

## PERFORMANCE ANALYSIS OF DIRECT METHANOL FUEL CELL WITH CATALYST AND GRAPHENE MIXTURE COATED ON TO FUEL CHANNELS

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This research respectively adds different proportions of Se catalyst, graphene and the mixture of Se catalyst and graphene to PDMS (Polydimethylsiloxane) fuel channel to discuss the effect of graphene powders and the mixture of Se catalyst and graphene on power generation efficiency of DMFCs. Respectively coating Se catalyst and graphene powders to fuel channel of fuel cells can promote the electrochemical reaction and be beneficial to the removal of CO<sub>2</sub> bubbles on anodic flow channel to improve the power generation efficiency of DMFC. However, the adding percentages of Se catalyst and graphene powers have their corresponding critical adding percentage values under different operational conditions. When the adding percentage of Se catalyst and graphene powers equals the critical value, the performance of DMFC can be enhanced to the maximum degree. With the increase in operational temperature, the critical value of adding percentage of Se catalyst and graphene powers will decrease accordingly to avoid the cross over situation of DMFC. But compared with Se catalyst, the effect of coating graphene powers on the fuel channel plate to enhance the power generation of DMFC is not apparent, and its maximum power density can be enhanced by 3%~12%. According to the results, the adding weight percentage of the mixture of Se catalyst and graphene also has the best critical proportion value. Compared with DMFC where the critical value of Se catalyst has been added on the fuel channel plate, adding graphene powders on flow channel will possibly cause the cross over problem of fuel cells. Thus, it is not necessarily conducive to the enhancement of power generation efficiency of DMFC.

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### 1. Introduction

The direct methanol fuel cell (DMFC) using methanol as fuel possesses some characteristics of high chemical stability and security for storage and transportation and is considered to have great potential to replace the traditional power source of portable electronic products. However, some drawbacks for DMFC are necessary to be overcome including methanol crossover poisoning, expensive catalysts, membrane instability, water management and so on. Finding and preparing suitable catalyst for DMFC to boost the stability and durability of membrane and avoid the problem of crossover poisoning are essential for the commercial applications of DMFCs.

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Platinum (Pt) or platinum-based materials are widely use as catalysts of DMFCs due to their high reactivity (Basri et al. [1]). A thin porous layer of Pt was first impregnated in a tubular polymer electrolyte membrane by Qiao et al. using a new plating process [2]. However, CO is generated in the electrochemical reaction, which may poison the Pt catalyst. In order to avoid the poisoning on the Pt catalyst, platinum-alternative catalysts binary or hybrid alloys of Pt are developed 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]). The bimetallic catalyst of PtRu is widely adopted in DMFCs due to its high electrocatalytic activity to methanol oxidation and decrease the overpotential at the anode (Ribeiro et al. [9]). Baglio et al. [4] adopted a low temperature method to prepare modified Pt catalyst with transition metals of Fe, Cu and Co. The DMFC single cell with catalyst of Pt-Fe presented high methanol tolerance and better output performance. Choi et al. [10] prepared a new type catalyst of Se/Ru and found that the performance of DMFC can be greatly improved under high methanol concentrations.

With regard to studies of fuel channel coating with hydrophobic particles and catalysts, Yeh et al. [11] and Yarn et al. [12] 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. Yarn et al. [13] added a specific weight percentage of active carbon catalyst onto anode and cathode channels made of PDMS and indicated that under the same operating conditions, the performances of the DMFCs with an active carbon catalyst can enhance the performance of DMFCs.

Xie et al. [14] reviewed the properties of carbon nanotubes compared with properties of graphene. As can be seen from Table 1 that graphene has a very low resistivity, but it has a high thermal conductivity (in-plane) and also has a high thermal stability, so the material of graphene is feasible to be used as thermal conductor. Graphene structure consisting of several axis layers, generally the axis layers are determined into three axis, i.e. a-axis, b-axis and c-axis. The term of in-plane refers to the combined layer of a-axis and b-axis. The corresponding properties of graphene are listed in Table 1.

