CHAPTER 6

STUDY OF BIOLOGICAL AND CHEMICAL COMPONENTS IN THE BFC

In this chapter, the effect of biological and chemical concentrations such as glucose, yeast, methylene blue and ferricyanide ($K_3Fe(CN)_6$), will be investigated. The performance of the BFC with different electron mediators such as methylene blue (MB), neutral red (NR) and rhodamine B (RhB) were compared for finding the good mediator in the BFC system. In addition, the performance of two electron acceptors such as ferricyanide and dissolved oxygen were explored for enhancing the BFC performance.

6.1 Bio-Fuel Cell Experiments

Firstly, the 2515010 compartment was used for studying of biological (yeast) and chemical (glucose, MB and $K_3Fe(CN)_6$) concentrations on the BFC performance. Carbon fiber electrode was used in both compartments. Each electrode had a surface area of 50 cm^2. The anodic compartment contained with 10 mg/ml of baker's yeast, 0.1 M of glucose and 1 mM of MB. One mM of ferricyanide in 0.1 M, pH 7.0 PB was used in the cathodic compartment. The compositions for both anodic and cathodic compartments were listed as follows:

Anodics : PB 0.1M (pH7)+yeast 10mg/ml+glucose 0.1M+MB 1mM

Cathodics : PB 0.1M (pH7)+$K_3Fe(CN)_6$ 1mM

In these experiments, the glucose, yeast, MB, ferriccyanide concentrations were changed in the range 1mM-0.1M, 2.5mg/ml–15mg/ml, 0.1mM–20mM and 0.05mM–5mM, respectively.

For the study on the effect of electron mediator and acceptor, the 0819010 compartment was used as the BFC compartment. Each carbon fiber electrode in the anodic or cathodic compartment had a surface area of 60.5 cm^2. The anolyte for both studies consisted of baker's yeast and glucose with the concentration of 21 mg/ml and 53 mM in 0.01 M phosphate buffer (pH 7), respectively. The effect of electron mediator study, the concentration of each electron mediator (MB, NR or RhB) was 3mM and 0.5 mM of ferricyanide was used as electron acceptor.

The effect of electron acceptor study, the catholyte consisted of 0.5 mM of ferricyanide solution and/or oxygen in a 0.01 M phosphate buffer (pH 7). Three mM of MB was used as electron mediator in the anodic compartment.

The compositions for both anodic and cathodic compartments were listed as follows:

Anodics : PB 0.01M (pH7)+yeast 21mg/ml+glucose 53mM+electron mediator (MB, NR or RhB) 3mM

Cathodics : PB 0.01M (pH7)+$K_3Fe(CN)_6$ 0.5mM and/or oxygen (500 min/ml)

6.2 Results and Discussions

6.2.1 Effect of Biological and Chemical Concentrations in the Bio-Fuel Cell

6.2.1.1 Glucose Concentration

The voltage-current density characteristics of the BFC with different glucose concentrations is shown in Fig. 6.1. It was found that the open circuit voltage of the BFC was in the range of 300-350 mV. For the current density generation, the highest glucose concentration could generate the current density up to 18 mA/m^2.

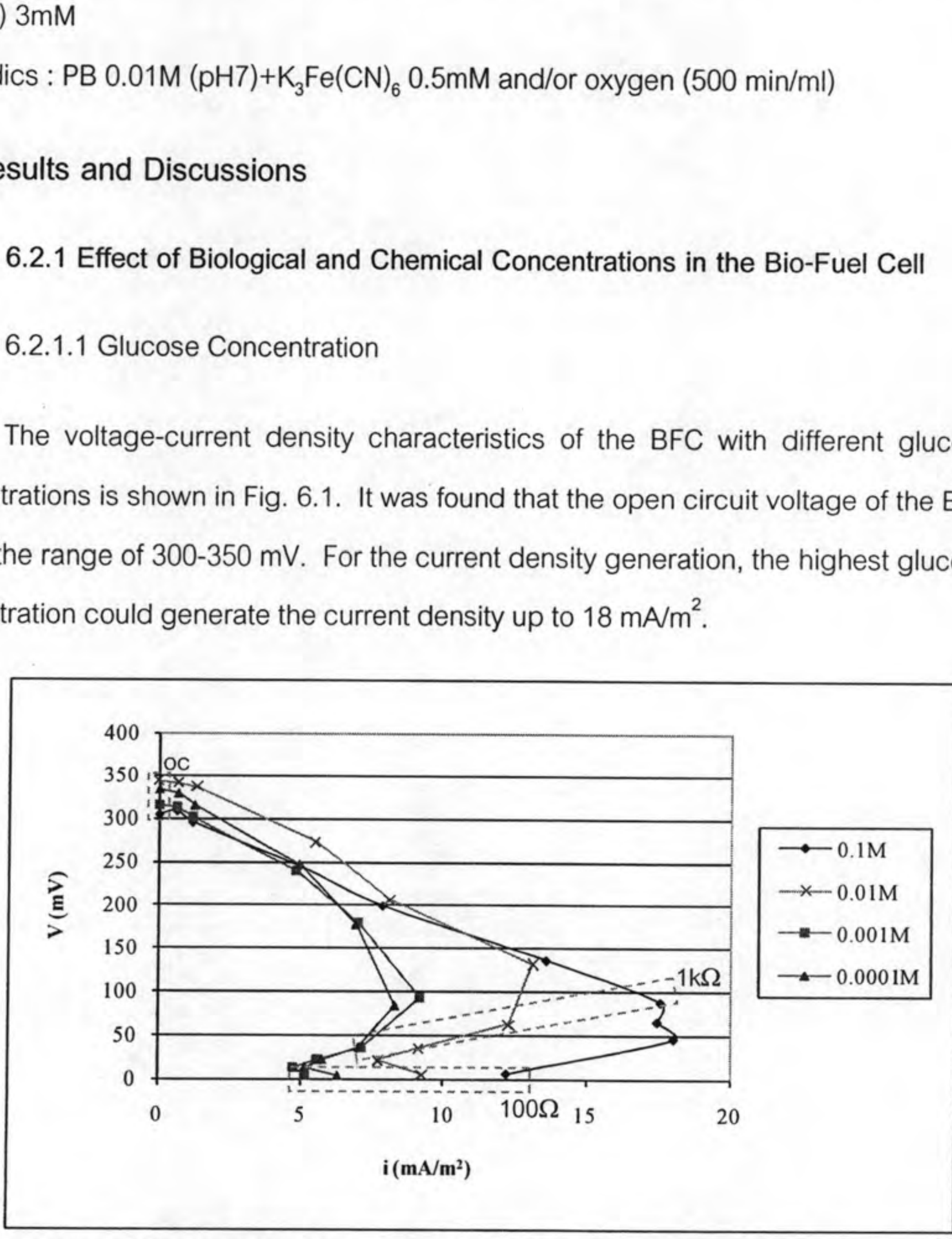


Fig. 6.1 Voltage vs. current density of the BFC with different glucose concentrations

The voltage generation vs. glucose concentration of the BFC at the open circuit and 1kΩ load is shown in Fig. 6.2.

