

Effect of Reactant Flow Rate and Operation modes on Direct Formic Acid Fuel Cell (DFAFC) Performance

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Abstract

Background/Objectives: The main focus of this research is to study the effects of reactant flow, i.e. formic acid and oxidant, and operation mode, i.e. passive, semi-passive or active conditions, on the Direct Formic Acid Fuel Cell (DFAFC) performances. **Methods/Statistical analysis:** A single cell DFAFC with 5 cm² electrode is used in this study. The DFAFC is operated with 10 M of formic acid concentration under four modes of reactant supply: air breathing, air flowing (80 to 600 mL min⁻¹), oxygen flowing (10 to 100 mL min⁻¹) at the cathode, and formic acid flowing (2 to 15 mL min⁻¹) at the anode to investigate their effects on cell performance. **Findings:** It is obtained that the DFAFC performances are affected by oxidant types, i.e., air and oxygen, flow rate, and the mode of operation. In passive operation, the maximum power density is obtained at 2.95 mW cm⁻². The highest performance is achieved in semi-passive using 50 mL min⁻¹ of oxygen with maximum power density of 10.92 mW cm⁻². Meanwhile, for semi-passive using air flow condition at 400 ml min⁻¹ shows a maximum power density at which 8.89 mW cm⁻². For active operation, the highest performance is obtained using 6 mL min⁻¹ with a maximum power density at 8.52 mW cm⁻². **Application/Improvements:** The semi-passive operation with oxygen could improve the DFAFC performances, and hence the DFAFC could be used as an energy source for electric and electronic applications.

Keywords: Active, DFAFC, Flow rate, Passive, Semi-passive

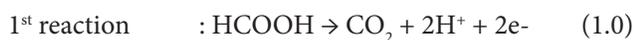
1. Introduction

Fuel cells are electrochemical devices that can realize direct conversion of chemical energy in the reactants to electrical energy with high efficiency and high environment compatibility¹⁻³. Fuel cell uses fuel, i.e., hydrogen or alcohol, and oxygen/ air as source of energy. As a reduction in polluting environment, fuel cell caught attention of researches as alternative way in replacing fossil type engine and battery for small size electronic devices⁴⁻⁸. Direct formic acid fuel cell (DFAFC) is a subcategory of direct liquid fuel cell. It has many advantages compare to other type of fuel cells, which includes; i) non-biohazard; ii) does not required special tank to store as formic acid exists in liquid form; and iii) lower crossover magnitude⁹.

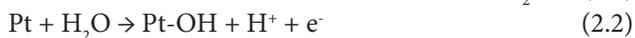
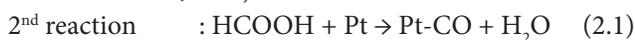
Theoretically, complete reaction of formic acid with oxygen can generate electromotive force (emf) of 1.48 V. The easiest mechanism that can be accepted is "series or dual mechanism"¹⁰. The first pathway is the dehydrogenation process, which involves complete oxidation of formic acid that will form carbon dioxide (CO₂) and hydrogen ion (H⁺). The second path forms carbon monoxide (CO) intermediate by dehydration method. Hydrogen ion will diffuse through Nafion membrane whereas electron will use the external circuit to reach cathode. Then, hydrogen ion and electron will combine with oxygen supplied to form water. Electron flows from external circuit forms complete circuit that will generate electric current. Equation below shows the overall reaction happen in DFAFC system¹⁰.

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Anode side:



Emf, $E^\circ \sim -0.25 \text{ V}$ (compare with standard hydrogen electrode, SHE)



Cathode side:



$E^\circ = 1.23 \text{ V}$ (compare with standard hydrogen electrode, SHE)

DFAFC system gets attention from many researches other than direct methanol fuel cell (DMFC). Nevertheless, DFAFC has many advantages compare to other fuel cell system, even though there are some constraints and issues need to be solved toward commercialization. Thus, all existing problems like dual reaction mechanisms slow in electro-oxidation activity, high manufacturing cost, and water as well heat management need to be solved to ensure constant performance all the time.

