FUEL CONCENTRATION AND OPERATING TEMPERATURE EFFECTS ON CRITICAL AMOUNTS OF CATALYSTS ADDED TO THE FUEL CHANNELS OF DIRECT METHANOL FUEL CELL

Y. D. KUAN[a], W. J. LUO[b*], C. C. CHANG[a], I. WELLID[c], Z. Y. ZHENG[a], C. N. CHEN[d]

[a]Department of Refrigeration, Air Conditioning and Energy Engineering, National Chin-Yi University of Technology, Taichung 411, Taiwan
[b]Graduate Institute of Precision Manufacturing, National Chin-Yi University of Technology, Taichung 411, Taiwan
[c]Refrigeration and Air Conditioning Department, Politeknik Negeri Bandung, Bandung 40012, Indonesia
[d]Department of Physics, Tamkang University, New Taipei, Taiwan

This study modifies the geometry of fuel channel corners in order to reduce the hydro-resistance of the fuel within the channels, and investigates fuel concentration and operating temperature effects on the loading weight percentages of catalysts added to the fuel channels. The intent of the study is to further improve the output efficiency of DMFCs (direct methanol fuel cells). In this study, different proportions of catalysts, including active carbon and selenium (Se), were coated onto anode and cathode channels composed of PDMS (polydimethylsiloxane) to promote a fuel decomposition reaction in the fuel channels. The output of the DMFCs was measured under different operational temperatures and different supply fuel concentrations in order to find suitable catalyst loading values under different operational conditions. The experimental results indicate that under identical operating conditions, the performances of DMFCs can be greatly boosted using rounded channel turns rather than right angle turns. Furthermore, the results indicate that critical catalyst loading values exist for each catalyst under different operating temperatures. Suitable coating weight percentages for each catalyst are recommended for different operating temperatures. It was found that under lower operating temperatures and lower fuel supply concentrations, the effect of adding catalysts to fuel channels on the performance enhancement of DMFC is more apparent than for cases with higher operating temperatures and fuel supply concentrations. We also found that the fuel concentration effect on the performance of DMFCs was not apparent for a range of fuel concentrations investigated under the same operating temperature. In other words, while the fuel cells are under operation, even the supplied fuel concentrations vary, although not beyond operational concentration limitations. The effects of concentration variations on the performance of DMFCs with catalysts added to the channels can therefore be neglected.

1. Introduction

Methanol possesses the properties of high energy density, superior chemical stability and high security for transportation and storage, and is considered a promising fuel for electrochemical reaction cells. The Direct Methanol Fuel Cell (DMFC), which utilizes a methanol solution as a fuel, possesses simple and compact characteristics. In comparison to other fuel cell systems, the DMFC has the potential to be widely used as a power source for portable electronic devices. However, before DMFCs can be approved as a reliable power source for portable applications,

---

*Corresponding author. wjluo@ncut.edu.tw

some major problems, including high production costs, expensive catalysts, catalyst instability, thermal and water management and methanol crossover poisoning, must be addressed. Researchers and industry engineers worldwide are studying DMFCs. Finding and preparing suitable catalysts to increase their tolerance to methanol and to further enhance performance are critical for the development of DMFCs.

Most DMFC catalytic electrodes are made of either platinum (Pt) or platinum-based materials (Basri et al. [1]). Qiao et al. [2] developed a new plating process for producing a cathode catalyst for a micro-tubular direct methanol fuel cell. In their method, a thin porous layer of a Pt electro-catalyst is first bound to a tubular polymer electrolyte membrane via the chemical reduction of a Pt complex impregnated in the membrane. The high reactivity of Pt makes it a suitable anode electrocatalyst for DMFCs. However, pure Pt is readily poisoned by carbon monoxide (CO), which is formed by an indirect reaction during methanol oxidation. In order to avoid the formation of CO on Pt electrodes, platinum-alternative catalysts, binary or hybrid alloys of Pt, such as PtRu, PtSn (Sandoval-González et al. [3]), Pt-M (Baglio et al. [4]), PtMO (Martínez-Huerta et al. [5]), PtPbMnO (Huang et al. [6]) and PtCo (Xu et al. [7]; Vinayan et al. [8]) are generally employed as electrocatalytic materials on DMFC anodes. Baranton et al. [9] developed new electron-conductive polymers that are stable under an oxidizing environment, and that possess a high doping capacity for using platinum-alternative cathode catalysts in DMFCs. Guo et al. [10] investigated the structural and surface features and the electrocatalytic properties of bimetallic PtRu/Oxidized carbon nanofibers (OCNF) and PtRu/Reduced carbon nanofibers (RCNF). The OCNF-supported catalysts provided better performance compared to commercial catalysts when the current density was greater than 50 mA cm,$^{-2}$ despite the low methanol oxidation peak current density. In DMFCs, bimetallic PtRu is the most widely used catalytic material because of its high electrocatalytic activity towards methanol oxidation at the anode. Ru improved the electronic properties of Pt to prevent the adoption of CO by decreasing the oxidation overpotential of the anode (Ribeiro et al. [11]). However, kinetic slow reaction is a significant limitation that reduces the performance and power output of DMFCs. Baglio et al. [4] used a low-temperature preparation procedure to modify Pt catalysts with transition metals (Fe, Cu and Co). According to a stripping analysis of the absorbed methanolic residues, the Pt–Fe system exhibits better methanol tolerance and enhanced activity toward oxygen reduction. An improvement in DMFC single cell performance was also observed in the presence of Pt–Fe catalysts. Wang et al. [12] used Ketjen Black EC 300J as an additive in the cathode catalyst layer to improve DMFC performance. The cathode catalyst layer with the Ketjen Black EC 300J additive showed greater single cell performance than the cathode catalyst layer without any additive, especially in the air-breathing mode. Choi et al. [13] developed a new type of Se/Ru catalyst called Se/Ru(aq) and studied the methanol tolerance and performance of the direct methanol fuel cell for the catalyst. They reported that the Se/Ru(aq) catalyst was highly tolerant to methanol crossing through the membrane (from the anode side) up to a feed concentration of 17 M. When compared to Pt cathodes, the performance of Se/Ru(aq) is significantly better under high methanol concentrations. Yao et al. [14] used a magnetron sputtering (MS) and a metal-plasma ion implantation (MPII) technique to prepare a Pt–M/C catalyst. They reported that the membrane electrode assembly for Pt–Ni/C, Pt–Fe/C and Pt–Cr/C catalysts can enhance DMFC cell performance more than the traditional Pt/C and Pt–Ru/C can.