Table 1. Properties of graphene. [14]

Property	Value
Specific density	2.26 g/cm <sup>3</sup>
Elastic modulus	1 TPa (in-plane)
Resistivity	50 μΩ cm (in-plane)
Thermal conductivity	3000 W m <sup>-1</sup> K <sup>-1</sup> (in-plane) 6 W m <sup>-1</sup> K <sup>-1</sup> (c-axis)
Thermal expansion	-1 x 10 <sup>-6</sup> K <sup>-1</sup> (in-plane) 29 x 10 <sup>-6</sup> K <sup>-1</sup> (c-axis)
Thermal stability	450-650°C

Pierson [15] investigated the physical properties of graphene and provided some relevance properties of graphene as well. The heat of vaporization of graphene is 355.8-598.2 kJ/mol, while the heat capacity of graphene at 25°C is 0.690-0.719 kJ/kg.K and the standard entropy of graphene at 25°C is 5.697-5.743 J/mol.K.

Along with its unique and typical characteristics, many kinds of graphene are widely used in some applications such metallurgy process, coating, lubricants, batteries, paint production, catalyst in chemical processes, aerospace and carbon brushes. Nakajima [16] investigated the lithium-graphite fluoride (Li/(CF)<sub>n</sub>) battery. The Li/(CF)<sub>n</sub> battery possesses some excellent properties, such as large capacity and energy density, high stability, long storage life and so on, which are derived from the highest electronegativity of fluorine and high stability of graphite fluoride cathode. Chandrashekara and Yadav [17] studied about exfoliated graphite solar thermal coating on a receiver with a Scheffler dish for desalination. They found that the maximum fresh water production is obtained to exfoliated graphite coating on the receiver. Thus, the enhanced productivity of 6.67 l/day with the single stage was achieved with exfoliated graphite coating, 13% more productivity is achieved compared to the case without exfoliated graphite coating. It is

also found that the exfoliated graphite coating has a high thermal stability of 420°C with a Scheffler dish and even the thermal stability can rise up to 700°C when tested in the microwave.

Recently, graphite was applied to fuel cells. Jiang et al. [18] fabricated a microbial fuel cell with an anode electrode made of microporous graphite carbon foam accompanied with polydopamine (PDA) to enhance the performance of the cell. The anode electrode possesses the characteristics of large surface area and improved surface hydrophilicity for bacterial attachment and adhesion. Thus, the microbial fuel cell equipped with MGCF-PDA as anode electrode shows high power density of 1735 mW/cm<sup>2</sup>. Kim et al. [19] evaluated the performance of tubular fuel cells fueled by pulverized graphite. They concluded that the maximum open-circuit voltage of 1.115 V and a power density of 16.8 mW/cm<sup>2</sup> for the studied tubular fuel cell are achieved at 950°C. Moreover, the performance of MGCF could be improved with smaller graphite particle sizes due to activation loss reduction. Zana et al. [20] used the “tool-box approach” studying for fuel cell catalysts by utilizing graphitized carbon (GCB) as supports for polymer electrolyte membrane fuel cells (PEMFCs). The results clearly demonstrated advantages and limits of GCBs as supports for PEMFC catalysts. The major advantage of GCBs as supports for PEMFC catalysts is its significant higher stability and the major limitation is the low number of anchor sites for nanoparticles on graphitized supports. Mansor et al. [21] developed the graphitic carbon nitride as a catalyst support in fuel cell and electrolyzer. It is found that graphitic carbon nitride supports have the potential to better anchor Pt and other metal nanoparticles, which can improve the catalyst dispersion and durability and reduce the catalyst loading and lead to improved catalyst performance.

In the previous studies, it is found that the performance of DMFCs can be enhanced by adding hydrophobic particles and different catalysts onto fuel channels and critical loading values exist for each catalyst under different operational conditions. Especially, the catalyst of Se adding onto fuel channels of DMFCs exhibited high performance and the graphene has the properties of low resistivity, high conductivity and hydrophobicity. Thus, this study aimed to investigate the output efficiency of DMFCs by coating different weight percentages of Se catalyst and graphene on the fuel channels to promote the fuel decomposition reaction and CO<sub>2</sub> bubble removal within the channels and to further enhance the output of the DMFCs. The effects of adding various proportions of Se catalyst and graphene on the output efficiencies of DMFCs were investigated under different operating temperatures and methanol concentrations.