In order to improve the electro-oxidation activity¹¹ discovered that alloy Pt/Ru and Pt/Pd were capable to reduce CO catalytic poisoning. Catalytic poisoning can limits activity of catalyst in formic acid oxidation at anode. In order to enhance the performance of Pd/C catalyst, a binary catalyst metal was introduced for reducing catalytic poisoning. Several studies have been implemented for this binary metal catalyst including using Pd-Ir/C¹, formic acid/formate blended solution¹², and PtSb/C¹³. Recently, a study has been done on Pd nanoparticles with phosphomolybdic acid (HPMo), poly (diallyldimethylammonium chloride) (PDDA), and functionalized multiwalled such as carbon nanotubes (CNT) supports. Pd/HPMo-PDDA-MWCNT shows higher activity and stabilization for electro-oxidation compare to Pd/C¹⁴.

The deficiency in formic acid fuel is a low volumetric power density with only 2104 Wh L⁻¹, which is lower than methanol fuel at 4600 Wh L⁻¹¹⁰. At anode side, direct oxidation of formic acid only forms two electrons per molecule. Theoretically, power density of formic acid should be 2.1 times less than the power density of DMFC¹⁵. In order to increase the power density, reactants flow rate and their concentration need to be increased. However, by increasing the reactant flow rate or concentration, it will affect other mechanisms like fuel

crossover, fuel diffusion, water and heat management. The fuel crossover and diffusion rate would increase with increasing or concentration while flooding issue might occur if not properly control⁸.

In order to commercialize the DFAFC for portable power source, the production of DFAFC system needs to be increase in a large scale. However, high manufacturing cost scared entrepreneur from taking the risk. Gross manufacturing cost consists of raw material cost and operating manufacturing cost. Raw material cost hard to minimize due to low capacity production of electrolyte membrane such as Nafion. Pd, Pt or binary precious catalyst also consider as an expensive materials. Thus, a proper research need to be investigated, i.e. method of fabrication and new materials development, to reduce manufacturing cost.

Electro osmosis force and back diffusion are types of water transport happen in DFAFC system. These two types of water transport happen naturally and not consistent because of changing in operating parameters. When the rate of water dispense lower than rate of generation of water, water will accumulate at cathode side and cause flooding. Flood will block the porous of gas diffusion and catalyst layer and reduce the diffusion of oxygen¹⁶. An active site for reaction will block and cause inconsistent distribution of current and sharply drop in performance at high current density¹⁷. Flooding can also happen at anode when flow rate of fuel too low to remove water from channel¹⁸. When the water removed rate is higher than generation of water (from electrochemical reaction), the dehydration of membrane will happen and cause in increase the cell resistance and hence the degradation of performance due to ohmic loss in cell¹⁷. Many researchers studied on the electrode structure to reduce the flooding phenomena including hydrophobic treatment on gas diffusion layer (GDL) layer using PTFE, adding the micro porous layer (MPL) on membrane electrode assembly (MEA) layer, and design of channel flow serpentine layout¹⁶.

Conversion of energy not efficient as expected in DFAFC system. More than half of electrochemical energy convert into thermal energy in process of generate electricity. Thermal energy generate in fuel cell consists of 55 % irreversible heat, 35% entropy heat and 10% resistant heat¹⁹. Thermal energy has to release to surrounding to ensure temperature is in optimum range. Trapped energy will contribute to hotspot that might destroy the structure of component especially MEA structure¹⁹. Besides, heat

also can cause dehydration at membrane and inconsistent temperature can cause performance degradation. In order to stabilize performance of fuel cell, the fuel cell system needs a good heat management system that successfully releases the heat and safety regarding when thermal out of control²⁰.

As mentioned previously, some exiting problems limit the commercialization of DFAFC, including catalytic poisoning²¹, high cost of catalyst and membrane, cross over that causing problem in heat management, and water management that might cause flooding issue. Based on literature review done, problems that slow down commercialization of DFAFC made up of dual electrochemical reaction, normal power density, high production cost, water and heat management. All these problems are related with flow rate at both anode and cathode side¹⁷⁻²⁰.