In regard to studies on fuel concentration effects on the performance of DMFCs, Shaffer and Wang [15] indicated that DMFCs must be designed to increase their energy density. One major hurdle in accomplishing this task is being able to use high concentration methanol fuel, thereby reducing the size of the fuel tank and the amount of water carried as part of the system. Umeda et al. [16] investigated cell temperature and methanol concentration dependencies of DMFC performance and its polarization characteristics using a single cell with a Ag/Ag_2SO_4 reference electrode. Their results demonstrate a decrease in the DMFC performance at 60℃ when feeding 10 mol dm^{-3} methanol. This was attributed to the simultaneous appearance of an O_2 cross leak and a methanol crossover causing a decline in the methanol oxidation performance at the anode and an O_2 reduction performance at the cathode. In a DMFC, there is an optimal methanol concentration where the efficiency of the fuel cell reaches its maximum (Arisetty et al. [17]). Na et al. [18] modified system layouts and operating strategies of DMFCs in terms of feedforward fuel

concentration control, thus enabling variable concentrations to be determined by fuel efficiency and varying with the current and other process variables. Halim et al. [19] adopted a passive vapor feed DMFC using high methanol concentration from 12M (molarity) to neat methanol, and found improved performance of the passive vapor feed DMFC. A linear dependence of current density on methanol concentration was established. Gago et al. [20] analyzed the performance of each electrode of an air breathing passive micro-direct methanol fuel cell (μDMFC) during polarization, stabilization and discharge with different methanol concentrations. Their experimental results indicated that with a high concentration of 20M, due to fuel crossover, maximum power density decreased by 85%.

In studies on fuel channels for DMFCs, Hwang et al. [21] investigated optimum flow channel design for DMFCs, and explored the effects of the pressure drop across inlets and outlets on the performance of the DMFCs with various flow channel designs. Sudaroli and Kolar [22] experimentally investigated the effects of single, double and triple serpentine flow field configurations on a DMFC with a $25cm^2$ MEA (membrane electrode assembly) with a constant open ratio. They found the cell efficiency of a double serpentine flow field to be 12.5% greater than for a single serpentine flow field due to the reduction of mixed potential. However, in the cell of the triple serpentine flow field, the maximum power density and cell efficiency were the lowest among the DMFCs due to high mass transfer resistance. Yeh et al. [23] and Yarn et al. [24] investigated the performance of DMFCs with different hydrophobic anode channels. They found that the performance of DMFCs made of PDMS with high hydrophobic particles can be greatly enhanced, while the hydrophobic property of the particles is unaffected by different operating conditions. Chung et al. [25] investigated the effect of anode channel width on the performance of DMFCs and found that that the performance of DMFCs with smaller anode channels can be enhanced by uniform distribution of fuel on the anode collectors and a longer retention period of the fuel within the anode channels. However, when the width of the anode channel was less than 600 μ m, hydro-resistance from CO_2 bubbles produced within the anode channels dramatically increased. Consequently, the output of the DMFCs showed a significant decrease. The performance of a DMFC can be significantly reduced by methanol crossover. One method of reducing methanol crossover is utilizing a flowing electrolyte channel (FE–DMFC). Yarn et al. [26] added a 0.09 wt% of active carbon catalyst to anode and cathode channels made of PDMS and indicated that under the same operating conditions, the performances of the DMFCs with the active carbon catalyst added onto their channels were always superior to those of DMFCs without an added catalyst. However, they did not investigate the proportional effect for different added catalysts on the performance of the DMFCs [26]. Kuan et al. [27] indicated that critical catalyst loading values for fuel channels exist for the investigated catalysts of platinum (Pt), active carbon and selenium (Se). When the amount of catalyst added is less than this critical value, the output of the DMFCs can be greatly enhanced by increasing the proportion of the catalyst added to the fuel channels. However, when the amount of catalyst added exceeds the critical value, enhanced efficiency is no longer apparent. A suitable coating weight percentage for the investigated catalyst was recommended. The fuel concentration effect on the performance enhancement of DMFC achieved by loading catalysts onto fuel channels was not investigated in their study. An increase in fuel concentration might promote an electro-chemical reaction in DMFCs, but excessive fuel concentrations could exceed the tolerance of DMFCs and result in methanol crossover poisoning problems, ultimately leading to deterioration of the DMFCs. Thus, the fuel concentration effect is crucial to the performance of DMFCs.

In order to further improve the output efficiency of DMFCs, this study modified the geometry of the fuel channel corners to reduce the hydro-resistance of the fuel within the channels and investigate the fuel concentration and operating temperature effects on the loading weight percentages of catalysts for the fuel channels. Two catalysts of active carbon and selenium (Se) were used in the study in order to understand the variations of critical catalyst loading values under different supplied fuel concentrations and operating temperatures. This study aimed to find suitable catalyst loading percentages for DMFCs under different fuel concentrations and operational temperatures.

2. Experimental

2.1 Channel fabrication

In this study, the channel for the DMFCs using PDMS as the substrate was fabricated by injecting the PDMS material into a master mold on which reverse channel patterns were fabricated using lathe machining. The related injection-molding processes are shown in Fig. 1 and described below [23-26]:

(1) PDMS preparation: the silicone resin (Agent A) and the hardener (Agent B) are mixed in a 10:1 weight ratio, and then the mixture is uniformly mixed with different weights of catalysts in terms of the designed weight percentage ratios. The total weight of the mixture is 35 g.

(2) Vacuum treatment: because the mixing of Agents A and B in the previous step produces a large amount of bubbles, the mixed PDMS is placed into a vacuum chamber for vacuum treatment to completely remove the bubbles.

(3) Injection mold solidification and catalyst coating: the master mold (8cm x 8cm) is placed on a balanced stage, and then the channel area (3.5 cm x 3.5 cm) of the master mold is isolated using a square glass plate before injection, and then the PDMS containing the catalyst is injected into the channel area. The PDMS without catalyst fills up the exterior of the mold. Then, the glass plate is removed, and the mold is placed on a hot plate and heated at 70℃ for 30-40 min to complete the solidification of PDMS.

