CHAPTER 5

EFFECT OF PHYSICAL PARAMETERS ON THE BIO-FUEL CELL PERFORMANCES

The effect of electrode material was described in chapter 4. However, there are still several physical parameters which might affect the performance of the BFC such as electrode surface area, distance between electrodes and compartment volumes. This chapter will investigate the effect of these parameters.

5.1 Bio-Fuel Cell Experiments

Firstly, the 2515006 chamber was used for investigation of electrode surface area on the BFC performance. Carbon fiber electrodes with different surface areas, $2cm^2$, $18cm^2$ and $50cm^2$, were used to explore the BFC performance such as voltage, current density and power density and the BFC impedance. The distance between anode and cathode was fixed at 2 cm.

For the study on the effect of distances between the two electrodes, the 2525010 chamber was used and the surface area of the electrodes was fixed at 50 cm^2. The BFC performance and BFC impedance were explored while the distance between the two electrodes was varied for three conditions such as, 2cm, 12cm and 20cm.

Finally, the effect of compartment volume was explored. Four compartments such as 2507502, 2515005, 2521007 and 2525010 compartments were used in the study. The carbon fiber electrode surface area and distance between electrodes were maintained at 50 cm^2 and 2 cm, respectively. The generated voltage, current density and power density were investigated.

5.1.1 Bio-Fuel Cell Performances

Ten mg/ml of yeast in 0.1M phosphate buffer (pH7) containing 0.1M glucose and 1mM methylene blue were used as fuel source and electron mediator, respectively.

One millimole of ferricyanide was used as the electron acceptor in the cathodic compartment. The compositions for both 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

5.1.2 Impedance Studies

The impedance analysis was performed by removing the PEM, microorganism, organic substrate, electron mediator and electron acceptor from the system. The surface area and distance electrode were varied to investigate their rolls. The compositions for the experimental setup consisted of 0.1M of PB and carbon fiber electrodes.

5.2 Results and Discussions

5.2.1 Effect of Electrode Surface Area

5.2.1.1 Electricity Generation of the Bio-Fuel Cell

The voltage-current and voltage-current density characteristics of the BFC with different electrode surface areas are shown in Fig. 5.1 and Fig. 5.2, respectively.

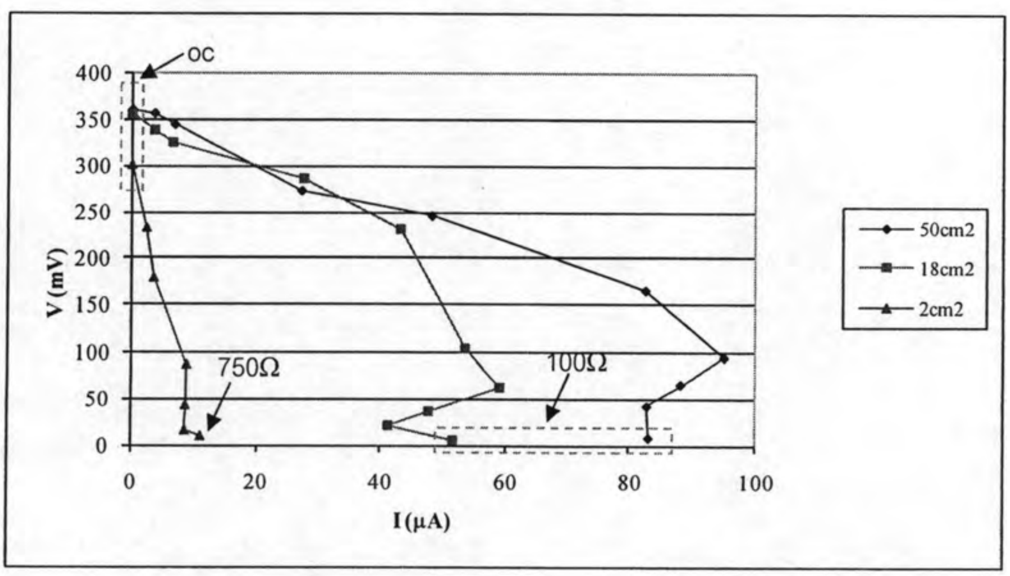

Fig. 5.1 Voltage-current characteristics of the BFC with different electrode surface areas

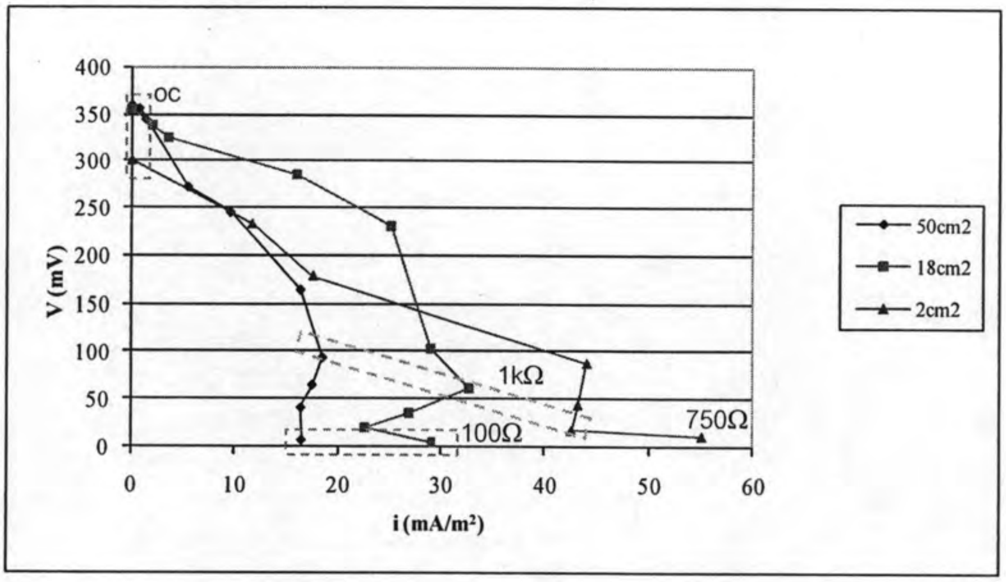

Fig. 5.2 Voltage-current density characteristics of the BFC with different electrode surface areas