By choosing an optimum flow rate can reduce catalytic poisoning that form Pd-CO complex, flooding issue or membrane drying issue and not influence the diffusion of oxygen and formic acid into DFAFC system. Many researches done regarding optimum flow rate but mostly focus on polymer electrolyte membrane fuel cell (PEMFC), including experimental studies on optimal operating conditions for different flow field designs of PEM fuel cells²², characterization of high performing passive DFAFC¹¹, performance of an active DMFC fed with neat methanol²³.

In PEMFC²² studied the effects of operating parameters condition including humidity temperature, cell temperature and flow rate of gas supply to cathode side using different types of flow channel towards cell performance. The number, angle and length of channel were considered in designing of flow channel. They concluded that PEMFC with baffles in flowing channel shows better performance due to baffle force reagent gas diffuse into GDL layer. The cell performance increased with increasing the flow rate until optimum value.

Meanwhile¹¹ investigated the operating parameters such as temperature, operation modes, fuel concentration towards the DFAFC performance. The performance test was measured by focusing on the polarization curve of DFAFC on three different conditions (passive, semi-passive and active). Based on their study, the passive DFAFC showed a lowest power density compared to that semi-passive and active types. They concluded that the performance of passive DFAFC limited by performance at cathode site due to unsatisfactory oxygen transportation.

Moreover, in DMFC,²³ studied the relationship of mass transport in anode using porous carbon plate (PCP) at high methanol concentrations in order to increase the DMFC performance at passive type operation. The methanol flow rate only slightly influenced the performance of cell due to existence of the PCP. The maximum power density achieved at lowest flow rate of 2 mL min⁻¹. The lower flow rate of fuel will benefit the DMFC system in reducing the outside power source for supplying fuel and increase system's efficiency. For the effect of air flow rate towards cell performance, an increasing flow rate till 400 mL min⁻¹ would increase the voltage and the maximum current density, and thus increasing the power density. The peak power density was achieved at 800 mL min⁻¹ flow rate is 56 mW cm⁻². However, they concluded that an increase in air flow rate would cause an increase in methanol crossover, and hence influence the MEA performance.

From the discussion above, it shows that the reactant's flow rates has significant effect towards phenomena such as mass transport, fuel crossover and flooding, and hence affect the fuel cell performance. However, only few papers reported on the effects of flow rate towards DFAFC performance. Moreover, previous researches only focus on one optimum operating condition, either in passive, semi-passive or active condition. The main objective of this research is to compare the performance of cell at different reactant flow rates on all operating modes condition, i.e., passive, semi-passive, active, in order to get optimum flow rate on each operating condition.

2. Experimental

2.1 MEA Fabrication and MEA Pre-Treatment

Active area for membrane electrode assembly (MEA) used is 5 cm². NRE 212 was used as the polymer electrolyte membrane. Palladium black (Alfa Aesar) and Platinum black (Alfa Aesar) were used as catalysts for the anode and cathode, respectively. The catalyst inks were prepared by dispersing an appropriate amount of the catalyst in a solution of de-ionized water, isopropyl alcohol, and 5 wt.% Nafion[®] solution (Wako Pure Chemical Industries, Ltd.). For the anode, Pd ink was coated with 2 mg cm⁻² of carbon black on carbon paper. For the cathode, Pt ink was coated on carbon paper with 2 mg cm⁻² of carbon black. Catalyst loadings were 4.0 mg cm⁻² for Pd (the anode) and 4.0 mg cm⁻² for Pt (the cathode). The MEA was then

fabricated by sandwiching the membrane between the anode and cathode and hot pressing them at 135 °C and 5 MPa for 3 minutes.

The MEA was conditioned initially within the test fixture at 70 °C under the H₂/air fuel cell operating mode for 1 hour, while holding the cell potential at 0.6 V. Cell potential was controlled by a fuel cell testing electric load (Paxitech). H₂ flow rate was set to 600 mL min⁻¹ and the flow rate of air to the cathode was set as 1200 mL min⁻¹; both streams were humidified at 70 °C prior to entering the cell. The humidified H₂ and air was used to activate the catalyst in order to maximize the performance of the DFAFC.

