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Parametric Studies of Direct Methanol Fuel Cell under Different Modes of Operation

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ABSTRACT

Direct methanol fuel cell (DMFC) performance tests were carried out in different modes of operation, namely, passive, active (air as oxidant) and active (oxygen as oxidant). Few parameters including methanol concentration (2 M, 4 M, 6 M, and 8 M) and methanol flow rate (1-4 mL min^{-1}) were considered to investigate their effects on the DMFC performance. Fuel consumption was indicated by refractive index tests. Results showed that the performance of DMFC increased with the increase of methanol concentration and flow rate, until they reach certain values, i.e., 4-6 M and 2 mL min^{-1}. Furthermore, for all parameters, the active mode with oxygen yielded the highest power density, followed by the active mode with air and passive DMFC system. The active mode with oxygen yielded the power density which peaks at 10.41 mW cm^{-2} during 6 M of methanol concentration and 2 mL min^{-1} rate of flowing methanol, followed by active mode with air at the cathode with 8.39 mW cm^{-2} and passive mode with 5.39 mW cm^{-2} respectively. It also records a better fuel consumption efficiency among all modes. These results indicate that investigating the level of fuel concentration and flow rate can lead to enhancement of mass transport and diffusion thus generating better performance of DMFC system.

Keywords: Modes operation; direct methanol fuel cell; methanol flow rate

ABSTRAK

Ujian prestasi Sel Fuel Metanol Langsung (DMFC) dijalankan dalam pelbagai mod operasi, iaitu pasif, aktif (udara sebagai oksidan) dan aktif (oksigen sebagai oksidan). Beberapa parameter termasuk kepekatan metanol (2 M, 4 M, 6 M, dan 8 M) dan kadar alir metanol (1-4 mL min^{-1}) dipertimbangkan untuk mengkaji kesannya terhadap prestasi DMFC. Penggunaan bahan api ditunjukkan melalui ujian indeks biasan. Keputusan menunjukkan bahawa prestasi DMFC meningkat dengan peningkatan kepekatan metanol dan kadar alir, sehingga mencapai nilai tertentu, iaitu, 4-6 M dan 2 mL min^{-1}. Selain itu, bagi semua parameter, mod aktif dengan oksigen menghasilkan ketumpatan kuasa tertinggi, diikuti dengan mod aktif dengan sistem udara dan pasif DMFC. Mod aktif dengan oksigen menghasilkan ketumpatan kuasa yang mencapai 10.41 mW cm^{-2} pada kepekatan metanol 6 M dengan kadar aliran metanol 2 mL min^{-1}, diikuti oleh mod aktif udara di katod dengan 8.39 mW cm^{-2} dan mod pasif dengan 5.39 mW cm^{-2}. Ia juga merekodkan kecekapan penggunaan bahan api yang lebih baik di kalangan kesemua mod. Keputusan ini menunjukkan bahawa kajian tehadap tahap kepekatan bahan api dan kadar alir dapat membawa kepada peningkatan pengangkutan dan penyebaran jisim, yang dengan itu mampu menghasilkan prestasi sistem DMFC yang lebih baik.

Kata kunci: Mod operasi; sel fuel metanol langsung; kadar alir metanol

INTRODUCTION

Electronic devices such as mobile phones, laptops and cameras are having a rapid development in power and complexity. Thus, conventional battery has now become insufficient and can no longer fulfill the demands of application due to limited power capacity, low energy density, poor durability and contribution to environmental pollution. The current technology of portable electronics specifically demands to a smaller, cheaper, environmentally friendly and high endurance power of portable energy. Thus, direct methanol fuel cell (DMFC) has been attracting attentions lately as one of the power sources for many applications (Rahman et al. 2018; Goor et al. 2019) due to its advantages such as high energy density, low operating temperature, instant refueling, convenient operation, zero emission and rapid start up and response (Chan et al. 2008; Achmad et al. 2011; Mansor et al. 2018). Furthermore, DMFC system can also be operated without complex external devices such as heat exchanger and humidifier (Qian et al. 2006).

In passive mode, the cell is consisted of a reservoir-included anode serves as the storage tank while the cathode is considered air-breathing and does not require pumps or blowers as in active system (Zhao et al. 2009). Hence, many studies put attention to the passive system in recent years (Zainoodin et al. 2014; Yuan et al. 2016). For instance, a study by Fang et al. (2017) shows that a passive system is able to operate in highly concentrated methanol from 10-15 M of methanol concentration. Another study by (Wu et al. 2014) found that the performance of a passive system decreases as the methanol concentration increases due to methanol crossover (MCO). This finding is coincident with the other researchers (Munjewar & Thombre 2019) where they found that the power density of a lower concentration (4 M) is higher than the power density of a high concentration (5 M) due to MCO and increase in cathode side water. However, a passive system may experience great loss in performance electrochemically due to mass transfer limitations and catalytic inactivity (Yuan et al. 2016).

