CrossMark

ORIGINAL PAPER

Experimental studying of the effect of active area on the performance of passive direct methanol fuel cell

R. Hashemi[1] · S. Yousefi[2] · M. Faraji[3]

Abstract This work experimentally studies the effect of the size and shape of active area on the performance of passive direct methanol fuel cell. The obtained results show that the cell performance strongly depends on the size and shape of active area. Experimental results of this study also demonstrate that the cell performance improves with an increase in the size of active area. Increasing the size of active area also leads to a lower internal resistance, lower OCV, and higher operating temperature. Furthermore, it was found that the smallest active area (4 cm^2) produced the longest stable discharging voltage (about 16.5 h). This study also reveals that the square active area has the best performance and the highest power density compared to the rectangular and circular active areas. Finally, the results prove that the place of applying the clamping force is an important parameter that should be considered in the cell design.

Keywords Passive direct methanol fuel cell · Active area · CO$_2$ bubbles · Operating temperature · Clamping system

✉ S. Yousefi
sasan_6262@yahoo.com; syousefi@mail.kntu.ac.ir

1 School of Mechanical Engineering, Iran University of Science and Technology, Tehran, Iran

2 Faculty of Mechanical Engineering, K. N. Toosi University of Technology, Tehran, Iran

3 Faculty of Mechanical Engineering, University of Applied Science and Technology, Babol, Iran

Introduction

In recent years, there have been notable interests on the use of fuel cells as a substitution for fossil fuels in electrical power generation. They provide a green, noiseless, and renewable means of producing power [1–10]. There are different types of fuel cell such as solid oxide (SOFC), direct liquid (DLFC), proton exchange membrane (PEMFC), molten carbonate (MCFC), and alkaline fuel cell (AFC) which is fueled with different fuels such as methanol, ethanol, and acids. Among all of these famous and recognized fuel cells, the direct methanol fuel cells (DMFCs) have received much attention because of their high theoretical energy density, low weight, compactness, easy recharging, simplicity, rapid start-up, using liquid fuel (methanol), being low pollution and green, and working under ambient conditions [3–15]. DMFC is an electrical power generator that uses methanol as a hydrogen source and convert the electrochemical energy into electrical energy directly by using aqueous or vaporized methanol as a fuel at the anode and air or pure oxygen as the oxidant at the cathode [2–23]. Based on fuel solution supply, DMFCs are classified into two major types, which are known as passive and active DMFCs [23–35]. The difference between these two types consists of pumping and delivering fuel to the reaction sites and electrical controls [3–9]. Contrary to active DMFCs, passive DMFCs do not have any ancillary devices such as pump or blower, so the parasitic energy and power losses, because of such external instruments, eliminate significantly. In passive DMFC, the fuel supply relies on the diffusion from a built-in fuel reservoir, while ambient air supplies the required oxidant through natural convection [6]. Through these characteristics, the passive DMFCs have recognized as a promising power source for portable applications [3–9]. In addition, some manufacturers combine the advantages of passive and active systems together, which are a combination

Springer

between passive and active type structures (semi-active (or semi-passive) DMFC).

In recent years, several researchers have studied passive DMFCs under a specific and constant active area. For example, S. Yousefi et al. [3–6] studied a single cell passive DMFC with a 100-cm^2 active area for the first time. They studied the effect of various operational parameters on the performance of passive DMFC single cell such as environmental conditions, open circuit voltage, sealing design, methanol concentration, and end frame design. Chang Hyun Lee et al. [10] fabricated a 10-cm^2 active area passive DMFC with a sulfonated polyimide–silica nanocomposite (SPI–SiO$_2$-1) membrane with high-proton conductivity, low-methanol permeability, and thin thickness compared with conventional membranes. N. Paust et al. [11] fabricated a portable passive DMFC with a 2.6-cm^2 active area that continuously run for 40 h in all orientations. H. Gharibi et al. [12] prepared carbon-supported Pd and Pd$_x$Co alloy electro-catalysts with different Pd$_x$Co atomic ratios by a fertilization synthesis method at room temperature by ethylene glycol reduction. The reported active area for the experiments was 4.75 cm^2. Takahiro et al. [13] designed and built a pumpless DMFC with a 36-cm^2 active area. Tang et al. [14] studied the effect of various structural features on the performance of a passive air-breathing DMFC with a 9-cm^2 active area. They considered three factors in their researches: different open ratios, different diffusion layers, and different membranes. Ahmad et al. [15] also developed a micro DMFC single cell with a 4-cm^2 active area successfully. S. Kamarudin et al. [16] reduced the cost of micro DMFCs for portable applications. They optimized the design of DMFC by combining a multi-physics model that consists of manufacturing features, costs, and species conservation with either single cell or stacking using a non-linear constrained optimization algorithm. In addition, they proved that the cell voltage affects the design features while the current is influenced by the active area of fuel cell. Finally, they proposed total active areas of 800, 100, 4, 9, and 5 cm^2 for the laptop, hand phone, calculator, laser pointer, and mini fan applications, respectively.

J.G. Liu et al. [20] studied the effect of methanol concentration on the performance of a passive DMFC with a 4-cm^2 active area. They reported that the cell performance was improved substantially with an increase in methanol concentration. N.K. Shrivastava et al. [2, 29] examined the feasibility of the stainless steel wire mesh as current collector in a passive direct methanol fuel cell with a 25-cm^2 active area. They also investigated the effect of diffusion layer compression on the performance of passive direct methanol fuel cell (DMFC) under a constant active area [30]. Their study revealed that the cell performance can be enhanced drastically (200 to 340 % higher) by using the optimum diffusion layer compression.

R. Chen et al. [31] proposed a membrane electrolyte assembly (MEA), in which the conventional cathode gas diffusion layer (GDL) was eliminated while utilizing a porous metal structure for transporting oxygen and collecting current. Their results showed that the passive DMFC with the new MEA (with 4 cm^2 active area) yielded better and much more stable performance than did the cell having the conventional MEA.