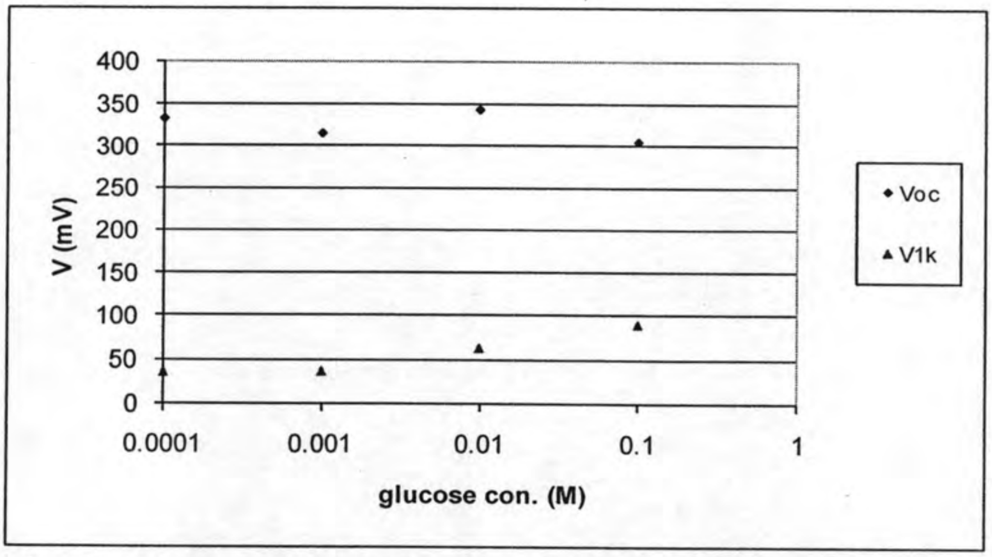


Fig. 6.2 Voltage generation of the BFC with different glucose concentrations

As shown in Fig. 6.2, it was found that the glucose concentration affects the current generation of the BFC. The current density of the BFC increases as the glucose concentration increases. The increasing of current density might be caused by the higher diffusion of the high glucose concentration into the yeast cell. The power density–load characteristics of the BFC with different glucose concentrations is shown in Fig. 6.3.

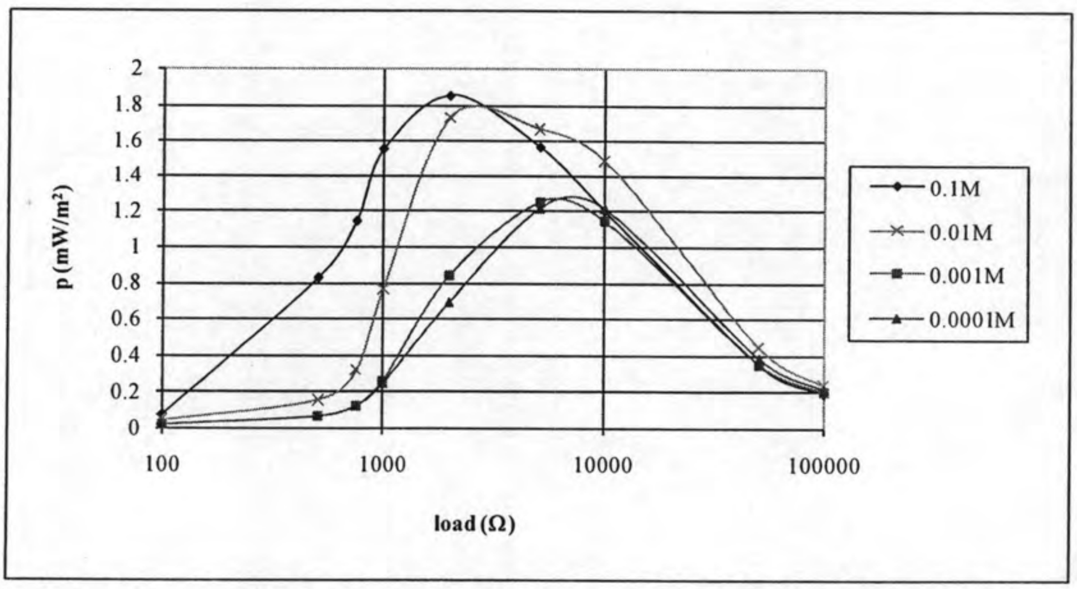


Fig. 6.3 Power density-load characteristics of the BFC with different glucose concentrations

The results show that the glucose concentration affects the power density generation of the BFC. The maximum power density of 1.8 mW/m^2 at 2 $k\Omega$ load was obtained from the highest glucose concentration. Considering the load at which the maximum power was obtained for each glucose concentration, it indicates that the Thevenin resistance decreases as the glucose concentration increases. The Thevenin resistance for each BFC with different glucose concentrations (slope of V-I characteristics at ohmic loss region in Fig. 6.1) is shown in Fig. 6.4.

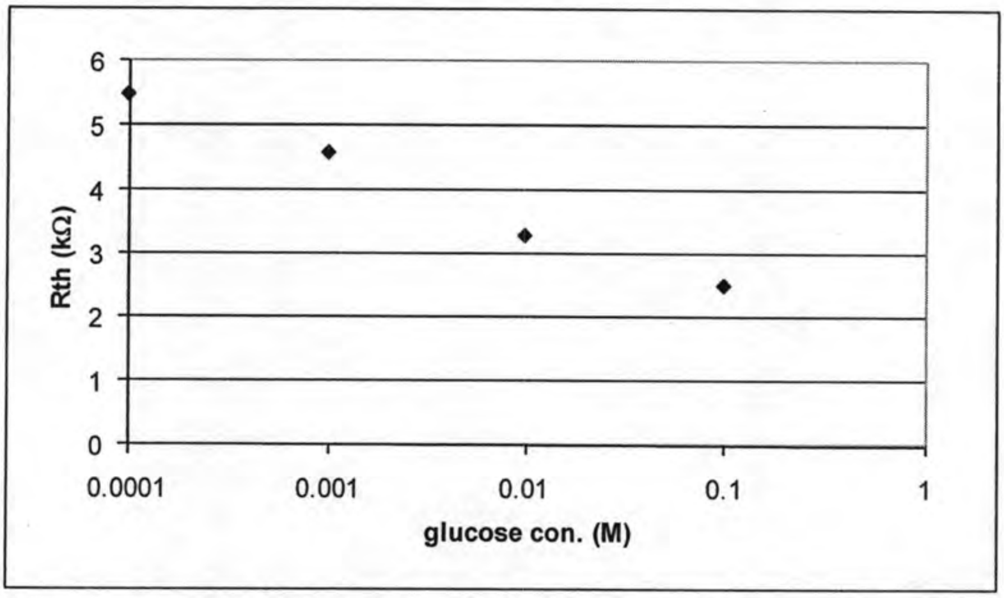


Fig. 6.4 Thevenin resistance of the BFC with different glucose concentrations

As shown in Fig. 6.4, it shows that the Thevenin resistance increases if the glucose concentration decreases. It implies that the increasing of the glucose concentration can enhance the electron transfer in the BFC.

6.2.1.2 Yeast Concentration

Fig. 6.5 presents voltage-current density characteristics of the BFC with different yeast concentrations. The yeast concentration was set to be less than 15 mg/ml because the concentration higher than 15 mg/ml will cause the solution overflows at the anodic chamber. It is obvious that the better performance can be obtained by increasing the yeast concentration. At the highest yeast concentration, the voltage and current density up to 350 mV and 20 mA/m^2 (at 100 Ω), respectively, could be generated. Considering the V-I characteristics of the BFC at high resistance load (low resistor), the results show that the different yeast concentrations affected the current density at the concentration loss region. The current at the concentration loss region dramatically dropped as the yeast concentration decreased. It is well known the yeast is the electron generator in the BFC, the increasing of yeast concentration will lead to the increasing of the energy producer. Then, the higher energy will be obtained as the yeast concentration is increased as found in Fig. 6.5.

