World Applied Sciences Journal 22 (4): 516-522, 2013
ISSN 1818-4952

DOI: 10.5829/idosi.wasj.2013.22.04.494

The Effect of Operating Parameters on the Performance of a Passive DMFC Single Cell

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Abstract: A passive direct methanol fuel cell was fabricated and investigated experimentally to study the characteristics of the open circuit voltages under the variation of some operating parameters such as cell orientation, cell temperature and also methanol concentration. Then the effect of cell orientation on the performance of such fuel cell was studied experimentally. The obtained results indicated that the best power output and the best performance were achieved under vertical orientation than others. Also, according to results, it can be concluded that the OCV values Depends on cell orientation, cell temperature and methanol concentration. The OCV values decrease regularly with an increase in methanol concentration and also decrease with an increase in cell temperature. Also the OCV values in vertical orientation are lower than the OCV values in horizontal orientations.

Key words: Passive direct methanol fuel cell · Open circuit voltage · Methanol cross over · Power output

INTRODUCTION

Direct methanol fuel cell (DMFC) has received much attention because of its high theoretical energy density, using liquid methanol fuel, employing polymer electrolyte, also low pollution (green) and working under ambient conditions [1-3]. A direct methanol fuel cell (DMFC) is able to directly convert the electrochemical energy into electricity by using aqueous or vaporized methanol at the Anode side and oxygen as the oxidant at the cathode side. According to the reactant delivery modes, it can be categorized into two types including passive and active cells [4, 5]. In passive DMFCs, fuel and oxidant are supplied passively (contrary to active) so fuel cell system becomes more simple and compact (with low weight) and also the parasitic energy losses due to ancillary devices eliminate significantly. Through these advantages, the passive DMFCs have been considered as a more promising power sources for portable power sources [6, 7]. Also It should be mentioned that the performance of active DMFCs is higher than that of passive cells but the passive system is simpler and have lower weight, as a result it is regarded as one of the most promising candidates to provide sustainable power output for portable applications [4,8,9]. In recent years, it was conducted numerous researches about passive DMFCs. For example,

M.M. Ahmad *et al.* [10] were developed a µDMFC with a power output of 56 mW and an active area of 4 cm^2. Zhen Guo and Amir Faghri [11] were developed a 1 (W) passive DMFC. A peak power output of 1.5 W was achieved with the dilute methanol solution feed.

On the other hand, as reported by Sasan Yousefi *et al*. [12], in high power portable devices like laptop or hand phone, one approach to use passive DMFC as a power source instead of stacking could be single passive DMFC with higher active area. Sasan Yousefi *et al.*, designed, manufactured and investigated a passive direct methanol fuel cell with 100 cm^2 active areas. Finally, with an optimized design, a maximum power output of 520 mW was achieved under ambient conditions.

The objective of this work is to design, fabricate and test an air-breathing single cell passive DMFC that operates under ambient condition. Then the effect of cell orientation on the performance of such fabricated passive DMFC and also the Characteristics of the open circuit voltages under operating conditions were investigated experimentally. These experiments are novel because the indicated operating parameters were studied for the first time in passive DMFCs with 100 cm^2 active areas.

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MATERIAL AND METHODS

Membrane Electrolyte Assembly: The conventional Nafion 117 MEA with a thickness of 256μm, which uses carbon cloth As the anode and cathode backing diffusion layers, was prepared for experiments. Single side ELAT electrodes from ETEK were used in both anode and cathode sides, where type (A) E-TEK carbon cloth was used as the backing support layer with a 30% wt. PTFE wet-proofing treatment.

Pt black and Pt–Ru black were used as catalyst for the cathode and anode, respectively. The catalyst loading on the cathode side was 2.0 $mgcm^{-2}$ using 40%wt. Pt on Vulcan XC-72 and the catalyst loading on the anode was 4.0 mg cm^{-2} with Pt-Ru black. Furthermore, 0.8 mg cm^{-2} dry Nafion® ionomer was applied onto the surface of each electrode. Finally, this MEA with an active area of 10×10 cm² was formed by hot pressing for 3 minute at 135°C and 5MPa. More detailed MEA fabrication procedures and information can be found elsewhere [13-15].