In real application view, a high power output is always preferred and become the ultimate goal. Hence, the active supply of fuel and oxidants can become another favorable option. Different than the passive system, an active system requires auxiliary devices to supply power that feed fuel and air or oxygen to the cell. Clearly, this system requires more cost and space. For the active case, the optimization of operating conditions such as concentration and feed rate has been among top priorities because it greatly affects the performance, efficiency, cost and durability of a system for commercial applications. Thus, we can say that operational modes of DMFC whether in active or passive system can contribute to mass transport behavior and its performance. Yuan et al. (2016; 2017) studied on different parameters for active DMFC and found the optimum methanol concentration and feed rate for all cases. A research by (Yang et al. 2005) focused on another parameters important in active system namely cell orientation and cell operating temperature. (Yuan et al. 2017) studied on the effects of the methanol concentration, methanol feed rate, gas bubble behavior and pressure drop to the performance of an active DMFC with different flow fields and found the condition with best performance.

Previous researches focused on the effect of operating parameters to the cell performance although they did not consider these parameters under different modes of operations. Thus, in this work, the influences of operating parameters such as methanol concentration and methanol flow rate under active (oxygen and air as cathode supply) and passive modes were investigated and compared.

MATERIALS AND METHOD

MEMBRANE ELECTRODE ASSEMBLY PREPARATION AND SINGLE CELL DMFC

The active area of the Membrane Electrode Assembly (MEA) was 2.0 cm x 2.0 cm. The catalysts used for all MEA were Pt-Ru Black (HiSPEC 6000, Alfa Easer USA) and Pt black (HiSPEC 1000, Alfa Easer USA) for the anode and cathode layers, respectively. The catalyst loading was 4 mg cm^{-2} in anode and 2 mg cm^{-2} in cathode, while Nafion 117 (DuPont™) was used as the electrolyte membrane. It was then combined by inserting the anode and cathode electrodes between electrolyte membrane by hot-pressing at 135 °C for 3 minutes. Single cell DMFC was used in all performance studies.

TESTING SETUP FOR DMFC PERFORMANCE AND FUEL CONSUMPTION

Concentration and flow rate of methanol were chosen as the parameters to investigate their effects on DMFC performance. The experiments were carried out using a self-constructed testing system. For instance, as shown in Figure 1 (a), in passive system, methanol was fed at the storage on the anode side while cathode side was considered air breathing. For the active modes shown in Figure 1 (b) and (c), the methanol solution was injected into the anode side by a peristaltic pump.

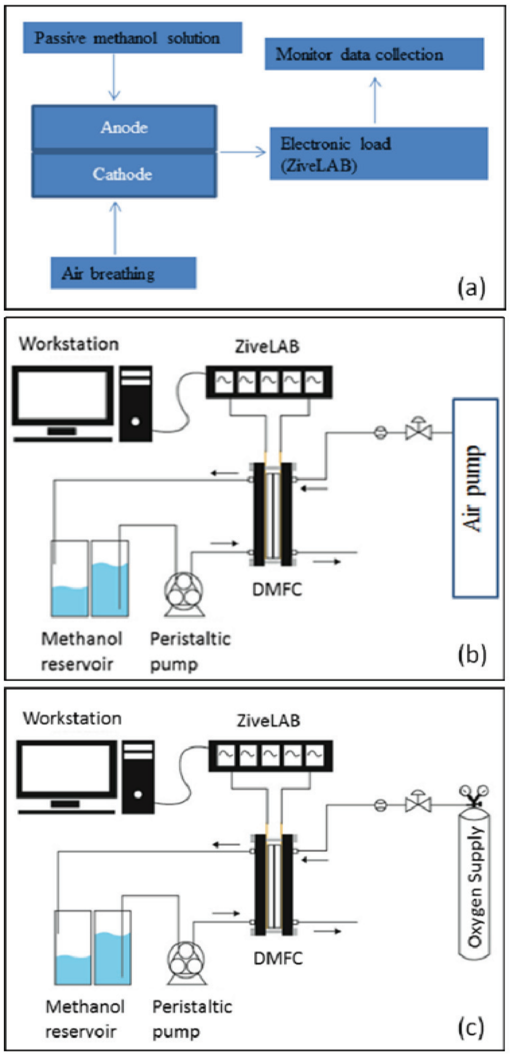

FIGURE 1. Schematic diagram of testing system in mode of operation (a) Passive; (b) Active-air; (c) Active-oxygen