2.2 Measurement of DFAFC Performance

The experiment was started by choosing two different formic acid concentrations with 4M and 10 M to obtain the optimum voltage from the polarization curve. The oxidant (air) flowed through the cathode side. Different reactants flow rates were tested during the two-hour operation using fabricated single cell DFAFC as shown in Figure 1. The DFAFC was operated under four modes of reactant supply: air breathing, air flowing, oxygen flowing, and formic acid flowing to investigate their effects on cell performance. The experimental setups for different operations are shown in Figure 2. The air was supplied at 80 to 600 mL min⁻¹ at the cathode and the formic acid was fed passively at the anode by injecting 8 ml formic acid solution to the reservoir (shown in Figure 1).

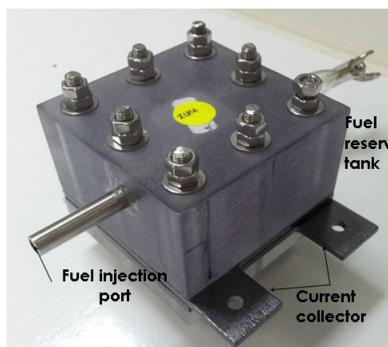


Figure 1. Single cell DFAFC used in this study.

Then, the oxidant was changed from air to oxygen, which was supplied at 10 to 100 mL min⁻¹ at the cathode. The oxidant flow at the cathode is also known as the semi passive cell mode. For active DFAFC operating condition, air flow rate was fix at 200 mL min⁻¹, while formic acid was fed at 2 to 15 mL min⁻¹ at the anode, which is also known

as the active cell mode. Passive operating condition was used as control experiment to compare with other operating conditions. The performance of the cell was investigated by operating the cell at a constant voltage of 0.4 V, and the current and power profiles were measured throughout the two-hour operation using a Potentiostat/Galvanostat (Wonatech WMPG 1000).

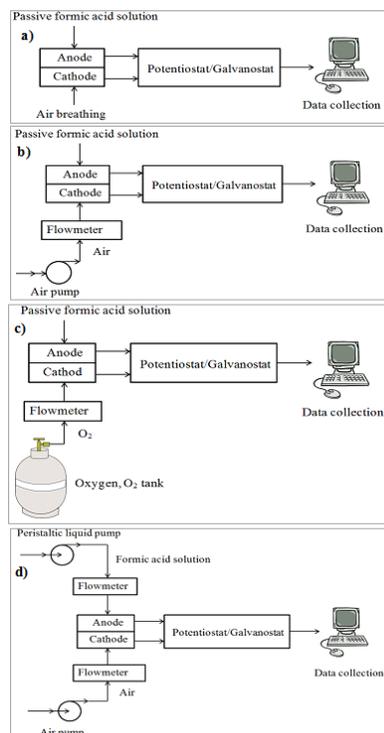


Figure 2. Experimental setup for DFAFC performance, a) Passive; b) Semi-passive – air; c) Semi-passive – O₂; d) Active.

3. Results and Discussion

3.1 Polarization curve of DFAFC

Pre-conditioning of MEA was implemented to activate the MEA catalyst of DFAFC. For the passive DFAFC, the operation conducted at room temperature or low temperature, hence the activation of MEA is required. The operation of PEMFC, the hydrogen absorption occurs rapidly due to the small molecular size. This is in contrast to the direct liquid fuel cell (DLFC) which requires activation on site reactions at the electrodes to provide a uniform absorption. According²⁴, activation of the MEA can reduce the resistance of the MEA which in turn increases the current drawn.

After pre-conditioning or MEA activation, single cell of DFAFC was tested for IV measurement, also known as polarization curve, in order to optimize the cell voltage that would be used for this study. In some cases, the testing performance would reduce the DFAFC performance after long term operation, i.e. above 2 h. Thus, regeneration of DFAFC was required to reactivate the MEA to its initial performance. This could be due to the attachment or adsorption of intermediate products such as CO in active site of catalyst. Based on previous reports^{11,25}, there are several methods to reactivate the MEA performance. For instance, Ha et al. applied a high potential on Pd catalyst at anode side, and hence the catalytic activity can be restored easily and fast⁹. Another method is by replacing the formic acid solution with pure water, i.e., washing method, to restore its performance²⁵.