A.M. Ali et al. [32] studied the effect of the ionomer content in the catalyst layers of both the anode and the cathode with the black catalyst on the performance of a passive DMFC. R. Chen et al. [33] investigated the effect of cell orientation on the performance of a passive DMFC with 4 cm^2 active area. Their experimental results showed that the vertical orientation always yielded better performance than did the horizontal orientation. J.G. Liu et al. [34] also studied the effect of membrane thickness on the performance and efficiency of a passive DMFC with 4 cm^2 active area. In [35], various pretreatment methods have been studied in order to investigate their effects on the performance of passive DMFCs. The reported active area for the experiments was 6 cm^2. The results proved that the cell performance is influenced by the pretreatment conditions, which included exposure of the MEA either to water or to a methanol solution prior to use.
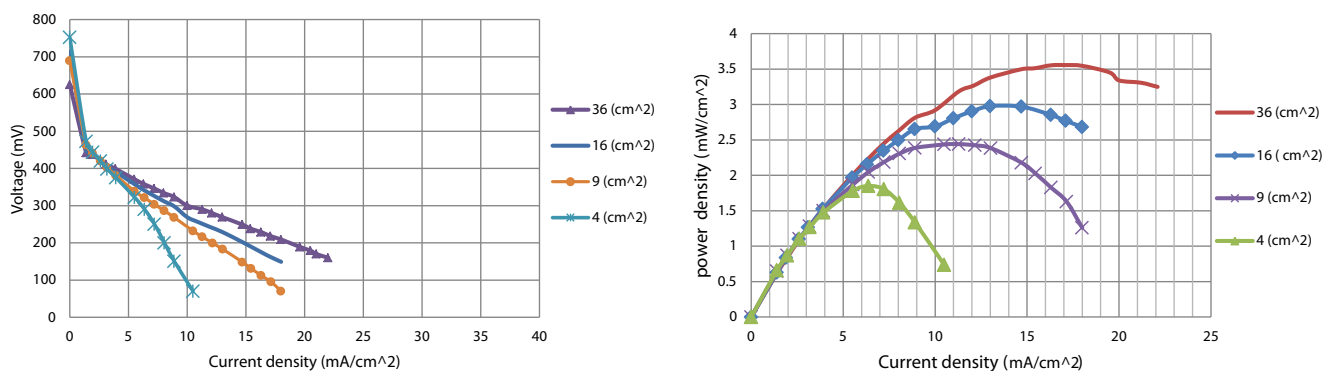
Fig. 1 Effect of the size of active area on the performance of passive DMFC single cell with a 4-M fuel concentration under surrounding condition
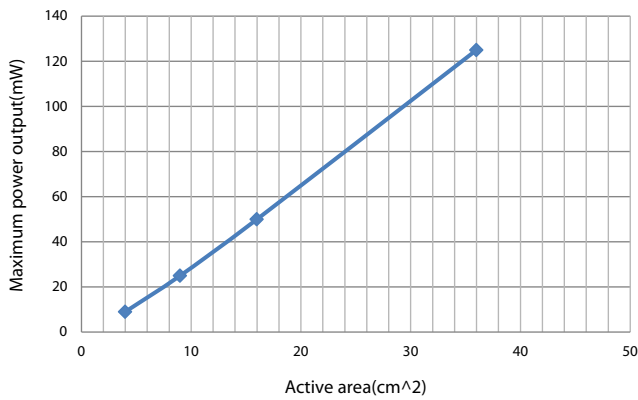
Fig. 2 The variations of cell maximum power output with different active areas under a 4-M fuel solution

Despite of all those mentioned studies and other published researches, the effect of the size and the shape of active area on the performance of passive DMFCs has not been studied comprehensively up to now [1–30]. The size and the shape of active area are important factors that have significant effects on the cell design, cell performance, total weight, and total cost, especially in portable applications [5]. To address the current issues, the main purpose of this research is to investigate the effect of the size and the shape of active area on the performance of passive DMFC single cells. At the end, the effect of the location of applying clamping force on the performance of passive DMFC has been determined experimentally.

Experimental procedures

Membrane electrolyte assembly

The membrane electrolyte assembly (MEA) of passive DMFC is composed of an anode diffusion layer (ADL), an anode catalyst layer (ACL), a polymer electrolyte membrane (PEM), a cathode diffusion layer (CDL), and a cathode catalyst layer (CCL). A conventional Nafion 117 with a thickness of 175 μm was employed in the research. The pretreatment approach included boiling the membrane in 5 vol.% H_2SO_4 at 60 °C and then washing it in deionized water for 1.5 h. Then, the pretreated membrane was kept in the deionized water before fabricating the desired MEA. Then, single-side ELAT electrodes from ETEK were used in both anode and cathode sides, where type (A) ETEK carbon cloth, due to its satisfactory performance in passive DMFCs, was used as the backing support layer with a 30 wt.% PTFE wet-proofing treatment. It should be noted that the same diffusion layers were used in the both electrodes. The catalyst loading on both cathode and anode sides were 4.0 mg cm^{-2}. Furthermore, 0.8 mg cm^{-2} dry Nafion® ionomer was applied onto the surface of anode and cathode electrodes. Finally, we formed the MEAs (with 4, 9, 16, 25, and 36 cm^2 active areas) by hot-pressing at 145 °C and 5 MPa for about 3 min. Prior to experiments, to improve the proton conductivity of PEM and electrodes, the MEAs were hydrated by filling the fuel reservoir with 1 wt.% methanol solution and allowing the cell to stand for about 9 h. Before each test, the MEA was activated under a constant load for about 7 h and to eliminate the effect of previous test, the MEA was washed in distilled water. In addition, to study the effect of the shape of an active area, we employed three different shapes (circular, square, and rectangular) of an active area with the same size (25 cm^2). More details about the MEA can be found elsewhere [10–19].

Single cell design

A single cell passive DMFC is composed of a built-in fuel reservoir, an anode current collector (ACC), a membrane electrode assembly (MEA), a cathode current collector (CCC), and/or endplates that act as a fixture [20]. The MEA is