## 2. Experimental

### 2.1 Channel fabrication

In this study, the channels for the DMFCs using PDMS as the substrate were 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 contain four major processes including PDMS preparation, vacuum treatment, injection mold solidification and catalyst coating and turning mold. The detailed fabrication can refer to [11-13]. Figure 1 shows the related injection-molding processes.

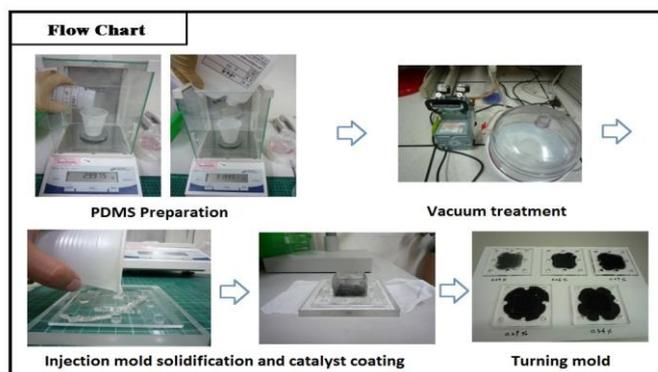


Fig. 1. Injection-molding processes of channel fabrication. [11-13]

## 2.2 Transparent cell

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. The single DMFC composed of bipolar plates and MEA was clamped between two end plates by eight M8 screw joints with a torque of 12 KGF-CM. The MEA is comprised anode and cathode single-sided electrodes used carbon cloth (E-TEK, Type A) and a Nacion 117 membrane, in which the active area is 3.5 cm x 3.5 cm. The material used for the bipolar is 316 stainless steel with thickness of 2.0 mm. The bipolar plate is composed of fuel channels and plate electrode. Serpentine fuel channels were designed in anode and cathode sides in the study, which consisted of a parallel channel with cross section area of 2.0 mm x 2.0 mm. The width of the ribs between the parallels was 2 mm as well. 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 [11-13].

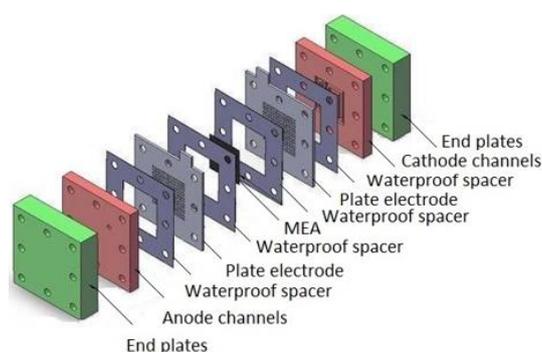


Fig. 2. Exploded view of the transparent DMFC test fixture. [11-13]

## 2.3 Experimental procedure

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. The detailed experimental procedure of the DMFC refer to the literatures [11-13].

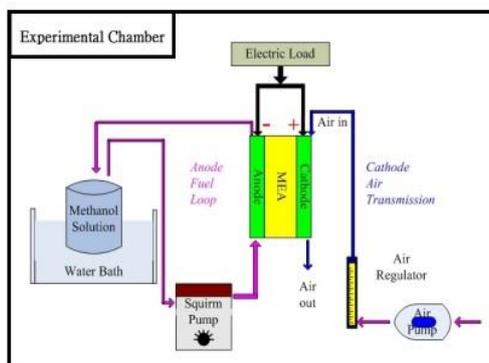


Fig. 3. Schematic diagram of experimental apparatus. [11-13].

