EFFECT OF COPPER CHANNEL WIDTHS ON THE PERFORMANCE OF DIRECT METHANOL FUEL CELLS UNDER VARIOUS OPERATING TEMPERATURES

C.W. CHUNG[a], J.S. LIN[b], J.S. WANG[c], W.J. LUO[d*], Z.Y. CHEN[d], C.N. CHEN[e]
[a]*Department of Electronic Engineering, Far East University, Tainan 744, Taiwan*
[b]*Department of Mechanic Engineering, National Chin-Yi University of Technology, Taichung 41170, Taiwan*
[c]*Department of Power Mechanical Engineering, National Taitung Junior College, Taitung, Taiwan*
[d]*Graduate Institute of Precision Manufacturing, National Chin-Yi University of Technology, Taichung 41170, Taiwan*
[e]*Department of Physics, Tamkang University, New Taipei City, Taiwan, 25137*

In this study, pure copper was used for the bipolar plates of the direct methanol fuel cells (DMFCs), and the anode and cathode channels were manufactured on the plates in order to reduce the electrical resistance and the volume of the DMFCs. To prevent the corrosion of the copper plates by the methanol fuel, nickel (Ni) and chromium (Cr) were electroplated onto the surface of the plates. Different anode channel widths of 2mm, 1.75mm, 1.5mm, 1.25mm, 1mm, 800 μm and 600 μm were, respectively, fabricated on the bipolar plates in order to investigate the effect of the anode channel width on the performance of the DMFCs. In this study, it was found that the performance of DMFCs with smaller anode channels was greatly enhanced due to the uniform distribution of the fuel on the anode channels and the longer retention period of the fuel within the anode channels. However, when the width of the anode channel was less than 600 μm, the hydro-resistance from the CO_2 bubbles produced within the anode channels significantly increased, which hindered the fuel from moving into the anode channels through the wriggle pump. Consequently, the output of the DMFCs decreased. In this study, the performance of the DMFCs was also tested under various operating temperature conditions and supplied fuel flow rates in order to understand the effect of the operating conditions on the output of DMFCs with different anode channel widths.

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1. Introduction

Fuel cells are energy conversion devices with high efficiency that allow electrochemical reactions between fuel and oxidant to convert the chemical energy of the fuel directly into electricity. The direct methanol fuel cell (DMFC) utilizes methanol solution as fuel is considered a promising power source for portable electronic devices. Methanol has high energy density and specific, superior chemical stability that is important for transport and storage. In comparison with other fuel cell systems, the DMFC is a simple and compact system that is also a potential power source for portable applications [1-4]. These reasons have motivated researchers and industry engineers all over the world to study DMFCs.

* Corresponding author: wjluo@ncut.edu.tw

The DMFC consists of a proton exchange membrane with an anode and a cathode catalyst layer on each side. Gas diffusion layers, usually made of carbon paper or carbon cloth, are used to cover the catalyst layers and form the membrane electrode assembly (MEA). The MEA is then sandwiched between two current collectors that have some flow channels machined on the surface for the supply of the fuel and oxidant. Typically, the DMFC is operated at a temperature lower than 100°C. Methanol is electrochemically oxidized to CO_2 at the anode and oxygen is reduced to water at the cathode. The flow field channel, which is integrated into bipolar plates, is an important component because it serves as a fuel or air distributor as well as a current collector. In general, the flow field channels influence the fuel and air distributions, the concentration polarization loss, the electrical current conduction, the heat conduction, etc. [5–9]. The flow field channel is especially important for water management inside the fuel cells since the products (CO_2 and H_2O) are removed through flow field channels. Therefore, an appropriate flow channel design is necessary for achieving high performance and durability of the cell as it resolves mass transport-related problems and improves the water management in the channel, the gas diffusion layer and the catalyst layer [10].