In this study, the purpose of fixing the constant voltage is to ensure the power produces by DFAFC cell always at optimum value. Fixing the optimum constant voltage for the single cell operation can be done by analysing the polarization curve and power-current profiles. For 20 h single cell DFAFC operation²⁶ obtained the performance at constant voltage 0.2 V and 0.4 V showed a higher power density compared to that at 0.6 V and 0.8 V.

Figure 3 (a) shows the polarization curve for formic acid solution with concentration 4 M and 10 M. The cell voltage decreased with increasing of current density, while the power density increased with increasing of current density until it reaches optimum point as shown in Figure 3 (b). For 4 M formic acid polarization curve, the peak power density achieved at 4.21 mWcm^{-2} with 0.40 V cell voltage while for 10 M obtained at 5.31 mWcm^{-2} with 0.35 V, which 1.5 times higher than peak power density at 4 M.

From Figure 3, it shows that the different in polarization curve and power-current profiles are due to the different in formic acid concentrations. It was easily understood that a higher formic acid concentration has a higher concentration gradient that assisting diffusion of formic acid across the GDL layer. Therefore, a greater numbers of molecule increase the reaction rate and form more hydrogen ions (H^+) and increase the generation of power density. Moreover, based on Figure 3, it shows that both peak power densities obtained at 0.35V and 0.40 V. The peak power density at this optimum voltage range was similar to that previous reported²⁶. Thus, a constant voltage of 0.4 V was fixed to compare the performance of single cell DFAFC cell at different operating conditions.

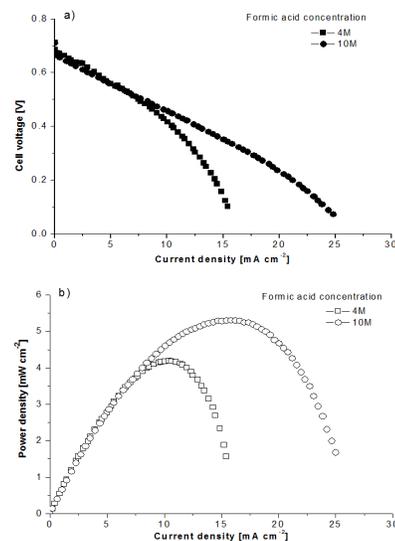


Figure 3. (a) Polarization curve; (b) Power-current profiles, for 4M and 10M formic acid concentrations.

3.2 Single Cell DFAFC with Passive Mode Operation

In passive condition, single cell DFAFC does not receive any flow supply, or any back pressure and humidification system at both sides of anode and cathode. Cathode side was exposed to surrounding ambient air, while 8 mL formic acid was injected into fuel reservoir tank in DFAFC cell. Both formic acid and air diffuse across the gas diffusion layer (GDL) layer by diffusion mechanism due to concentration gradient. Figure 4 shows a single DFAFC cell performance during 2 h operation in passive mode condition. From the figure, the current density and the power density increase initially and then slowly decrease with time. The maximum current density and power density obtained at 7.39 mA cm^{-2} and 2.95 mW cm^{-2} , respectively. It was easily understood that the decreasing of current density with time because of formic acid was consumed in the anode reaction and hence, the remaining formic acid in the reservoir would be diluted.

On the other hand, from previous studies by other researchers^{28,29}, it was obtained that the CO poisoning was one of the factor to degrade the DFAFC performance. A higher degradation rate occurred at high current density and vice versa. Therefore, it was suggested that the CO intermediate product produced from formic acid oxidation at high current density using 10 M. Those, the DFAFC performance, i.e. current and power profiles for 10 M, (as shown in the Figure 4) could be affected by CO

poisoning phenomenon and hence, the degradation rate would be increased.

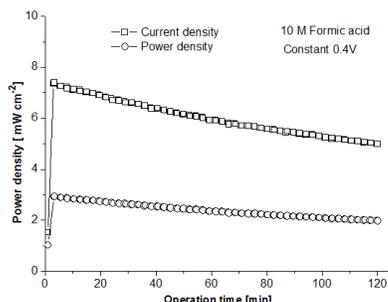


Figure 4. Power and current profiles of DFAFC with operation time at 0.4 V using 10 M formic acid concentration.