### 3. Experimental results and discussion

Table 2 shows that the maximum generation power densities of DMFCs under the operational conditions of different temperatures and fuel concentrations when different proportions of Se catalysts are added to fuel channels of DMFCs. For the methanol percentage concentrations of 5%, 10% and 15%, the corresponding mole concentrations are 1.23M, 2.47M and 3.7M, respectively. It can be seen from the table that under the operational conditions of the same temperature and fuel concentration, the suitably adding Se catalyst to the fuel channel can help the reactant to conquer the required activation energy in electrochemical reaction and accelerate the reactant's cracking reaction to improve the power generation efficiency of DMFCs. However, it can also be seen from the table that the best critical values of adding weight percentages of Se catalyst exist and the proper catalyst adding proportion can be beneficial to the power generation output of DMFCs. When the excessive catalysts are added to fuel channel to make the adding weight percentage of catalyst be greater than the critical percentage value, the power generation output of DMFCs will decrease because the excessive half-reaction resultants  $H^+$  may accumulate on the anode side and cause  $H^+$  cannot infiltrate into the cathode side timely to impede the proceeding of chemical reaction on the anode side. Besides, it can also be found from the table that when the fuel cell's operational temperature is lower, more catalysts are needed to be added to fuel channel to conquer the activation energy required by electrochemical reaction, so the critical value of adding percentage of catalyst is higher. Relatively, when the fuel cell's operational temperature is higher, it is easier to conquer the activation energy required by chemical reaction. Thus, the critical value of adding weight percentage of catalyst will also gradually decrease accordingly. Besides, in order to avoid producing the cross over phenomenon in the fuel cell, the concentration percentage of general fuel is often not greater than 15%. According to the table, under the same operational temperature, the critical value of adding weight percentage of catalyst will not be affected by fuel concentration. It can be known from the table that when operational temperature is 70°C, methanol concentration is 10% and the adding percentage of Se catalyst is 0.09%, the maximum generation power density obtained for this fuel cell is 42.56 mW/cm<sup>2</sup>.

Table 2 Maximum power density of adding Se catalyst to the fuel channels of DMFCs under different temperatures and different methanol concentrations

Adding percentage of catalyst	Operational Temperature								
	50°C			60°C			70°C		
	Methanol concentration			Methanol concentration			Methanol concentration		
	5%	10%	15%	5%	10%	15%	5%	10%	15%
Not added	26.23	27.94	29.17	31.13	32.16	33.33	35.78	36.47	37.15
0.09%	26.91	34.16	32.82	31.91	33.92	34.6	38.28	42.56	41.58
0.14%	36.67	37.05	30.22	32.11	34.53	34.92	37.3	42.47	40.68
0.29%	26.72	38.01	29.65	32.89	35.78	35.12	35.66	33.38	31.44
0.43%	28.41	41.46	35.84	31.35	35.27	34.46	31.25	35.76	33.09
0.57%	28.11	31.3	29.53	30.73	33.28	33.5	30.02	34.14	30.37

(Unit: mW/cm<sup>2</sup>)

The graphene possesses the characteristics of low resistivity, high conductivity and hydrophobicity, so it is often applied to increase the transfer efficiency of electricity and heat. In the anodic electrochemical reactions, it is used to remove the CO<sub>2</sub> resultants from the fuel channels in time, which are produced in fuel channel and to avoid the concentration polarization phenomenon resulting from CO<sub>2</sub> bubbles blockage in the fuel channel and insufficient fuel supply in the reaction area timely. Besides, in order to increase the transmission efficiency between electron and charged ion, the different weight percentages of graphene powders are coated on the surface of the fuel channel. The density of graphene powder is much lighter than PDMS materials, so the concentration of graphene powder in the mixture is quite high in spite of adding a very small amount of weight percentage mixture of graphene. Therefore, in this study, the highest weight percentage of graphene added in fuel channel is 0.15%. In order to know about the