Many researchers have studied the effects of flow channel geometry on the homogeneous distribution of the reactants and on cell performance. Shimpalee et al. [11] investigated the effects of the channel and rib cross-sectional areas on the reactant distribution and cell performance with serpentine flow field patterns and showed that narrower channels with wider rib spacing resulted in higher performance. Yoon et al. [12] reported that a narrower rib width led to improved performance of proton exchange membrane fuel cells (PEMFCs) because the diffusion of the gas appeared to be a more important factor than the electrical conduction for better cell performance. Wang et al. [13, 14] investigated the effects of the number of flow channel bends, the number of serpentine loops, and the flow channel width ratio on the cell performance of PEMFCs with serpentine flow fields. Manso et al. [15] numerically investigated the influence of the channel cross-section aspect ratio (defined as the ratio height/width) on the performance of a PEMFC with a serpentine flow field design, and analyzed the local current density distributions in the membrane, velocity distributions, liquid water saturation and hydrogen and oxygen concentrations to understand the channel cross-section aspect ratio effect. These studies demonstrated that flow channel geometry influences the performance of PEMFCs in terms of fuel distribution, mass transport and water removal.

In DMFCs, the flow channel is a critical component for minimizing the mass transport-related issue raised by the two-phase flow of liquid (CH_3OH and H_2O) and gas (CO_2 and air) and for removing a large amount of liquid water on the cathode side, which results from product water by oxygen reduction reaction and electro-osmotically dragged water from the anode. Yang et al. [16] experimentally examined the effect of the anode flow field pattern on the performance of a DMFC and reported that both the open ratio and the flow channel length had a significant influence on the cell performance and the pressure drop. Park et al. [17] experimentally and numerically investigated the effects of four different types of serpentine flow-field geometry on the performance of direct methanol fuel cells (DMFCs). They found a narrow rib width and a suitable channel/rib aspect ratio are needed to increase the cell performance of serpentine DMFCs. Seo and Lee [18] experimentally determined the methanol crossover and efficiency of a direct methanol fuel cell (DMFC) under various operating conditions such as cell temperature, methanol concentration, methanol flow rate, cathode flow rate, and cathode backpressure. They indicated that methanol crossover increased by increasing cell temperature, methanol concentration, methanol flow rate, cathode flow rate and decreasing cathode backpressure. Also, they revealed that the efficiency of the DMFC was closely related with methanol crossover, and significantly improved as the cell temperature and cathode backpressure increased and methanol concentration decreased. Luo et al. [19-20] investigated the performance of the DMFCs with different hydrophobic anode channel. They found that the performance of the DMFCs made of PDMS with high hydrophobic particles, can be greatly enhanced and the hydrophobic property of the particles can be unaffected by different operation conditions. Despite these important facts, there have been few papers that dealt with the effect of the flow channel geometry on the performance of DMFCs.

In this study, pure copper was used to be the electric collectors of the direct methanol fuel cells (DMFCs), and the anode and cathode channels were manufactured upon the collectors in order to reduce the electric resistance and the volume of the DMFCs. For avoiding the corrosion of the copper bipolar plates by the methanol fuel, the materials of nickel (Ni) and chromium (Cr) were electroplated on the surface of the plates. In order to find the effect of the anode channel widths on the performance of the DMFCs, the performance of the DMFCs with different anode channel widths were investigated under various operation conditions including the aqueous methanol solution flow rate and temperature. Through this investigation, the effects of the copper anode channel widths on the performance of the DMFC can be further understood.