Single Cell Fixture: Figure 1 shows a schematic diagram of the configuration of the single cell passive air-breathing DMFC. For the visualization of the entire cell, the transparent acrylic Plexiglas material was used to fabricate the methanol solution reservoir and cathode window end frame by using milling and polishing techniques. A built-in reservoir with a volume of 50mL was machined to store the methanol solution. Four through holes were drilled at the top of the methanol solution reservoir. These holes are used for injection methanol solution as fuel and also for exhausting generated CO_2 bubbles at anode side. So the role of these holes is vital in order to prevent the poisoning of Pt in catalyst layers. Both the anode and cathode current collectors were made of two 1.5mm 316L stainless steel plates with perforated hole-arrays distributed within the active area (Fig. 2). In this study a plurality of 289 holes with a diameter of 4mm were drilled inside the active area of the both current collectors, which resulted in an open ratio of 36% approximately. Open ratio is calculated as follow:

$$289\times\frac{\pi d^2}{4}\Rightarrow 256\times\frac{\pi 4^2}{4}\Rightarrow 3629.84\left(mm^2\right)$$

$$open\ ratio=\frac{3629.84\left(mm^2\right)}{100\times100\left(mm^2\right)}\times100\Rightarrow 36.3\%$$

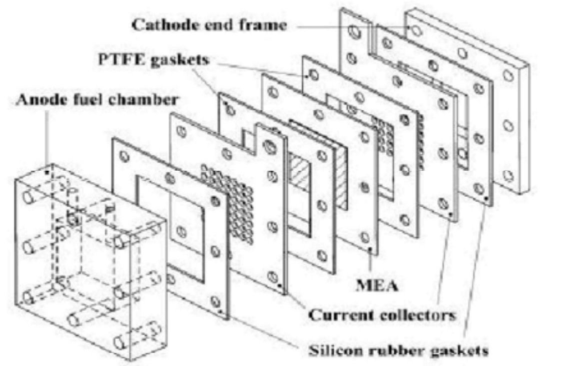

Fig. 1: Schematic of the passive air-breathing DMFC [11]

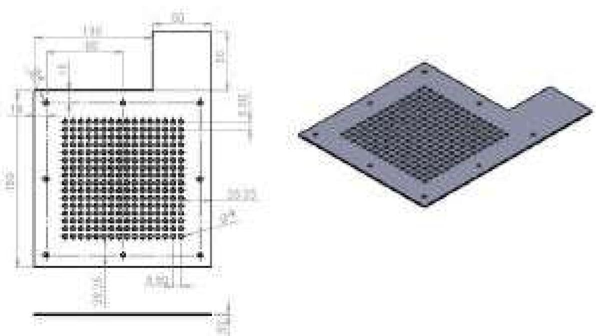

Fig. 2: Schematic of the fabricated current collectors

Fig. 3: Electro-load instrument during experiments

Also eight M6 screw bolts were used to assemble the entire cell. A silicon-rubber strip was used to seal the gaps between anode-cathode current collectors and the end plates, while an in-house PTFE film served as the gasket between anode-cathode current collectors (CC) and the edged membrane of the MEA.

A commercial electronic load was used to test the fuel cell discharge performance and a Lab VIEW-based data acquisition (DAQ) program was used to record the current and voltage outputs for polarization curves at different conditions. Commercial electronic load is shown in Fig. 3.

Before tests, the MEA was activated under a very low constant load for 6h and also to eliminate the effects of previous tests, the MEA was washed in distilled water. Over the experiment, the fuel cells were tested at an ambient pressure and a room temperature of approximately 25 °C. The relative humidity was conditioned at around 75%.

RESULTS AND DISCUSSIONS

Characteristics of the Open Circuit Voltages under Operating Conditions: Here two parameters which affected open circuit voltages of fabricated cell significantly are discussed. These parameters are methanol concentration and cell temperature and cell orientation. The effect of cell temperature which varies from 20 $^{\circ C}$ to 50 $^{\circ C}$, on the OCV values was investigated experimentally. As shown in Figs. 4 and 5 increasing cell temperature leads to decreasing OCV values.

Because the OCV values reflect methanol crossover degree in passive DMFCs, it can be concluded that (as shown in Figs.4 and 5 too) higher temperature leads to higher methanol crossover which finally caused decreasing the OCV values. This phenomenon can be attributed to the larger mixed potential as a result of methanol cross over at cathode side [16-18]. It should be noted that higher fuel cell temperature also leads to the improved electrochemical kinetics of methanol oxidation and oxygen reduction reaction.

Higher surrounding temperature leads to the increased temperature differences between the inside temperature of fuel cell and the ambient temperature. This phenomenon will lead to the increased natural convection at the both anode and cathode side [19].