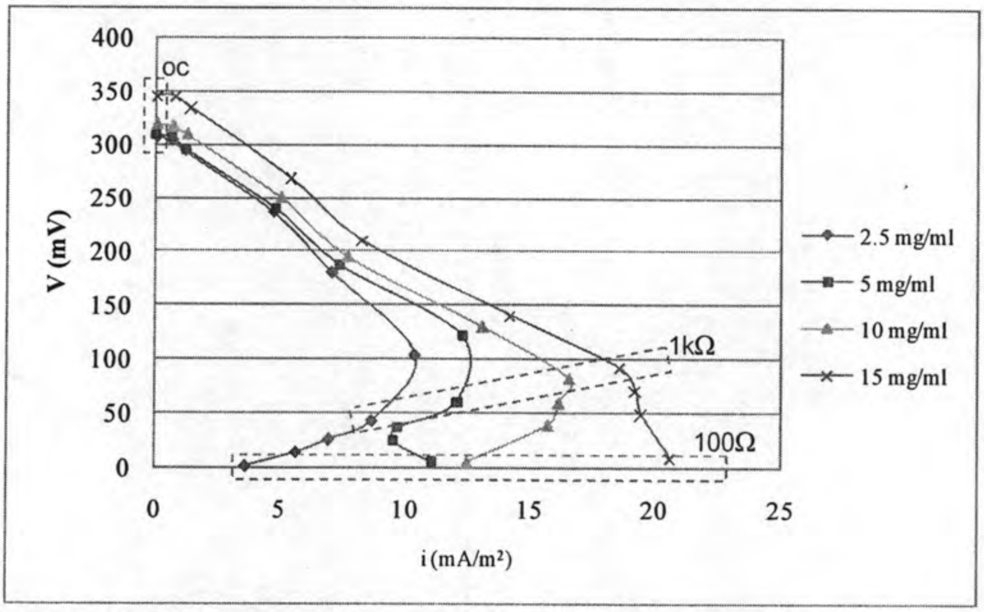


Fig. 6.5 Voltage-current density of the BFC with different yeast concentrations

The voltage generation of BFC with different yeast concentrations is shown in Fig. 6.6. It indicates that the yeast concentration affects the voltage and current generation of the BFC. The voltage and current generation increases with increasing yeast concentration.

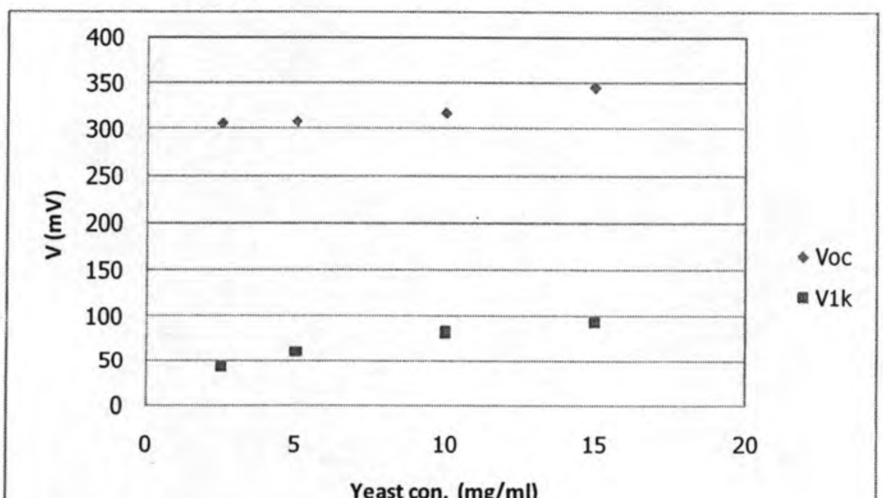


Fig. 6.6 Voltage generation of the BFC with different yeast concentrations

The power density of the BFC with different yeast concentrations is presented in Fig. 6.7. It shows that the highest power density was obtained when using the highest yeast concentration. The yeast concentration do affect the power generation of the BFC.

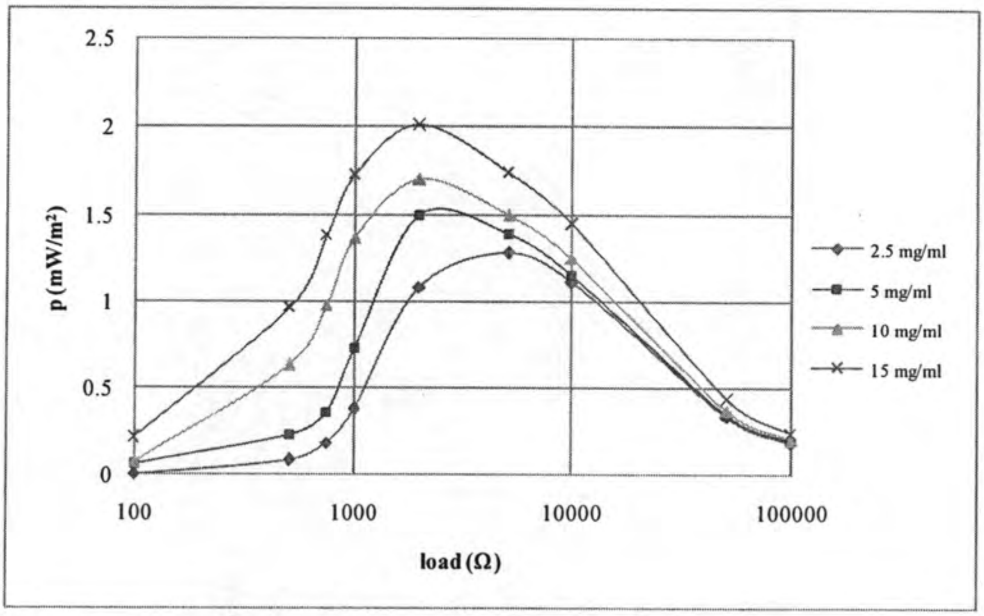


Fig. 6.7 Power density-load characteristics of the BFC with different yeast concentrations

The Thevenin resistance of the BFC with different yeast concentrations (slope of V-I characteristic at ohmic loss region in Fig. 6.5) is shown in Fig. 6.8. It was found that the Thevenin resistance decreases when the yeast concentration increases. It implies that the increasing of the yeast concentration can enhance the electron transfer in the BFC.

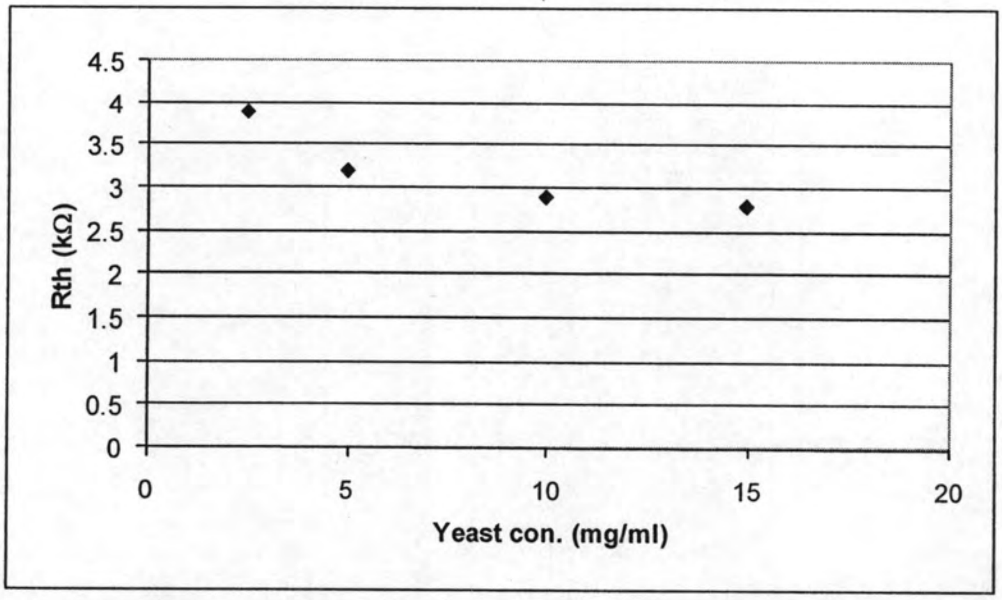


Fig. 6.8 Thevenin resistance of the BFC with different yeast concentrations

6.2.1.3 Methylene Blue Concentration

The results of the BFC performance (V-I characteristics) and voltage generation with different methylene blue concentrations are shown in Fig. 6.9 and 6.10, respectively.