(4) Turning mold: the solidified PDMS is removed from the master mold.
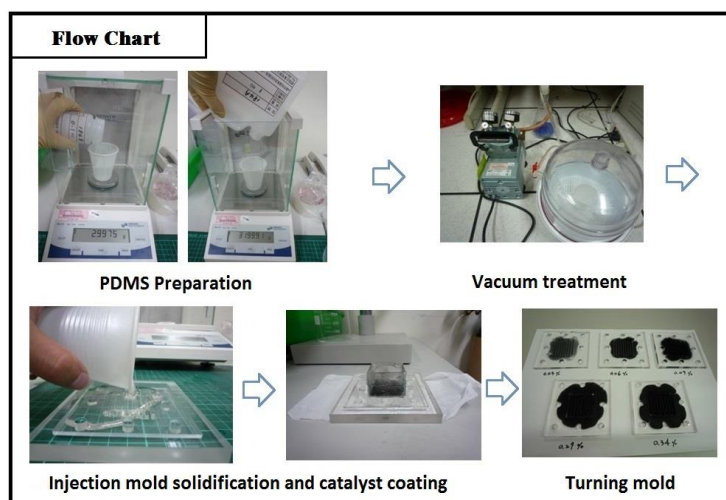

Fig. 1. Injection-molding processes of channel fabrication (Yarn et al [24]).

2.2 Transparent cell and experimental procedure

Fig. 2 presents an exploded schematic of the transparent DMFC test fixture that was designed and fabricated for the visualization study presented in this paper [26]. The MEA (membrane electrode assembly) was sandwiched between two bipolar plates with a gasket on either side of the MEA. This assembly, including the bipolar plates and MEA, was clamped between two enclosure plates using eight M8 screw joints (each having a torque of approximately 12 KGF-CM). The active area of the MEA used in this study is 3.5 cm×3.5 cm, which consisted of two single-sided ELAT electrodes from E-TEK and a Nafion[R]117 membrane. Both the anode and cathode electrodes used carbon cloth (E-TEK, Type A) as a backing support layer with a 30% PTFE water-proofing treatment. The catalyst loading on the anode side was 4.0 mg cm^{-2} with unsupported [Pt:Ru] Ox (1:1 a/o), where as 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[R] was applied to the surface of each electrode. The bipolar plates (shown in Fig. 3) were composed of 316 stainless steel with a thickness of 2.0 mm to avoid corrosion.
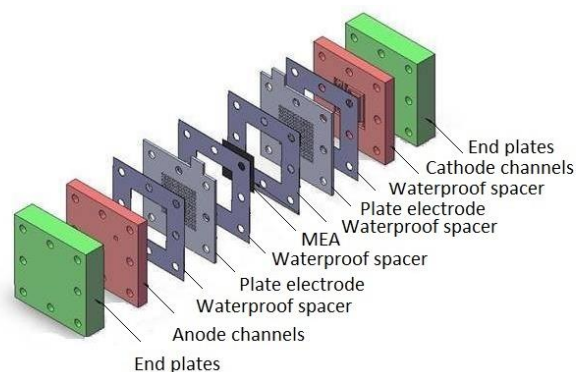
Fig. 2. Exploded view of the transparent DMFC test fixture (Yeh et al. [24]).

A schematic of the experimental setup is shown in Fig. 3. The methanol solution was driven by a squirm pump, which can precisely control the liquid flow rate from 3 to 15 ml/min with an error of 2%. Before entering the cell, the methanol solution was pre-heated to a desired temperature by placing the methanol solution tank in a temperature-controllable water bath. Simultaneously, ambient air with approximately 21% oxygen as an oxidant was provided to the cathode side of the cell without humidification. The oxygen flow rate was controlled using an air mass flow regulator, which has an error of 5% of the full scale. As shown in Fig. 3, all of the measurements of the investigated DMFCs were performed in an experimental chamber in which the temperature and humidity can be controlled.
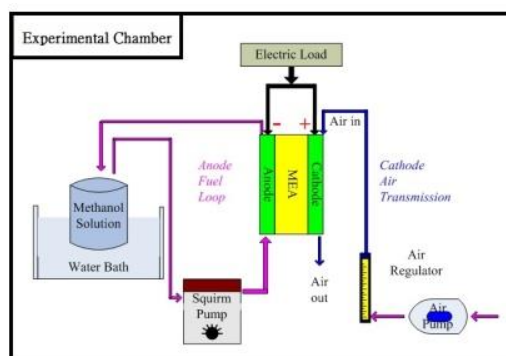

Fig. 3. Schematic diagram of experimental apparatus (Yeh et al. [24]).

3. Results and discussion

In this study, serpentine fuel channels with 2 mm width, 3 mm depth and 2 mm ribs, as shown in Fig. 4, were applied to distribute fuel into the electrochemical reaction area of DMFCs. As shown in Fig.4, the total length of the serpentine fuel channel was 322 mm. Due to the DMFC's limited reaction area of 3.5 cm×3.5 cm, 8 turns of the serpentine channels were designed along the fuel channels. However, the production of CO_2 bubbles generated from the electrochemical reaction in the anode channel could block the fuel channels and hinder fuel being supplied into the anode channels. As a result, performance of the DMFCs would gradually decline because fuel on the anode side could not be supplied in time or evenly distributed in the reaction area during an electrochemical reaction. In order to enhance the performance of DMFCs, effective removal of the CO_2 bubbles from the anode channels and reduction of the hydro resistance for the fuel supply in the channels are essential. In the past, turns with right angles were commonly used in the anode and cathode fuel channels which could cause a high hydro-resistance for the fuel supply. In this study, in order to reduce the hydro-resistance in the fuel channels, instead of right angle turns in the fuel channels, rounded corners were designed, as shown in Fig. 4. Table 1