As a result, this improved natural convection increases the methanol concentration gradients between the MEA and the methanol solution reservoir. Therefore, these high gradients generate higher diffusion force which improve the transfer rate of methanol solution from reservoir to the anode side and so aid the diffusion of fuel to the catalyst layers. Consequently, higher methanol concentration at the anode catalyst layer leads to a higher methanol permeation rate. Finally, such enhanced methanol diffusion, as a result of the natural convection, causes a higher rate of methanol crossover which decreases the open circuit voltage (OCV) of fabricated passive air-breathing DMFC as a result of larger mixed potential which occurs at cathode compartment.

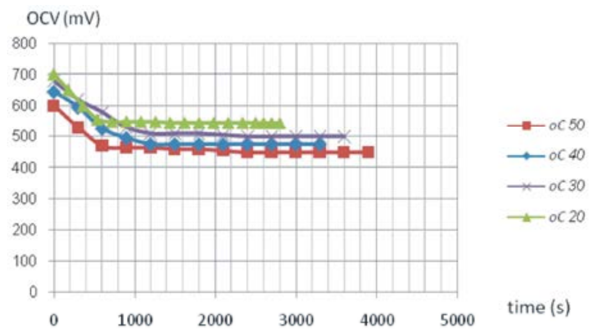

Fig. 4: OCV variations of fabricated fuel cell under various cell temperatures with 2M methanol solution

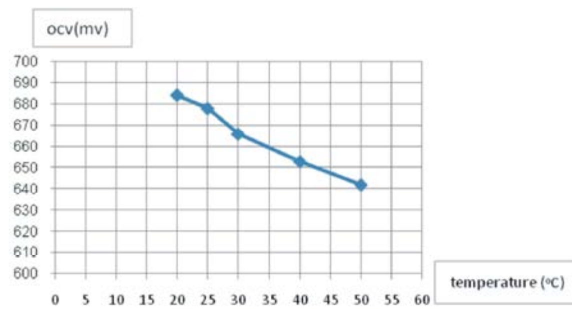

Fig. 5: Effects of the cell temperature on the OCV values of fabricated fuel cell with 3M methanol solution

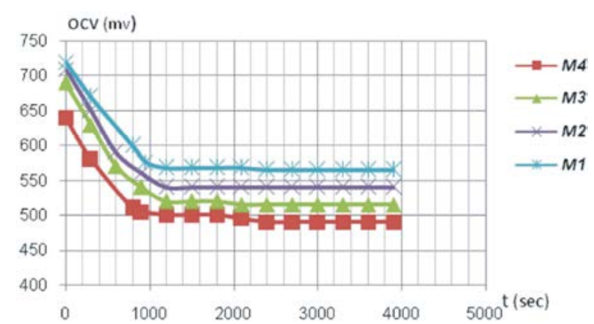

Fig. 6: Effects of the methanol concentrations on the values of open circuit voltages

As discussed earlier, the open circuit voltage (OCV) of a passive air-breathing DMFC is usually a concerned technical target because its value reflects the methanol crossover degree. Fig.6 shows the OCV characteristics of the fabricated single cell with different methanol solutions. It can be seen that the OCV of fabricated single cell enters into a stable period after about 30 min. As shown in the Fig.6 the OCV values decreases regularly with an increase in methanol concentration from 1M to 4M. This phenomenon is related to this fact that

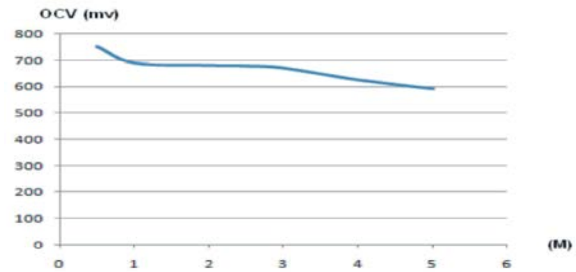

Fig. 7: Variations in OCV values with methanol concentration

the methanol crossover becomes increasingly severe with increase in methanol concentration and also because of a higher mixed potential, the OCV values decrease and accordingly, the methanol utilization efficiency reduced significantly [9, 20, 21]. When methanol concentration increase from 1M to 4M, the methanol concentration gradients between the anode and the methanol reservoir increase, so these higher gradients generate higher diffusion force which improve the transfer rate of methanol from reservoir to the anode side and catalyst layers [12]. As a result, the concentration of methanol increases in anode catalyst layer which finally results in higher rate of methanol crossover through the membrane from anode to cathode compartment.

