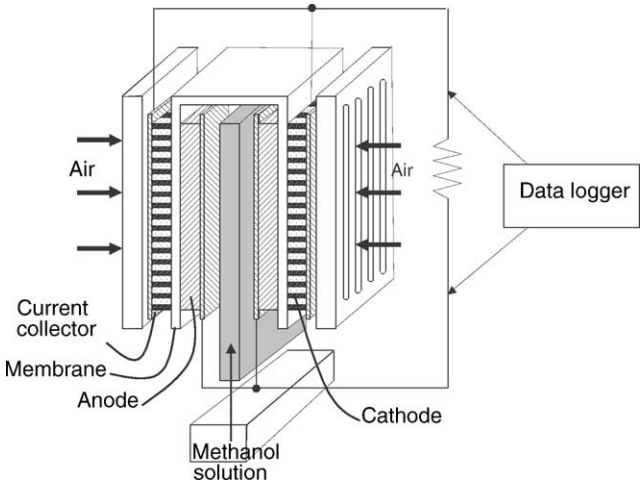

Fig. 7. Experimental set-up for the anode fuel feed.

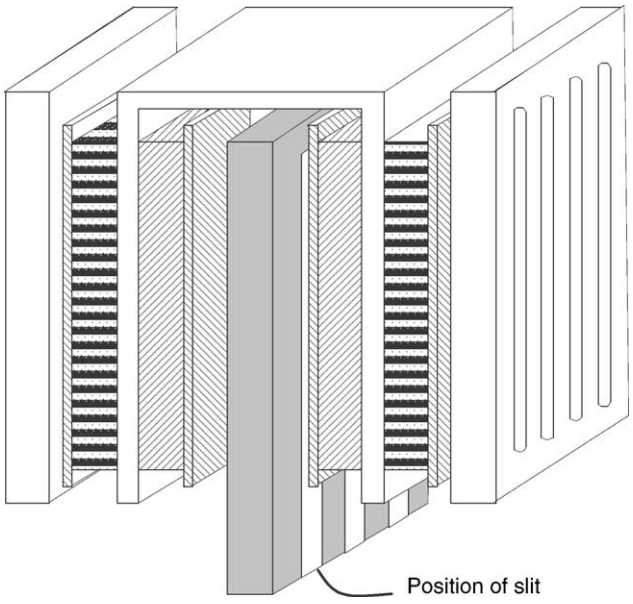

Fig. 8. Position of slit in fuel feed materials.

4. Results and discussion

4.1. Fuel feed for the anode

4.1.1. Performance validation

In order to determine the time characteristics, the anode folded cell and the basic cell were run using a constant load resistance (5.6 or 300 Ω). The voltage of the module is shown in Fig. 10. The temperature surrounding the unit was maintained between 19 and 23 °C. The anode folded cell initially showed a sharp decrease. The dry filter paper quickly soaked up the methanol solution, but methanol diffusion was slow once the filter paper became wet. At first, the methanol feed in the upper side of the anode was sufficient, but a fuel shortage gradually developed. The power decreases as the methanol concentration decreases. The anode folded cell generates low output voltage more steadily than the basic cell. When the load resistance is low (5.6 Ω), the drop of the output voltage is larger than when the load resistance is high (300 Ω). If the load resistance is low, it is easy to apply a current to the load. The methanol consumption increases as the current increases. When the load resistance is low, it is more difficult to transport sufficient reactant to the electrode surface. In a steady state, the voltage of the anode folded cell with slits was higher than that without slits.

The polarization curves are shown in Fig. 11. When the current density was 10 mA cm^{-2}, the power density for the cell with slits was twice as high as that for the cell without slits, because methanol solution was taken up through the slits by the capillary phenomenon. Methanol diffusion in the methanol solution taken up by the capillary phenomenon via the slits was faster than that via the filter paper. Replenishment of the feed solution in the anode was improved.