indicates the maximum power densities of two DMFCs, one with a right angle turn and one with a rounded corner, with different proportions of Se catalyst added onto the fuel channels. The table also shows the corresponding performance increments of the two DMFCs, respectively, with 10% methanol fuel supplied under different operating temperatures. As shown in the table, the maximum power density of the two DMFCs gradually increased with the increase in the operating temperature because high temperatures can boost the electrochemical reaction in the MEA. In the DMFC with right angle turns and without a catalyst coated onto the fuel channels, a maximum power density of 10.4 mw cm^{-2} could be attained at an operating temperature of 70°C. However, in the DMFCs with rounded corners and without a catalyst coated onto the fuel channels, due to a great reduction in the hydro-resistance, the CO_2 bubbles in the anode channels can be effectively removed, and a maximum power density of 39.99 mw cm^{-2} can be attained at an operating temperature of 70°C. The increments of maximum power density for the two DMFCs, from 190% ~ 284% without a catalyst added onto the fuel channels can be attained under the investigated operating temperatures.
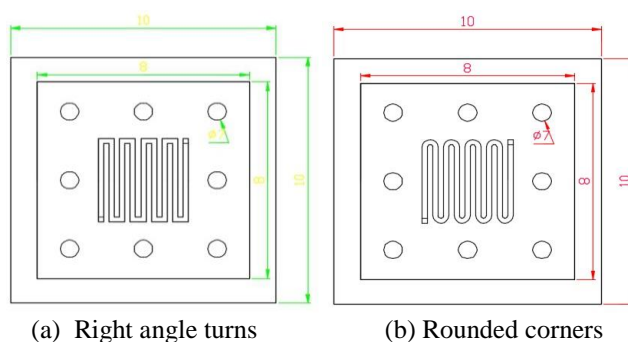

(a) Right angle turns   (b) Rounded corners

Fig. 4. Geometry of fuel channels with right angle turns and rounded corners.

Table 1 Maximum power densities of two DMFCs with right angle and rounded corners, respectively, with different proportions of Se catalyst added onto the fuel
channels and the corresponding performance increments of the two DMFCs with 10% of methanol fuel supplied under different operating temperatures.

Temperature	50°C			60°C			70°C		
catalyst adding proportion	Right angle turns (mW cm^{-2})	Round angle turns (mWcm^{-2})	Increment percentage (%)	Right angle turns (mWcm^{-2})	Round angle turns (mW cm^{-2})	Increment percentage (%)	Right angle turns (mWcm^{-2})	Round angle turns (mWcm^{-2})	Increment percentage (%)
0%	8.34	28.75	244.7	9.36	27.16	190.2	10.4	39.99	284.5
0.09%	14.29	34.16	139.0	14.95	30.92	106.8	15.35	42.56	177.3
0.14%	15.83	37.05	134.0	16.12	32.2	99.8	16.02	42.47	165.1
0.29%	18.77	38.01	102.5	18.92	34.9	84.5	19.16	33.38	74.2
0.43%	12.65	41.47	227.8	14.01	33.06	136.0	14.46	37.1	156.6
0.57%	11.54	31.31	171.3	12.82	30.67	139.2	13.6	37.71	177.3

(1)   Power density increment percentage is defined as $(E_{RO} - E_{RI})/E_{RI} \times 100$ % , where E_{RO} is the maximum power density of a DMFC with rounded channel corners and E_{RI} is the maximum power density of a DMFC with right angle channel turns at the same Se catalyst proportion added.

(2)   For the weight proportions of 0.09%, 0.14%, 0.29%, 0.43% and 0.57%, the amount of Se catalyst added in the channel area accounts for 2.57mg cm^{-2}, 4.0mg cm^{-2}, 8.28mg cm^{-2}, 12.28mg cm^{-2} and 16.28mg cm^{-2}, respectively.

In order to further enhance the performance of the DMFCs and boost the electrochemical reaction of the DMFCs, different proportions of Se catalyst were added onto the fuel channels of the two DMFCs, respectively. As shown in Table 1, under the same operating temperature, the maximum power densities of the two DMFCs with right angle turns and rounded corners could be greatly enhanced due to the Se catalyst added onto the fuel channels. For the two DMFCs, when the Se catalyst was added in the fuel channel, the boost in the electrochemical reaction could generate more hydro-pressure within the fuel channel to overcome the adhesive force on the interface of the bubbles and the channels. Especially in the case of DMFCs with right angle turns, the pressure drops along the fuel channel were much greater, but CO_2 bubbles in the channels are difficult to remove under different operating temperatures. Thus, DMFCs with right angle turns possess high potential to improve the pressure drop along the fuel channel. Maximum power density increments can be reached by adding a Se catalyst under different operating temperatures for DMFCs with right angle turns compared to the DMFCs with rounded corners.

Yarn et al. [26] added a 0.09 wt% of active carbon catalyst onto the fuel channels to enhance the performance of single and twin stack DMFCs and found that by adding the catalyst in the fuel channels, performance enhancement of 90% to 118% for the DMFCs could be achieved under different operating temperatures. In Table 1, the maximum power densities of the two DMFCs with different proportions of Se catalyst added to the fuel channels under different operating temperatures are shown as well. According to the table, under the same operating temperature and fuel concentration, an increase in the added catalyst proportions can gradually enhance the maximum power density of a DMFC. However, critical values of the added catalyst exist under different operating temperatures. If the proportion of the catalyst added is greater than the critical value, under the same operating conditions, the fuel decomposing rate in the anode channel may be too fast and exceed the tolerance of the MEA. Excessive protons with positive charges generate in the anode channel and cannot be transported to the cathode side of the DMFC through the MEA due to limited tolerance of the MEA. The excessive protons may hinder the fuel decomposing reaction in the anode channel and cause crossover phenomena in the DMFC. Thus, the maximum power density gradually decreases and the performance of the DMFC deteriorates as well when the proportion of catalyst added is greater than the critical values. As shown in the table, at an operating temperature of 50°C, the critical values of the proportion of added Se catalyst for the two type DMFCs are about 0.29% and 0.43%, respectively. With an increase in the operating temperatures, the critical values of the added Se catalyst gradually decrease. This raises a concern since higher proportions of Se catalyst might lead to a higher risk of poison.