Especially, when the methanol concentration is at 4M, the OCV is reduced significantly. This fact demonstrates that the methanol concentration has a significant effect on the value of OCV. In other words, it can be concluded that OCV values decrease with increase in methanol concentration because higher methanol concentration leads to a higher mixed potential and this phenomenon leads to lower OCV value in different conditions (Fig. 6 and 7).

Effects of Cell Orientation: Figure 8 shows the transient discharging voltage of DMFCs with different cell orientations at a constant current of 300 mA. As shown in Fig.8, the fabricated cell with horizontal orientation with anode facing upwards and vertical orientation shows better performance than horizontal orientation with anode facing downward due to the easy removal of CO_2 bubbles at anode and produced water at cathode [19]. Also the fabricated cell with horizontal orientation with anode facing downward shows the highest open-circuit voltage (OCV). It is believed that the lower OCV in horizontal anode facing upward is attributed to this fact that the rate of methanol crossover from the anode to the cathode is

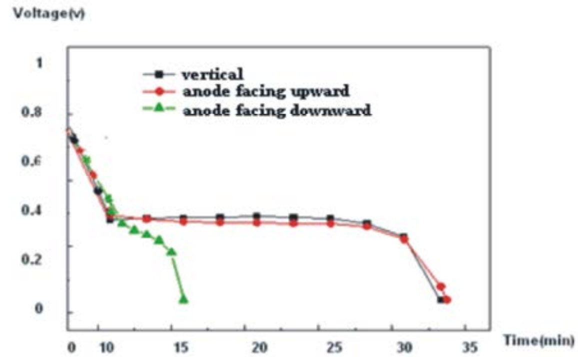

Fig. 8: Transient discharging voltage at a constant current (300 mA) with a start from the cell to be fueled with 2.5M Methanol solution

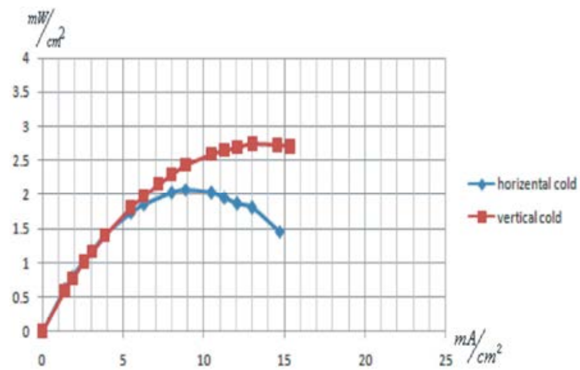

Fig. 9: Comparison in the cell performance among vertical and horizontal anode facing upward cell orientations with2.5M Methanol solution

higher due to the gravity force. As the passive cell with horizontal orientation with anode facing downward, a large amount of generated CO_2 bubbles accumulated at the anode catalyst layer and a large amount of generated water accumulated at the cathode catalyst layer (flooding) due to the buoyancy force and gravity, blocked the paths for methanol and oxygen transferring to the reaction sites (the removal of CO_2 and water Bubbles became rather difficult).

As shown in Fig.8, the performance of passive cell with vertical orientation and that of passive DMFC with horizontal orientation with anode facing upward are similar so we compared these orientations separately. Fig.9 shows the performance of fabricated cell with vertical orientation and horizontal orientation with anode facing upward. It can be seen than the vertical orientation always yielded better performance than the horizontal orientation with anode facing upward. Also, as shown in Fig.10, vertical operation produced higher power output

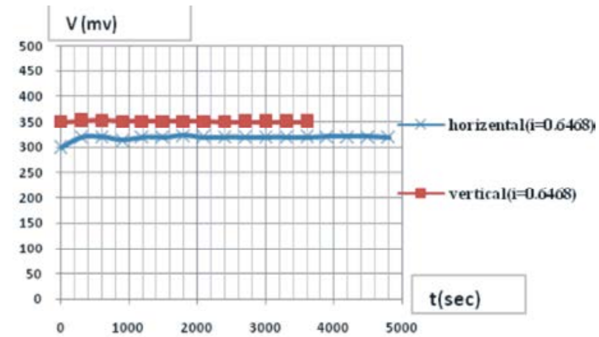

Fig. 10: Effect of the cell orientation on the voltage output of the fabricated cell with2.5M Methanol solution and under a constant load at 600 mA