2. Experimental Methods

2.1 Transparent cell

Fig 1 is the exploded view of the transparent DMFC test fixture designed and fabricated for the visualization study in this paper. The MEA, (detailed in the subsequent paragraph) was sandwiched between two bipolar plates with a gasket on either side. This assembly, including the bipolar plates and the MEA, was clamped between two enclosure plates by using eight M8 screw joints (each having a torque of about 12 KGF-CM). The active area of the MEA adopted in this paper was 3.5 × 3.5 cm^2, which consisted of two single-side ELAT electrodes from E-TEK and a Nafion® membrane 117. Both anode and cathode electrodes used carbon cloth (E-TEK, Type A) as the backing support layer with 30% PTFE wet-proofing treatment. The catalyst loading on the anode side was 4.0 mg/cm^2 with unsupported [Pt:Ru] Ox (1:1 a/o), while the catalyst loading on the cathode side was 2.0 mg/cm^2 with 40% Pt on Vulcan XC-72. Furthermore, 0.8 mg/cm^2 Nafion® was applied to the surface of each electrode. The bipolar plates (shown in Fig. 2) were made of pure copper plates with a thickness of 4.0 mm, on which nickel (Ni) and chromium (Cr) were electroplated to avoid corrosion [21-23]. As shown in Fig. 2, the rectangular bipolar plate consisted of two portions: the channel area and the extension area. The channel area acted as the distributor for supplying fuel and oxidant to the MEA. The parallel serpentine channels, with an area of 3.4 × 3.4 mm^2, were machined using wire-cut technology. The deepness of the channels of the DMFCs was 2 mm, and the ratios of the channel area to the reactant area (3.4 × 3.4 mm^2) for all DMFCs in this study all kept in the range of 56%~59%. The extension area of the bipolar plates served as a current collector. In addition, a tape heater was attached to the extension area to adjust the cell operation temperature to a desired value during the experiments. Two enclosure plates (2.0 cm thick) were made of well-insulated transparent Lucite which can effectively keep the heat in the MEA and the bipolar plates from dissipating into the surroundings under higher operation temperatures, as shown in Fig.1.

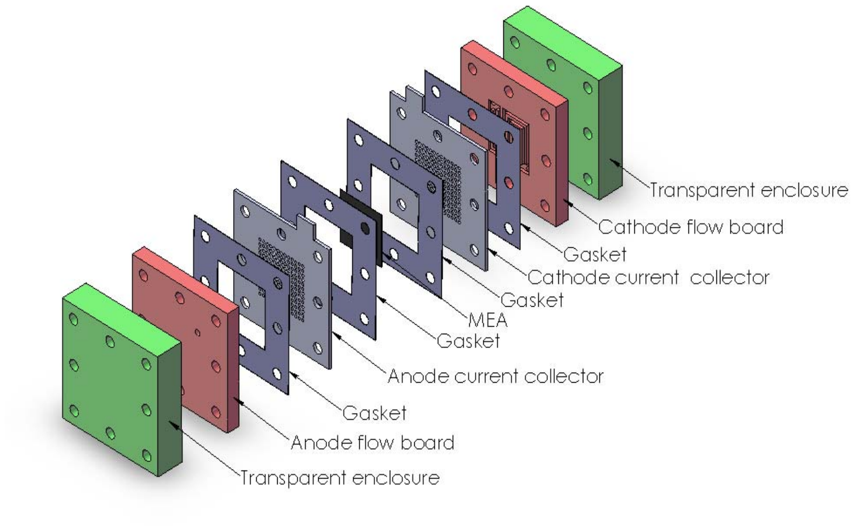

Fig. 1 Exploded view of the DMFC test fixture.

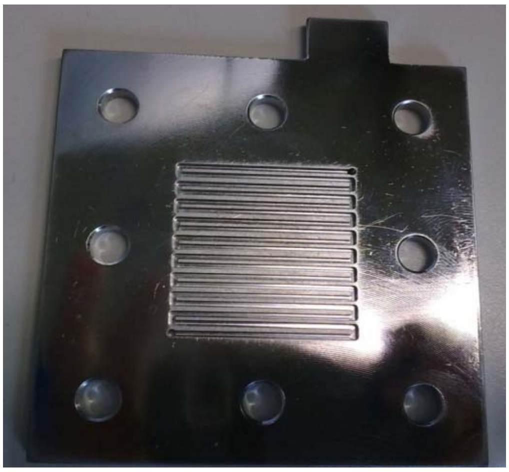

Fig. 2 The copper bipolar plate on which nickel (Ni) and chromium (Cr) were electroplated.