The result in Fig. 5.2 shows that the lowest open circuit voltage of ~300 mV was obtained from the BFC with 2 cm^2 electrode, while the 18 and 50 cm^2 electrode ones generated open circuit voltage of ~360 mV. The highest current density of 44 mA/m^2 (at 1kΩ load) was obtained from the BFC with 2cm^2. On the contrary, the lowest current of the BFC obtained was 11μA at 1kΩ load from the BFC with 2cm^2 electrode. At the same load, the current density generated from the BFC with 18 cm^2 and 50 cm^2 electrodes were 34 and 19 mA/m^2, respectively.

Fig. 5.3 shows the relation between electrode surface area and the current/ current density at 2 kΩ load. The current is a linear function with respect to the electrode surface area. The results indicate that the BFC's current increases as the electrode surface area increases. On the contrary, the current density decreases as the electrode surface increases. However, it should be noted that if the surface area is zero, the current is not zero because all current data were calculated from the voltage generation.

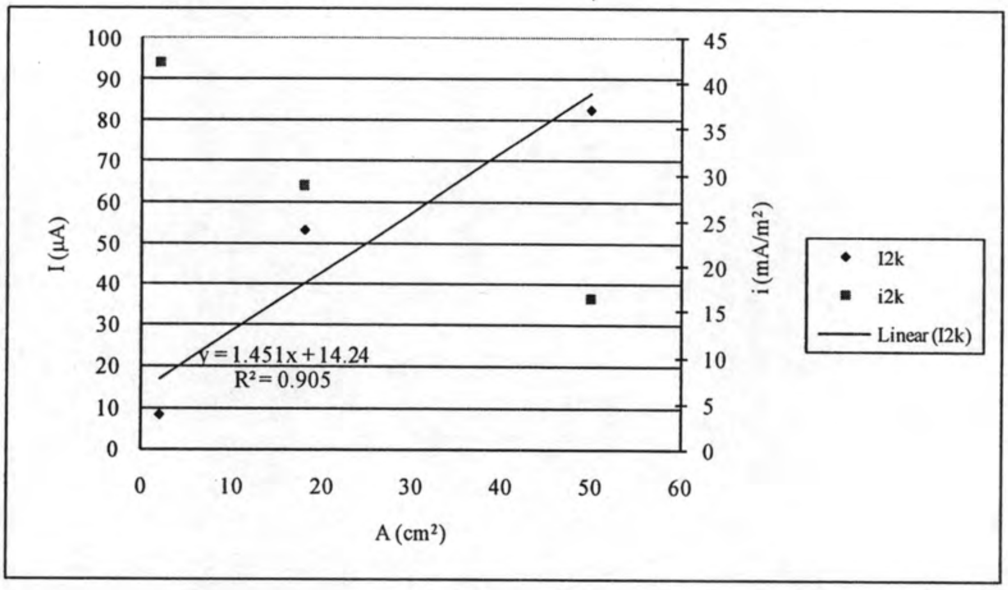

Fig. 5.3 Current and current density vs. the different electrode surface areas at 2kΩ load

The power-load and power density–load characteristics of the BFC with different electrode surface areas are shown in Fig. 5.4 and Fig. 5.5, respectively.

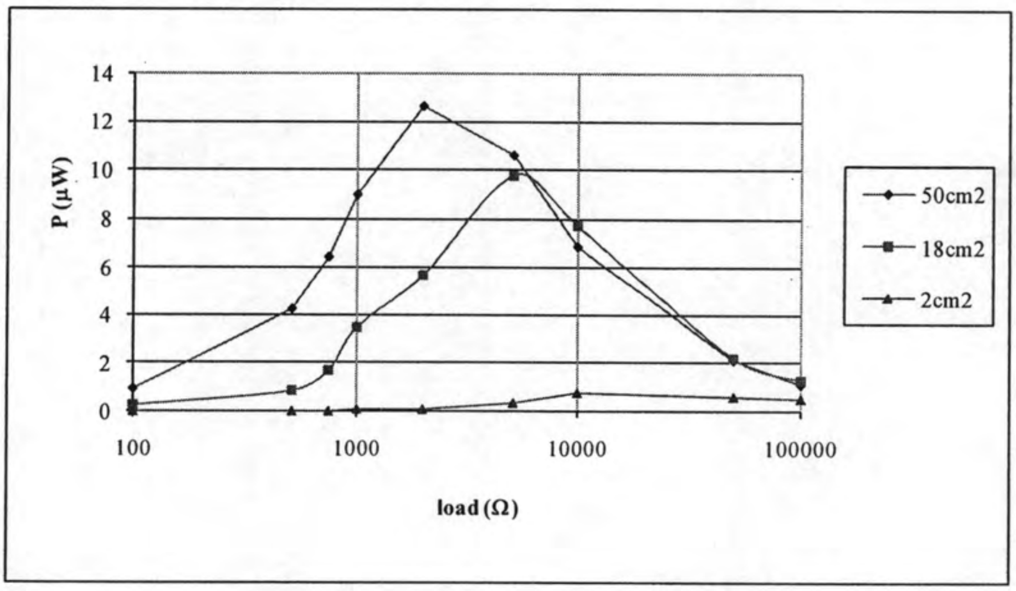

Fig. 5.4 Power-load characteristics of the BFC with different electrode surface areas