Table 2 indicates the maximum power densities of the two DMFCs with right angle and rounded corners, respectively, when different proportions of active carbon catalyst were added with corresponding performance increments of the two DMFCs with 10% methanol fuel supplied under different operating temperatures. In comparison to the DMFCs with right angle turns, the maximum power densities of the DMFCs with rounded corners are highly superior under the same operating conditions and with the same proportions of active carbon catalyst added. The table shows that the critical values of active carbon catalyst added decrease with the increase in the operating temperature as well. With the same proportion of the catalyst added, maximum power density increments ranging from 15.9% to 284.5% can be attained.

Table 2 Maximum power densities of two DMFCs with right angle and rounded corners, respectively, with different proportions of active carbon catalyst added onto fuel channels and the corresponding performance increments of the two DMFCs with 10% of methanol fuel supplied under different operating temperatures.

Temperature	50°C			60°C			70°C		
catalyst adding proportion	Right angle turns (mW cm^{-2})	Round angle turns (mWcm^{-2})	Increment percentage (%)	Right angle turns (mWcm^{-2})	Round angle turns (mW cm^{-2})	Increment percentage (%)	Right angle turns (mWcm^{-2})	Round angle turns (mWcm^{-2})	Increment percentage (%)
0%	8.34	28.75	244.7	9.36	27.16	190.2	10.4	39.99	284.5
0.03%	8.69	29.46	239.0	9.67	35.02	262.2	10.64	39.92	275.2
0.06%	14.32	29.9	108.8	15.08	37.74	150.3	15.99	37.47	134.3
0.17%	13.53	32.16	137.7	13.82	33.7	143.8	14.6	35.02	139.9
0.29%	18.19	30.44	67.3	19.98	31.13	55.8	21.73	31.08	43.0
0.34%	16.37	27.72	69.3	18.73	30.44	62.5	21.61	25.05	15.9

(1) Power density increment percentage is defined as $(E_{RO} - E_{RI})/E_{RI} \times 100$ % , where E_{RO} is the maximum power density of a DMFC with rounded channel corners and E_{RI} is the maximum power density of a DMFC with right angle channel turns at the same active carbon catalyst proportion added.

(2) For the weight proportions of 0.03%, 0.06%, 0.17%, 0.29% and 0.34%, the amount of active carbon catalyst added in the channel area accounts for 0.857mg cm^{-2}, 1.71mg cm^{-2}, 4.86mg cm^{-2}, 8.28mg cm^{-2} and 9.71mg cm^{-2}, respectively.

Fig. 5 illustrates the output of the DMFC with right angle channel turns and without a catalyst being adding onto the fuel channels, in terms of voltage, current density and power density with a 10% fuel concentration supplied. With an increase in the operating temperature, the power density output of the DMFC also gradually increases and the maximum power density can reach a value of 10.4 mw cm^{-2} under an operating temperature of 70°C. Fig. 6 illustrates the output of the DMFC with rounded channel corners without a catalyst being added onto the fuel channels, in terms of voltage, current density and power density with a 10% fuel concentration supplied. In comparison to the output of the DMFC with right angle channel turns shown in Fig. 3, with the increase in the operating temperature, the power density output of the DMFC with rounded channel corners gradually increases as well. However, in the DMFC with rounded channel corners, the hydro-resistance in the fuel channels can be greatly reduced and the current density output of the DMFC can be significantly raised at the same voltage output. Thus, the power density output of the DMFC with rounded channel corners can be substantially enhanced. The maximum power density of the DMFC can reach a high value of 42.56 mW cm^{-2} under the operating temperature of 70°C.
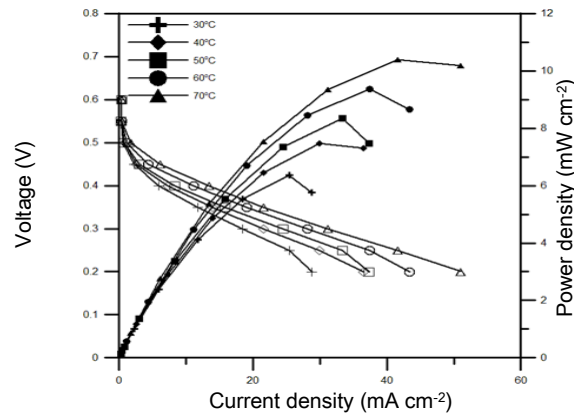
Fig. 5.Output of DMFC with right angle channel turns and without catalyst added onto the fuel channels in terms of voltage, current density and power density with 10% fuel concentration supplied.
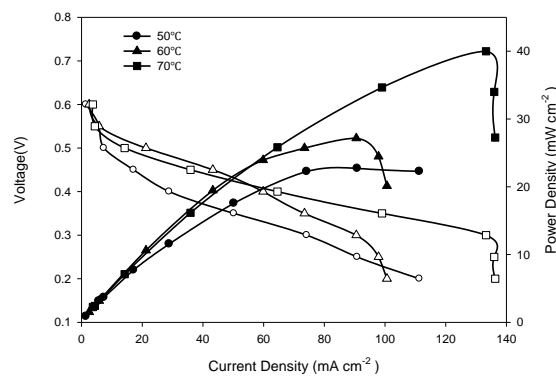

Fig. 6. Output of DMFC with rounded channel corners and without catalyst added onto the fuel channels in terms of voltage, current density and power density with 10% fuel concentration supplied.

3.2 The fuel concentration and operating temperature effects on critical proportion values of Se and active carbon catalysts added for DMFCs with rounded turns

In this study, different proportions of Se and active carbon catalysts were added onto the fuel channels of a DMFC with rounded corners, and the effects of the proportion of catalyst added, fuel concentration and fuel operating temperature on the performance of the DMFC were further investigated. Table 3 indicates the maximum power densities of the DMFCs with rounded channel corners and different proportions of Se catalyst added under different operating temperatures and different methanol fuel supply concentrations. As shown in Table 1, at the same operating temperature, a critical value for the proportion of Se catalyst added can be found, i.e. 0.43% at 50°C operating temperature, 0.29% at 60°C operating temperature and 0.09% at 70°C operating temperature. It can be observed that, with the increase in the operating temperature, the critical value of the added catalyst gradually decreases as well. Under higher operating temperatures, the fuel decomposing rate in the anode channel is greater in comparison to those at lower operating temperatures. The catalyst added to the fuel channel might exceed the tolerance of the MEA and cause deterioration of the DMFC in high operating temperatures. Thus, when the operating temperature is lower, a greater amount of the catalyst is required in order to achieve higher performance. In Table 3, it can also be observed that, at the same operating temperature, with an increase in the fuel supply concentration, the corresponding critical value of catalyst added is almost maintained at a constant value. In other words, the investigated fuel concentration effects on the performance of the DMFCs are a great deal less in comparison to that of the operating temperature. Notably, for DMFCs a concentration of supply fuel less than 15% is recommended in