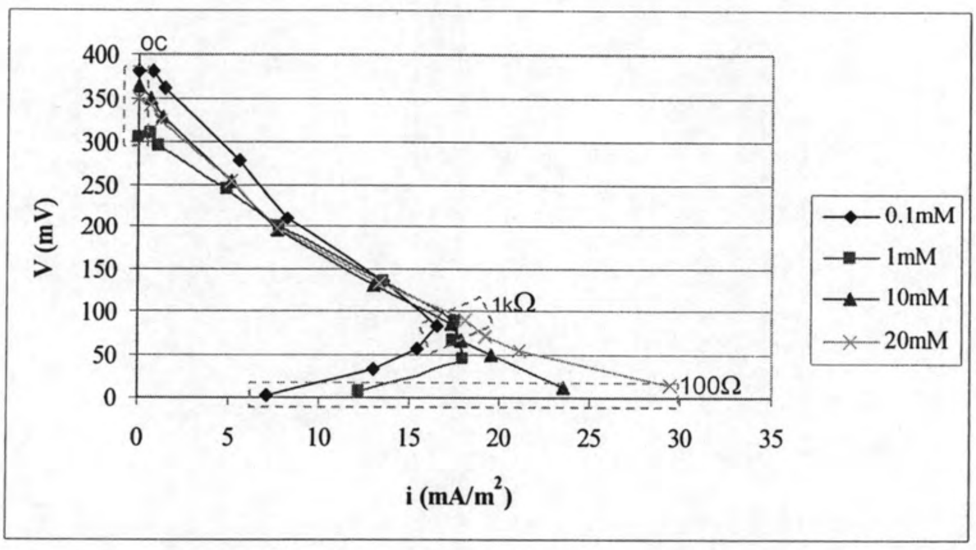


Fig. 6.9 Voltage-current density of the BFC with different methylene blue concentrations

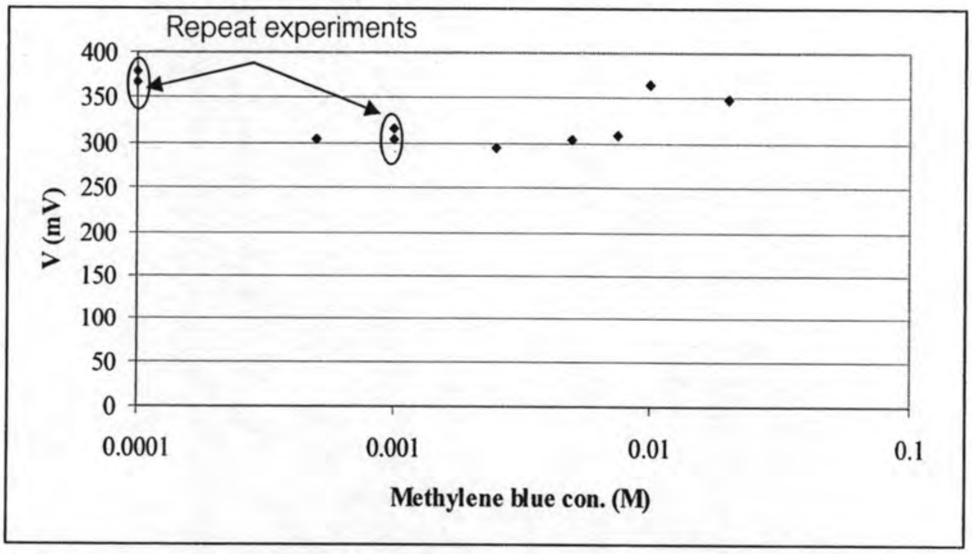


Fig. 6.10 Voltage generation of the BFC from different methylene blue concentrations

As found at the concentration loss region in Fig. 6.9, the higher current density was obtained from the higher methylene blue concentration. Since methylene blue acts as electron mediator, then the higher methylene blue concentration will lead to the higher electron transfer in the system. However, the relation between methylene blue concentration and the open circuit voltage could not be observed.

The power density characteristics of the BFC from different methylene blue concentrations are shown in Fig. 6.11. The power density outputs were in the range of 1.6-1.8 mW/m^2 at 2 kΩ load without any obvious effect from the methylene blue concentration. However, it was found that there was a drop on the power density as the MB concentration decreased in the low resistor load.

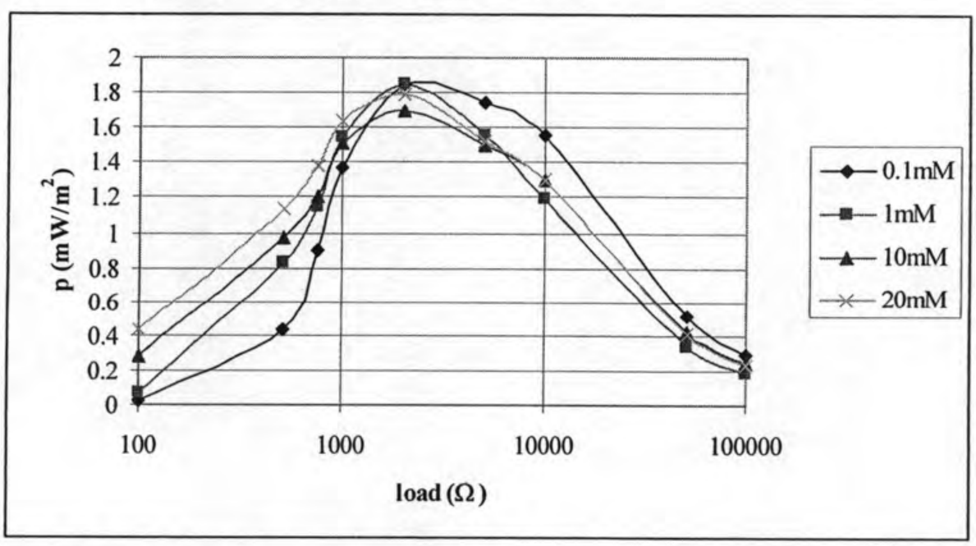


Fig. 6.11 Power density vs. load of the BFC with different methylene blue concentrations

The Thevenin resistances of the BFC with different methylene blue concentrations (slope of V-I characteristic at the ohmic loss region in Fig. 6.9) are shown in Fig. 6.12. At low methylene blue concentration, the Thevenin resistance was high, so the current generation was low. At higher MB concentrations, the Thevenin resistances were fluctuated around 3 kΩ.

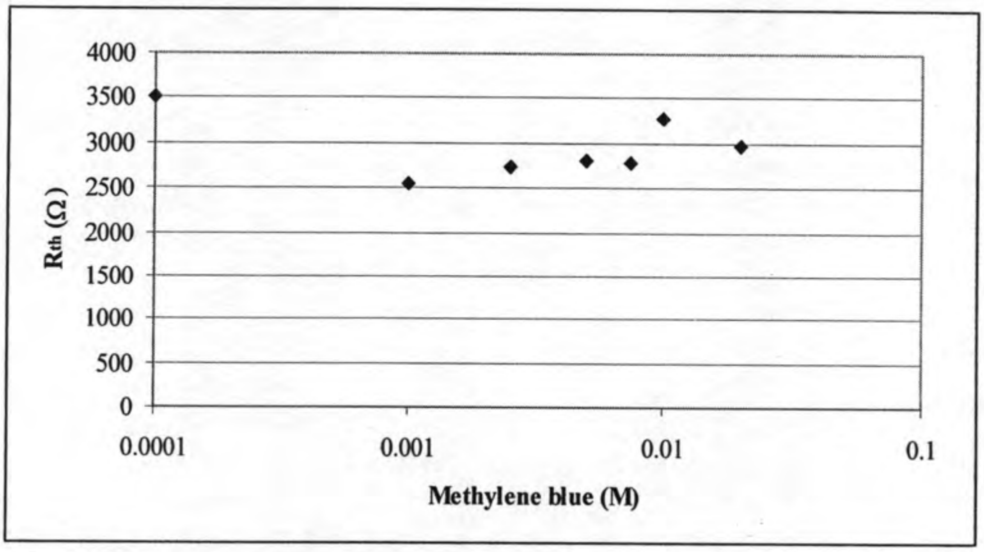


Fig. 6.12 Thevenin resistance with different methylene blue concentrations

6.2.1.4 Ferricyanide Concentration

The voltage-current density characteristics of the BFC with different ferricyanide concentrations is shown in Fig. 6.13.