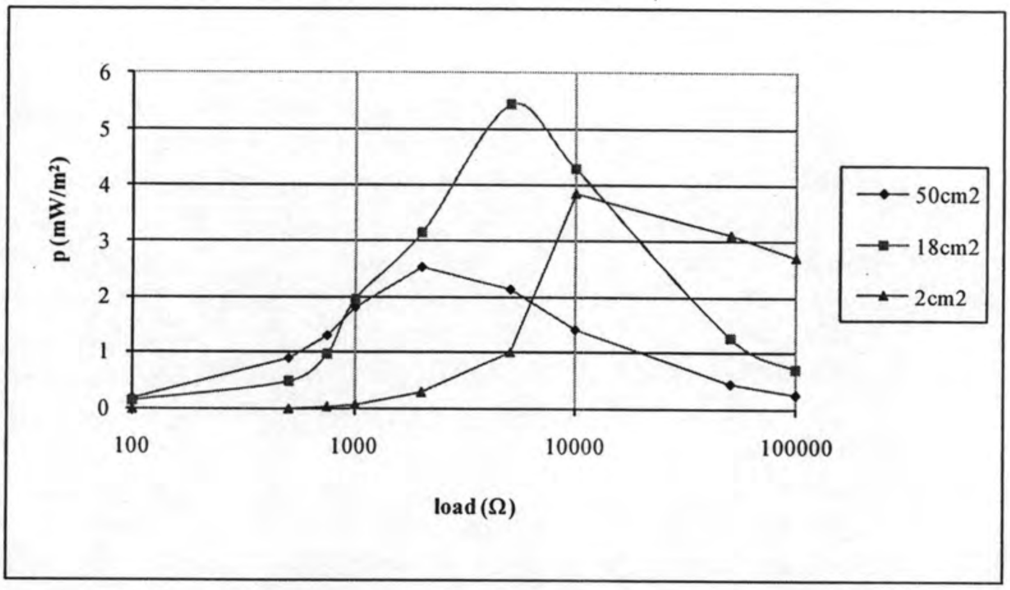

Fig. 5.5 Power density-load characteristics of the BFC with different electrode surface areas

It was found that the highest power of 12.6 μW was obtained from the BFC with 50 cm^2 electrode at load of 2kΩ. The power obtained from the BFC with 18 cm^2 and 2 cm^2 electrodes were highest at 10 μW (5.1kΩ) and 1 μW (10kΩ), respectively. The maximum power was found at lower resistance load as the electrode area was increased. These results imply that the internal resistance decreases as the electrode surface area increases. Even the BFC with higher electrode surface area could supply higher power output, but the power density does not have this trend. The highest power density was obtained from the BFC with 18 cm^2 electrode.

5.2.1.2 Impedance Analysis of the Bio-Fuel Cell with Different Electrode Surface Areas

Fig. 5.6 shows the Cole-Cole plots of different electrode surface areas in PB from the ac-impedance measurement.

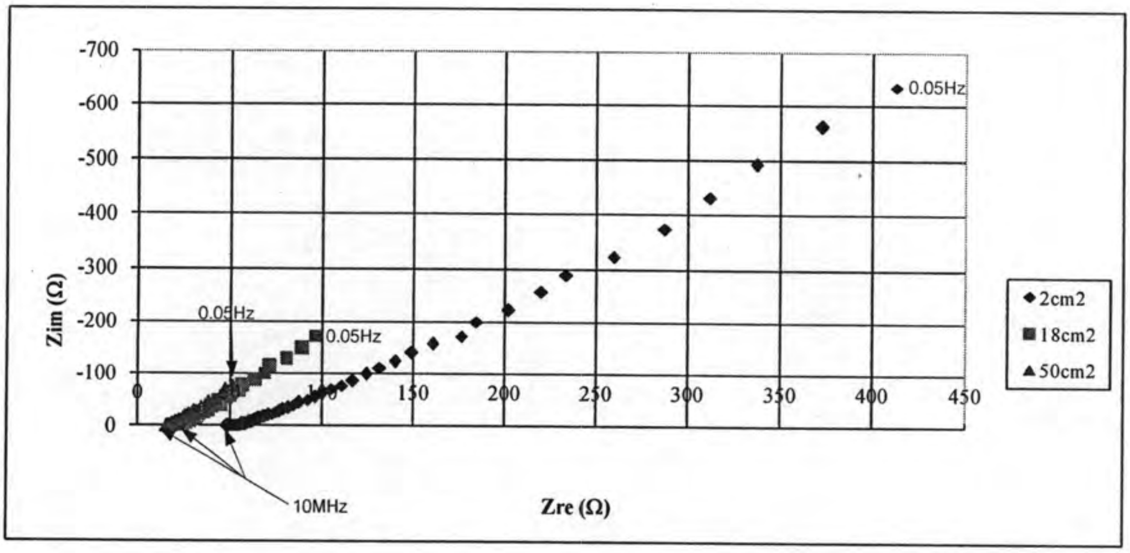

Fig. 5.6 Cole-Cole plots of the BFC with different electrode surface areas

Using Eq. (4.2), the constants R_{SE}, R_I, *A* and α were extrapolated using numerical estimation technique in fitting the experimental results (Fig. 5.6). The results are summarized in Table 5.1.