2.2 Test loop

The schematic of the experimental setup is shown in Fig. 3. The methanol solution was driven by a squirm pump and precisely controlled the liquid flow rate from 5 to 15 ml/min with a 2% error rate. Before entering the cell, methanol solution was pre-heated to a desired temperature by placing the methanol solution tank in a temperature controlled water bath. The mixture of CO_2 and un-reacted methanol solution was drained from the cell and cooled down by passing through a cooling system. The CO_2 produced at the anode was separated from the methanol solution tank and released into the atmosphere, while the un-reacted methanol solution was re-collected into a chemical liquid tank. Simultaneously, the ambient air, almost 80% oxygen, as oxidant was provided to the cathode side of the cell without humidification. The flow rate of oxygen was controlled by an air mass flow regulator with a of 5% error rate.

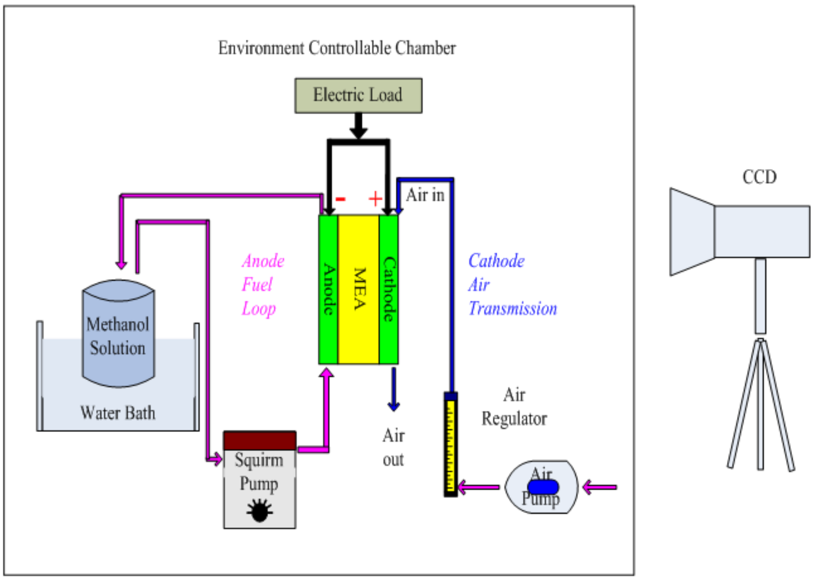

Fig. 3 Schematic of the experimental setup.

3. Results and Discussion

In this study, pure copper was used for the bipolar plates of the DMFCs, and the anode and cathode channels were manufactured on the plates in order to reduce the electrical resistance and the volume of the DMFCs. To prevent the corrosion of the copper plates by the methanol fuel, nickel (Ni) and chromium (Cr) were electroplated onto the surface of the collectors. In order to enhance the performance of the DMFC, the produced CO_2 bubbles had to be efficiently removed from the anode channel during the electrochemical reaction. In this study, different anode channel widths of 2mm, 1.75mm, 1.5mm, 1.25mm, 1mm, 800 μm and 600 μm were fabricated on the copper plates in order to investigate the effect of the anode channel width on DMFC performance.

3.1 Performance of DMFCs under the operation conditions of low fuel flow rate (5 cc/ min) and various operating temperatures

The performance of DMFCs with different anode channel widths was investigated under the operating conditions of low fuel flow rate and various operating temperatures. Figure 4 illustrates the power density distributions for DMFCs with different anode channel widths under the operating conditions of 40℃, 5 cc/min and 10% methanol concentration. Table 1 shows the maximum power densities of DMFCs with different anode channel widths under the operating conditions of 5 cc/min and 10% methanol concentration. As shown in Fig. 4 and Table 1, the DMFC with an anode channel width of 800 μm possessed the best power generating efficiency in comparison with the DMFCs with larger channel widths. This phenomenon indicated that for DMFCs with smaller anode channel widths, the fuel in the channels were uniformly distributed on the electrochemical reaction area; thus, the fuel was also uniformly distributed above the reactant area. Furthermore, the length of the anode channels with smaller widths was also greater than that of anode channels with larger widths. Therefore, the retention times of the fuel within the anode channels with smaller widths were also longer than for those with larger widths. Consequently, under the same operating conditions, the power generating efficiencies of DMFCs with smaller anode channel widths were superior to the DMFCS with larger anode channel widths. Table 2 shows the percentages of the maximum power densities of the DMFCs with different anode channel widths to that of the DMFC with a 2mm channel width under the operating conditions of 5 cc/min and a 10% methanol concentration. The maximum power density of the DMFC with a 800