For consistency of measurement, a non-recycling mode for methanol supply is applied. Meanwhile, air or high-purity oxygen was placed as the oxidants, and was allowed to flow continuously at a flow rate of 300 mL min^{-1} and its flow rate was regulated by a flow meter. For the methanol concentration as the parameter, the concentrations were varied with 2 M, 4 M, 6 M and 8 M for all three modes while for methanol flow rate as the parameter, flow rate of 1-4 mL min^{-1} was varied in the active mode only. A programmable electronic load (ZIVELAB) was employed to measure the power generated by the DMFC single cell.

The refractive index tests to analyze fuel consumption were carried using a refractometer (Reichert USA). Concentration of 2 M was monitored for each mode. Specifically, after each run of test, small amount of fuels were collected from either the storage tank and the concentration was determined using the refractometer. The efficiency was then calculated using the following equation:

$$FCCE\ (\%) = [(C_{before} - C_{after}) / C_{before}] * 100 \qquad (1)$$

where *FCCE* (%) is the fuel concentration consumption efficiency and *C* (M) is the concentration of diluted methanol.

RESULTS AND DISCUSSION

EFFECT OF AQUEOUS METHANOL SOLUTION CONCENTRATION

Figure 2 (a), (b) and (c) shows the voltage-current (V-I) and power-current (P-I) curves when single cell is operated at different modes and concentrations. It is shown that the cell performance increases directly with an increase in methanol concentration at different current densities. In Figure 2 (b) and (c) for the case of active modes, both experience the same output where the cell performance increases continuously with increasing methanol concentration from 2 to 6 M, reaching the maximum level of 8.39 mW cm^{-2} and 10.41 mW cm^{-2} at 6 M whereas the limiting current is obtained at approximately 90 mA cm^{-2} and 125 mA cm^{-2} respectively.

At higher concentration of 8 M, its value reversely decreases. This finding is coincident to many previous studies by other researchers (Yuan et al. 2017). These findings can be explained by the phenomena called concentration polarization (Yuan et al. 2016). This phenomenon happens when a concentration that is lower than optimal value is used because the fuel supply near the catalyst layer experiences exhaustion which can limit the cell performance at higher current densities. Hence, the use of higher fuel concentration can help the cell to maintain a strong performance at high current operation.

However, it is important to consider another effect of using excessively high concentration of methanol which is severe methanol crossover (MCO) from an anode to cathode. This explain why when 8 M of methanol concentration is used, it yields a lower performance than 6 M. Thus, it is important to find the optimum fuel concentration to avoid degrading performance at low concentration and fuel waste at high concentration. For the case of passive system in Figure 2 (a), the best concentration for highest power was obtained at 4 M followed by 6 M while the lowest at 8 M where this occurrence might be due to the same reason with active system. However, in passive system, the methanol crossover phenomena may occur at a slightly lower concentration at 6M compared to active at 8M.