Table 5.1 Parameters estimated from fitting process for the equivalent circuit of Fig. 5.6

A (cm^2)	R_{SE} (Ω)	R_I (Ω)	α	*A* (s^α/Ω)	$R_{SE}+R_I$ (Ω)
2	57	8539	0.68	0.0027	8596
18	24	3525	0.75	0.0123	3549
50	17	1270	0.74	0.0265	1287

It was found that both the solution-electrode impedance (R_{SE}) and electrode-solution interfacial impedance (R_I) decrease as the electrode surface areas increases. In theoretical aspect, it is known that the resistance of electrode and solution depend on the geometry such as, surface area and length, as shown in Eq. (5.1).

$$R = \rho l/A \qquad (5.1)$$

where R: the electrical resistance [Ω]

ρ: resistivity [Ω.cm]

l: length [cm]

A: the cross-sectional area [cm^2]

Surface area of the electrode also affects the solution and the electrode-solution interfacial capacitance. The capacitance of the solution increases as the electrode surface area increases as shown in Eq. (5.2).

$$C = \varepsilon_0 \varepsilon_r A/d \quad (5.2)$$

with, C: capacitance [F]

ε_0: electrical permittivity [8.854×10^{-12} F/m]

ε_r: relative electrical permittivity [F/m]

A: surface of one electrode [cm^2]

d: distance between two electrodes [cm]

Since the reactance of solution and electrode were relatively low compared to the solution and electrode resistance (at high frequency region as shown in Fig. 4.6 (d)), the values of the reactance were dismissed. Furthermore, it is obvious from Eq. (5.1) and (5.2) that the interfacial impedance was affected by the electrode surface area. Therefore, the R_I and *A* of the BFC with different electrode surface areas were not the same.

Due to the slow rate reaction in the biological component, Z_{CPE} can be eliminated. This implies that the frequency does not affect the total impedance. Therefore, the total impedance (Z_T) can be expressed as a simple resistance.

$$Z_T = R_{SE} + R_I \quad (5.3)$$

Fig. 5.7 displays the total impedance of the BFC with different electrode surface area. It was found that the total resistance decreases if the surface area of electrode increases. These data support the performance data (current and power not current density or power density) as mentioned above. It was also found that the impedance data changed as an inverse function of the electrode surface area.

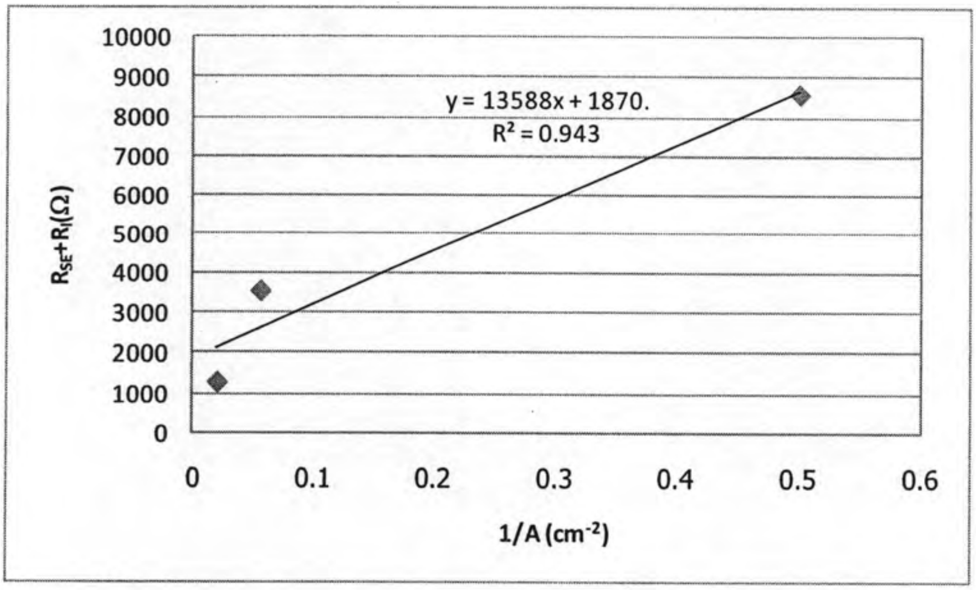

Fig. 5.7 Total impedance vs. the different electrode surface areas

Table 5.2 summarized the Thevenin resistance (R_{th}) and total impedance (Z_T) of the three different electrode surface areas. The R_{th} was estimated from a slope of the voltage-current characteristics (Fig. 5.1) at the ohmic loss region. The Z_T was obtained from Table 5.1. It should be noted that the R_{th} of all electrode surface areas were higher than the Z_T because the R_{th} was the internal resistance of the complete BFC system (with yeast, glucose, MB, ferricanide and PEM) while, the Z_T was the total impedance of the PB and electrode.

Table 5.2 Comparison of R_{th} and Z_T of the electrode with different surface areas

A (cm^2)	50	18	2
$Z_T=R_{SE}+R_I$ (Ω)	1287	3549	8596
R_{th} (Ω)	2612	4359	26195
$R_{th}-Z_T$ (Ω)	1325	810	17599

5.2.2 Effect of Distance between Electrodes

5.2.2.1 Electricity Generation of the Bio-Fuel Cell

The voltage-current density characteristics of the BFC with different distance between electrodes is shown in Fig. 5.8.