order to avoid crossover problems. Therefore, the fuel supply concentration effect on the performance enhancement of DMFCs by adding a catalyst to the fuel channel can be neglected. Table 4 indicates the maximum power density increments of DMFCs with rounded channel corners and different amounts of Se catalyst added under different operating temperatures and different methanol fuel supply concentrations. It can be seen in the table that the maximum power density increments of the DMFC can be achieved in the range of -16.53% to 60.71% in comparison to the DMFCs without an added catalyst. Especially, under lower operating temperatures and lower fuel supply concentrations, the effect of adding a Se catalyst to the fuel channels on the performance enhancement of the DMFC is more apparent in comparison to the cases under higher operating temperatures and fuel supply concentrations. It can be observed that, under high operating temperatures, i.e. 70°C, and high supply fuel concentrations, i.e. 15%, the increments of the maximum power densities become negative values, which indicates that an added catalyst can worsen the performance of the DMFC under these operating conditions.

Table 3 Maximum power densities of DMFCs with rounded channel corners and different amounts of Se catalyst added under different operating temperatures and different methanol fuel supply concentrations

Temperature	50°C			60°C			70°C		
Concentration proportion	5%	10%	15%	5%	10%	15%	5%	10%	15%
0%	16.57	28.75	28.57	21.74	27.16	26.06	25.37	39.99	35.63
0.09%	21.31	34.16	32.82	27.43	30.92	29.07	38.28	42.56	41.59
0.14%	20.02	37.05	30.22	31	32.2	31.18	35.66	42.47	40.68
0.29%	21.31	38.01	29.65	32.08	34.9	32.47	31.96	33.38	30.61
0.43%	26.63	41.47	35.84	31.34	33.06	28.6	31.25	37.1	33.09
0.57%	26.09	31.31	29.53	30.4	30.67	26.6	30.02	37.71	30.37

Unit: mw cm^{-2}

Table 4 Maximum power density increments of DMFCs with rounded channel corners and different amounts of Se catalyst added under different operating temperatures and different methanol fuel supply concentrations.

Temperature	50°C			60°C			70°C		
Concentration proportion	5%	10%	15%	5%	10%	15%	5%	10%	15%
0.09%	28.61	18.82	14.88	26.17	13.84	11.55	50.89	6.43	16.73
0.14%	20.82	28.87	5.78	42.59	18.56	19.65	40.56	6.20	14.17
0.29%	28.61	32.21	3.78	47.56	28.50	24.60	25.98	-16.53	-14.09
0.43%	60.71	44.24	25.45	44.16	21.72	9.75	23.18	-7.23	-7.13
0.57%	57.45	8.90	3.36	39.83	12.92	2.07	18.33	-5.70	-14.76

(1) Power density increment is defined as $(E_X - E_P)/E_P \times 100$ %, where E_X is the maximum power density of a DMFC with different percentages of catalyst added onto the channels and E_P is the maximum power density without the addition of catalyst to the channels at the same operating temperature and fuel supply concentration.

(2) For the weight proportions of 0.09%, 0.14%, 0.29%, 0.43% and 0.57%, the amount of Se catalyst added in the channel area accounts for 2.57mg cm^{-2}, 4.0mg cm^{-2}, 8.28mg cm^{-2}, 12.28mg cm^{-2} and 16.28mg cm^{-2}, respectively.

Unit: %

Fig. 7 shows the output of a DMFC with rounded channel corners, 0.09% Se catalyst added onto channels and different fuel concentrations supplied under the operating temperature of 70°C. From the figure, it can be seen that, for DMFCs with the same amount of catalyst added, outputs are not apparent with different supply fuel concentrations in this study. The maximum power density of the DMFC ranges from 38.28 to 42.56 mW cm^{-2}, as shown in the figure. Fig. 8 shows the output of the DMFC with rounded channel corners, 0.29% Se catalyst added onto the channels and different fuel concentrations supplied under the operating temperature of 60°C. Similar phenomena can be observed in the figure as well.
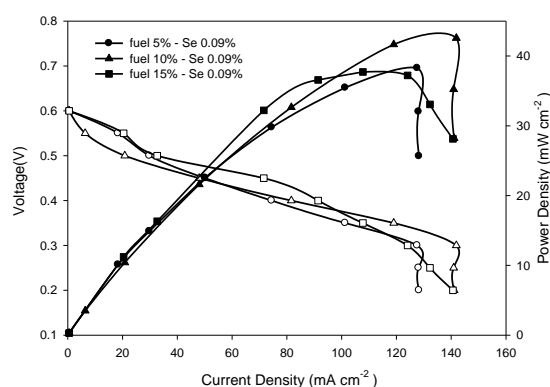

Fig. 7. Output of DMFC with rounded channel corners, 0.09% proportion of Se catalyst added onto channels and different fuel concentrations supplied under the operating temperature of 70°C.
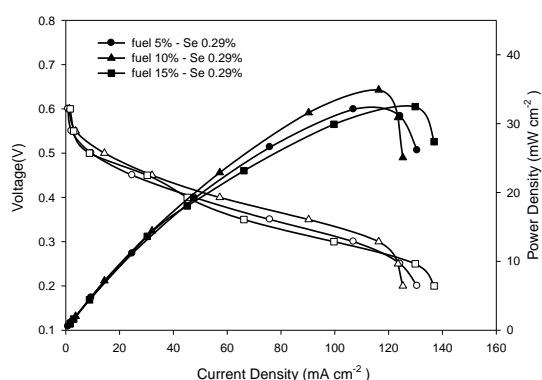

Fig. 8. Output of DMFC with rounded channel corners, 0.29% proportion of Se catalyst added onto channels and different fuel concentrations supplied under the operating temperature of 60°C.