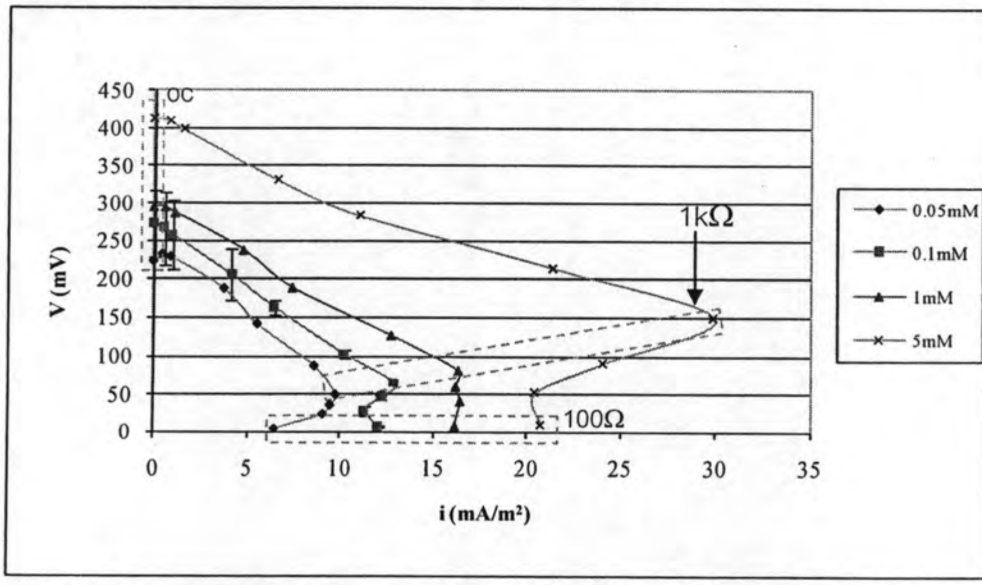


Fig. 6.13 Voltage-current density characteristics of the BFC with different ferricyanide concentrations

From, Fig.6.13, it was obvious that the voltage and current generation increase as ferricyanide concentration increases. Relation between the voltage generation and ferricyanide concentration is shown in Fig. 6.14.

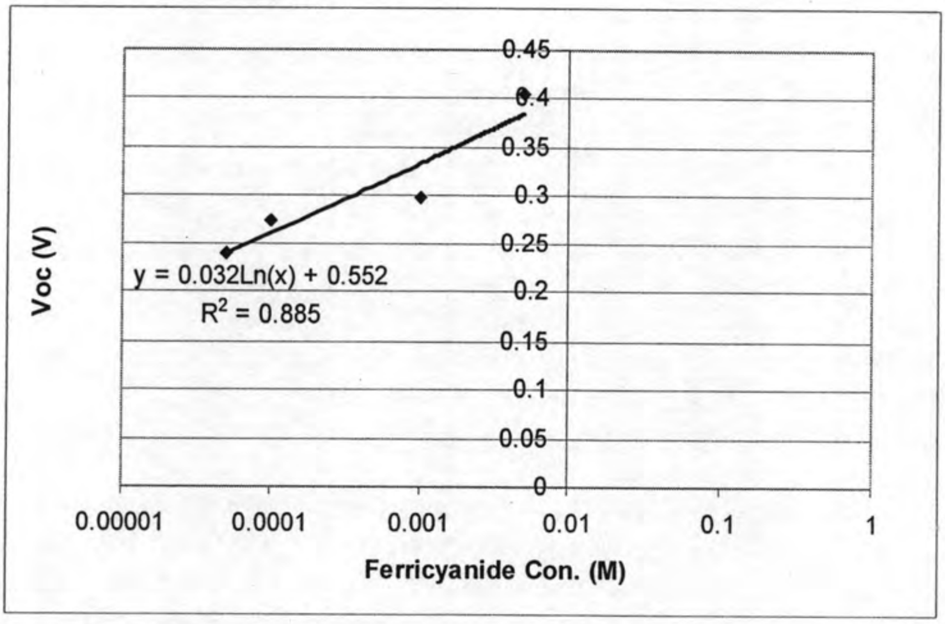


Fig. 6.14 Relation between the voltage generation and the ferricyanide concentration (at 0.1mM, the average open circuit voltage was used)

Generally, the voltage generation of the BFC will follow the Nernst equation as shown in Eq. (6.1) [44].

$$E = E^0 + \frac{RT}{nF}\ln\frac{[concentration\ \ of\ \ electron\ \ acceptor]}{[concentration\ \ of\ \ electron\ \ donor]} \qquad (6.1)$$

where E^0: standard electrode potential [V]

R: gas constant [8.31441 J mol^{-1} K^{-1}]

T: temperature [K]

n: number of electron involved in the reaction

F: Faradaic constant [96,485.3415 C / mol]

As shown in Eq. (6.1), if the ferricyanide is decreased for ten folds, the half-cell potential of the cathode will decrease for 59 mV at room temperature (25°C). However, the experimental result shows that the open circuit voltage increases up to 74 mV/decade. It is still unclear why this high slope was obtained.

From Eq. (2.4) the BFC voltage is

$$V_{BFC} = V_{cathode} - V_{anode}$$

As shown in Eq. (2.13), the half cell reduction potential of ferricyanide (1M and 25°C) is 0.36 V.

Therefore, $V_{BFC} = V_{cathode} - V_{anode} = 0.552 + 0.032 \cdot \ln(\text{ferricyanide concentration; M})$

$$V_{BFC} = 0.36 + 0.032 \cdot \ln(\text{ferricyanide concentration; M}) - (-0.192)$$

Then, the anodic voltage should be -0.192 V that was similar with the open circuit voltage of the BFC when the BFC operated with glucose, yeast and methylene blue and without ferricyanide as shown in Fig. A5 (same condition).

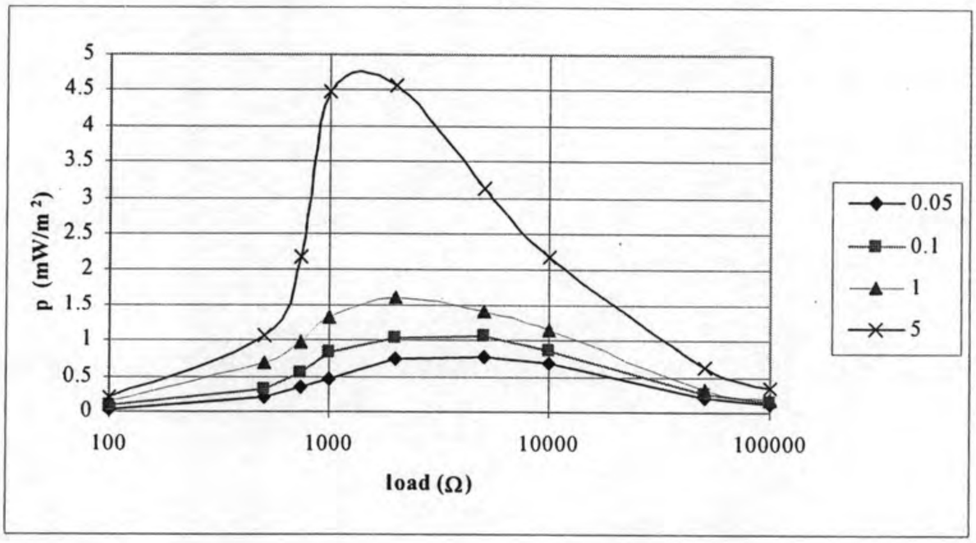


Fig. 6.15 Power density-load characteristics of the BFC with different ferricyanide concentrations

Fig. 6.15 shows power density – load characteristics of the BFC with different ferricyanide concentrations. It shows that the higher power density was obtained when the higher ferricyanide concentration was used. The Thevenin resistance of the BFC with different ferricyanide concentration (slope of V-I characteristic at the ohmic loss region in Fig. 6.13) is shown in Fig. 6.16. It was found that the Thevenin resistance decreased when ferricyanide concentration increased. This implies that the increasing of the ferricyanide concentration can enhance the electron transfer in the BFC.