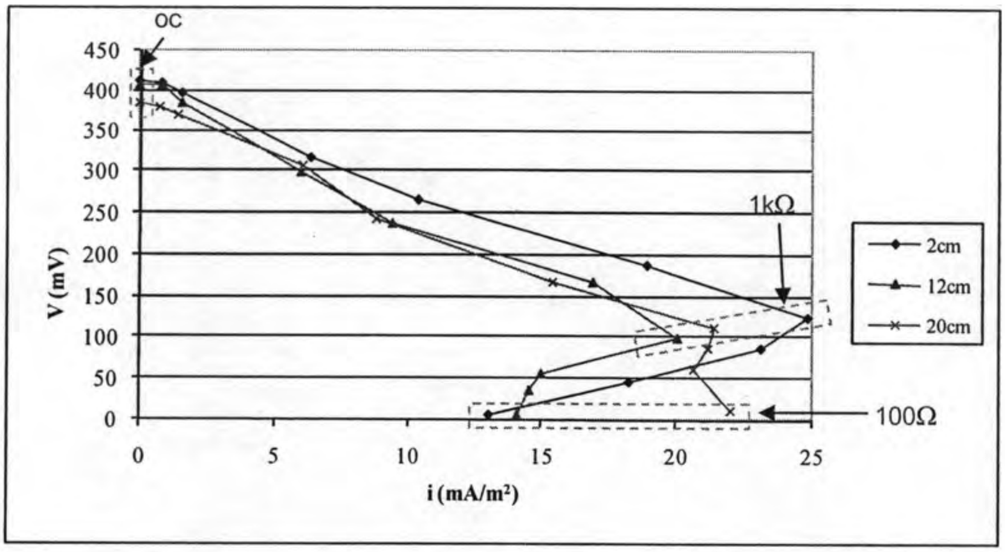

Fig. 5.8 Voltage vs. current density of the BFC with different distances between electrodes

The results show that all different distances between electrodes gave the open circuit voltage and the current density at 1kΩ load in the range of 386-412 mV and 3-5 mA/m^2, respectively. The effect of distance between electrodes was not clear (Fig. 5.8), even the Eq. (5.1) and (5.2) indicate that the longer distance the higher resistance should be observed. The different distances between electrodes affect the solution resistance and capacitance between two electrodes as shown in Eq. (5.1) and (5.2), respectively.

The power density–load characteristics of the different distances between electrodes is displayed in Fig. 5.9. The maximum power density for all different distances between electrodes was in the range of 2.8-3.6 mW/m^2 at 2 kΩ. The relation between voltage generation and distance between electrodes is plotted as shown in Fig. 5.10.

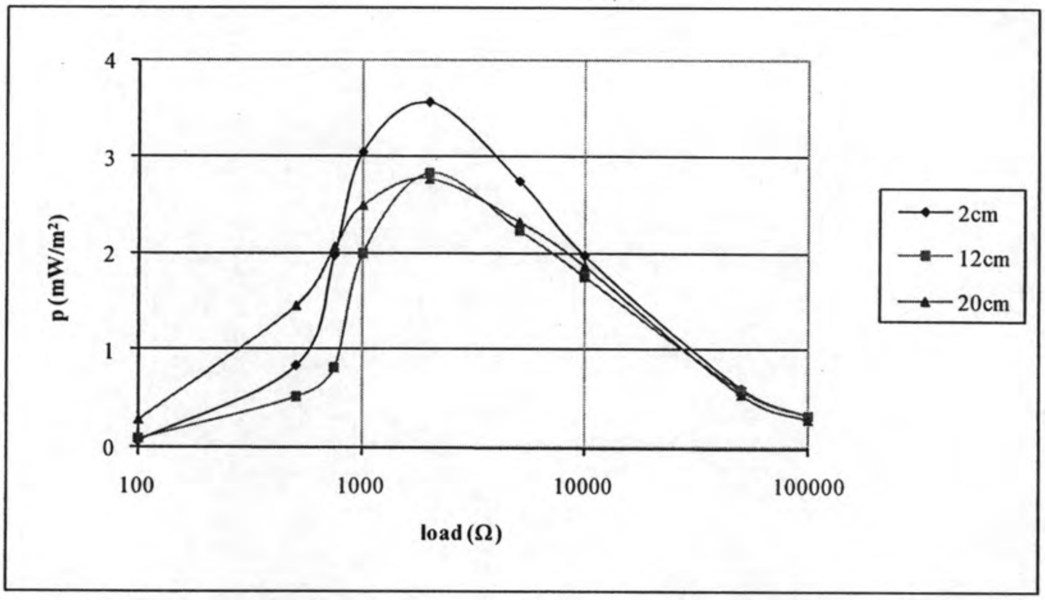

Fig. 5.9 Power density vs. load of the BFC with different distances between electrodes