3.3 Single Cell DFAFC with Semi Passive Mode Operation

3.3.1 Effect of air flow rate at cathode

In semi-passive condition, normally cathode flow is the manipulated variable rather than anode side. The first part of this study is by controlling the air flow rate supply to the cathode. Figure 5 (a) shows the profile of power density for different air flow rate during 2 h cell operation in semi-passive mode condition. Similar profiles were obtained which the power density increased sharply then followed by slowly decreased.

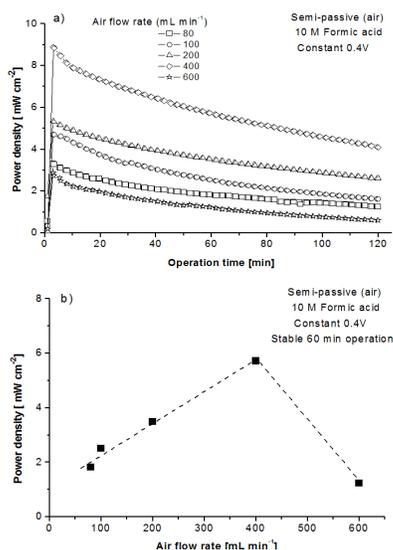


Figure 5. (a) Profile of power density with different air flow rate during 2 h operation time; (b) The relationship between stable power density and flow rate of air; under semi-passive mode operation using 10M formic acid concentration and constant 0.4V.

As mentioned previously, the performance drop could be due to several factors such as dilution of formic acid concentration, MEA degradation (CO poisoning) and fuel crossover. By comparing Figure 4 and Figure 5, the air flow rate at 80 mL min⁻¹ showed a higher peak power density than in passive mode system. This situation shows that the air convection using air pump can ensure the excess of oxygen supply to the cathode and improve the electrochemical reaction. Thus, a higher rate of oxygen will diffuse to the catalyst layer due to concentration gradient, and hence improve the oxygen reduction reaction (ORR) at cathode.

Figure 5(b) shows the relationship between the flow rate of air and power density under stable operating conditions (60 min). From the figure, it was clearly showed that the stable power density increased with the increasing flow rate of air up to 400 mL min⁻¹ before its decreased above 400 mL min⁻¹, i.e., 600 mL min⁻¹. The maximum stable power density obtained is 5.82 mW cm⁻² at 400 mL min⁻¹. This tendency was similar to that Nakagawa et al. research³⁰. They found that the increasing flow rate increased the cell voltage at low current density. This will increase maximum current density and power density. They concluded that a higher flow rate support the air diffusion process into GDL layer and react with hydrogen ion and form water. Water formed will be removed by air convection.

Increasing the flow rate of air at the cathode enhances the oxygen mass transfer at cathode, and hence improve the driving force for mass transfer through the MEA. Moreover, by increasing the flow rate of air also prevents flooding at the cathode by increasing the rate of water removal by evaporation. However, at higher rates of air flow, the power density starts to drop severely, possible because of the dehydration of electrolyte membrane due to higher forced convection at cathode. Therefore, it would slow the proton transport, and hence decreased the current density³⁰.

3.3.2 Effect of oxygen flow rate at cathode

For the effect of oxygen flow rate on the DFAFC performance, oxygen supplied through oxygen tank with high purity of 99.9 %. Oxygen was supplied from tank with 1 bar (pressure gauge), while flow meter was used to control the oxygen flow rate. Figure 6 (a) shows the profile of power density with different oxygen flow rate from 10 to 100 mL min⁻¹ using 10 M concentration and

fixed 0.4V. Again, a similar profiles were obtained which the power density increased sharply then followed by slowly decreased could due to the fuel dilution and MEA degradation.

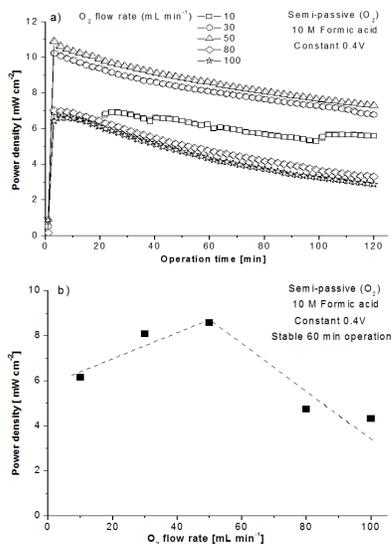


Figure 6. (a) Profile of power density with different oxygen flow rate during 2 h operation time; (b) The relationship between stable power density and flow rate of oxygen; under semi-passive mode operation using 10M formic acid concentration and constant 0.4V.