μm anode channel width reached 37.061mW/cm^2 under the operating conditions of 40℃, 5 cc/min and 10% methanol concentration, for a maximum power density enhancement of 57.64% in comparison to that of the DMFC with a channel width of 2mm. From the over-potential （η_{act}） equation: $\eta_{act} = \frac{RT}{\alpha nF} \times \ln\left(\frac{i}{i_0}\right)$, it can be seen that the increase of the operating temperature can lead to the reduction of the over-potential. By increasing the operating temperature, both the diffusivity of the supplied fuel and the activity of the catalyst could also be increased. Thus, the reactants in the anode channel possessed sufficient chemical energy to allow the reaction to proceed. For the DMFC with a 800μm channel width, the retention time of the fuel within the anode channels was longer than those for the DMFCs with greater widths, and the size of the generated CO_2 bubbles was insufficient to hinder the movement of the fuel at a low flow rate and low operating temperature. Thus, the maximum power density of the DMFC with a 800μm channel width was reached at a 40℃ operating temperature, and this enhanced output was most apparent in the DMFCs when there was an increase in the operating temperature from 30℃ to 50℃. When the operating temperature was greater than 50℃, the CO_2 bubbles generated in the anode channel were bigger than the width of the anode channel; they blocked the anode channel and hindered the supply of fuel. This phenomenon resulted in the output decline of the DMFC. When the anode channel width was less than 0.8mm, as the size of the generating CO_2 bubbles was almost the same as the width of the anode channel, the bubbles hindered the movement of the fuel. Consequently, the performance of the DMFC seriously decayed.

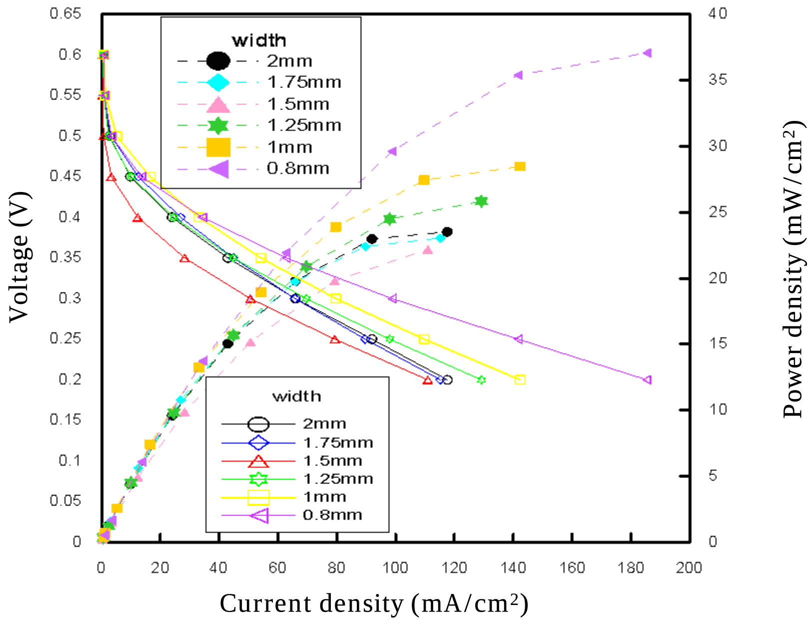

Fig. 4 Power density for the DMFCs with different anode channel widths under the operation conditions of 40 ℃, 5 cc min^{-1} and a 10% methanol concentration.