situation of hydrophobic property on the surface of fuel channel when graphene powders are evenly coated on the PDMS fuel channel, this research especially analyzed the contact angle between channel plate and water drop. Figure 4 (a) shows that the contact angle of the case in which graphene powders are not added on fuel channel is about 72.75 degrees. As shown in the figure, the contact angle is defined that, when the water drop is located on the contact surface, the angle from the contact surface inside the water drop to the tangent of the interface between air and water drop is called contact angle. When the contact angle is smaller, it means that the contact surface is inclined to hydrophily; on the contrary, when the contact angle is larger, it means that the contact surface is inclined to the hydrophobic property. In order to measure the contact angle on the fuel channel plate, this research took 9 points evenly on the area covered by the fuel channel plate and then measured the contact angle of each position respectively. Lastly, the average of the values measured for the 9 positions was regarded as the contact angle of this fuel channel plate. In this research, the difference between the measurement values of the contact angle obtained at the 9 positions on the fuel channel plate is less than 2%, indicating that this graphene was evenly distributed and coated on flow path plate. Figure 4 (b) shows that when 0.15% graphene powders are added on PDMS fuel channel plate, the contact angle of the surface of fuel channel plate can be increased to be 100.76 degrees, showing that coating graphene powders on fuel channel plate will make the hydrophobic property of fuel channel plate more apparent. Table 3 shows the contact angle distribution state when the different proportions of graphene powders are coated on the fuel channel plate. According to the table, with the increase in adding proportion of graphene, the contact angle also increases gradually. The contact angle has gradually increased from 72.75 degrees (not adding graphene powders) to 100.76 degrees (adding 0.15% graphene powders).

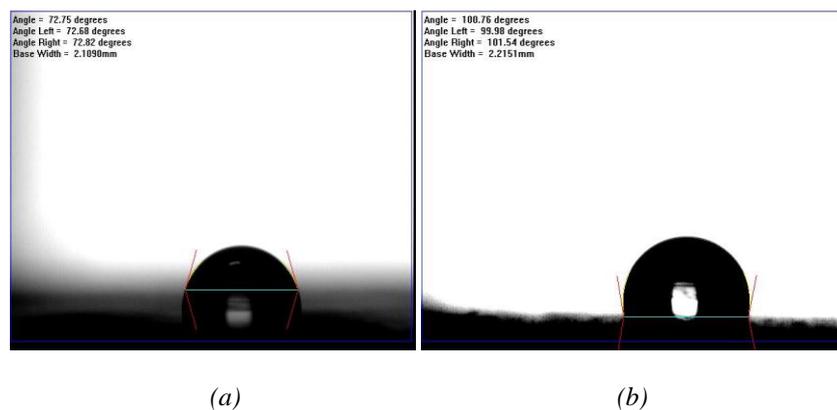


Fig. 4. Contact angle of water drop on fuel channel plate where different proportions of graphene are added

Table 3 Contact angle distribution where different proportions of graphene are added

Graphene concentration on fuel channel plate	0%	0.001%	0.01%	0.05%	0.15%
Contact angle (degrees)	72.75	84.52	89.49	91.84	100.76

Table 4 shows that when different proportions of graphene are coated on the flow path plate of fuel cells, the maximum generation power densities of DMFCs under different temperatures and different fuel concentrations can be gained. It can be seen from the table that properly adding graphene powders on the fuel channel plate under the operational conditions of the same temperature and fuel concentration can be conducive to removing CO<sub>2</sub> resultants in the fuel channel and accelerating the cracking reaction of resultants to improve the power generation performance of DMFCs. However, it can also be seen from the table that the best critical values of the adding weight percentage of graphene exist and the proper adding proportion of graphene is conducive to the output of electricity generation power of DMFCs. When the excessive graphene is added on the fuel channel plate, it makes the adding weight percentage of graphene be greater than critical percentage values; the excessive graphene powders with hydrophobic