Figure 6(b) shows the relationship between the flow rate of oxygen and power density under stable operating conditions (60 min). From the figure, it was obtained that the stable power density increased with the increasing flow rate of oxygen from 10 to 50 mL min⁻¹ before the performance dropped above 50 mL min⁻¹. The maximum stable power density of 8.58 mW cm⁻² is achieved by a 50 mL min⁻¹ O₂ flow rate. As mentioned previously, an increasing the flow rate of oxygen at the cathode would enhance the oxygen mass transfer at cathode, and hence improve the driving force for mass transfer through the MEA. Meanwhile, for low oxygen flow rate at 10 mL min⁻¹, the fluctuate profile could be due to the flooding occurred at cathode. The water accumulated at cathode during small convection force would affect the current distribution, and hence affects the power profile at 10 mL min⁻¹ as shown in Figure 6 (a).

Similar profile trend was obtained²⁷ for DMFC performance. They concluded that increasing oxygen flow rate can increase cell current and increase maximum current density and power density. However, the

performance drop after 50 mL min⁻¹ O₂ is due to high oxygen purity flavor to occur a formic acid crossover, and hence reduce the DMFC performance. Meanwhile, for this study, the performance drops with flow rates higher than 50 mL min⁻¹ of O₂ due to high O₂ purity, which could affect the stoichiometric balance of the overall reaction, and hence reduces the performance of DFAFC as shown in decreasing power density at 80 and 100 mL min⁻¹ O₂.

In conclusion, in case of semi-passive mode operation at high flow rate, i.e. when the slope changed to negative, it was suggested that the rate determining step changed and would be controlled by the electrodes reaction rates. It was probably due to the oxidation of formic acid on anode which more rapid than reduction of oxygen on the cathode. At high flow rate, dehydration of electrolyte could be occurred and slowed the movement of proton (H⁺). Therefore, it would be reduced the cathode reaction rate (reduction of oxygen), and hence reduced the current density of DFAFC as shown in Figure 5 (b) and Figure 6 (b).

3.4 Single Cell DFAFC with Active Mode Operation

In active mode condition, formic acid solution was placed in a reagent bottle and peristaltic liquid pump (Compulab® 3 72-777-100 model) was used to pump the fuel to the anode of DFAFC cell. Figure 7 (a) shows the profile of power density with different formic acid flow rate from 2 to 15 mL min⁻¹ using 10M formic acid concentration and fixed 0.4V during 2 h operation time.

A similar profiles were obtained which the power density increased sharply then followed by slowly decreased could due to the MEA degradation. However, unstable power density at low flow rate especially at 2 mL min⁻¹ because inconsistent formic acid flows at low flow rate through peristaltic pump.

Figure 7 (b) shows the relationship between stable formic acid flow rate and DFAFC performance using 10 M concentration and fixed 0.4V. In Figure 7 (b), it shows that the power density increases from 2 to 6 mL min⁻¹ formic acid and decreases linearly with increasing formic acid flow rate from 6 to 15 mL min⁻¹. The highest stable power density of 5.85 mW cm⁻² is obtained at a flow rate of 6 mL min⁻¹. The power density of the formic acid flow rate is much lower compared with the semi passive DFAFC, as shown in Figure 5 and Figure 6.

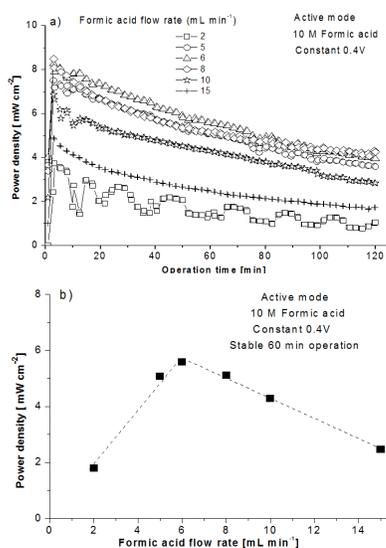


Figure 7. (a) Profile of power density with different formic acid flow rate during 2 h operation time; (b) The relationship between stable power density and flow rate of formic acid; active mode operation using 200 mL min⁻¹ air flow, 10 M formic acid concentration and at constant 0.4V.

