

CHAPTER 4

IMPEDANCE ANALYSIS OF BIO-FUEL CELL ELECTRODE MATERIALS

The BFC needs two electrodes, anode and cathode for supplying and receiving electrons to and from an external load, respectively. There were a number of reports on using different materials for electrode as mentioned in chapter 1. However, there has been no report presenting the criteria for the selection of electrode materials. The selection of an effective electrode material for electron transfer in the system is clearly important for improving the efficiency of the BFC. The requirements for a suitable electrode are detailed as follow:

(a) The electrode should not be toxic to microorganisms. This requirement has not been fulfilled by many of the reactive electrodes employed in electrochemistry so far, such as lead or mercury electrodes.

(b) For practical application over a long period, it should be physically and chemically stable in extreme environments since the activated sludge or wastewater may be used as a fuel source. The degradation of the conventional electrode such as carbon and graphite composite electrodes will affect the stability of the power supply from the BFC.

(c) Impedance of the electrode material should be low to prevent the loading effect in connection with an external load and also to reduce the power loss inside the electrode itself. This means the conductivity of the material used should be as high as possible.

(d) Interfacial impedance between the electrode and the solution should also be low to facilitate electron transfer between the microorganism/mediator and the electrode. This criterion implies that the electrode should not act as a polarized electrode.

(e) From the commercial aspect, the electrode should not be expensive. This limits the use of noble metals, such as platinum and gold, even though they are relatively stable in most environments.

The purpose of this chapter is to study the effect of different electrodes on the performance of the BFC. An electrical equivalent circuit model of the electrodes impedance will be proposed to describe the BFC characteristics. The CPE model was also applied to analyze the impedance data for determining values of each component in the equivalent circuit.

4.1 Bio-Fuel Cell Experiments

The 0800801 chamber was used in the following experiments. Five types of electrode were used in the experiments: carbon fiber (CF), silver (Ag), nickel (Ni), stainless steel (St) and aluminum (Al). Platinum and gold electrodes were not use in our experiment because both electrodes are expensive. The carbon fiber electrode replaced the carbon or graphite electrode because of its flexible structure. The dimension of each electrode was 3.2 cm x 6.0 cm. The same electrode materials were used for both compartments which made it symmetrical in configuration. Two experimental setups were investigated as follows.

4.1.1 Bio-Fuel Cell Performances

This experimental setup was designed for investigation of the relation between the BFC performance and electrode materials. Twenty five mg/ml of baker's yeast was used as a microorganism in the experiments. Fifty three mM of glucose, 3mM MB and 5mM ferricyanide ($K_3Fe(CN)_6$) in 0.1 M, pH 7.0 PB, were used as the organic substrate, electron mediator and electron acceptor, respectively. The compositions for both anodic and cathodic compartments were listed as follows:

Anodics : PB 0.1M (pH7)+yeast 25mg/ml+glucose 53mM+MB 3mM

Cathodics : PB 0.1M (pH7)+ $K_3Fe(CN)_6$ 5mM

4.1.2 Impedance Studies

For the electrode impedance analysis experiments, all other variables such as the PEM, microorganism, organic substrate, electron mediator and electron acceptor,

except for electrode and PB, were removed to eliminate their impedances as shown in Fig. 4.1.

Anodics : PB 0.1M (pH7)

Cathodics : PB 0.1M (pH7)

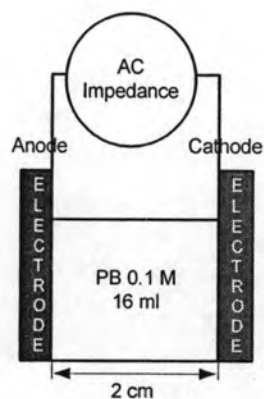


Fig. 4.1 An ac-impedance measurement

Since this system consisted of two electrodes and PB, the impedances of the system were the results of the summation of the electrode (Z_E), solution (Z_S) and electrode-solution interface (Z_I) impedance as shown in Fig. 4.2.