Fig. 3 The variations in the cell operating temperature with a 4-M methanol solution and under 250 (mA) constant load (ambient condition)
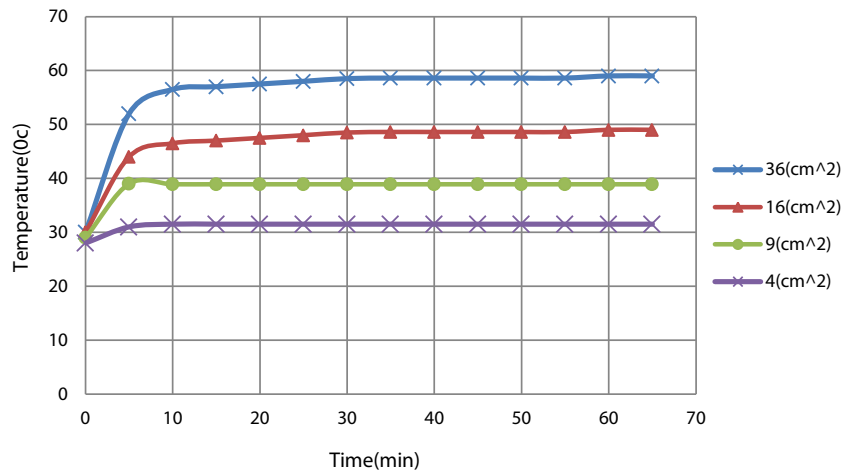
Fig. 4 The effect of the size of active area on the values of open circuit voltages with a 4-M methanol solution
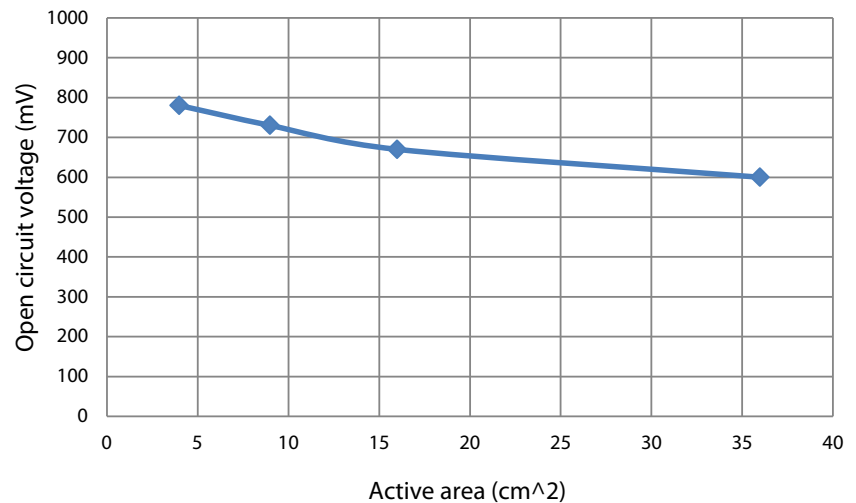
sandwiched between the anode current collector and the cathode current collector. Both the cathode and anode current collectors must have high electrical conductivity, proper mechanical strength, and low thermal conductivity [5, 6, 21–23]. To address current issues, in this study, we employed 304-L stainless steel plates with 1.5 mm thickness as the current collectors. A plurality of holes with a diameter of 2 mm was drilled inside the active area of current collectors, which finally resulted in an open ratio of 41 %. It is important to note that the shape and the open ratio of the current collectors were same in all of the experiments. To reduce the contact resistance, the current collectors were coated with a gold layer (with a thickness of 500 μm). In this study, for the convenience of visualization, transparent acrylic plexiglas with a thickness of 35 mm was milled and polished to build the anode and cathode end plates. The use of this transparent material as the end plates allowed the monitoring and visualization of the internal activity of the fuel cell and provided sufficient rigidity to support and fix the entire cell. A built-in reservoir with a volume of 36 mL was machined on one side of the anode end plate for methanol solution storage. It is important to mention that the same fuel tank capacity (36 mL) has been used in all the single cell experiments. Three small holes with 1 mm diameter were drilled on the upper side of the fuel reservoir for solution injection and CO_2 bubbles exhaust. In addition, a hollow window was cut in the cathode end frame (cathode window) to expose the cathode compartment to the surrounding air. We used silicone rubber gasket to seal the gaps between the current collectors and the end plates, while an in-house PTFE film served as the gasket between the current collectors and the edges of the MEA. Sixteen M6 screw bolts with an appropriate clamping torque (10 Nm) fixed and clamped the entire fuel cell. The same 10-Nm clamping torque was used for all of the active areas and experiments.

Experimental set-up test conditions

We employed an Arbin electrical load system interfaced to a computer to control the condition of discharging and record the polarization curves. For each set of obtained polarization curves, a waiting period (after fuel injection) about 50 s after fuel injection was used to reach stable condition for measurements. We measured the cell internal resistance by BT2000 built-in function. The internal resistance of the cell was the average of 35 applied pulses. We also used a K-type thermocouple to control and measure the cell temperature. We installed the sensor of this thermocouple in the fuel solution reservoir to control and record the cell operating temperature. This means that the internal cell temperature was determined by measuring the temperature of the fuel reservoir, as an indicator for cell operating temperature. Given the methanol concentration at the beginning and end of each test and the total mass of methanol solution consumed, the mass of methanol and the mass of water that were removed from the methanol reservoir during the test were calculated. By integrating the current density for a given 14-hour test, the amount of methanol reacted at the anode was calculated. The difference between the total mass of methanol removed from the methanol reservoir and the mass of methanol reacted at the anode is the mass of methanol lost due to methanol crossover. We repeated these steps to calculate the mass of water reacted at the anode and the mass of water lost due to water crossover.

Table 1 The internal resistance of the fabricated passive DMFC with different active areas

Active area (cm^2)	4	9	16	36
Internal resistance (mΩ)	86	80	77	70

Fig. 5 A statistical overview about the usage percent of different active areas that have been used in fabricated passive DMFCs up to now
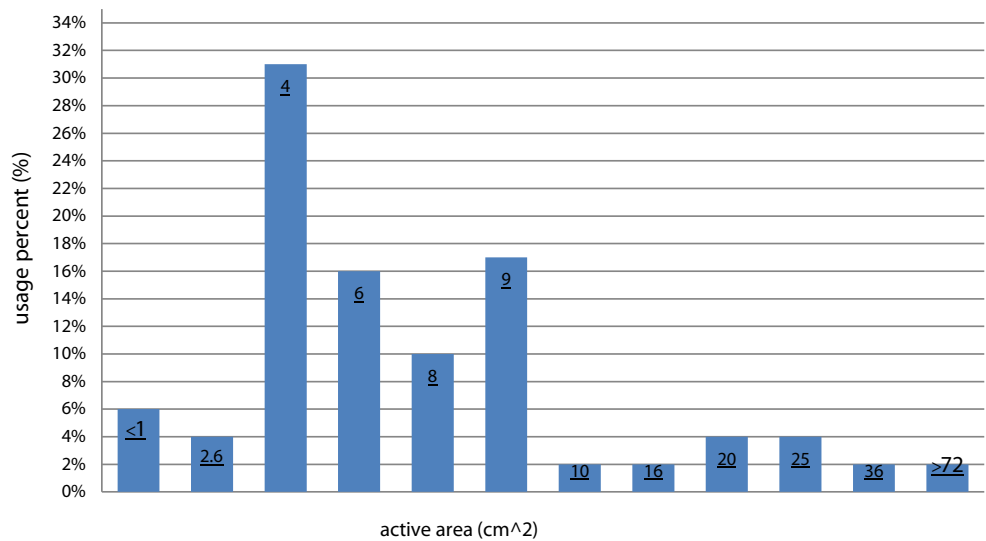
Results and discussions

### The effect of the size of active area on the performance of passive DMFC

Besides design features and cost considerations, active area has significant effects on the performance of passive DMFCs because all the electrochemical reactions occur on the surface of active area. In order to study the effect of active area, we conducted various tests and examined the performance of passive DMFC single cell under different active areas. There are different shapes of active area that we studied, some of them such as square, rectangular, and circular [25]. The shape of active area strongly depends on the required dimension and the size of fuel cell system.

To study the effect of active area on the performance of passive DMFCs, we examined the performance of the fabricated cell with 4, 9, 16, and 36 cm^2 active areas and a fuel concentration of 4 M, under ambient condition (25 °C and 1 atm). In the experiments, square active areas (4, 9, 16, and 36 cm^2) were used. Figure 1 shows the cell performance with different active areas (4, 9, 16, and 36 cm^2). As shown in Fig. 1, the cell performance decreases with an increase in the size of active area.