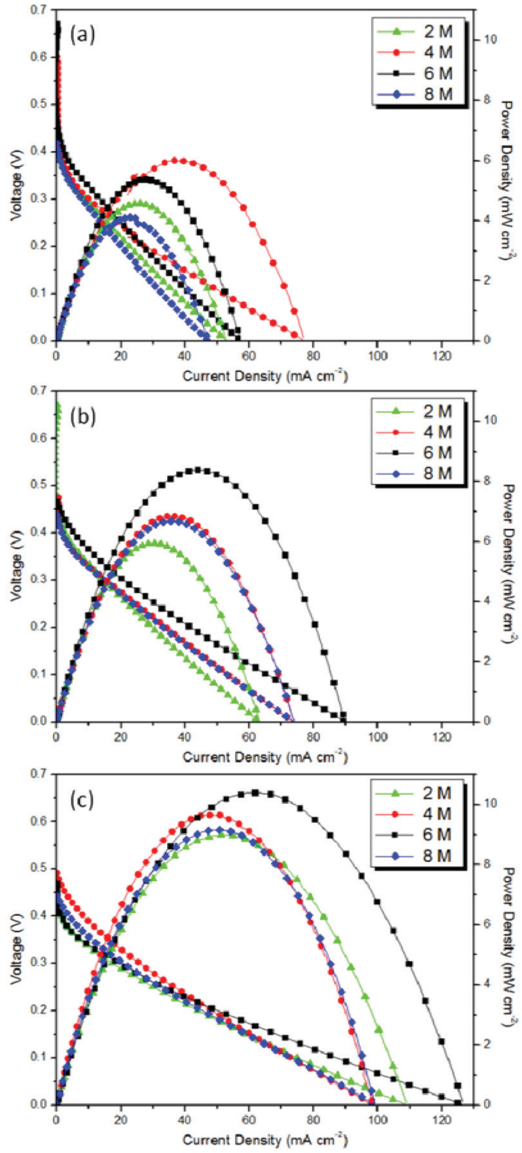

FIGURE 2. Effects of methanol concentration on the performance of the DMFC with different operational modes: (a) Passive; (b) Active-air; (c) Active-oxygen

EFFECT OF FLOW RATE OF AQUEOUS METHANOL SOLUTION

Figure 3 (a) and (b) shows the effects of methanol flow rate on the performance of DMFC system under both active modes. The concentration of methanol was kept constant at 6 M. It is found that the power density records the highest at 2 mL min^{-1} for both cases.

This flow rate value is considered the best speed to remove the gas CO_2 produced according to the electrochemical reaction that takes places at the anode side : $CH_3OH + H_2O \rightarrow CO_2 + 6H^+ + 6e^-$ (anode reaction).

At a lower and higher flow rates than this boundary, the cell gains poor performance. Different causes can lead to this finding. At lower methanol flow rate, i.e., 1 mL min^{-1}, the slower flow is not helpful to remove the gas bubbles produced in the anode channel thus blocking an efficient flow of methanol transport to the catalyst layer. Hence, a slightly higher flow rate is favorable which can open up to more fuel supply and mitigate methanol exhaustion (Yuan et al. 2016). However, when the flow is too fast, it can lead to heat loss which can reduce the cell operating temperature. Mass transfer of fuel methanol is the process occurs in the DMFC system at the anode side. Thus, a faster transport of the methanol will quickly remove the heat produced by the anode reaction and resulted in the decrease of cell temperature (Yuan et al. 2016). On one hand, this cooling effect can lead to low catalytic activity but on the other hand, it is an advantage to reduce MCO to some extent. One of the consequences may counteract each other and become the dominator.

Besides, a higher feed rate can result in increase of pressure difference between both sides of membranes thus can exacerbate MCO (Liao et al. 2007). Thus, flow rate of fuel is an important parameter to be considered in order to obtain a better performance especially in real application.

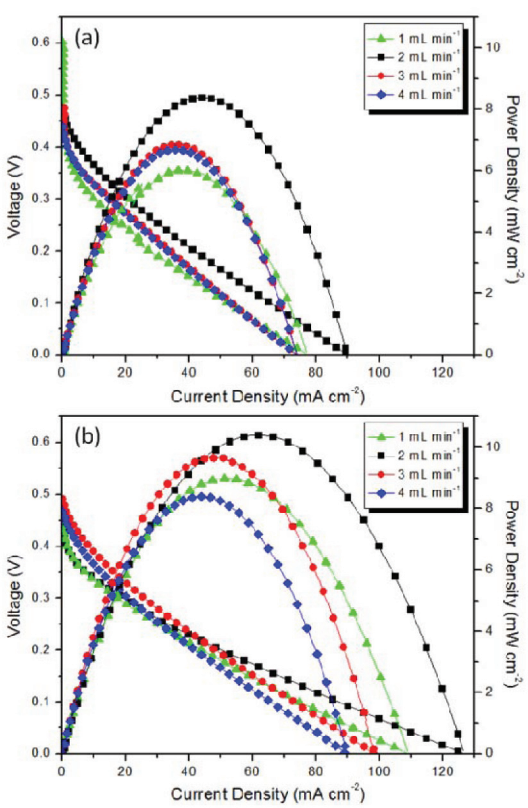

FIGURE 3. Effects of methanol flow rate on the performance of the DMFC with different operational modes: (a) Active-air; (b) Active-oxygen

COMPARISON OF DMFC PERFORMANCE AT DIFFERENT OPERATIONAL MODES AND PARAMETERS

Figure 4 (a) compares the power density of DMFC at different concentrations in passive, active-air and active-oxygen modes of operations. It is clearly shown that DMFC system with oxygen at the cathode exhibited the highest performance and yielded a maximum power density of up to 10.41 mW cm^{-2} followed by system with air at the cathode with 8.39 mW cm^{-2} and passive system with 5.39 mW cm^{-2} respectively. The same trend is also illustrated when different flow rate of methanol is applied to the anode side in active modes, Figure 4 (b).