Table 1 Maximum power densities of DMFCs with different anode channel widths under the operating conditions of 5 cc min^{-1} and 10% methanol concentration.

width	temperature					
	30°C	40°C	50°C	55°C	60°C	70°C
0.8mm	28.767	37.061	36.784	35.2	32.849	32.441
1mm	28.522	28.457	29.927	31.004	29.845	28.865
1.25mm	26.841	25.829	31.396	31.461	29.437	29.224
1.5mm	17.502	22.188	24.539	26.204	26.873	26.939
1.75mm	24.245	23.037	24.359	24.506	23.102	23.2
2mm	24.98	23.51	24.457	24.735	23.592	23.037

Unit:mW/cm^2

Table 2 Percentages of the maximum power densities of DMFCs with different anode channel widths to that of the DMFC with a 2mm channel width under the operating conditions of 5 cc min^{-1} and 10% methanol concentration.

width	temperature					
	30°C	40°C	50°C	55°C	60°C	70°C
0.8mm	115.16%	157.64%	150.40%	142.31%	139.24%	140.82%
1mm	114.18%	121.04%	122.37%	125.34%	126.50%	125.30%
1.25mm	107.45%	109.86%	128.37%	127.19%	124.78%	126.86%
1.5mm	70.06%	94.38%	100.34%	105.94%	113.91%	116.94%
1.75mm	97.06%	97.99%	99.60%	99.07%	97.92%	100.71%

3.2 Performance of DMFCs under the operating conditions of middle fuel flow rate (10 cc/ min) and various operating temperatures

Fig. 5 illustrates the distributions of the power density for DMFCs with different channel widths under the operating conditions of 50℃, 10 cc/min and a 10% methanol concentration. Table 3 shows the maximum power densities of DMFCs with different channel widths under the operating conditions of 10 cc/min and 10% methanol concentration. Figure 5 and Table 3 also show that the DMFC with a 800 μm anode channel possessed the best power generating efficiency as compared to the DMFCs with larger channel widths under different operating temperatures. As the retention times of the fuel within the anode channels with smaller widths were longer than for those with larger widths under the same operating conditions, the power generating efficiencies of the DMFCs with smaller anode channel widths were also greater. For DMFCs with anode channel widths of less than 1.5mm, when the operating temperature was 50℃~55℃, the maximum power densities of the DMFCs reached their maximum values. The maximum power densities of the DMFCs reached their maximum value, 39.641 mW/cm^2, with a 800 μm anode channel and under the operating conditions of 50℃ and 10% methanol concentration. Table 4 shows the percentages of the maximum power densities of DMFCs with different anode channel widths to that of the DMFC with a 2mm channel width under the operating conditions of 10 cc/min and 10% methanol concentration. Under a low operating temperature of 40℃, the maximum enhancement of the maximum power density, i.e. 48.1%, was reached for the DMFC with a 800 μm anode channel width; the maximum power density enhancements gradually decreased with the increase in the operating temperature.

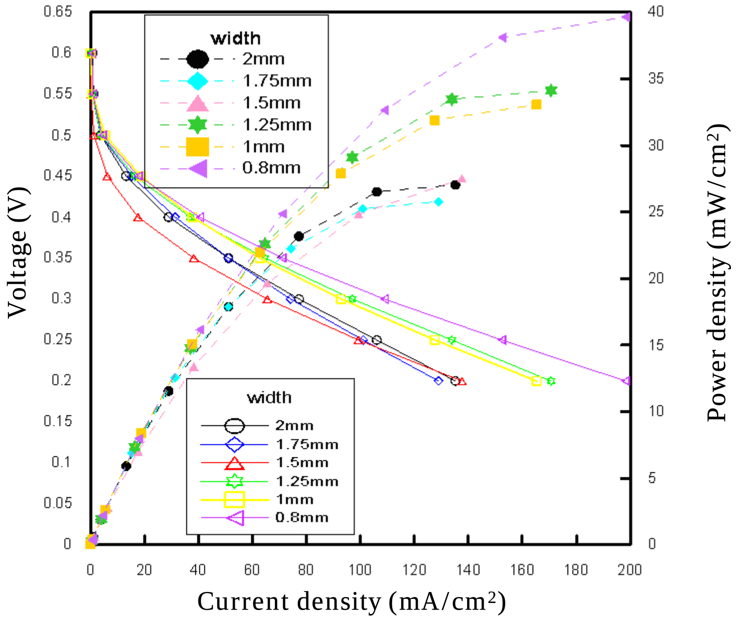

Fig. 5 Power density for the DMFCs with different anode channel widths under the operation conditions of 50 ℃, 10 cc min^{-1} and a 10% methanol concentration.