property will also cause the concentration polarization phenomenon where the fuels are not easy to be transmitted to the fuel channel, so the output of power generation of DMFCs will conversely decrease. Besides, it can also be found from the table that when the operational temperature of fuel cells is lower, more graphene is needed to be added on the flow path plate to remove the CO<sub>2</sub> bubbles accumulated on the fuel channel, so the critical adding percentage of catalyst is higher. Relatively, when the operational temperature of fuel cells is higher, it is easier to remove the CO<sub>2</sub> bubbles from the flow path. Therefore, the critical value of adding weight percentage of graphene will also gradually decrease accordingly. Besides, in order to avoid producing cross over phenomenon in the fuel cells, the concentration percentage of the general fuel concentration is often not greater than 15%. Based on the table, under the same operational temperature, the critical values of adding weight percentage of graphene will not be affected by fuel concentration. Based on the table, it can be seen that when the operational temperature is 70°C, methanol concentration is 15% and a smaller amount of graphene is added, the maximum electricity generation power for this fuel cell is 37.15 mW/cm<sup>2</sup>. Table 4 shows the increment percentages of maximum power density of DMFCs when different weight percentages of graphene powders are coated on the fuel channel plate of DMFCs. It can be seen from the table that coating the graphene powders on the fuel channel plate of DMFCs can make the maximum power density of DMFCs improve by 3~12%. When the operational temperature of DMFCs is lower, the effect of coating graphene powders on the fuel channel plates to improve the power generation efficiency of DMFCs is more apparent.

Table 4 Maximum power density under different temperatures and methanol concentrations by coating graphene on the fuel channels plate of DMFCs

Adding percentage	Operational Temperature								
	50°C			60°C			70°C		
	Methanol concentration			Methanol concentration			Methanol concentration		
	5%	10%	15%	5%	10%	15%	5%	10%	15%
Not added	26.23	27.94	29.17	31.13	32.16	33.33	35.78	36.47	37.15
0.001%	28.19	28.41	29.63	32.16	33.75	35.19	33.09	34.53	35.93
0.01%	29.51	30.12	32.06	31.57	31.86	32.64	32.57	33.26	35.19
0.05%	28.87	29.22	30.86	29.66	30.39	31.59	30.44	31.13	31.91
0.15%	25.84	26.18	26.87	26.16	26.77	27.89	25.4	26.69	27.11

(Unit: mW/cm<sup>2</sup>)

Table 5 Increment percentages of maximum power densities by coating different weight percentages of graphene powders on the flow path plates of DMFCs

Adding percentage	Operational Temperature								
	50°C			60°C			70°C		
	Methanol concentration			Methanol concentration			Methanol concentration		
	5%	10%	15%	5%	10%	15%	5%	10%	15%
0.001%	7.5	1.7	1.6	3.3	4.9	5.6	-7.5	-5.3	-3.3
0.01%	12.5	7.8	9.9	1.4	-0.9	-2.1	-9.0	-8.8	-5.3
0.05%	10.1	4.6	5.8	-4.7	-5.5	-5.2	-14.9	-14.6	-14.1
0.15%	-1.5	-6.3	-7.9	-16.0	-16.8	-16.3	-29.0	-26.8	-27.0

(Unit: %)

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 graphene coated and  $E_{RI}$  is the maximum power density of a DMFC without graphene coated.