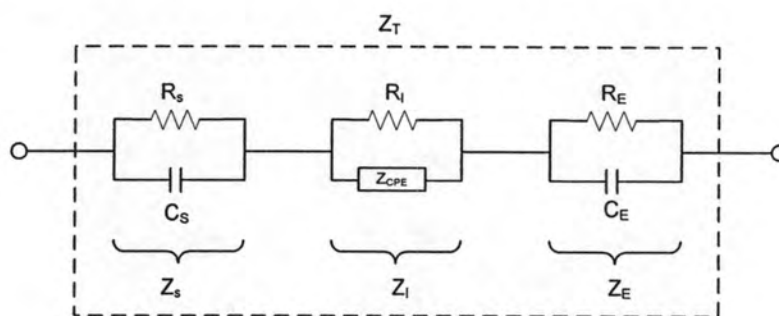


Fig. 4.2 The estimation of total BFC impedance when the system consists of electrodes and PB

where Z_E : the electrode impedance [Ω]

Z_S : the solution impedance [Ω]

Z_I : the electrode-solution interface impedance [Ω]

Z_{CPE} : the CPE impedance which related to the electrodes-solution interface defined as shown in Eq. (2.22).

The total impedance (Z_T) of the electrodes in solution could be calculated as follows:

$$Z_T = \left(\frac{R_s}{1 + j\omega C_s R_s} \right) + \left(\frac{R_l}{1 + AR_l(j\omega)^\alpha} \right) + \left(\frac{R_E}{1 + j\omega C_E R_E} \right) \quad (4.1)$$

Each parameter in Eq. (4.1) was investigated from the impedance analysis.

4.2 Results and Discussions

4.2.1 Voltage Generation from the Bio-Fuel Cell Electrode Materials

Fig. 4.3 shows a typical voltage versus time data measured from the BFC when carbon fiber was used as electrode. All reagents, including glucose, MB, microorganism and ferricyanide were loaded into the measuring compartments.

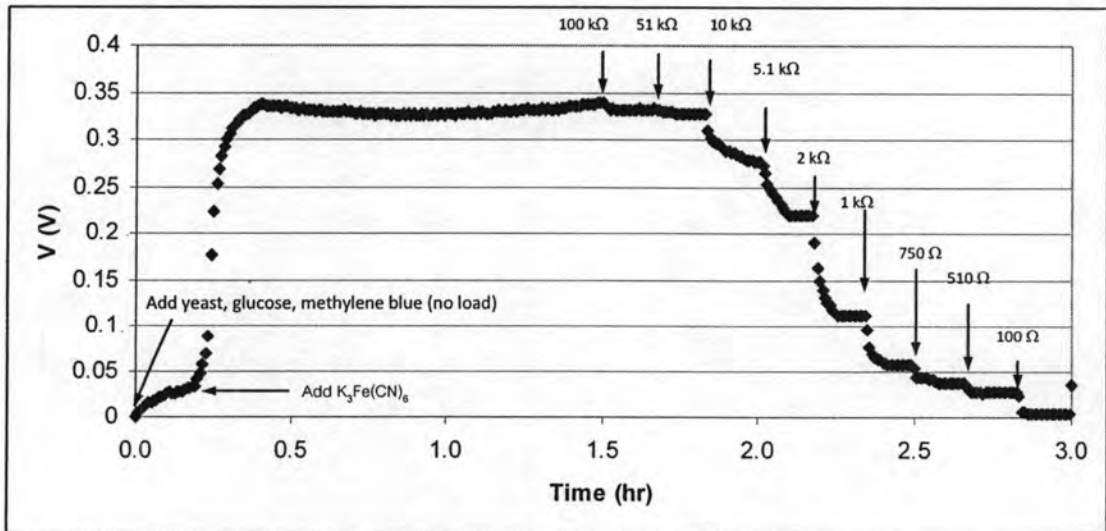


Fig. 4.3 Voltage generation from BFC when using carbon fiber as an electrode

Before all the components were added, approximately 0 mV was observed from the BFC at open circuit condition. The addition of only one component, such as microorganism, glucose and MB changed the BFC voltage in the range of 10~50 mV. It was observed that the potential dramatically increased at the beginning to 337 mV when all components were loaded to the cell. This implied that the cell started the metabolism of glucose and generated the electrical potential. The current and power

outputs were measured by changing the values of external resistance across the anode and the cathode from $100\text{ k}\Omega$ to $100\ \Omega$.