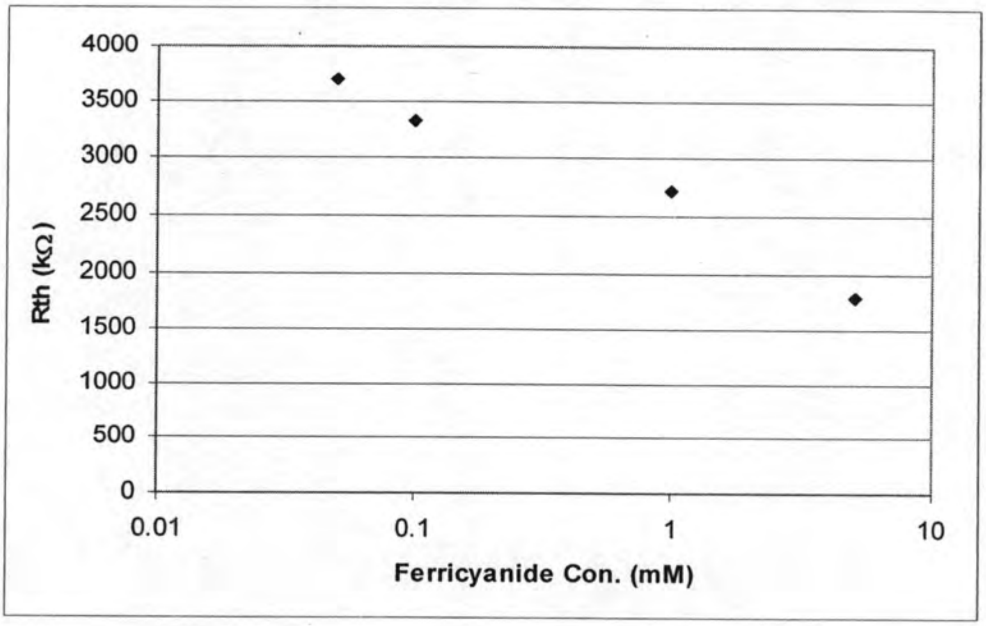


Fig. 6.16 Thevenin resistance of the BFC with different ferricyanide concentrations

6.2.2 Effect of Electron Mediator Types

Fig 6.17 shows the voltage – current density characteristics of the BFC with different electron mediators. The result shows that, the highest open circuit voltage of 392 mV was obtained when methylene blue was used as electron mediator while the open circuit voltages of 330 mV and 285 mV were obtained when using neutral red and rhodamine B as electron mediator, respectively. The maximum current density of 33.3, 20.5 and 11.6 mA/m^2 were obtained when methylene blue, neutral red and rhodamine B were used as electron mediator. The result shows that methylene blue gave the better current generation than neutral red and rhodamine B.

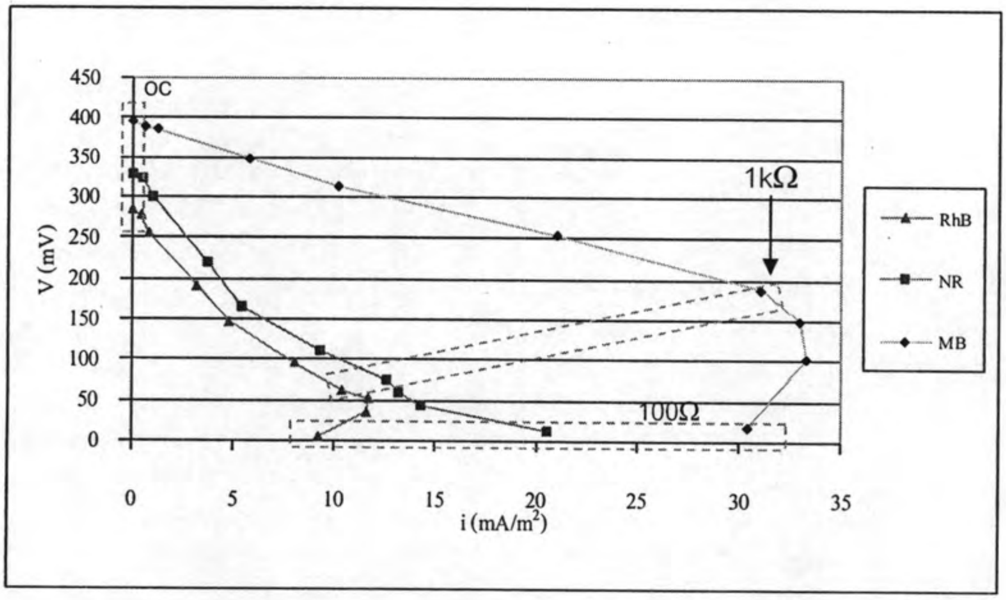


Fig. 6.17 Voltage – current density characteristics of the BFC with different electron mediators

Fig. 6.18 shows power density – load characteristics of the BFC with different electron mediators. It was found that the highest power density of 5.8 mW/m^2 (1 kΩ) was achieved when using methylene blue while the power density of 1.02 mW/m^2 (2 kΩ) and 0.78 mW/m^2 (2 kΩ) were obtained from neutral red and rhodamine B, respectively.

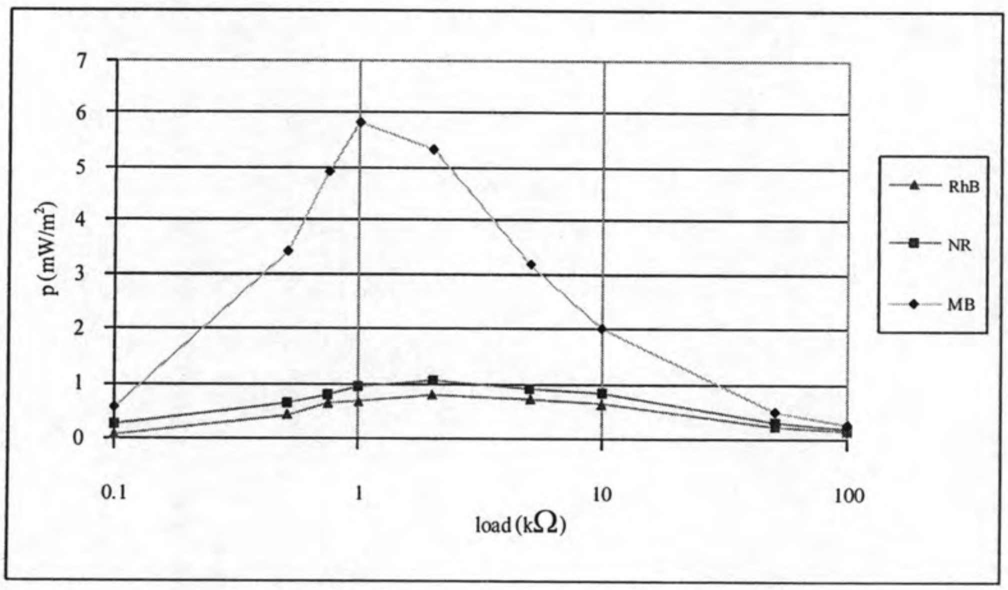


Fig. 6.18 Power density – load characteristics of the BFC with different electron mediators

The Thevenin resistances of the BFC with different electron mediators (slope of V-I characteristics at the ohmic loss region in Fig. 6.17) are shown in Fig. 6.19. It was found that the type of electron mediator affects the Thevenin resistance in the BFC. The results show that the MB shows the lowest Thevenin resistance. It implies that the best electron transfer will be occurred when the MB is used as electron mediator.