The electrochemical evaluation of each single cell performance (in Fig. 1) showed that the passive DMFC with larger active areas had good electrochemical performance. As shown in Fig. 1, it is obvious that the cell power density increases by increasing the size of active area from 4 to 36 cm^2. Therefore, a maximum power density of 3.5 mW cm^{-2} was obtained by a 36-cm^2 active area, which was the largest active area. It should mention that in passive DMFCs, voltage affects the design parameters for the manufacturing purposes while the current is influenced by the size of active area [16].

Fig. 6 Effect of the size of active area on the mass of water lost due to crossover in the fabricated fuel cell
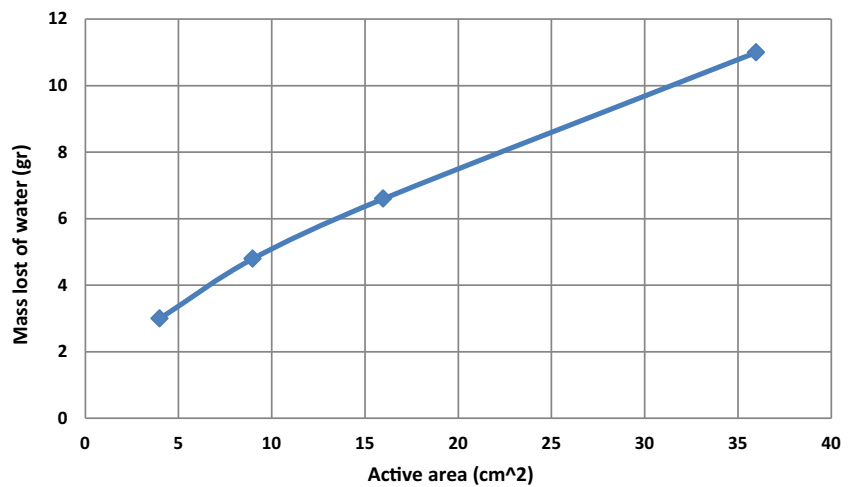
Table 2 The duration of stable discharging voltage of the cell with different active areas

Active area (cm^2)	4	9	16	36
Stable discharging voltage duration (h)	16.5	15.7	14	11

As depicted in Fig. 2 too, decreasing the size of active area lead to a decrease in the maximum power output of the fabricated passive single cell. The drop in power output is mainly due to a decrease in the size of active area as well as a drop in the cell operating temperature. Because in larger active areas the places where the exothermic reactions occur are larger, more heat is generated during the cell operation, and as a result, the cell performance improves significantly. To prove this claim, studying the variations of the cell operating temperature under different active areas will be necessary. Hence, at a given constant load (250 mA), we studied the variations of cell operating temperature with a 4-M methanol solution. The obtained results are shown in Fig. 3. As shown in Fig. 3, the cell operating temperature increases with increasing in the size of active area from 4 to 36 cm^2. This behavior can relate to the variations of current density in different active areas (current density is the current per unit area of the surface). Under a given constant load (250 mA), larger active areas have a lower current density compared to smaller active areas. For example, by applying 250 mA of constant load in the cell with a 36-cm^2 active area, current density will be about 4.2 mA cm^{-2} and in the cell with a 25-cm^2 active area, current density will be 6 mA cm^{-2}. Current density has an important effect on methanol crossover and water electro-osmotic drag. The reactants' concentration at the catalyst surface depends on current density. Higher current density leads to a lower surface concentration. The surface concentration reaches zero when the rate of consumption exceeds the diffusion rate, and the reactant is consumed faster than it can reach the surface [26]. If the current density is smaller, the methanol will be consumed slowly. Therefore, the local concentration at the membrane will be higher, which finally results in more methanol crossover. As a result, in large active areas, because of a smaller current

density, a more intense methanol crossover occurs. The exothermic reaction, which occurs between the permeated methanol and oxygen on the cathode catalyst layer, produces more heat, which finally leads to a higher operating temperature. The higher operating temperature results in a better electrochemical kinetics of methanol oxidation and oxygen reduction reactions, which finally lead to a better cell performance, as shown in Figs. 1 and 2. To prove this claim, we investigated the OCV variations at different active areas experimentally because the open circuit voltage (OCV) value reflects the methanol crossover degree in passive DMFC.

Figure 4 illustrates the variations of OCV value under different active areas. As shown in Fig. 4, the OCV value decreases with increasing in the size of active area. Thus, as the OCV value reflects the methanol crossover degree, we can infer that in larger active areas, a higher rate of methanol crossover occurs. This higher rate of methanol crossover results in a higher operating temperature (see Fig. 3). As discussed earlier, this higher operating temperature leads to the improved electrochemical kinetics of methanol oxidation and oxygen reduction reactions, which finally result in better cell performance. The internal resistance of fuel cell is another important parameter that has a key effect on the cell performance. Therefore, we evaluated the internal resistance of the cell under different active areas. The obtained results are indicated in Table 1.

As indicated in Table 1, the internal resistance decreases with increasing the size of active area. This fact is completely compatible with the achieved results shown in Figs. 1, 2, 3, and 4. Although the cell performance and power output increased by increasing the size of active area, previous literatures have reported that small active area has its own advantages such as slower charge transfer resistance, lower flooding, uniform fuel distribution, more efficient current collecting, lower cost of machining and manufacturing, and also total less dimension and weight [5, 10, 26]. A statistical overview about the usage percent of different active areas, which have been used in passive DMFCs from 2004 to 2014, is shown in Fig. 5. In Fig. 5, micro size active areas are depicted as <1 cm^2. As mentioned earlier and as shown in
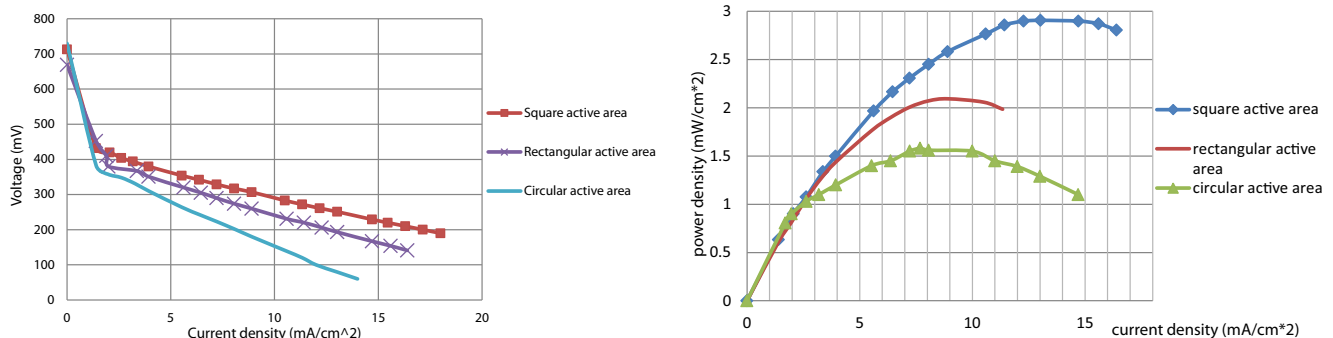
Fig. 7 Effect of the shape of active area on the performance of passive DMFC single cell