Fig. 4.4 shows the voltage - current density characteristic of the BFC when different electrodes were applied. These results had shown that nickel electrodes gave the highest open circuit voltage up to 540 mV. The open circuit voltage of stainless steel, carbon fiber, aluminum and silver were 455, 337, 268 and 213 mV, respectively. These results obviously denoted that the electrode materials affect the voltage generation of the BFC. For the current density supplied from the BFC, it was found that the highest value of 31 mA/m^2 (at $1\text{ k}\Omega$ load) was obtained from the carbon fiber electrode. At the same load of $1\text{ k}\Omega$, the current density supplied from the silver, nickel, stainless steel and aluminum electrodes were 29, 10, 10 and 2 mA/m^2 , respectively.

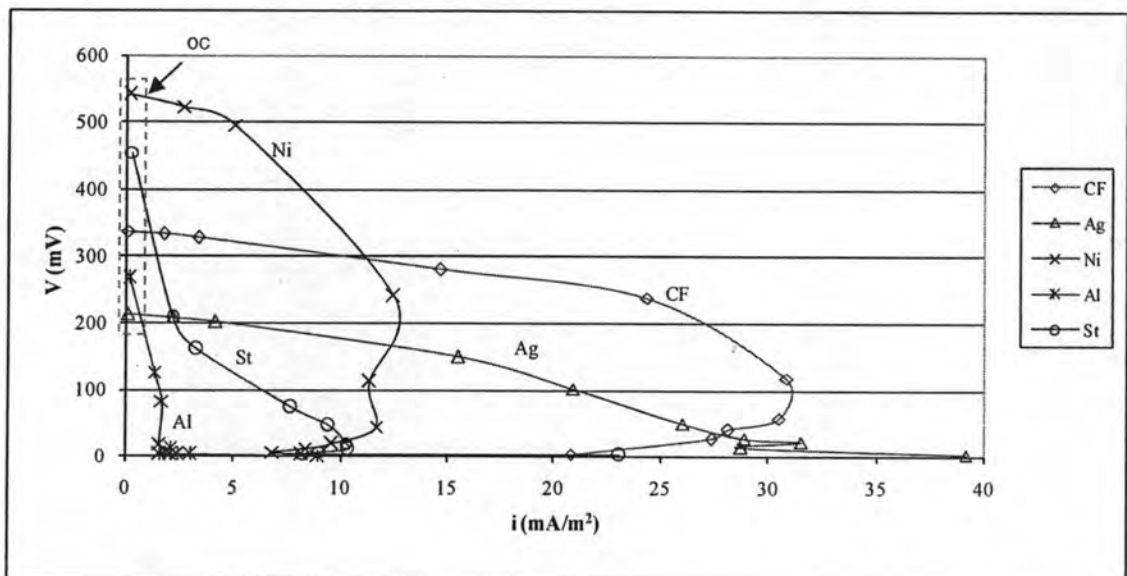


Fig. 4.4 Voltage vs. current density of the BFC when using different electrodes

Fig. 4.5 shows power density - load characteristics of the BFC with different electrodes. The maximum power density of 1.8 mW/m^2 at $1\text{ k}\Omega$ load was gained from the carbon fiber electrode. For the silver, nickel, stainless steel and aluminum electrodes, the obtained power density at $1\text{ k}\Omega$ load were 0.8, 0.2, 0.1 and 0.004 mW/m^2 , respectively. This rank is consistent with the rank of the current density obtained from the BFC.