Table 5 indicates the maximum power densities of the DMFCs with rounded channel corners and different amounts of active carbon catalyst under different operating temperatures and different methanol fuel supply concentrations. As shown in Table 5, at the same operating temperature a critical value for the addition of the active carbon catalyst can be found, i.e. 0.17% at 50°C operating temperature, 0.06% at 60°C operating temperature and 0.03% at 70°C operating temperature. Table 6 indicates the maximum power density increments of DMFCs with rounded channel corners and different amounts of active carbon catalyst added under different operating temperatures and different methanol fuel supply concentrations. It can be seen in the table that the maximum power density increments of the DMFC can be achieved in the range of -37.36% to 141.6% in comparison to the DMFCs without an added catalyst. The characteristics of the DMFCs with an active carbon catalyst added onto the fuel channels are similar to those of DMFCs with a Se catalyst added. The maximum power density of the DMFCs with an active carbon catalyst

added can attain a maximum value of 40.19mWcm^{-2} with a 0.03% catalyst added under the operating temperature of 70°C and a fuel supply concentration of 15%. From Tables 5 and 6, it can be observed that the fuel supply concentration effect on the performance enhancement of DMFCs by the added catalyst can be neglected.

Table 5 Maximum power densities of DMFCs with rounded channel corners and different proportions of active carbon catalyst added under different operating temperatures and different methanol fuel supply concentrations

Temperature	50°C			60°C			70°C		
Concentration proportion	5%	10%	15%	5%	10%	15%	5%	10%	15%
0%	16.57	28.75	28.57	21.74	27.16	26.06	16.37	39.99	35.63
0.03%	28.87	29.46	31.13	33.36	35.02	36.88	39.55	39.92	40.19
0.06%	27.26	29.9	32.6	35.98	37.74	39.21	36.81	37.47	38.69
0.17%	31.22	32.16	33.23	34.56	33.7	35.17	34.73	35.02	35.83
0.29%	29.04	30.44	31.25	33.77	31.13	32.74	30.37	31.08	32.23
0.34%	26.03	27.72	29.12	30.1	30.44	31.32	24.81	25.05	27.58

Unit: mw cm^{-2}

Table 6 Maximum power density increments of DMFCs with rounded channel corners and different amounts of active carbon catalyst added under different operating temperatures and different methanol fuel supply concentrations.

Temperature	50°C			60°C			70°C		
Concentration proportion	5%	10%	15%	5%	10%	15%	5%	10%	15%
0.03%	74.23	2.47	8.96	53.45	28.94	41.52	141.60	-0.18	56.81
0.06%	64.51	4.00	14.11	65.50	38.95	50.46	124.86	-6.30	50.96
0.17%	88.41	11.86	16.31	58.97	24.08	34.96	112.16	-12.43	39.80
0.29%	75.26	5.88	9.38	55.34	14.62	25.63	85.52	-22.28	25.75
0.34%	57.09	-3.58	1.93	38.45	12.08	20.18	51.56	-37.36	7.61

(1)   Power density increment is defined as $(E_X - E_P)/E_P \times 100$ % , where E_X is the maximum power density of a DMFC with different percentages of catalyst added onto the channels and E_P is the maximum power density without the addition of catalyst to the channels at the same operating temperature.
(2)   For the weight proportions of 0.03%, 0.06%, 0.17%, 0.29% and 0.34%, the amount of active carbon catalyst added in the channel area accounts for 0.85mg cm^{-2}, 1.71mg cm^{-2}, 4.85mg cm^{-2}, 8.28mg cm^{-2} and 9.71mg cm^{-2}, respectively.

Unit: %

Figs. 9 and 10 illustrate the output of the DMFCs with rounded channel corners, when 0.06% and 0.03% proportions of active carbon catalyst were added onto the channels and different fuel concentrations were supplied under the operating temperatures of 60°C and 70°C, respectively. It can also be found that the fuel concentration effect on the performance of DMFCs is not apparent in the range of fuel concentration investigated. In other words, while the fuel cells are under operation even the supplied fuel concentrations vary but not beyond the operational concentration limitations, the effect of concentration variations on the performance of DMFCs with catalysts added onto the channels can be neglected.
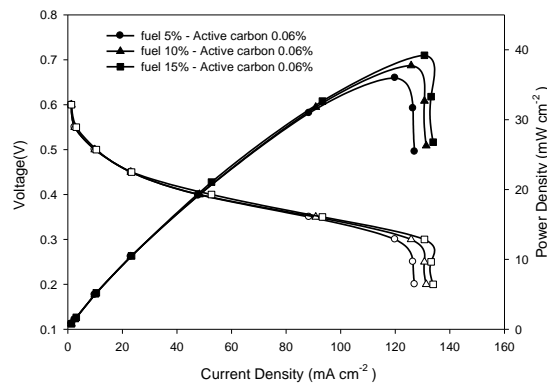

Fig. 9. Output of DMFCs with rounded channel corners, 0.06% proportion of active carbon catalyst added onto channels and different fuel concentrations supplied under the operating temperature of 60°C.
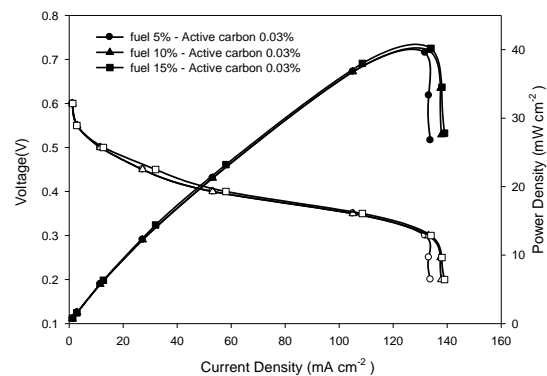

Fig. 10. Output of DMFCs with rounded channel corners and 0.03% proportion of active carbon catalyst added onto channels at different fuel concentrations supplied under the operating temperature of 70°C.