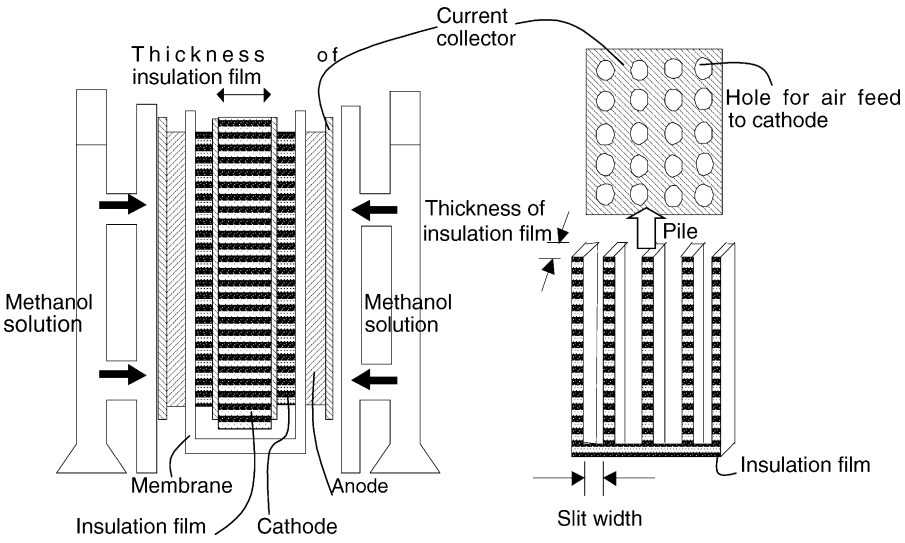

Fig. 9. Experimental set-up for the cathode air feed.

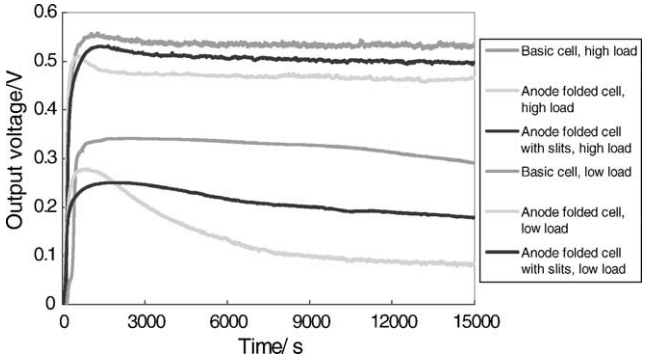

Fig. 10. Unit cell output voltage through three slits.

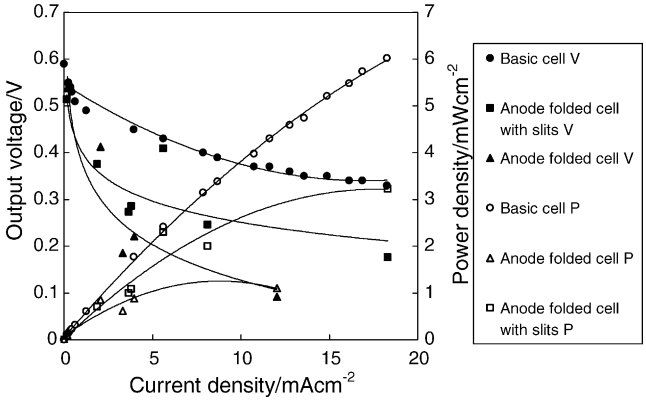

Fig. 11. Current–voltage characteristics for cells with and without slits.