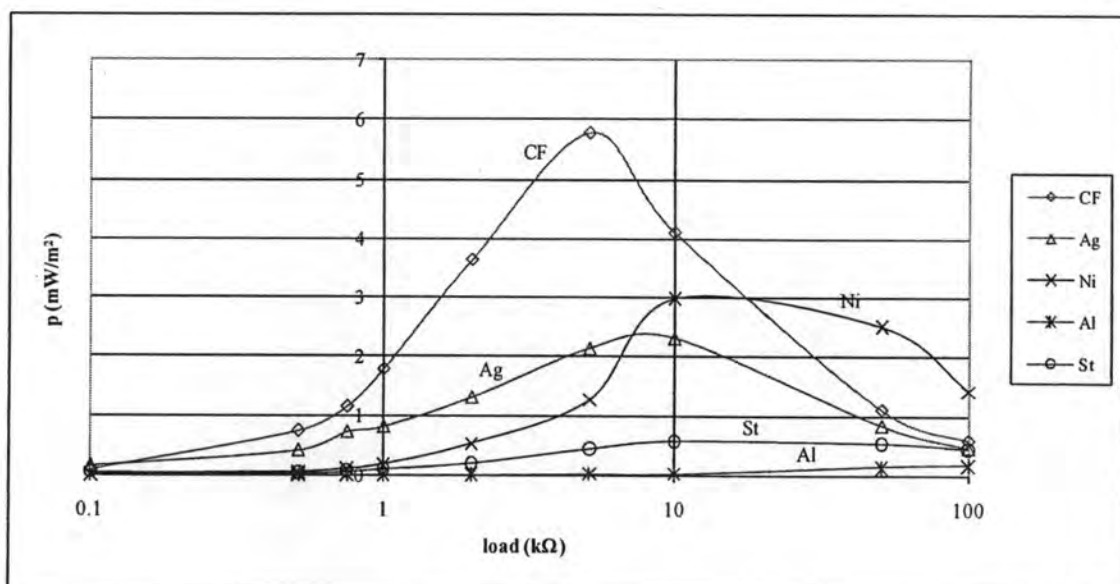


Fig. 4.5 Power density vs. load of the BFC when using different electrodes

The above results indicated that even the nickel electrode could generate the highest open circuit voltage but when it connected to an external load the current density was lower than the carbon fiber and silver electrode. The carbon fiber electrode could supply current and power of more than 3 times and 9 times, respectively, over nickel. These results implied that there must have losses somewhere in the system which made the nickel electrode not able to supply current and power as it should. The BFC voltage, current density, power density and internal resistance (R_{th}) of five electrodes are summarized in Table 4.1.

Table 4.1 Voltage, current density and power density of the bio-fuel cell

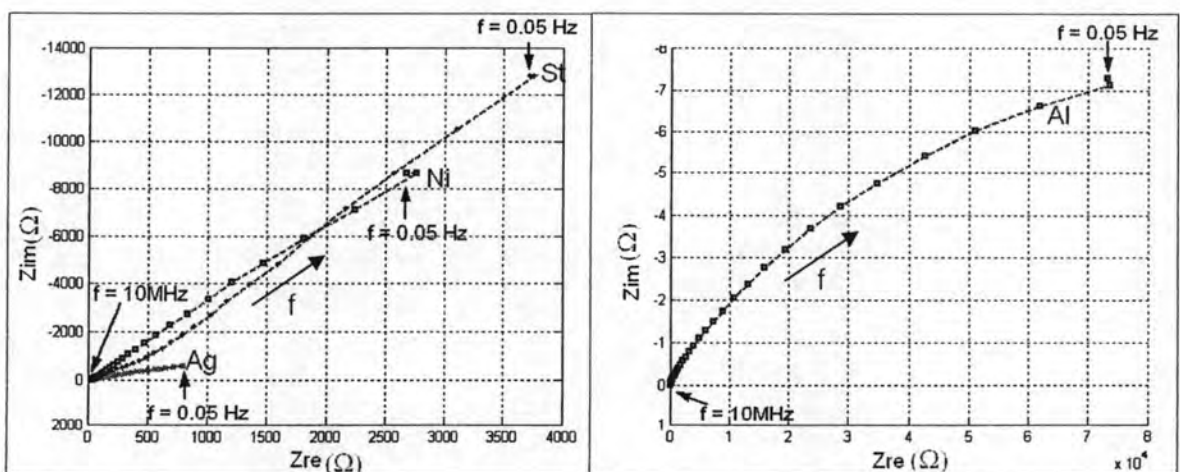
Electrode	$V_{no\ load}$ (mV)	$V_{1k\Omega}$ (mV)	$i_{1k\Omega}$ (mA/m ²)	$p_{1k\Omega}$ (mW/m ²)	R_{th} (kΩ, from p vs. load curve)
Carbon fiber	337	58	31	1.8	5.1
Silver	213	27	29	0.8	10
Nickel	540	18	10	0.2	10
Stainless steel	455	10	10	0.1	10
Aluminum	268	2	2	0.004	100

As shown in Table 4.1, the carbon fiber electrode had the smallest internal resistance (R_{th}) of $5.1 \text{ k}\Omega$, while the R_{th} of other electrodes were $10 \text{ k}\Omega$ except for aluminum electrode which had the R_{th} of $\sim 100 \text{ k}\Omega$. The results show the estimation values of all losses causing the loading effect in the system. Hence, we assume that the loading effect of the BFC was due to the use of different electrodes and ac-impedance measurement was performed for each electrode in PB solution to prove our assumption.