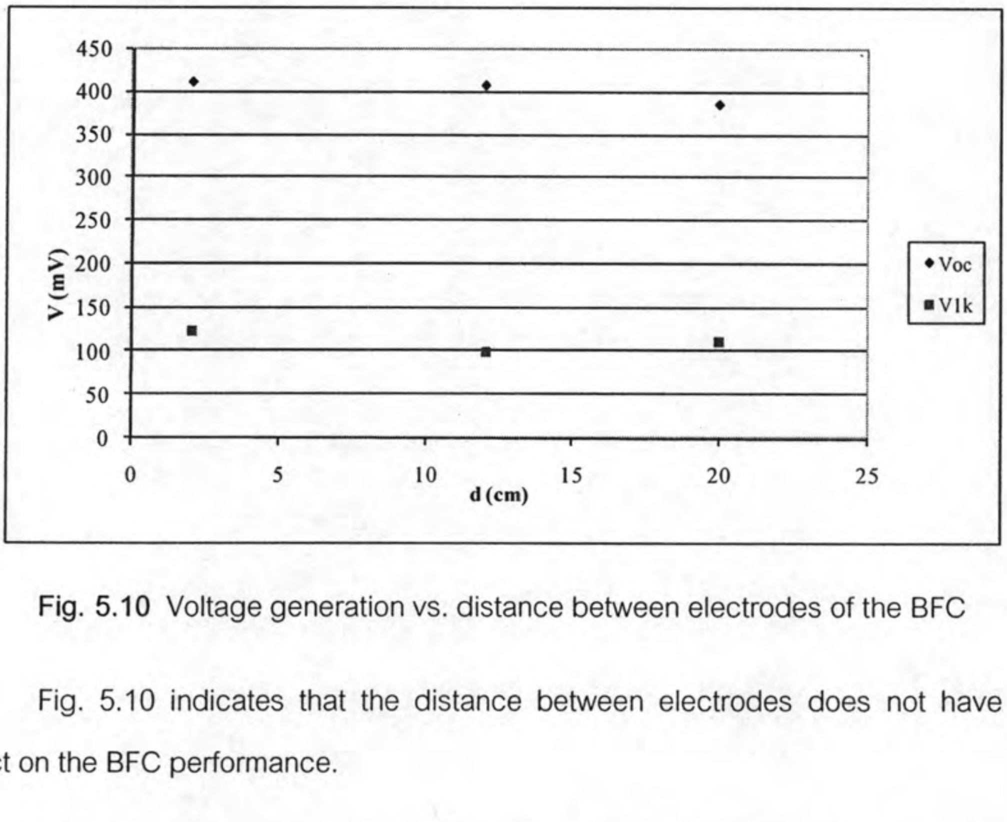

Fig. 5.10 Voltage generation vs. distance between electrodes of the BFC

Fig. 5.10 indicates that the distance between electrodes does not have any effect on the BFC performance.

5.2.2.2 Impedance Analysis of the Bio-Fuel Cell with Different Distances between Electrodes

Fig. 5.11 shows the Cole–Cole plots of the BFC with different distances between electrodes in PB, from ac-impedance measurement.

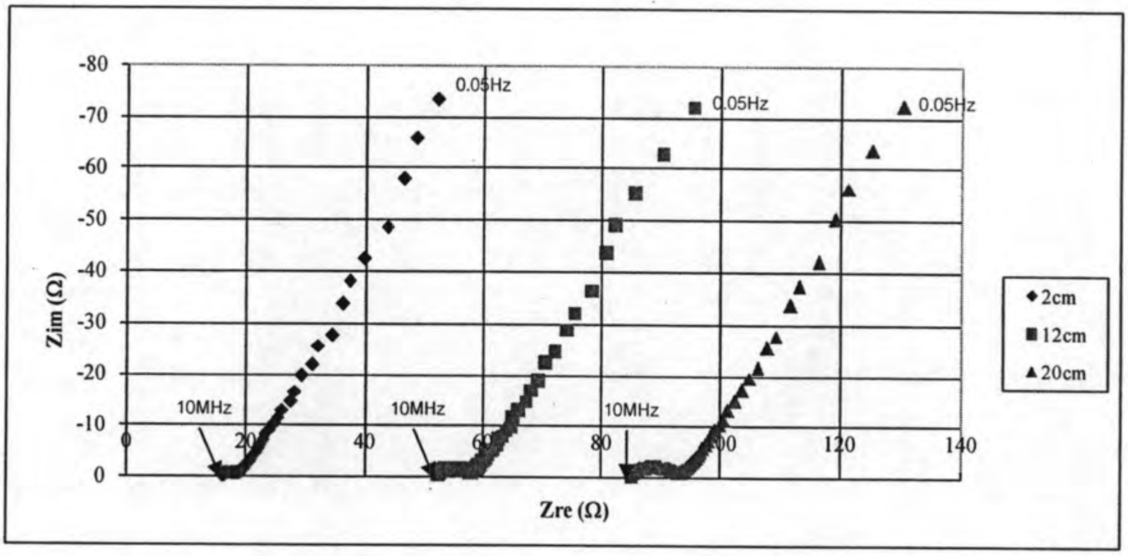

Fig. 5.11 Cole-Cole plots of the BFC with different distances between electrodes

Using Eq. (4.2), the constants R_{SE}, R_I, A and α were extrapolated using numerical estimation technique in fitting the experimental results (Fig. 5.11). The results are summarized in Table 5.3.

Table 5.3 Parameters evaluated from fitting process for the equivalent circuit of Fig. 5.11

d (cm)	R_{SE} (Ω)	R_I (Ω)	α	A (s^{α}/Ω)	$R_{SE}+R_I$ (Ω)
2	19	1039	0.73	0.0268	1058
12	58	989	0.71	0.0266	1047
20	93	1027	0.70	0.0261	1120

These data show that the different distances between electrodes do affect the R_{SE} but not on the interfacial impedance (R_I, α and A). However, the R_I was much higher than the R_{SE} for 11-55 folds. Since the R_I is the interfacial resistance then it is not affected by the distance between electrodes. This is why we could not observe the effect of distance between the two electrodes on the BFC performances (Fig.5.9 - 5.10) in our experiments. Fig. 5.12 shows the relationship between the total impedance and distances between electrodes.

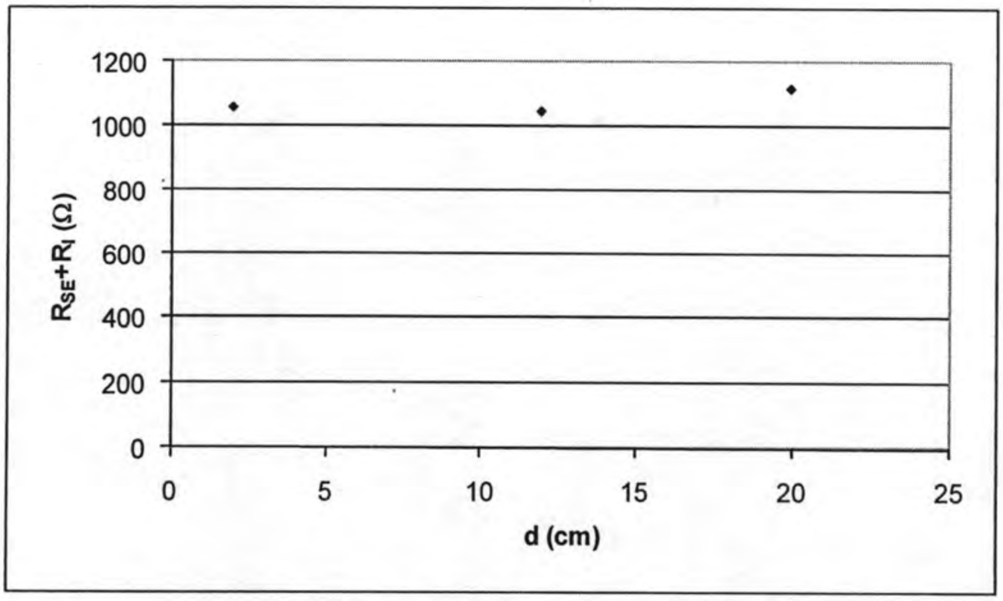

Fig. 5.12 The relationship between the total impedance and the different distances between electrodes