4.1.2. Capillary phenomenon

The slits in the fuel feed material improved the fuel feed, but the power of the anode folded cell was lower than that of the basic cell. The fuel uptake depends on the width of the slit, so the optimal slit width was calculated. The capillary attraction F is the sum of the surface tension components, as follows:

$$F = 2aT\cos\alpha + 2bT\cos\beta = 2T(a\cos\alpha + b\cos\beta)$$

where T is the surface tension; a, the space between folded cells; b, the slit width; α, the angle of contact between water

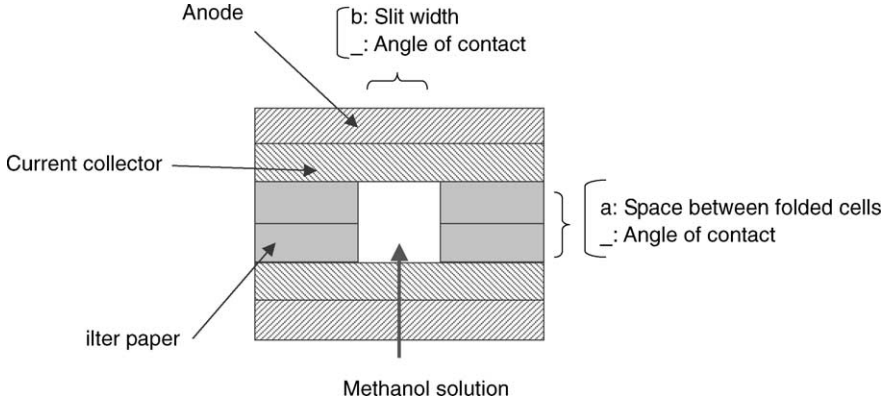

Fig. 12. Cross-sectional diagram of slit.

Table 1
Constants used to calculate the capillary phenomenon of slits

a (m)	2.0×10^{-4} (single)	
	4.0×10^{-4} (double)	Ref. [5]
T (N m^{-1})	0.073	Ref. [5]
	0	
	1.21	Ref. [5]
	1×10^{3}	Ref. [5]
g (m s^{-2})	9.8	Ref. [5]

and filter paper; and β, the angle of contact between water and aluminum. The parameters of the slits are shown in Fig. 12. The mass of the methanol solution taken up M is given as follows:

$$M = abH\rho g$$

where ρ is the mass density of water; g, the acceleration of gravity; and H, the height of the methanol solution taken up by the capillary phenomenon. In a steady state, the capillary attraction F is equal to the mass M of the methanol solution taken up. Therefore, the height H of the methanol solution taken up by the capillary phenomenon is given by the following equation:

$$H = 2T(a \cos \alpha + b \cos \beta)/ab\rho g$$

The values of the parameters used for the calculation are listed in Table 1. The height of the methanol solution taken up by the capillary phenomenon for different slit widths is shown in Fig. 13. When the slit width decreases, the height of the methanol solution taken up by the capillary phenomenon increases as the volume of the methanol solution taken up decreases. In order to promote even reaction of the anodes on both sides, the optimal slit width is the height of methanol solution taken up by the capillary phenomenon, which is larger than the cell height, and the mass of methanol solution taken up by the capillary phenomenon is as large as possible. The optimal slit width is 1 mm when one filter paper was used and the cell height was 4 cm.

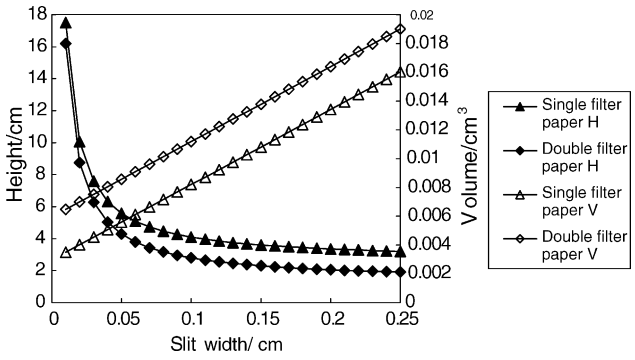

Fig. 13. Capillary phenomenon of slits.