4.2.2 Impedance Analysis of the Bio-Fuel Cell Electrode Materials

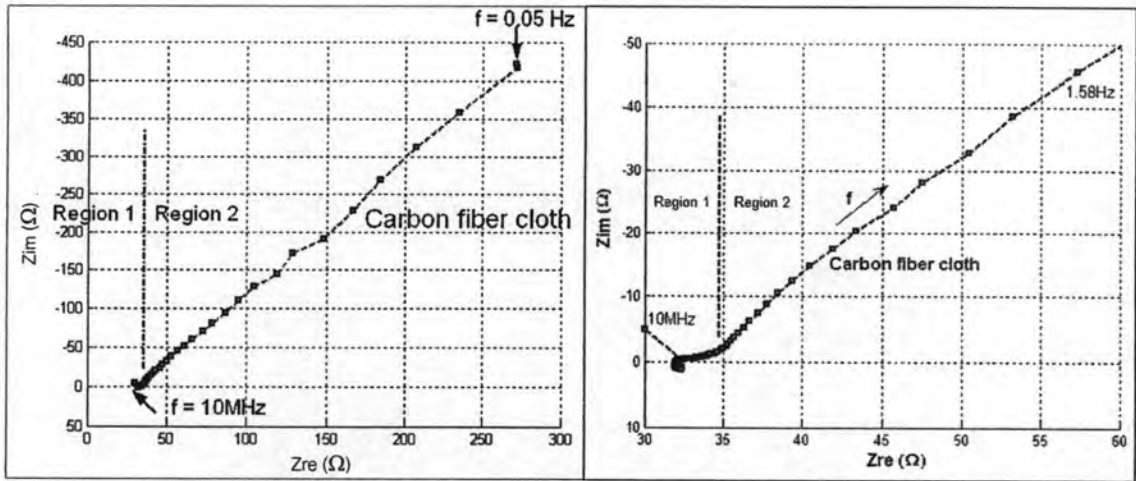
Since the configuration of the measuring system were the same for all experiments, except for the electrode used then the loss mentioned above should come from the electrode properties. To investigate the electrical characteristics of the electrode, ac-impedance measurement was performed using the same electrodes in phosphate buffer solution, without PEM, glucose, methylene blue and ferricyanide (Fig. 4.1). The frequency of the measurement was ranged from 0.05 Hz to 10 MHz .

Fig. 4.6 shows the impedance plots or Cole–Cole plots of the electrode in PB, using ac-impedance measurement. The x-axis and y-axis represent the real part (Z_{re} : resistive component) and the imaginary part (Z_{im} : reactive component) of the impedance, respectively.



(a)

(b)



(c)

(d)

Fig. 4.6 Cole-Cole plots using (a) silver, nickel, and stainless steel electrodes (b) aluminum electrode (c) carbon fiber electrode (d) the enlarged Fig. 4.6 (c) in the high frequency region

As shown in Fig. 4.6 (c and d), the impedance characteristic can be divided into two regions: region 1 and region 2 representing a high and low frequency region, respectively. The results show that the impedance at high frequency was nearly the same and low for all electrodes. As 0.1M PB solution and electrodes had low impedance, it is reasonable to assume that region 1 related to these two components. In addition, the reactance was relatively low compared to the resistance (Fig. 4.6 (d)), so the impedance at this region can be simplified to only the resistance component ($R_{SE} = (R_s // C_s) + (R_e // C_e) \cong R_s + R_e$). The differences found in the region 2 for all electrodes were assumed to be the contribution of the solution-electrode interfacial impedance. It is known that an electrical double layer occurs at the interface when the electrode is in contact with the solution. This electrical double layer acts as a capacitive component as found in region 2.

Therefore, the total impedance (Z_T) was then simplified to the following equation:

$$Z_T = R_{SE} + \left(\frac{R_I}{1 + AR_I(j\omega)^\alpha} \right) \quad (4.2)$$

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. 4.6). The target sum square error of the estimated value was set to be less than 6%. The results are summarized in Table 4.2.