Fig. 8 Effect of the shape of active area on the operating voltage under a 250-mA constant load
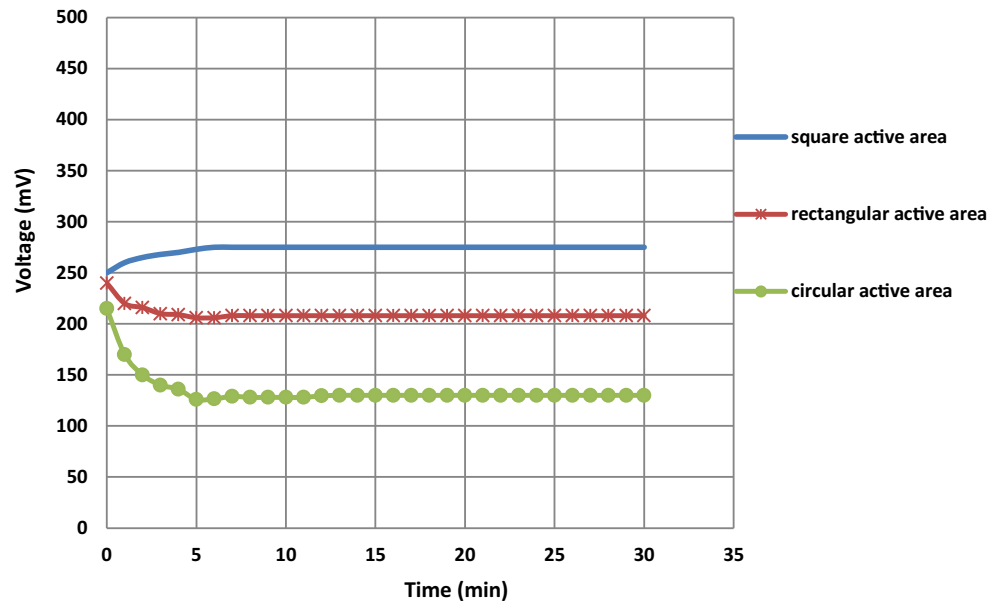

Fig. 5, we can conclude that active areas less than 10 cm^2 due to cost and weight considerations have more applications than larger active areas.

As discussed earlier, although larger active area leads to higher power output, there are major challenges that limit their application. In large active areas, the higher costs of machining and manufacturing are one of those challenges. Other important challenges include serious water flooding and intense CO_2 generation (due to more electrochemical reactions). During the cell operation, water can accumulate as a form of the water droplet at cathode side. The liquid water blocks the pores of cathode diffusion layer and therefore obstructs the oxygen transport. The insufficient oxygen at cathode catalyst layer may cause decrement in the cell performance [27]. In larger active areas, because of larger reaction surfaces and more electrochemical reactions, large amounts of CO_2

bubbles are generated at the anode catalyst layer. The CO_2 bubbles act as a gas barrier and block the fuel supply to the anode catalyst layer. In addition, the elimination of the large amount of CO_2 bubbles needs an efficient approach. The large amount of CO_2 bubbles at the anode and severe water flooding at the cathode block the access of fuel and air to the catalyst layers, respectively, and thus degrade cell performance [4, 27, 28]. Figure 6 shows the variations of the mass of water, which was lost due to water crossover in different active areas. Given the water content at the beginning and the end of each test (14-hour test) and the total mass of water consumed during the cell operation, the mass of water that was removed from the fuel reservoir during the experiment is calculated. By integrating the current density for a given 14-hour test, the amount of methanol and the water reacted at the anode are calculated. The difference between the total mass of

Fig. 9 Effect of the shape of active area on the OCV variation
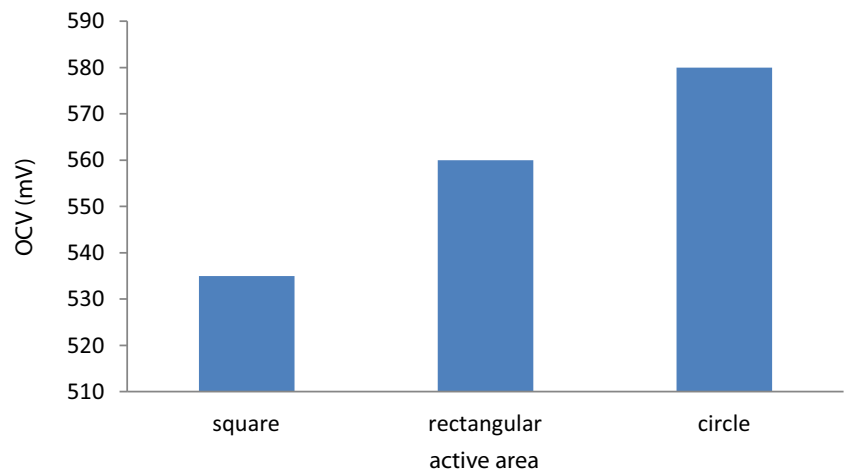
Fig. 10 Effect of the shape of active area on the operating temperature
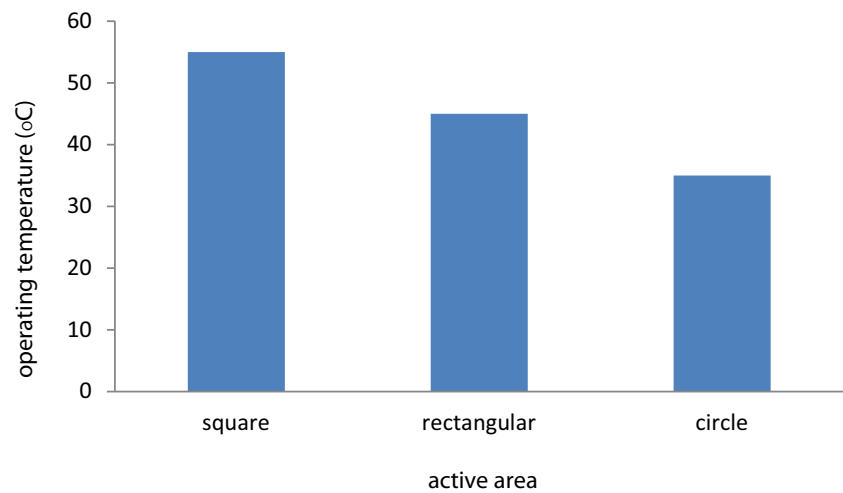
water removed from the fuel reservoir and the mass of water reacted at the anode is the mass of water lost due to the cross-over phenomenon. We repeated those steps to calculate the mass of methanol reacted at the anode and the mass of methanol lost because of methanol crossover. As indicated in Fig. 6 too, the mass of water lost due to the crossover increases with increasing in the size of active area. As a result, the large amounts of water that accumulate at the cathode side exacerbate the rate of water flooding. Therefore, this higher rate of flooding blocks even more pores of the cathode diffusion layer. Thus, during a longtime operation, in large active areas, the large amount of produced CO_2 bubbles and the severe water flooding will be important challenges. We can prove these claims by the experimental data that are listed in Table 2. Table 2 shows the duration of stable discharging voltage of the fuel cell at the current of 250 mA and with a 4-M fuel solution.