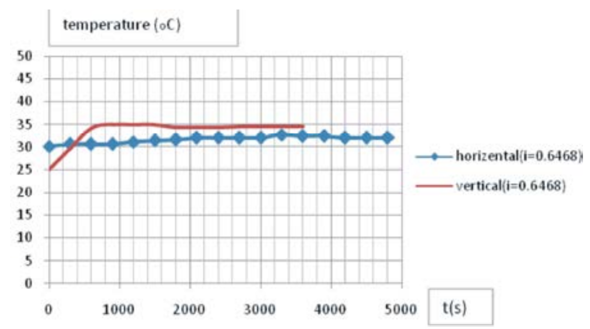

Fig. 11: Variation in the cell operating temperature with 2.5M Methanol solution and under a constant load at 600 Ma at different orientations

than that of horizontal orientation with anode facing upward under a constant load and 2.5M methanol solution.

Also we measured the cell operating temperature when the passive DMFC was oriented differently. The temperature was measured by installing a thermocouple at the outer surface of the anodic diffusion layer. Fig.11 shows the transient cell operating temperature when the cell started operating with the 2.5M methanol solution. Apparently, the vertical orientation exhibited a higher operating temperature than did the horizontal orientation with anode facing upward. The higher operating temperature in vertical orientation was mainly caused by the exothermic reaction between the permeated methanol and oxygen on the cathode. Thus, the rate of methanol crossover is higher in the vertical case than in the horizontal case.

This explains why the vertical orientation cell yielded a higher performance in all conditions. On the other hand, the higher temperature in the vertical case led to the improved electrochemical kinetics of methanol oxidation

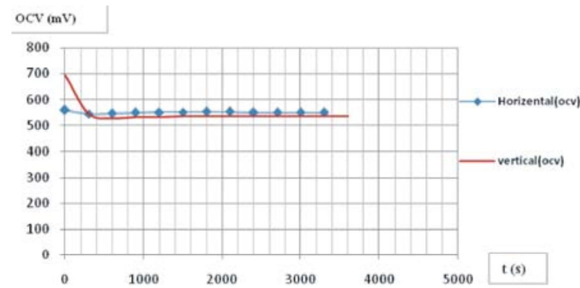

Fig. 12: Effects of the cell orientation on the values of open circuit voltages

and oxygen reduction reaction and thereby a better performance. In summary, the increased operating temperature as a result of the increased methanol crossover is the major reason that yields a higher performance of the fabricated cell operated at the vertical orientation. So as discussed earlier, it can be concluded that the cell orientation has a significant effect on the cell performance. As shown in Fig.8, the horizontal fabricated passive DMFC with anode facing downward results in the worst performance due to flooding in cathode and CO_2 bubbles accumulation in anode. Also the vertical orientation always yielded the best performance than did the horizontal operation. The improved performance in the vertical cell orientation was caused by the increased operating temperature as a result of a higher rate of methanol crossover which resulted in higher electrodes electrochemical kinetics.

The higher operating temperature in vertical orientation was mainly caused by the exothermic reaction between the permeated methanol and oxygen on the cathode [19]. This can be also concluded from Fig.12, because OCV values reflect the methanol crossover degree. This phenomenon is related to this fact that the rate of methanol crossover becomes higher in vertical orientation than the methanol crossover in horizontal orientation with anode facing upward and accordingly, because of a higher mixed potential, the OCV values decrease in vertical orientation. Thus, the exothermic reaction between this higher rate of permeated methanol and oxygen, on the cathode reaction sites, generates more heat and therefore causes a higher operating temperature in vertical orientation than did the horizontal orientation with anode facing upward.

CONCLUSIONS

A passive direct methanol fuel cell was fabricated and investigated experimentally to study the characteristics of the open circuit voltages under some operating parameters such as cell orientation, surrounding temperature and also methanol concentration. Then the effect of cell orientation on the performance of such fuel cell was studied. It was observed that the OCV values decrease with increase in methanol concentration because higher methanol concentration leads to a higher mixed potential and this phenomenon leads to lower OCV values in fabricated cell. Also experimental results showed that higher surrounding temperature leads to the increased natural convection inside the fuel cell. This enhanced natural convection increases Methanol crossover and finally, as a result of larger mixed potential, the open circuit voltage (OCV) of fabricated passive air-breathing DMFC decreases consequently.

According to the experimental results, it was concluded that the cell orientation has a significant effect on the cell performance and on the open circuit voltage (OCV) of fabricated fuel cell. The fabricated passive DMFC with anode facing downward results in the worst performance due to flooding in cathode and CO_2 bubbles accumulation in anode. Also the vertical operation always yielded the best performance than did the horizontal orientations. The improved performance in the vertical cell orientation was caused by the increased operating temperature as a result of a higher rate of methanol crossover which resulted in higher electrochemical kinetics of electrodes.