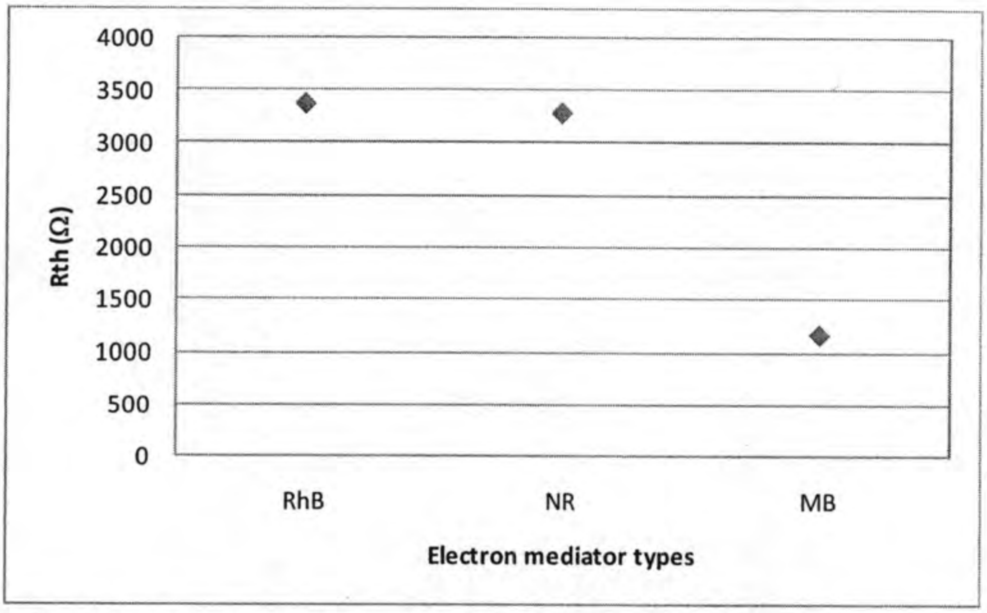
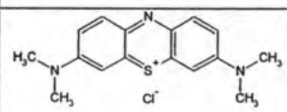
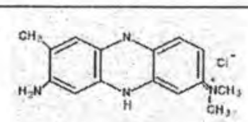
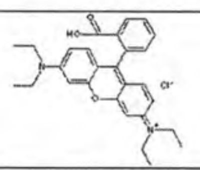


Fig. 6.19 Thevenin resistance of the BFC with different electron mediators

The chemical structures of the mediators are shown in Table 6.1.

Table 6.1 Chemical structure of electron mediators (at pH 7.0, 25°c)

Name	Chemical structure	Molecular formula	Molecular weight	Half-cell potential (V)
MB		$C_{16}H_{18}ClN_3S$	319.85	+0.011 [45]
NR		$C_{15}H_{17}ClN_4$	288.78	-0.325 [10]
RhB		$C_{28}H_{31}ClN_2O_3$	479.02	-0.542 [45]

The open circuit voltage from the BFC experiment versus the half cell reduction potential of the electron mediator is shown in Fig. 6.20.

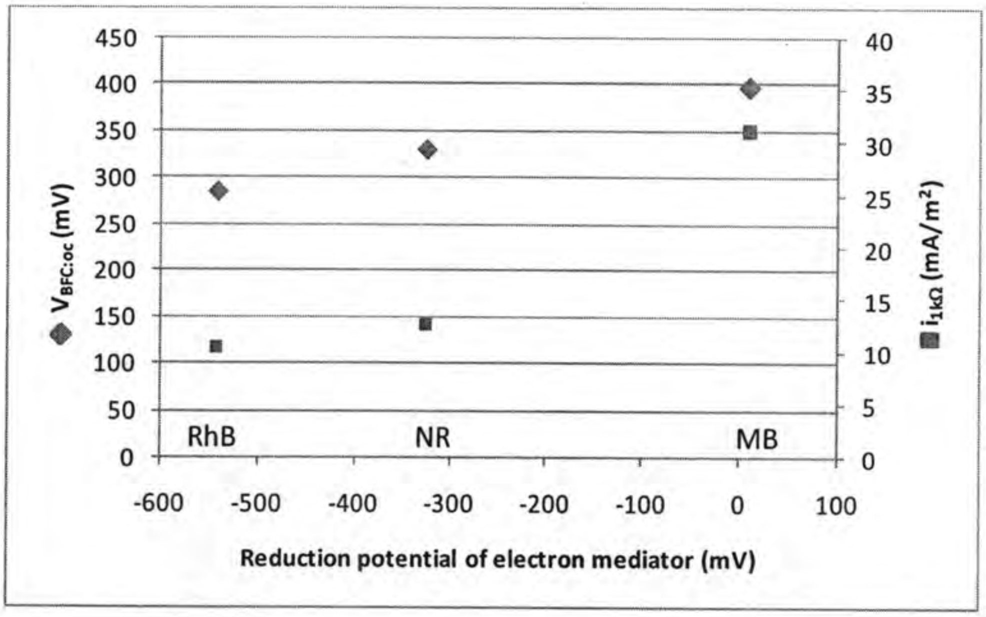


Fig. 6.20 Open circuit voltage and current density at 1kΩ load of the BFC vs. reduction potential of each electron mediator

Fig. 6.20 shows that the type of electron mediator affects the open circuit voltage generation of the BFC. The highest open circuit voltage and current density were obtained when using the MB which has the highest reduction potential. The decreasing of reduction potential of electron mediator reduces the open circuit voltage and current generation of the BFC.

It is known that the higher reduction potential, the better electron acceptability the material will be, while the material with lower reduction potential will behave as a better electron donor. Therefore, in the experiment, the MB should be the best electron acceptor while NR and RhB are the electron donor better than MB. Hence, the MB will receive the electrons from yeast better than NR and RhB. As the MB receives more electrons from the yeast, then it will transfer more electrons to electrode. Considering molecular weight of these mediators, although molecular weight of neutral red is the lowest, the NR is not the best electron mediator of the BFC in our system. This implies that the half cell reduction potential plays more contribution than the diffusion.

6.2.3 Effect of Electron Acceptor Types

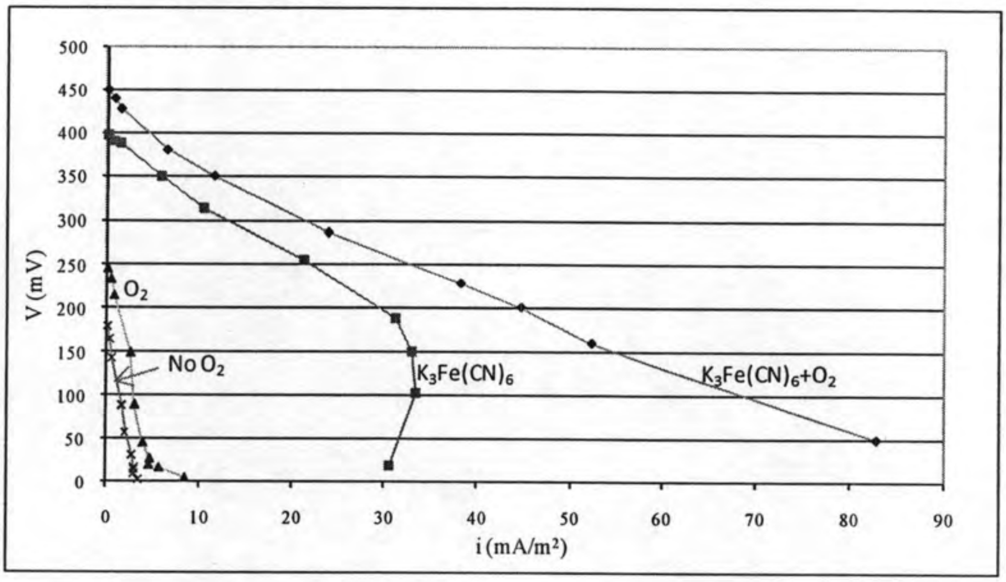


Fig. 6.21 Voltage – current density characteristics of the BFC with different electron acceptors

The voltage-current density generation of the BFC is shown in Fig. 6.21. The result shows that the BFC generates a very small voltage and current density when the electron acceptor is absent. It should be emphasized that carbon fiber electrode can work even though the electron acceptor was not added into the system. This small voltage generation might come from the small amount of dissolved oxygen (<8ppm) in the solution. When oxygen was used as electron acceptor, the cell voltage and current density of 245 mV and 9 mA/m^2, respectively, was generated. The voltage and current generation of 396 mV and 33 mA/m^2 were obtained when ferricyanide was used as electron acceptor. This is higher than the BFC with the oxygen for ~150 mV, even the reduction potential of the oxygen is higher than the ferricyanide. Value of the redox potential for the oxygen depends on the condition of the environments as shown in Eq. (6.2)-(6.4) [46].