From Table 2, we can see that the cell with a 4-cm^2 active area produced the longest stable discharging voltage (16.5 h). This means that the single cell with a 4-cm^2 active area, during 16.5 h, produced a stable voltage at a 250-mA

constant current. Although the cell with a 4-cm^2 active area generated the lowest power compared with other active areas, it produced the longest stable voltage (16.5 h). This longtime stable voltage can relate to the amounts of generated CO_2 bubbles and water flooding. As showed in Table 2, fuel cell with a 36-cm^2 active area, because of a large amount of produced CO_2 bubbles and serious water flooding, despite the highest power output, produced the shortest stable discharging voltage. Therefore, it can be concluded that in large active areas, the large amount of generated CO_2 bubbles at anode and severe water flooding at cathode can be important challenges in long-term operations, which deteriorate the cell performance.

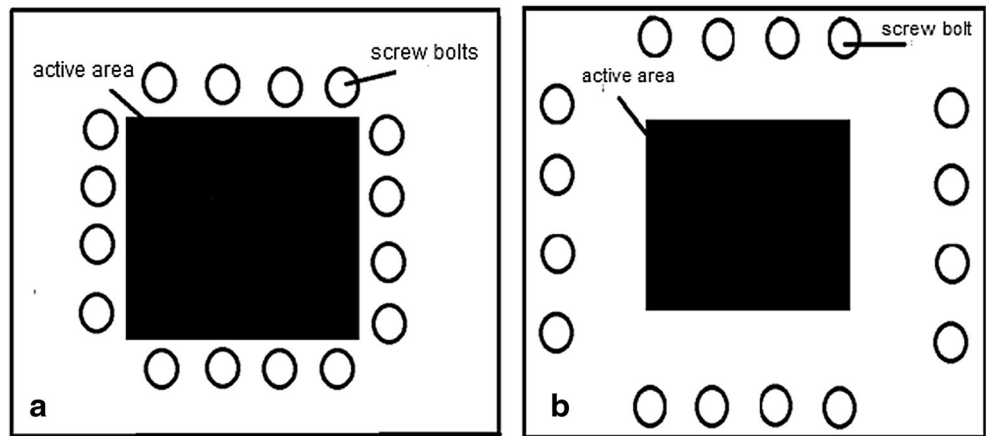**The effect of the shape of active area on the performance of passive DMFCs**

In order to examine the effect of the shape of active area, we studied three different shapes of active area with the same size (25 cm^2). These shapes were circular, square, and rectangular.

Fig. 11 The variations of the mass of methanol lost due to the crossover in different active areas
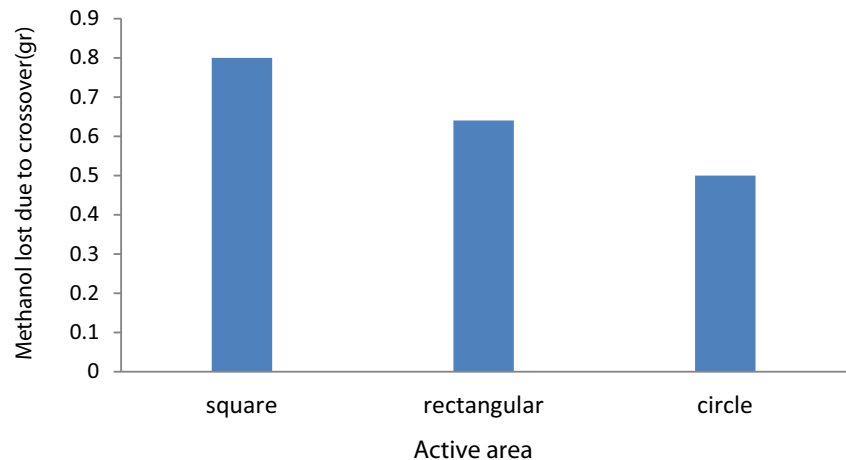
**Fig. 12** Two different designs for clamping system

To investigate the effect of the shape of active area, we conducted various tests and examined the cell performance with different shapes of active area. We performed these tests with a fuel concentration of 3 M and under ambient condition (25 °C and 1 atm). Figure 7 shows the performance of the fabricated passive DMFC single cell with different shapes of active areas (circular, square, and rectangular). As shown in Fig. 7, the cell with square and circular active areas produced the best and the worst performance, respectively. As a result, a maximum power density of 2.9 mW cm^{-2} was achieved with the square active area. In addition, as shown in Fig. 8, the square active area produced the highest voltage under 250 mA constant load and with a 3-M fuel solution (under ambient conditions). This high performance can be due to the distribution of reactants throughout the active area.

Studying the variations of operating temperature and open circuit voltage shows interesting results. As shown in Figs. 9 and 10, the square active area has the highest operating temperature and the lowest OCV value. As the OCV value reflects the methanol crossover degree in passive DMFCs, it can be concluded that in the square active area, more serious methanol crossover occurs compared with rectangular and circular active areas. This subject is obvious in Fig. 11, which shows the variations of the mass of methanol lost due to crossover.

As illustrated in Fig. 11, the amount of methanol lost, due to methanol crossover in the square active area, is more than the rectangular and circular active areas. In the square active area, the exothermic reactions that occur between this large amount of permeated methanol and oxygen on the cathode catalyst layer produce more heat, which finally lead to a higher operating temperature in the passive DMFC. The higher generated temperature leads to a better electrochemical kinetics of methanol oxidation and oxygen reduction reactions, which finally result in better performance, as shown in Figs. 7, 8, 9, 10, and 11.