It can be known from the results of Table 2 and Table 4 that adding Se catalyst or graphene powders on the fuel channel plate can help to improve the power generation of DMFCs. However, both of them have the best critical values of adding weight percentage under the specific operational conditions. Regarding to the critical value of adding weight percentage, excessive and insufficient catalysts and graphene powders coating onto the fuel channels will be harmful to the power generation efficiency of DMFCs. In order to better improve the power generation efficiency of methanol fuel cell, this research investigated the effect of mixture of the best adding weight percentage of the corresponding Se catalyst and graphene powders under different operational conditions on the power generation efficiency of DMFCs. Under the operational temperatures of 50°C, 60°C and 70°C, the best adding weight percentage of Se catalyst is 0.43%, 0.29% and 0.09% respectively, and the best adding weight percentage of graphene powders is 0.01%, 0.001% and 0.0005% respectively. Therefore, the best weight percentages of Se catalyst and graphene powder are mixed and investigated its power generation efficiency under the same operational temperature. From Table 6, it can be seen from the table that the adding weight percentage of Se catalyst and graphene mixture also has the best critical percentage value. Under the specific operational temperature, the critical percentage value of mixture happens to be the mixture of best percentage values of the separate Se catalyst and separate graphene powders under the corresponding operational temperature. The proper mixture adding proportion will be conducive to the power generation output of DMFCs; when the excessive mixtures are added on the fuel channel plate, it will also cause concentration polarization and activation polarization phenomena to the cells due to the excessive electrochemical reaction and surface characteristic of excessive hydrophobic property. Thus, the output of electricity generation power of fuel cells will conversely decrease. Moreover, it can be found from the table that when the operational temperature of fuel cell is lower, more mixtures are needed to be added on the fuel channel plate to conquer the activation energy required and remove the CO<sub>2</sub> bubbles accumulated in flow channels, so the critical adding percentage value of mixtures is higher. Relatively, when the operational temperature of fuel cells is higher, electrochemical reaction is easier to be triggered and CO<sub>2</sub> bubbles are easier to be removed from the fuel channels. Thus, the critical value of adding weight percentage of mixtures will also gradually decrease accordingly. It can be seen from the table that the maximum generation power density is 43.59 mW/cm<sup>2</sup> when the operational temperature is 70°C, methanol concentration is 10%, and the percentage for graphene powders and Se catalyst is respectively 0.0005% and 0.09%.

Table 6 Maximum power density under the different temperatures and different methanol concentrations by coating the different weight percentages of mixtures on the fuel channel plates of DMFCs

Adding percentage of catalyst	Operational Temperature								
	50°C			60°C			70°C		
	Methanol concentration			Methanol concentration			Methanol concentration		
	5%	10%	15%	5%	10%	15%	5%	10%	15%
Not added	26.23	27.94	29.17	31.13	32.16	33.33	35.78	36.47	37.15
Graphene 0.0005%+Se 0.09%	27.11	31.76	30.69	30.51	32.4	35.78	39.45	43.59	42.15
Graphene 0.001%+Se 0.29%	26.86	37.22	32.47	33.28	34.65	36.24	32.72	33.33	31.42
Graphene 0.01%+Se 0.43%	28.24	39.36	33.45	31.52	33.09	29.27	31.57	35.41	33.58

(Unit: mW/cm<sup>2</sup>)

Table 7 shows the increment percentages of maximum power densities when different mixtures of Se catalysts and graphene powders are added on fuel channel plate in comparison to the case without mixture added in fuel channels. It can be seen from the table that when the operational temperature is 50°C and Se catalyst and graphene powders are mixed by the best

weight percentage, no matter what the concentration of the methanol fuel is, it can achieve the better increment percentage of maximum power density and its maximum increment percentage of power density can reach up to 40.9%. Similarly, when the operational temperature is 60 and 70°C, and Se catalyst and graphene powders are mixed by the best weight percentage, no matter what the concentration of the methanol fuel is, it can achieve the better increment percentage of maximum power density and its maximum increment percentages of maximum power densities can lie between 7% and 20%.

Table 8 shows the increment percentages of maximum power densities of DMFCs by adding the mixture of Se catalyst and graphene powders on fuel channel plate in comparison to the cases by adding the same percentages of Se catalyst in Table 2 to understand the effect of the adding of graphene powders on the power generation performance of DMFCs where Se catalyst has been added on the fuel channel. It can be found from the table that graphene powers can help to remove the CO<sub>2</sub> bubbles generated in anodic fuel channel to improve the power generation efficiency of DMFCs. But, the DMFC of the best percentage of Se catalyst has been added on fuel channel plate and then graphene powders are added on fuel channel plate, which can not necessarily help to improve the power generation efficiency. Additional graphene powders are added on the fuel channel of the critical values of this Se catalyst which may cause the fuel cross over problem of fuel cells, it is not necessarily conducive to the enhancement of power generation efficiency of DMFC.