REFERENCES

1. Yang, H., T.S. Zhao and Q. Ye, 2005. In situ visualization study of CO2 gas bubble behavior in DMFC anode flow fields J. Power Sources, 139: 79-90.
2. Achmad, F., S.K. Kamarudin, W.R.W. Daud and E.H. Majlan, 2011. Passive direct methanol fuel cells for portable electronic devices, Applied Energy, 88: 1681.
3. Deryn Chu, Rongzhong Jiang, 2006. Effect of operating conditions on energy efficiency for a small passive direct methanol fuel cell, Electrochimica Acta, 51: 5829-5835.
4. Wei Yuan, Yong Tang, Zhenping Wan and Minqiang Pan, 2010. Operational characteristics of a passive air-breathing direct methanol fuel cell under various structural conditions, J. hydrogen energy, xxx: 1-13.
5. Kamarudin, S.K., W.R.W. Daud, S.L. Ho and U.A. Hasran, 2007. Overview on the challenges and developments of micro-direct methanol fuel cells (DMFC). J. Power Sources, 163: 743-754.
6. Shrivastava, N.K. and S.B. Thombre, 2011. Barriers to commercialization of passive direct methanol fuel cells: A review, J. IJEST., 3: 6000-6007.
7. Kamarudin, S.K., F. Achmad and W.R.W. Daud, 2009. Overview on the application of direct methanol fuel cell (DMFC) for portable electronic devices, J. Hydrogen Energy, 34: 6902-6916.
8. Zhen Guo and Amir Faghri, 2006. Development of planar air breathing direct methanol fuel cell stacks J. Power Sources, 160: 1183-1194.
9. Zhao, T.S., R. Chen, W.W. Yang and C. Xu, 2009. Small direct methanol fuel cells with passive supply of reactants J. Power Sources, 191: 185-202.
10. Ahmad, M.M., S.K. Kamarudin, W.R.W. Daud and Z. Yaakub, 2010. High power passive μDMFC with low catalyst loading for small power generation J. Energy Conversion and Management, 51: 821-825.
11. Yang Tang and Wei Yuan, 2010. Effects of structural aspects on the performance of a passive air-breathing DMFC, J. Power Sources, 195: 5628-5636.
12. Yousefi, S. and D.D. Ganji, 2012. Experimental investigation of a passive direct methanol fuel cell with 100 cm2 active areas. Electrochimica Acta, 85: 693-699.
13. Suzhen Ren and Gongquan Sun, 2006. Organic silica/Nafion® composite membrane for direct methanol fuel cells, J. Membrane Science, 282: 450-455.
14. Wang, L., D.O. Northwood, X. Nie, J. Housden, E. Spain, A. Leyland and A. Matthews, 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.
15. Basri, S., S.K. Kamarudin, W.R.W. Daud and M.M. Ahmad, 2010. Non-linear optimization of passive direct methanol fuel cell (DMFC)J. hydrogen energy, 35: 1759-1768.
16. Zhen Guo, Amir Faghri, 2008. Development of a 1 W passive DMFC, International Communications in Heat and Mass Transfer, 35: 225-239.
17. Liu, J.G., T.S. Zhao, R. Chen and C.W. Wong, 2005. The effect of methanol concentration on the performance of a passive DMFC, Electrochemistry Communications, 7: 288-294

18. Xu, C., X. Amir and T. Faghri, Li, 2010. Ward, Methanol and Water Crossover in a Passive Liquid- feed Direct Methanol Fuel Cell, International Journal of Hydrogen Energy, 35: 1769-1777.
19. Chen, R., T.S. Zhao and J.G. Liu, 2006. Effect of cell orientation on the performance of passive direct methanol fuel cells, Journal of Power Sources, 157: 351-357.
20. Park, J.Y., J.H. Lee, S.K. Kang, J.H. Sauk and I. Song, 2008. A small mono-polar direct methanol fuel cell stack with passive operation. J. Power Sources, 178: 181-187.
21. Lai, Q.Z., G.P. Yin, Z.B. Wang, C.Y. Du, P.J. Zuo and X.Q. Cheng, 2008. Influence of methanol crossover on the fuel utilization of passive direct methanol fuel cell Fuel Cells, 8: 399-403.