Therefore, we can conclude that varying the shape of active area alters the cell performance. The characteristics that vary with the shape of active area are as follows: the internal resistance, the mass of methanol lost due to crossover, the cell operating temperature, and the OCV value.
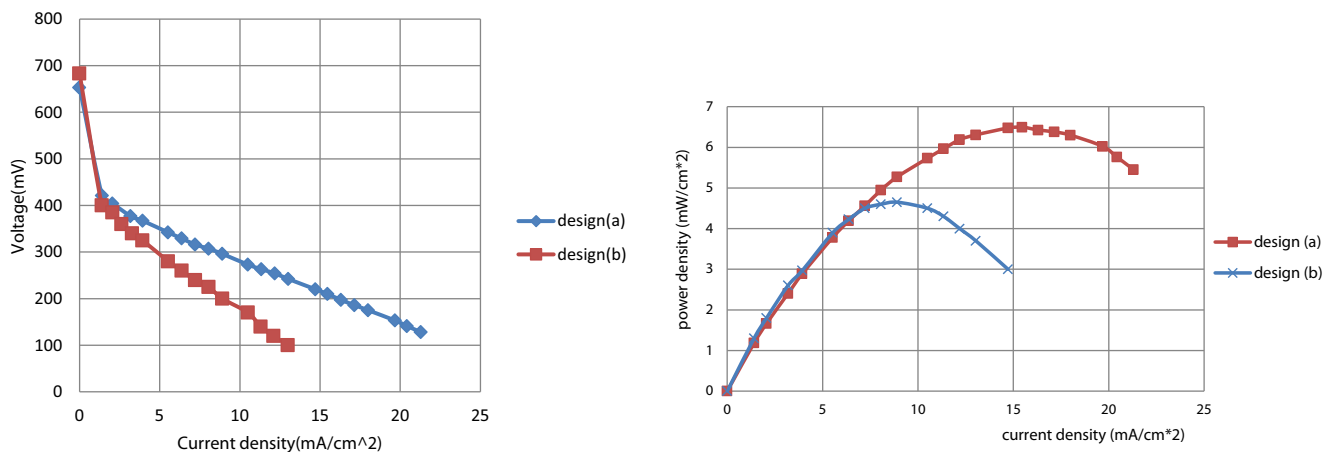

Fig. 13 The cell performance with different clamping designs (methanol concentration of 4 M and ambient condition)

Effect of the location of applying the clamping force on the performance of passive DMFC

Clamping force has an important effect on the performance and the efficiency of passive DMFC. On the one hand, inadequate applied clamping force leads to the leakage of reactants and high-contact resistance. On the other hand, excessive applied clamping force results in damage of the MEA and GDLs, which finally increase the transport resistance of both reactants and byproducts. Thus, to obtain the best power density, the optimal clamping force should be determined carefully. The location of applying the clamping force is another important factor, which affects the cell performance. Here, it will be shown that the place of applying the clamping force is a critical factor that should be considered carefully in the design of passive DMFCs. In this domain, the distances between the screw bolts (as the main component of clamping system) and the edge of active area are a key factor. To discover the effect of the place of applying the clamping force on the performance of passive DMFC single cell, two different designs with the same 5×5 cm^2 active area (design (a) and design (b)) were examined. These two designs are shown in Fig. 12. As shown in Fig. 12, the distances between the screw bolts and the edge of the active area in the design (b) are more than the design (a). Figures 13 and 14 show a comparison of the cell performance for the two clamping designs that already have been explained.

As shown in Figs. 13 and 14, the cell performance with the design (a) clamping system is better than that with the design (b) clamping system (about 40 %). The variations of internal resistance under these two clamping designs are listed in Table 3. The better performance of fuel cell with the design (a) is largely because of the lower internal resistance (see Table 3). In the design (b), insufficient compression force, which applies to the center of the active area, leads to the end plate deformation especially at the center of active area, and as a result, the contact resistance of the cell increases significantly.
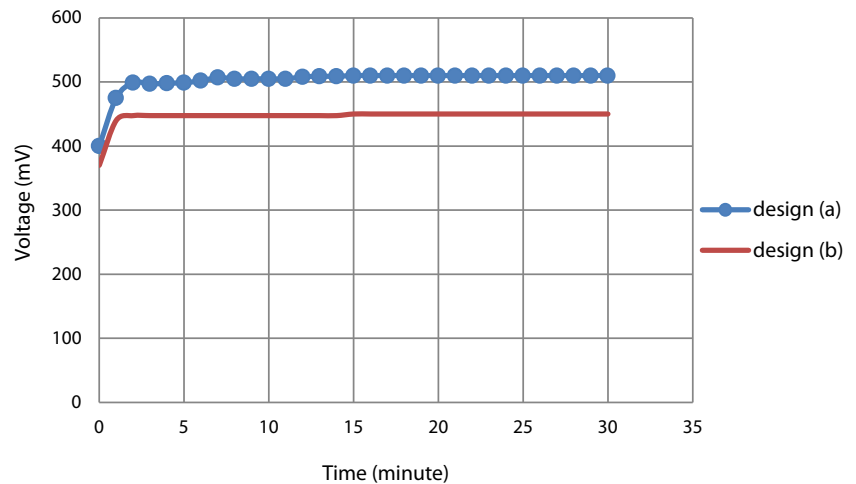
Table 3 The cell internal resistance under the two clamping designs

Clamping design	Internal resistance (mΩ)
Design (a)	70
Design (b)	86

Conversely, in the design (a), a higher compression force is applied, and thus, the contact resistance decreases drastically, and the cell performance improves consequently. Therefore, a less distance between the edge of the active and the screw bolts creates an adequate compressive force over the active area, which finally results in a lower contact resistance. This means that clamping system should apply adequate compressive force uniformly over the active area. Therefore, with a proper clamping design, the internal resistance will reduce significantly and the fuel cell efficiency will improve consequently. It is interesting to note that in passive DMFCs with large active area, to have a high electrochemical performance, it is more effective to assemble the cell with screws through the current collectors [10]. Finally, as discussed earlier, in designing the clamping system for a passive DMFC, a proper balance should be established between contact resistance and transport resistance to prevent fuel cell degradation and guarantee a high performance level [6].

At the end, a practical example about selecting a proper size for the active area will be helpful. If a single cell requires producing 1 kW of power, cell needs to produce current about higher than 1000 (A) [25]. A large active area with very thick cables can produce such current. Such a big active area and thick cables can lead to a high manufacturing cost and increase the total weight of the system. Another practical solution is to have multiple cells that electrically connect in series, which is called stacking. As a result, the active area of single cells and the cross-sectional area of the connecting cables with such stacking method will decrease significantly. The size of

Fig. 14 Effect of the location of clamping force on the voltage of the fabricated cell with 5×5 cm^2 active area and under a constant load at 250 mA

active area depends on the cost considerations, the application and the required power and current. On the one hand, it is difficult in large active areas to have a uniform electrochemical condition and clamping force. On the other hand, the number of single cells in stacking method should be determined carefully which depends on the clamping force, structural rigidity, total cost, and weight considerations. For example, a large number of single cells with small active area will be difficult to align and assemble. On the other hand, a small number of single cells with large active areas would result in high current-low voltage combination and would result in significant resistive losses in connecting cables [25]. Therefore, a designer should consider these factors and determine the optimal condition, which depends on the size and shape of active area, the number of cells, the clamping design, etc.