*Table 7 Increment percentages of maximum power densities by coating different weight percentage mixtures on the fuel channel plates of DMFCs, compared with the DMFC not adding catalyst*

Adding percentage of catalyst	Operational Temperature								
	50°C			60°C			70°C		
	Methanol concentration			Methanol concentration			Methanol concentration		
	1.23M	2.47M	3.70M	1.23M	2.47M	3.70M	1.23M	2.47M	3.70M
0.0005%+Se0.09%	3.4	13.7	5.2	-2.0	0.7	7.4	10.3	19.5	13.5
0.001%+Se0.29%	2.4	33.2	11.3	6.9	7.7	8.7	-8.6	-8.6	-15.4
0.01%+Se0.43%	7.7	40.9	14.7	1.3	2.9	-12.2	-11.8	-2.9	-9.6

(Unit: %)

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 mixture of graphene and Se catalyst coated and  $E_{RI}$  is the maximum power density of a DMFC without graphene and Se catalyst coated.

*Table 8 Increment percentage of maximum power densities by coating the mixtures on the fuel channel plates of DMFCs, compared with the direct methanol fuel cell not adding catalyst*

Adding percentage of catalyst	Operational Temperature								
	50°C			60°C			70°C		
	Methanol concentration			Methanol concentration			Methanol concentration		
	1.23M	2.47M	3.70M	1.23M	2.47M	3.70M	1.23M	2.47M	3.70M
0.0005%+Se0.09%	0.7	-7.0	-6.5	-4.4	-4.5	3.4	3.1	2.4	1.4
0.001%+Se0.29%	0.5	-2.1	9.5	1.2	-3.2	3.2	-8.2	-0.1	-0.1
0.01%+Se0.43%	-0.6	-5.1	-6.7	0.5	-6.2	-15.1	1.0	-1.0	1.5

(Unit: %)

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 mixture of graphene and Se catalyst coated and  $E_{RI}$  is the maximum power density of a DMFC with Se catalyst coated.

#### 4. Conclusions

This research respectively adds different proportions of Se catalyst, graphene and the mixture of Se catalyst and graphene to PDMS (Polydimethylsiloxane) fuel channel to discuss the effect of graphene powders and the mixture of Se catalyst and graphene on power generation efficiency of DMFCs. Respectively coating Se catalyst and graphene powders to fuel channel of fuel cells can promote the electrochemical reaction and be beneficial to the removal of CO<sub>2</sub> bubbles on anodic flow channel to improve the power generation efficiency of DMFC. However, the adding percentage of Se catalyst and graphene powers has the critical adding percentage value. When the adding percentage of Se catalyst and graphene powers equals the critical value, the performance of DMFC can be enhanced to the maximum degree. When the adding percentage of Se catalyst and graphene powers is greater than the critical value, the power generation efficiency of DMFC will decrease with the increase in adding percentage. This critical value of adding percentage will be affected by fuel's operational temperature, but the effect of fuel concentration on performance of DMFCs is not apparently. With the increase in operational temperature, the critical value of adding percentage of Se catalyst and graphene powers will decrease accordingly to avoid the cross over situation of DMFC. But compared with Se catalyst, the effect of coating graphene powers on the fuel channel plate to enhance the power generation of DMFC is not apparent, and its maximum power density can be enhanced by 3%~12%.

Under different operational conditions, the corresponding critical adding weight percentages of Se catalyst and graphene powers are mixed to further discuss the performance of DMFC. According to the results, the adding weight percentage of the mixture of Se catalyst and graphene also has the best critical proportion value. Under the specific temperature, the critical proportion value of the mixture happens to be the mixture of critical percentage value of separate Se catalyst and separate graphene powers under this operational temperature. When the operational temperature of fuel cells is higher, it is easier to trigger to electrochemical reaction and remove the CO<sub>2</sub> bubbles from the flow path and the critical value of adding weight percentage of the mixture will also gradually decrease accordingly. Compared with DMFC where the critical value of Se catalyst has been added on the fuel channel plate, adding graphene powers on flow channel will possibly cause the cross over problem of fuel cells. Thus, it is not necessarily conducive to the enhancement of power generation efficiency of DMFC.

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