DMFC system with oxygen recorded better performance than the other. This result is related to the difference in composition of oxygen in air, where only 21% of oxygen is available for oxidants supply from air compared to high purity oxygen in gas oxygen supply (Azam et al. 2019). Therefore, we can say that oxygen content for oxygen reduction reaction (ORR) in pure oxygen supply is higher than the one detected when only surrounding air is used at the cathode.

FUEL CONSUMPTION

Table 1 shows the fuel concentration at anode compartment before and after each test. Figure 5 clearly compares the

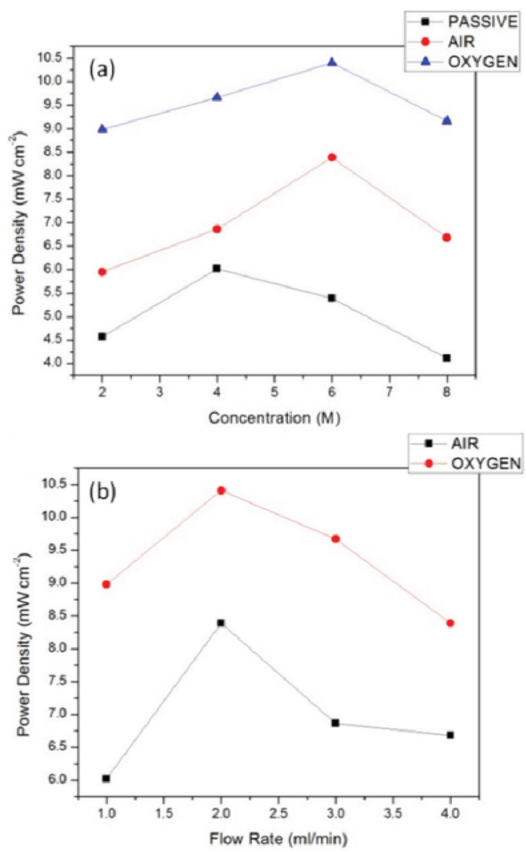

FIGURE 4. The peak power density at different modes with the use of (a) different methanol concentrations (b) different methanol flow rates

difference in fuel consumption among the operational modes. The fuel concentration in passive mode after the test recorded the highest which indicated less fuel is consumed during the operation which results to low efficiency.

Meanwhile, system with oxygen achieved the highest efficiency at 17.5%. The more fuel consumed, the higher power generated is expected to be produced due to a higher supply of fuel concentration. This explains why active system with oxygen produced the highest power density compared to the other modes.

TABLE 1. Fuel concentration measured before and after performance test and the efficiency

Mode	Concentration (M)		Fuel consumption efficiency (%)
	Before	After	
Passive	2	1.75	12.50
Active-air	2	1.70	15.00
Active-oxygen	2	1.65	17.50

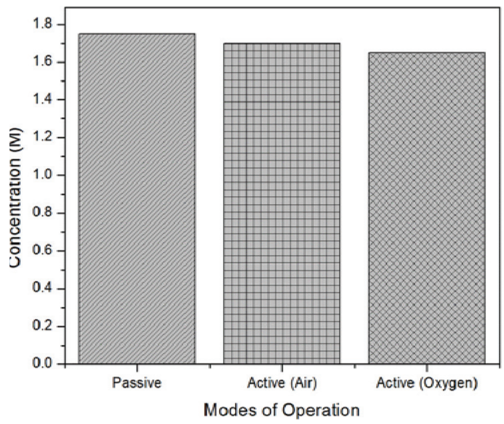

FIGURE 5. Methanol concentration at reservoir after one cycle of operation at different modes of operation

CONCLUSION

A performance study was carried out to determine the effect of operating conditions namely methanol concentration and flow rate on the performance of single DMFC system under different operational modes. The performance increases with increasing methanol concentration until it reaches optimum value. Besides, the performance also improves when flow rate of methanol increases until the value limits the optimum rate. Under all modes of operation, the active mode with oxygen yielded the highest value which peaks at 10.41 mW cm^{-2} during 6 M of methanol concentration and 2 mL min^{-1} rate of flowing methanol. It also records a better fuel consumption efficiency among all modes. These results indicate that investigating the optimum level of fuel concentration and flow rate can lead to enhancement of mass transport and diffusion thus generating better performance of DMFC system.

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