Table 3 Maximum power densities of DMFCs with different anode channel widths under the operating conditions of 10 cc min^{-1} and 10% methanol concentration.

width	temperature					
	30 °C	40 °C	50 °C	55 °C	60 °C	70 °C
0.8mm	29.845	38.155	39.641	37.437	33.763	33.453
1mm	27.641	29.992	33.061	33.208	32.343	32.408
1.25mm	27.918	31.951	34.122	33.486	31.673	34.816
1.5mm	19.804	24.147	27.51	29.143	29.649	31.641
1.75mm	24.294	23.837	25.796	25.763	24.261	24.98
2mm	24.751	25.763	27.037	27.624	27.086	26.955

Unit:mW/cm^2

Table 4 Percentages of the maximum power densities of DMFCs with different anode channel widths to that of the DMFC with a 2mm channel width under the operating conditions of 10 cc min^{-1} and 10% methanol concentration.

width	temperature					
	30 °C	40 °C	50 °C	55 °C	60 °C	70 °C
0.8mm	120.58%	148.10%	146.62%	135.52%	124.65%	124.11%
1mm	111.68%	116.42%	122.28%	120.21%	119.41%	120.23%
1.25mm	112.80%	124.02%	126.20%	121.22%	116.93%	129.16%
1.5mm	80.01%	93.73%	101.75%	105.50%	109.46%	117.38%
1.75mm	98.15%	92.52%	95.41%	93.26%	89.57%	92.67%

3.3 Performance of DMFCs under the operating conditions of high fuel flow rate (15 cc/min) and various operating temperatures.

Fig. 6 illustrates the power density distributions for DMFCs with different anode channel widths under the operating conditions of 40℃, 15 cc/min and 10% methanol concentration. Table 5 shows the maximum power densities of DMFCs with different anode channel widths under the operating conditions of 15 cc/min and 10% methanol concentration. As seen in Fig. 6 and Table 5, the DMFC with the anode channel of 800 μm also possessed the best power generating efficiency in comparison to the other DMFCs with larger channel widths under different operating temperatures. As the retention times of the fuel within the anode channels with smaller widths were longer than for those with larger widths under the same operating conditions, the power generating efficiencies of DMFCs with smaller anode channel widths were also greater. For DMFCs with anode channel widths of less than 1.25mm, at an operating temperature of 50℃, the maximum power densities of the DMFCs reached their maximum values. For DMFCs with anode channel widths larger than 1.25mm, due to their wider anode channels, the generated bubbles could not hinder the supply of fuel. Thus, the maximum power densities of the DMFCs also gradually increased with the increase in the operating temperature. Table 6 shows the percentages of the maximum power densities of the DMFCs with different anode channel widths to that of the DMFC with a 2mm channel width under the operating conditions of 15 cc/min and 10% methanol concentration. Under a low operating temperature of 30℃, the maximum enhancement of the maximum power density, i.e. 47.38%, was reached for the DMFC with a 800 μm anode channel width; the maximum power density enhancement gradually decreased with the increase in the operating temperature.