Conclusions

This work studied the effect of the size and shape of active area on the performance of single cell passive air-breathing DMFC. Experimental results proved that the size of active area has a significant effect on the cell performance. The cell performance improves with an increase in the size of active area (from 4 to 36 cm^2). In the large active areas, because the current density is smaller than the smaller active areas, the methanol is consumed slowly. Therefore, the local concentration at the membrane is higher, which results in more methanol crossover. The exothermic reaction, which occurs between this permeated methanol and oxygen on the cathode catalyst layer, produces more heat, which leads to a higher operating temperature. The higher operating temperature results in a better electrochemical kinetics of methanol oxidation and oxygen reduction reactions, which finally lead to a better cell performance. Experimental results of this study also demonstrated that in large active areas, a large amount of produced CO_2 bubbles at anode catalyst layer and severe water flooding at cathode catalyst layer might be important challenges in long-term operation. Existed results also showed that the shape of active area is another important factor that has a significant effect on the cell performance. The square active area had the best performance and the highest power density compared to the rectangular and circular active areas. The results showed that in the square active area, methanol crossover is higher than that of rectangular and circular active areas. The obtained results proved that a less distance between the edge of the active and the screw bolts creates an adequate compressive force over the active area, and as a result, the contact resistance decreases drastically and the cell performance improves significantly.

References

1. Yuan W, Zhang X, Zhang S, Hu J, Li Z, Tang Y (2015) Lightweight current collector based on printed-circuit-board technology and its structural effects on the passive air-breathing direct methanol fuel cell. Renew Energy 81:664–670
2. Mallick RK, Thombre SB, Shrivastava NK (2015) A critical review of the current collector for passive direct methanol fuel cells. J Power Sources 285:510–529
3. Yousefi S, Zohoor M (2013) Investigating the effect of operating parameters on the open circuit voltage of a passive DMFC. Ionics 19:1195–1201
4. Yousefi S, Shakeri M, Sedighi K (2013) The effect of cell orientations and environmental conditions. Ionics 19:1637–1647
5. Yousefi S, Zohoor M (2014) Conceptual design and statistical overview on the design of a passive DMFC single cell. Int J Hydrog Energy 39:5972–5980
6. Yousefi S, Ganji DD (2012) Experimental investigation of a passive direct methanol fuel cell with 100 cm2 active areas. Electrochim Acta 85:693–699
7. Achmad F, Kamarudin SK, Daud WRW, Majlan EH (2011) Passive direct methanol fuel cells for portable electronic devices. Appl Energy 88:1681–1689
8. Woolard DG (2010) Performance characterization of a passive DMFC over a range of operating temperatures and relative humidity -Virginia polytechnic Ins-M.S. thesis
9. Faghri A, Guo Z (2008) Innovative passive DMFC technology. Therm Eng 28:1614–1622
10. Lee CH, Park CH, Lee SY, Jung BO, Lee YM (2008) Passive DMFC system using a proton conductive hydrocarbon membrane. Desalination 233:210–217
11. Paust N, Krumbholz S, Munt S (2009) Design of a passive and portable DMFC operating in all orientations -Micro Electro Mechanical Systems . MEMS2009. IEEE 22nd International Conference – (10.1109/MEMSYS.2009.4805577)
12. Gharibi H, Golmohammadi F, Kheirmand M (2013) Fabrication of MEA based on optimum amount of Co in PdxCo/C alloy nanoparticles as a new cathode for oxygen reduction reaction in passive direct methanol fuel cells. Electrochem Acta 89:212–221
13. Shimizu T, Mohamedi M, Osaka T, Sarangapani S (2004) Design and fabrication of pumpless small passive DMFC for portable applications. J Power Sources 137:277–283
14. Tang Y, Yuan W (2010) Effects of structural aspects on the performance of a passive air-breathing DMFC. J Power Sources 195:5628–5636
15. Ahmad MM, Kamarudin SK (2010) High power passive micro DMFC with low catalyst loading for small power generation. Energy Convers Manag 51:821–825
16. Basri S, Kamarudin SK, Daud WRW, Ahmad MM (2010) Nonlinear optimization of passive direct methanol fuel cell (DMFC). J Hydrog Energy 35:1759–1768
17. Ren S, Sun G, Li C, Liang Z, Wu Z, Jin W, Qin X (2006) Organic silica/Nafion® composite membrane for direct methanol fuel cells. Membr Sci 282:450–455
18. Wang L, Northwood DO, Nie X, Housden J (2010) Corrosion properties and contact resistance of TiN, TiAlN, and CrN coatings in simulated proton exchange membrane fuel cell environments. J Power Sources 195:3814–3821
19. Kamarudina SK, Hashima N (2012) Materials, morphologies and structures of MEAs in DMFCs. Renew Sust Energ Rev 16:2494–2515
20. Lio JG, Zhao TS, Chen R (2005) The effect of methanol concentration on performance of a passive DMFC-electrochemistry. Communications 7:288–294

21. Yang WM, Shu C (2007) Effect of current-collector structure on performance of passive micro direct methanol fuel cell. J Power Sources 164:549–554

22. Yuan W, Tang Y (2011) Dominance evaluation of structural factors in a passive air-breathing direct methanol fuel cell based on orthogonal array analysis. Appl Energy 88:1671–1680

23. Esquivel JP, Sabaté N (2009) Influence of current collectors design on the performance of a silicon-based passive micro direct methanol fuel cell. J Power Sources 194:391–396

24. Zhao TS, Chen R, Yang WW, Xu C (2009) Small direct methanol fuel cells with passive supply of reactants. J Power Sources 191: 185–202

25. Frano B (2005) PEM fuel cells: theory and practice. Academic, Burlington

26. Chang H, Kim JR, Cho JH, Kim HK, Choi KH (2002) Materials and processes for small fuel cells. Solid State Ionics 148:601–606

27. Kamarudin SK, Achmad F, Daud WRW (2009) Overview on the application of direct methanol fuel cell (DMFC) for portable electronic devices. Int J Hydrog Energy 34:6902–6916

28. Chenggang X, Bostaph J, Pavio J (2004) Development of a 2W direct methanol fuel cell power source. J Power Sources 136:55–65

29. Shrivastava NK, Thombre SB, Motghare RV (2014) Wire mesh current collectors for passive direct methanol fuel cells. J Power Sources 272:629–638

30. Shrivastava NK, Thombre SB, Mallick RK (2014) Effect of diffusion layer compression on passive DMFC performance. Electrochim Acta 149:167–175

31. Chen R, Zhao TS (2007) A novel electrode architecture for passive direct methanol fuel cells. Electrochem Commun 9:718–724

32. Mohammad Ali A, Tsujiguchi T, Nakagawa N (2010) Effect of black catalyst ionomer content on the performance of passive DMFC. J Power Sources 195(19):6287–6293

33. Chen R, Zhao TS, Liu JG (2006) Effect of cell orientation on the performance of passive direct methanol fuel cells. J Power Sources 157(1):351–357

34. Liu JG, Zhao TS, Liang ZX, Chen R (2006) Effect of membrane thickness on the performance and efficiency of passive direct methanol fuel cells. J Power Sources 153(1):61–67

35. Kho BK, Oh I, Hong S, Yong Ha H (2005) The effect of pretreatment methods on the performance of passive DMFCs. Electrochim Acta 50:777–782