$O_2(g)+2H^++2e^- \leftrightarrow H_2O_2(aq) \quad E^0 = +0.682$ V (6.2)

$O_2(g)+4H^++4e^- \leftrightarrow 2H_2O \quad E^0 = +1.229$ V (6.3)

$O_2(g)+2H_2O+2H_2O \leftrightarrow 4OH^- \quad E^0 = +0.401$ V (6.4)

All of these reduction potential values for the oxygen also are higher than the ferricyanide one. It is still unclear why the system with ferricyanide is better than the oxygen one. One possible explanation might be that the concentration on oxygen in solution is very low because the oxygen will be saturated at 8 ppm (8 mg/l) [46], under the bubbling condition.

The best performance of the BFC using carbon fiber electrode was obtained when both oxygen and ferricyanide were used as electron acceptor. The highest open circuit voltage and the maximum current density of 450 mV and 83 mA/m^2 were obtained. It was found that the adding of oxygen in ferricyanide increased the open circuit voltage for 50 mV. It is also found that the open circuit voltage increased ~70mV when oxygen was added to the BFC without the electron acceptor. It looks like that the addition of oxygen to the BFC could enhance the voltage generation for 50~70mV.

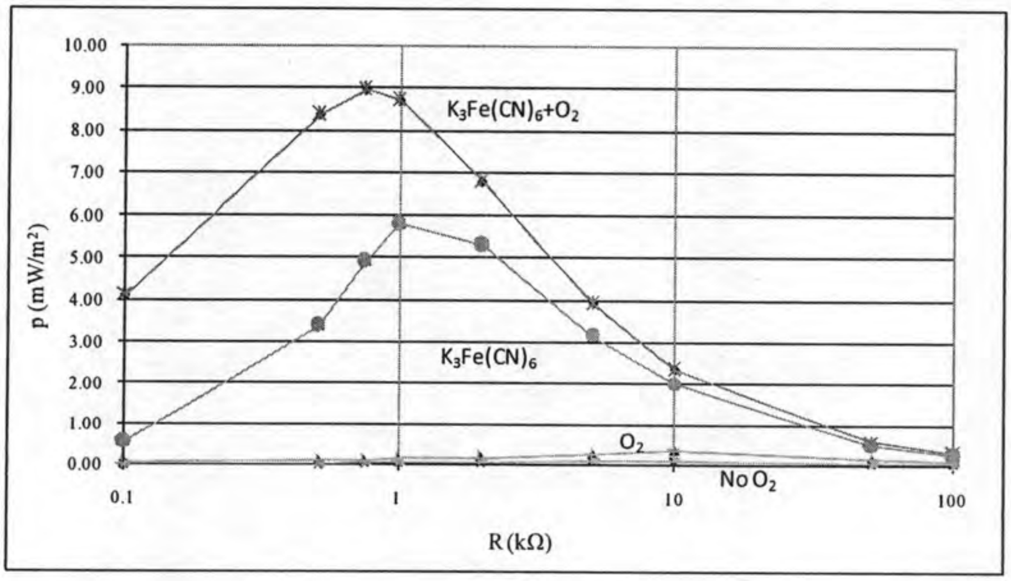


Fig. 6.22 Power density – load of the BFC with different electron acceptors

Fig. 6.22 shows power density – load characteristics of the BFC with different electron acceptors. It is obvious that the maximum power rely on the type of electron acceptor. The combination use of oxygen and ferricyanide drastically enhanced the cell power. The maximum power of 9 mW/m^2 was obtained at 750 Ω load when using oxygen together with ferricyanide as electron acceptor. Moreover, the combination use of electron acceptor also reduced the internal equivalent resistance.

The Thevenin resistance of the BFC with different electron acceptors (slope of V-I characteristics at the ohmic loss region in Fig. 6.20) is shown in Fig. 6.23. It was found that these electron acceptors affect the Thevenin resistance in the BFC. The results show that the combination of ferricyanide and oxygen gave the lowest Thevenin resistance (797Ω). Therefore, the lowest limiting of electron transfer was obtained when using the combination of ferricyanide and oxygen as electron acceptor.

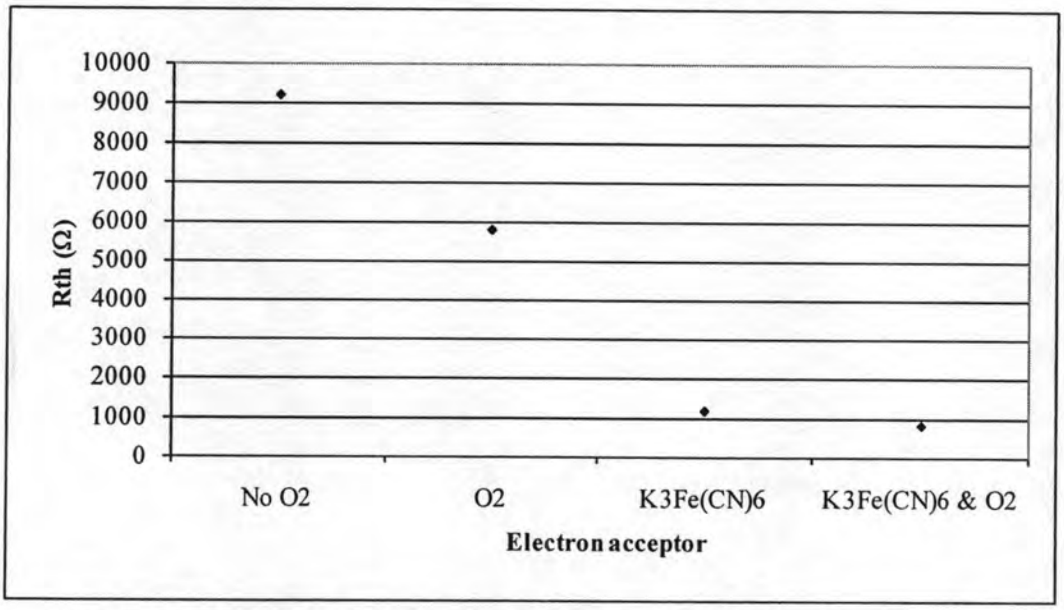


Fig. 6.23 Thevenin resistance of the BFC with different electron acceptors

6.3 Summary

Firstly, the experimental results show that the concentration of each component in the BFC does affect the BFC performance. The yeast and ferricyanide will affect the voltage generation of the BFC. The increasing of yeast and ferricyanide concentration will lead to the increasing of the voltage generation. The current generation of the BFC is affected by the concentration of yeast, glucose, methylene blue and ferricyanide. The increasing of concentration for these components can increase the current density. The power generation of the BFC increases as the concentration of glucose, yeast or ferricyanide increases. On the contrary, if the concentration of glucose, yeast or ferricyanide increases the R_{th} of the BFC will decrease.

Secondly, the type of electron mediator affects the voltage, current and power generation of the BFC. The methylene blue is the best electron mediator for the BFC in our experiments. Three hundred and ninety six mV, 33.3 mA/m^2 (510 Ω) and 5.8 mW/m^2 (1 kΩ) of highest open circuit voltage, current density and power density, respectively, were obtained when using MB as electron mediator. The R_{th} of the BFC system when using MB as electron mediator was found to be 1.2 kΩ.

Finally, the results of different electron acceptors shows that the electron acceptors play an important role in the voltage, current and power generation of the BFC. It was found that ferricyanide is better than oxygen. Moreover, the combination use of both the ferricyanide and oxygen will produce the best BFC characteristics. For both oxygen and ferricyanide were used as electron acceptor, the highest open circuit voltage of 0.45V, the maximum current of 83 mA/m^2 and the maximum power of 9 mW/m^2 were obtained. The internal resistance of the cell was found to be 797 Ω.