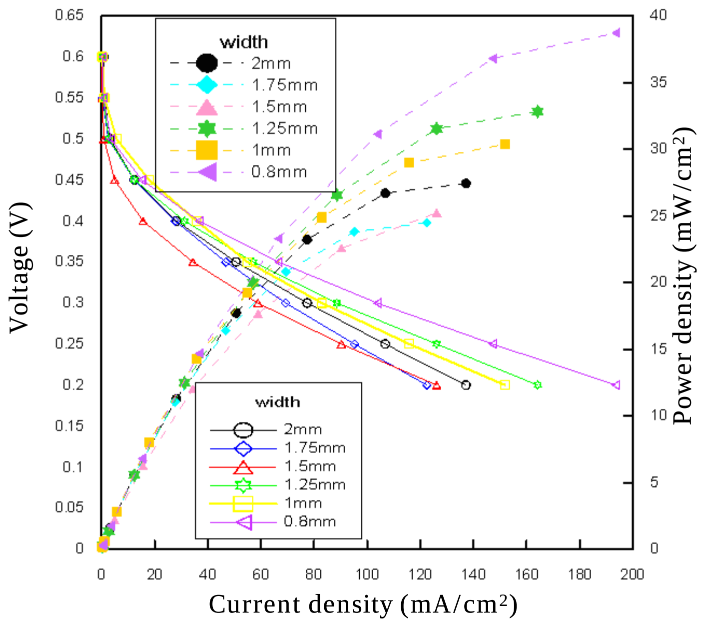

Fig. 6 Power density for the DMFCs with different anode channel widths under the operation conditions of 40 ℃, 15 cc min^{-1} and a 10% methanol concentration.

Table 5 Maximum power densities of DMFCs with different anode channel widths under the operating conditions of 15 cc min^{-1} and 10% methanol concentration.

width	temperature					
	30 °C	40 °C	50 °C	55 °C	60 °C	70 °C
0.8mm	36.261	38.71	39.788	38.449	35.314	35.02
1mm	26.939	30.384	34.465	34.09	33.453	35.069
1.25mm	24.996	32.833	35.771	35.412	33.673	37.673
1.5mm	20.751	25.224	29.469	31.118	31.918	35.167
1.75mm	23.559	24.49	26.498	26.694	25.616	26.429
2mm	24.604	27.429	30.122	30.122	29.812	31.449

Unit:mW/cm^2

Table 6 Percentages of the maximum power densities of DMFCs with different anode channel widths to that of the DMFC with a 2mm channel width under the operating conditions of 5 cc min^{-1} and 10% methanol concentration.

width	temperature					
	30°C	40 °C	50 °C	55 °C	60 °C	70 °C
0.8mm	147.38%	141.13%	132.09%	127.64%	118.46%	111.35%
1mm	109.49%	110.77%	114.42%	113.17%	112.21%	111.51%
1.25mm	101.59%	119.70%	118.75%	117.56%	112.95%	119.79%
1.5mm	84.34%	91.96%	97.83%	103.31%	107.06%	111.82%
1.75mm	95.75%	89.29%	87.97%	88.62%	85.92%	84.04%

4. Conclusions

In this study, pure copper was used for the bipolar plates of the DMFCs, and the anode and cathode channels were manufactured on the plates in order to reduce the electrical resistance and the volume of the DMFCs. Different anode channel widths of 2mm, 1.75mm, 1.5mm, 1.25mm, 1mm, 800 μm and 600 μm were fabricated on the copper plates in order to investigate the effect of the anode channel width on the performance of the DMFCs. It was found that the performance of DMFCs with smaller anode channels was enhanced due to the uniform distribution of fuel on the anode collectors and the longer retention period of the fuel within the anode channels. However, when the width of the anode channel was less than 600 μm, the hydro-resistance from the CO_2 bubbles produced within the anode channels seriously increased, which then hindered the fuel from moving into the anode channels through the wriggle pump. Consequently, the output of the DMFCs showed an obvious decrease. In this study, the performance of the DMFCs was also tested under various operating temperature conditions and supplied fuel flow rates. It was found that not only the fuel channel widths of the DMFCs could affect the performances of the DMFCs, but their corresponding operating temperatures did. Whether under low or high flow rates, the performance of the DMFC with a 800 μm channel width at an operating temperature of 40℃~50℃ obtained the maximum power density and the maximum output enhancement of the DMFCs under consideration. For the DMFCs with narrow channel widths, lower operating temperatures were suitable. In this study, the maximum power density of the DMFCs reached the maximum value of 39.788 mW/cm^2 with a 800 μm anode channel and under the operating conditions of 50℃, 15cc/min and 10% methanol concentration.

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