Table 5.4 summarized the Thevenin resistance (R_{th}) and total impedance (Z_T) of the three different distances between electrodes. The R_{th} was evaluated from the slope at ohmic loss region of the V-I characteristic (Fig. 5.8). It was found that for all cases, the R_{th} were higher than the total impedance. These results support the data as mentioned above in section 5.2.2.1.

The R_{th}-Z_T as shown in Table 5.2 and 5.4, had value in the range of 810-1985Ω, except for the BFC with 2cm^2 electrode surface area. The physical meaning of the R_{th}-Z_T is the total impedance of PEM, anodic solution (yeast, glucose and MB components) and cathodic solution (ferricyanide component).

Table 5.4 Comparison of R_{th} and Z_T of the electrode with different distances between electrodes

d (cm)	2	12	20
$Z_T=R_{SE}+R_I$ (Ω)	1058	1047	1120
R_{th} (Ω)	2357	3032	2535
R_{th}-Z_T (Ω)	1299	1985	1415

5.2.3 Effect of Compartment Volume

Fig. 5.13 show voltage and current density characteristics obtained from the BFC with different compartment volumes.

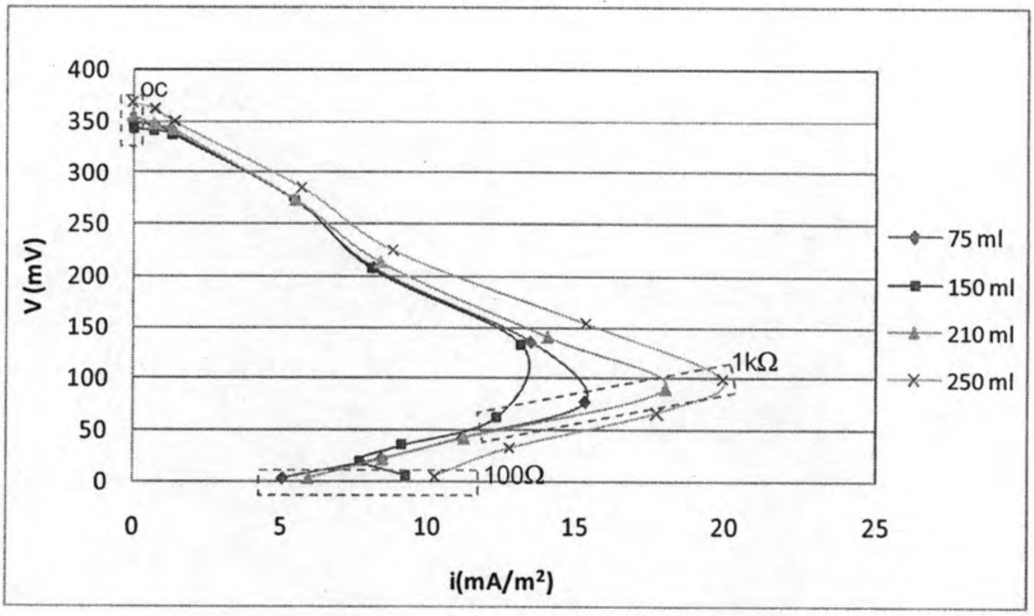

Fig. 5.13 Voltage-current density characteristics of the BFC with different compartment volumes

The results show that the open circuit voltages of all compartment volumes were in the range 342-367 mV. The increasing of compartment volume increased the maximum current density. The BFC with volume of 150 ml and 250 ml had the total impedance of 1287 and 1058 Ω, respectively (Table 5.1 and Table 5.3).

Fig. 5.14 shows power density of the BFC as a function of load resistance. The power density of 2.4 mW/m^2 was achieved from the highest volume at 2 kΩ load. The total charge generated by the BFC can be calculated from the area under current-time curves. The relationship between the total charge and the compartment volume of the BFC experiment is shown in Fig. 5.15.

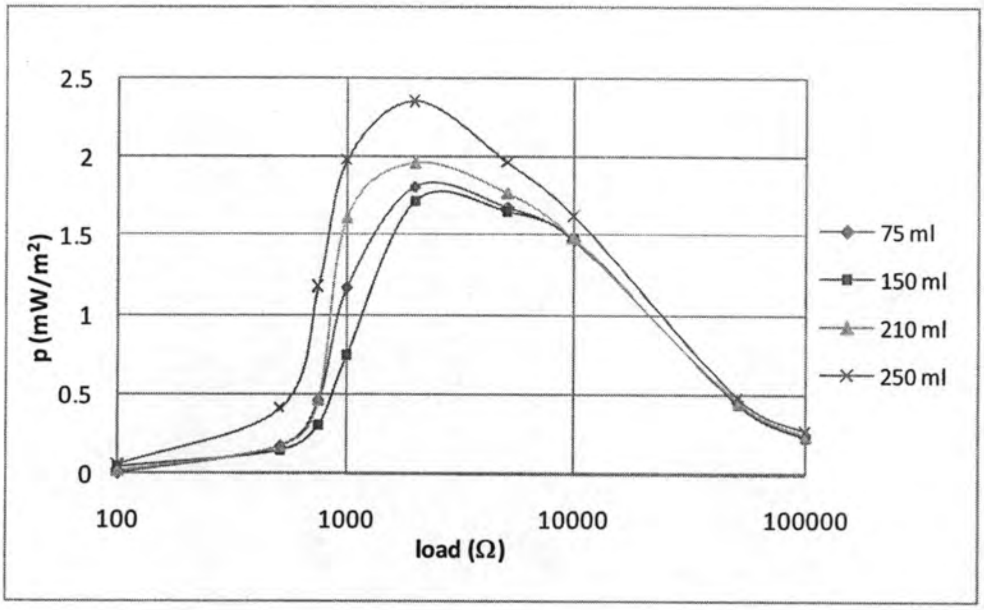

Fig. 5.14 Power density-load characteristics of the BFC with different compartment volumes