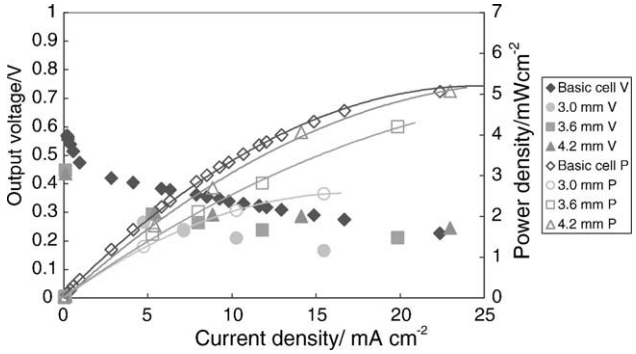

Fig. 14. Current–voltage characteristics for the folded cell for cathodes of various insulation film thickness (slit width is 5 mm).

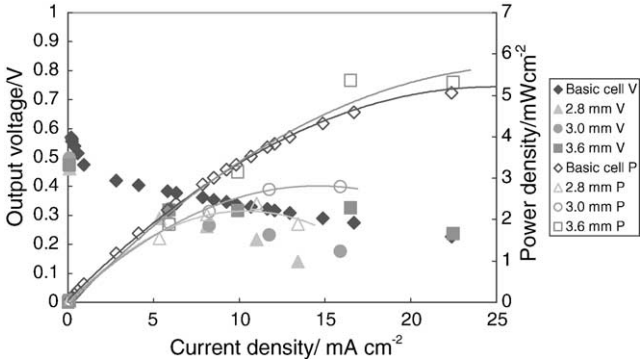

Fig. 15. Current–voltage characteristics for the folded cell for cathodes of various insulation film thickness (slit width is 7 mm).

4.2. Cathode fuel feed

Polarization curves for cathode folded cells of different slit widths and insulation film thicknesses are shown in Figs. 14 and 15. For a slit width of 5 mm and an insulation film thickness of 4.2 mm, the polarization curve is equivalent to that of the basic cell. On the other hand, for a slit width of 7 mm and an insulation film thickness of 3.6 mm, the polarization curve is equivalent to that of the basic cell. The cell power depends on the slit area. The relationship between the power density and the slit area is shown in Fig. 16. For the

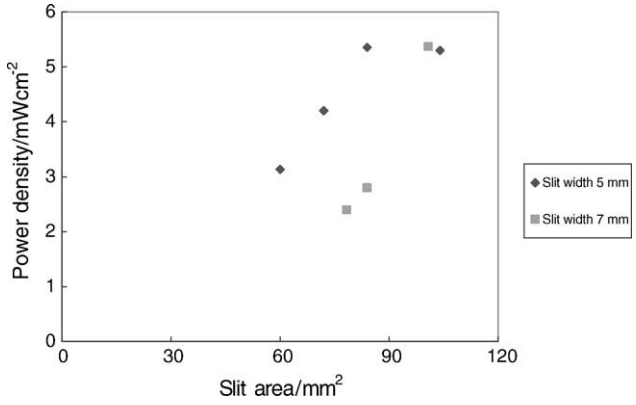

Fig. 16. Power density vs. area of slits.

slit width of 5 mm, the slit area of maximum power is smaller than for the slit width of 7 mm. Therefore, the insulation film thickness has a greater influence on the power density than does the slit width.

5. Conclusions

The zigzag-folded DMFC can achieve a high output voltage through easy in-series connection, because unlike in the conventional fuel cell, the connection of electrodes is not necessary, and a natural-drive-type DMFC is expected. Furthermore, the zigzag-folded DMFC can be operated at high temperatures by using the reaction heat in the cell.

The supply of methanol to the anodes was inadequate for the anode folded cell but was improved by introducing slits for the fuel feed materials to pass through. For the current density of 10 mA cm^{-2}, the power density was double compared to the no-slits case.

The capillary phenomenon improves the supply of methanol to the anodes. The effect of the slit width on the capillary phenomenon was investigated. The optimal slit width was 1 mm when one sheet of filter paper was used and the cell height was 4 cm.

The experimental results for the cathode folded cell revealed that the shape of the slit area used to feed air to cathodes affects the cell power.

With further improvements, if the supply of methanol is as good as in conventional cells, which supply liquid methanol to the anode, the zigzag-folded DMFC will be able to generate high output voltage electric power.

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