4. Conclusions

This study modified the geometry of the fuel channel corners in order to reduce the hydro-resistance of the fuel within the channels, and investigated the enhancement effects of adding different weight percentages of catalysts into the fuel channels on the output performance of DMFCs under different operating temperatures and different supplied fuel concentrations. Two types of catalysts: active carbon and Se, were added to fuel channels composed of PDMS. The results indicate that the performances of the DMFCs can be greatly enhanced with rounded channel turns under identical operating conditions due to considerable hydro-resistance reduction within the channels. Moreover, critical values for the percentage of added catalyst exist for every DMFC investigated in this study. When the added percentages are greater than the corresponding critical value, the maximum power densities of the DMFCs may decrease due to the limited tolerance of MEA. In this study, suitable loading weight percentages for every catalyst were

recommended under different operating temperatures. The highest maximum power density of 42.56 mW·cm^{-2} was obtained for the DMFC with a 0.09% Se catalyst at an operating temperature of 70℃. In comparison to the maximum power densities of the PDMS channel without catalysts at various operating temperatures, the highest maximum power density increment of 60.71% was attained for the DMFC with 0.43% Se catalyst added to the channels at an operating temperature of 30℃. Furthermore, the results indicate that for DMFCs with the same percentages of loading catalyst, higher maximum power density increments can usually be obtained under lower operating temperatures and fuel concentrations; this is attributed to the lower temperatures and concentrations retarding the crossover effect in the DMFCs. We also found that the fuel concentration effect on the performance of DMFCs is not apparent in the range of fuel concentration investigated under the same operating temperature. In other words, while the fuel cells are under operation, even the supplied fuel concentrations vary, although not beyond operational concentration limitations. The effect of concentration variations on the performance of DMFCs with catalysts added onto the channels can thus be neglected.

References

[1] S. Basri, S. K. Kamarudin, W.R.W. Daud, Z. Yaakub, International Journal of Hydrogen Energy **35,** 7957 (2010).

[2] H. Qiao, M. Kunimatsu, T. Okada, Journal of Power Sources **139**, 30 (2005).

[3] A. Sandoval-González, E. Borja-Arco, J. Escalante, O. Jiménez-Sandoval, S.A. Gamboa, International Journal of Hydrogen Energy **37**, 1752 (2012).

[4] V. Baglio, A. Stassi, A. Di Blasi, C. D'Urso, V. Antonucci, A.S. Aric`o, Electrochimica Acta **53**, 1360 (2007).

[5] M. V. Martínez-Huerta, N. Tsiouvaras, M.A. Peña, J.L.G. Fierro, J.L. Rodríguez, E. Pastor, Electrochimica Acta **55**, 7634 (2010).

[6] Y. Huang, J. Cai, Y. Guo, International Journal of Hydrogen Energy **37**, 1263 (2012)

[7] C. Xu, J. Hou, X. Pang, X. Li, M. Zhu, B. Tang, International Journal of Hydrogen Energy **37**, 10489 (2012).

[8] B.P. Vinayan, R.I. Jafri, R. Nagar, N. Rajalakshmi, K. Sethupathi, S. Ramaprabhu, International Journal of Hydrogen Energy **37**, 412 (2012).

[9] S. Baranton, C. Coutanceau, J.M. L´eger, C. Roux, P. Capron, Electrochimica Acta **51**, 517 (2005).

[10] J. Guo, G. Sun, Q. Wang, G. Wang, Z. Zhou, S. Tang, L. Jiang, B. Zhou, Q. Xin, Carbon **44**, 152 (2006).

[11] V.A. Ribeiro, O.V. Correa, A.O. Neto, M. Linardi, E.V. Spinacé, Applied Catalysis A: General **372**, 162 (2010).

[12] G. Wang, G. Sun, Q. Wang, S. Wang, J. Guo, Y. Gao, Q. Xin, Journal of Power Sources **180**, 176 (2008).

[13] J. H. Choi, C. M. Johnston, D. Cao, P.K. Babu, P. Zelenay, Journal of Electroanalytical Chemistry **662**, 267 (2011).

[14] K. S. Yao, Y.C. Chen, C.H. Chao, W.F. Wang, S.Y. Lien, H.C. Shih, T.L. Chen, K.W. Weng, Thin Solid Films **518**, 7225 (2010).

[15] C.E. Shaffer, C.Y. Wang, Handbook of fuel cells, Advances in Electrocatalysis, Materials, Diagnostics and Durability, Advanced Diagnostics, Models and Design Low-temperature Fuel Cells (2010).

[16] M. Umeda, K. Sayama and M. Inone, Journal of Renewable and Sustainable Energy

3, 043107 (2011).

[17] S. Arisetty, C.A. Jacob, A.K. Prasad, and S.G. Advani, Journal of Power Sources, **187(2)**, 415 (2009).

[18] Y. Na, F. Zenith, U. Krewer, Energies, **8**,10409 (2015).

[19] F.A. Halim, U.A. Hasran, M.S Masdar, S.K Kamarudin, Journal of clean energy technologies, **1**(4), 292 (2013).

[20] A.S. Gago, J.P. Esquivel, N. Sabate, J. Santander and Nicolas Alonso-Vante, Beilstein Journal of Nanotechnology, **6**, 2000 (2015).

[21] Y.S. Hwang, S.W. Cha, H. Choi, D.Y. Lee, S.Y. Kim, Journal of Fuel Cell Science and Technology **6**(1), 011023 (2008).

[22] B.M. Sudaroli and A. K. Kolar, Fuel cells, **15**(6), 826 (2015).

[23] H.C. Yeh, R.J. Yang, W.J. Luo, J.Y. Jiang, Y.D. Kuan, X.Q. Lin, Journal of Power Sources **196**, 270 (2011).

[24] K.F. Yarn, Y.J. Pan, K.Y. Huang, W.J. Luo, C.N. Chen, Journal of Biobased Materials and Bioenergy **7**, 184 (2013).

[25] C.W. Chung, J.S. Lin, J.S. Wang, W.J. Luo, Z.Y. Chen, C.N. Chen, Digest Journal of Nanomaterials and Biostructures **9**, 681 (2014).

[26] K.F. Yarn, M.C. Hsieh, M.H. Shih, W.J. Luo, Y.H. Kuo, C.N. Chen, Digest Journal of Nanomaterials and Biostructures **9**, 1417 (2014).

[27] Y. D. Kuan, W. J. Luo, C.C. Chang, Y.H. Kuo, G.C. Cheng, C.N. Chen, Digest Journal of Nanomaterials and Biostructures **11**(2), 651 (2016).