According to²³ in DMFC, highest power density reached at lowest flow rate, which is at 2 mL min⁻¹ with pure methanol is used. In this study, different optimum flow rate of formic acid power obtained at 6 mL min⁻¹ could be due to the difference in concentration, i.e., 10 M formic acid and 24.7 M methanol, and MEA structure, i.e., different catalyst used.

On the other hand, the performance drops at high flow rate of formic acid, i.e. above 6 mL min⁻¹, could be affected by the increasing of magnitude fuel crossover with flow rate. It can be understood that by increasing the formic acid flow rate at anode, hence it would increase the driving force at anode, and influence the fuel transport to the cathode. The fuel crossover is causing formic acid directly reacts with oxidant at cathode and forming the flooding. Therefore, it would affect the DFAFC performance by reducing the power density as shown in Figure 7.

3.5 Effect of Operation Mode in DFAFC

Figure 8 shows the power density profile the current profile for different operational modes of DFAFC: passive, semi-passive (air), semi-passive (O₂), and active. The different types of DFAFC mode operation were compared for each flow rate parameter at 10 M and fixed 0.4V. From the figure, the passive mode shows the lowest DFAFC

performance. It could be due to less oxygen transport (oxygen starvation) and slows the oxygen reduction reaction (ORR) at cathode. Meanwhile, it is obtained that the semi-passive with O₂ flow obtained the highest maximum power density followed by semi-passive with air flow. By operating the single cell in semi-passive mode, it would improve the oxygen driving force for mass transfer at cathode and improve the ORR, and hence increase the DFAFC performance.

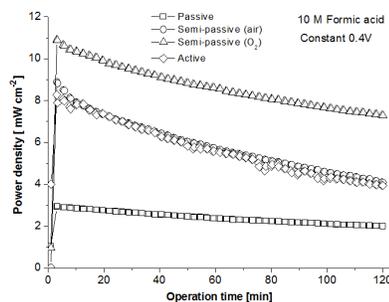


Figure 8. Profile comparison effect flow rate against DFAFC cell performance.

Active DFAFC exhibited only a small improvement on the cell performance; the change in flow rate at the cathode affected the performance of the cell more than that at the anode. This could be related to the transfer of formic acid fuel through the MEA, i.e., fuel crossover, and therefore, the change in the formic acid flow rate has only a slight effect on the mass transfer rate. Varying the methanol flow rate also had a slight effect on the mass transfer rate, as reported²³.

Moreover, for active DFAFC, maximum power density is less than semi-passive operating condition is due to limitation of air mass transport. Therefore, it was suggested that a higher oxygen mass transport, i.e., increase the air flow rate or use higher flow rate of oxygen, could be improved the electrochemical reaction in the cell, and hence increase the performance of DFAFC.

4. Conclusion

The effects of reactant flow, i.e. formic acid and oxidant, and operation mode, i.e. passive, semi-passive or active conditions, on the DFAFC performances were investigated. The change in oxidant flow rate, i.e., oxygen and air, at the cathode caused a greater effect on the performance of the cell compared with that at the anode. A high flow rate increases the driving force and

improves the mass transport by reducing the flooding at cathode and reducing the fuel crossover in the DFAFC. Furthermore, it was suggested that the overall DFAFC performance was mainly determined by the rate-determining step, i.e. fuel and oxygen supply, and electrode reaction (ORR). The semi passive DFAFC gave the highest cell performance compared with the active DFAFC and passive DFAFC. Therefore, semi passive DFAFCs are preferable because they are less complex and do not need additional equipment such as an auxiliary pump unit at anode. Hence, by optimizing the reactant flow rate, it would improve the performance of DFAFC and give opportunities for DFAFC use as an energy source for electric and electronic applications.

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