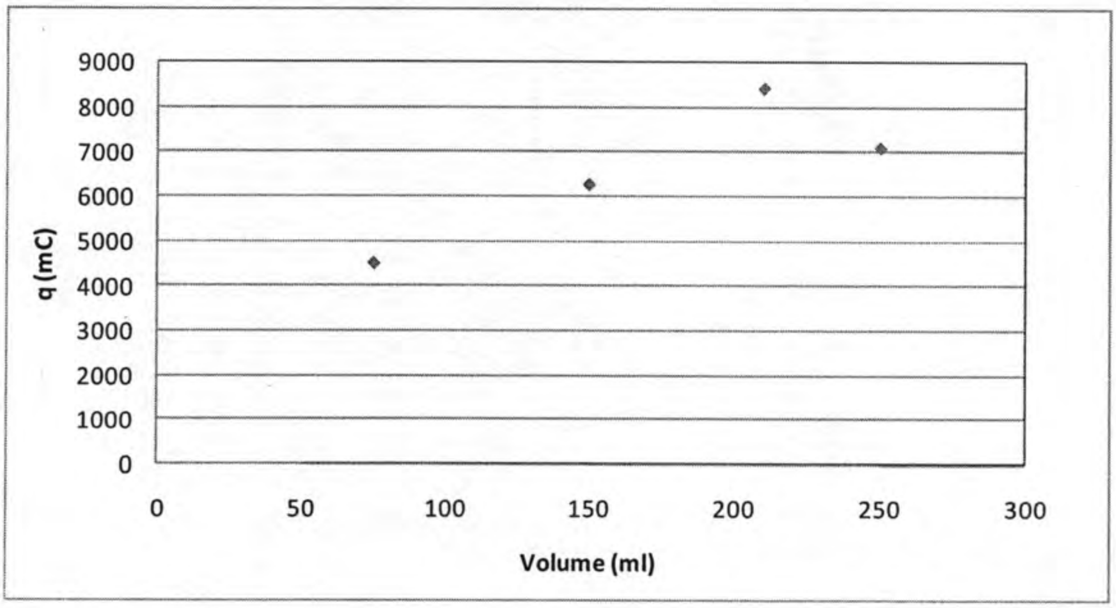

Fig. 5.15 The relationship between the total charge and volume of the BFC

Since the all experiments were operated in the batch operation, so the BFC can generate charge until one of the components was totally exhausted. In our experiments, it was found that the ferricyanide ($Fe(CN)_6^{3-}$) exhausted before other components because it was observed that the color of ferricyanide changed from the yellow to pale (reduction: $Fe(CN)_6^{3-} + e^- \rightarrow Fe(CN)_6^{4-}$).

Theoretically, the concentration of each component relates with the amount of charge (Q_{th} [C]) as shown in Eq. (5.3).

$$Q_{th} = nFMv \quad (5.3)$$

n: number of moles of electrons produced per mol of substrate

F: Faraday's constant [96,485 C/mol]

M: concentration of the substrate [mol/l]

v: substrate volume [l]

Since ferricyanide exhausted before other components, then the amount of charge was limited by concentration of ferricyanide. For the BFC with 210 ml compartment volume, the amount of charge was 40.5 C (Qth=nFCV=2*96485*0.001*0.21 C). However, the total of charge from the BFC experiment with 210 ml compartment volume was 8.4 C. The loss of charge in this BFC was 79%. The loss of charge is summarized in Table 5.5.

Table 5.5 Charge of the BFC with different compartment volumes

Compartment volume (ml)	Q_{th} (C)	Q_{ex} (C)	% loss of charge
75	14.5	4.5	68.6
150	28.9	6.3	78.2
210	40.5	8.5	79.1
250	48.2	7.1	85.2

where Q_{ex} [C] is the charge from the BFC experiment.

As shown in Fig. 5.15, it was found that the lower volume the lower charge was obtained. It could say that the amount of charge increases as the increasing of volume while the concentration of the substrate is fixed (following as Eq. 5.3). However, the increasing of the compartment volume increased the loss of charge in the BFC (Table 5.5). Moreover, it was found that the BFC with 250 ml compartment generated the charge lower than the 210 ml one. Since the experiments were operated under un-stirring condition, the distribution of yeast in the system with the larger volume is higher than the smaller volume one. Hence, the loss in the system with larger volume should be also high. This indicates that for the BFC volume design, the volume should not be so large. However, if the system has to be large, the system should be stirred.

5.3 Summary

It was found that the electrode surface area affects the electrode, solution, electrode-solution interfacial impedance. The smaller the electrode surface area results in the higher impedances (PEM, yeast, glucose, MB and ferricyanide). Therefore, the current of the BFC can be increased by increasing of electrode surface area which will lead to the decreasing of the BFC impedance. However, the increasing of electrode surface area will lead to the decreasing of the current density. It was found that the distances between electrodes do not have much effect to the solution impedance because the value of the interfacial impedance was much higher than the solution. Hence, the effect of distance is not the high important for this system. Finally, it was found that as the compartment volume increases, the higher charge will be results.