Table 4.2 Parameters estimated from a fitting process for the equivalent circuit of Fig. 4.6

Electrode	R_{SE} (Ω)	R_i ($k\Omega$)	α	A (s^α/Ω)	$1/A$ (Ω/s^α)
Carbon fiber	34.7	5	0.71	0.00442	226
Silver	30.6	3	0.56	0.00137	730
Nickel	33.8	3662	0.82	0.00029	3448
Stainless steel	31.8	2453	0.82	0.00019	5263
Aluminum	30.0	224	0.76	0.00002	50000

As shown in Table 4.2, the R_{SE} values for all electrodes were in the range of 30-35 Ω . Since the R_{SE} is the series combination of electrode (Z_E) and solution (Z_S) impedance, moreover all experiments used the same PB, so the difference in the R_{SE} value should come from the difference in conductivity of the electrode material used. It should be noted that the R_{SE} values were quite low comparing to other components, so this impedance should not be the limiting factor for the electron transfer in the system. Hence, it can be surmised that the interfacial impedance between electrode and solution (Z_{CPE} and R_i) is the key parameter which plays an important role in the electron transfer in the system.

The interfacial impedance is defined by R_i and Z_{CPE} . Theoretically, both components should be small to minimize the total impedance. It was found that R_i of silver electrode had the smallest resistance of 2.6 $k\Omega$, while the R_i of carbon fiber and aluminum were 5 and 224 $k\Omega$, respectively. It should be noted that the R_i of nickel and stainless steel were higher than 1 $M\Omega$, so it is difficult for the electron to transfer through the R_i . However, there was Z_{CPE} in parallel with the R_i therefore the Z_{CPE} has to be

considered together with the R_i one since Z_{CPE} will be another conduction path for the electron transfer.

As shown in Eq. (2.22), the Z_{CPE} value depends on the parameter A and α . To reduce the Z_{CPE} , A and α should be high. It was found that the α values varied with the electrode type in the range of 0.71-0.82 except for the silver electrode which has α of about 0.56. This implies that the Z_{CPE} of all electrode materials used in this experiment are not pure resistive and neither has a capacitive component. Therefore, the CPE model could be expressed by the series of resistance and capacitance. According to this model, the better electron transfer can be obtained when the resistance is low and the capacitance is high. Since the α value of silver electrode was nearly 0.5, this denotes that the resistive and capacitive components of the impedance are of nearly the same order. This implies that both components make the same contribution in the electron transfer in the system. For the other electrodes, the α values were around 0.75 which indicates that the capacitive component plays more important role on the electron transfer between electrode and solution. However, not only the α value but also the A parameter is necessary for describing the electron transfer between electrode and solution. It should be noted that the A value of aluminum electrode was only 0.00002 which is too low comparing to the other electrodes which have magnitude of 10~200 times higher. This clearly indicates that aluminum electrode do not allow the electron to transport through the aluminum and solution interface. For other electrodes, the A value were rather high indicating that the impedances were low and allowed the electron flow through their electrode-solution interface. To explore the electron transportation pathway, the magnitude of $1/A$ and R_i have to be considered as to whether the Z_{CPE} or R_i are the limiting factor for the electron transfer between electrode and solution interface.

In the Table 4.2, it is obvious that the R_i and $1/A$ of the carbon fiber, and silver were low compared to other metal electrodes. This indicates that electrons could transfer through electrode-solution interface of the carbon, and silver electrode better than other metal electrodes. The better electron transfer in the system means there is less loss and smaller loading effect when the electrodes were connected to external load. Then, it is possible to say that the loading effect of the carbon fiber and silver

were less than other metal electrodes. This data clearly supports the results of the BFC performance as mentioned above that carbon and silver distribute a higher power and current than nickel, stainless steel and aluminum. Consider the Eq. (2.22), it should be noted that the Z_{CPE} magnitude decreases as the frequency increases implying that at higher frequency the electron will flow through Z_{CPE} while at low frequency the electron will flow through the R_i .

R_i and $1/A$ for all electrodes were plotted together in Fig. 4.7, except for the aluminum electrode which had very high $1/A$ ($\sim 57,400 \text{ } \Omega/s^\alpha$).

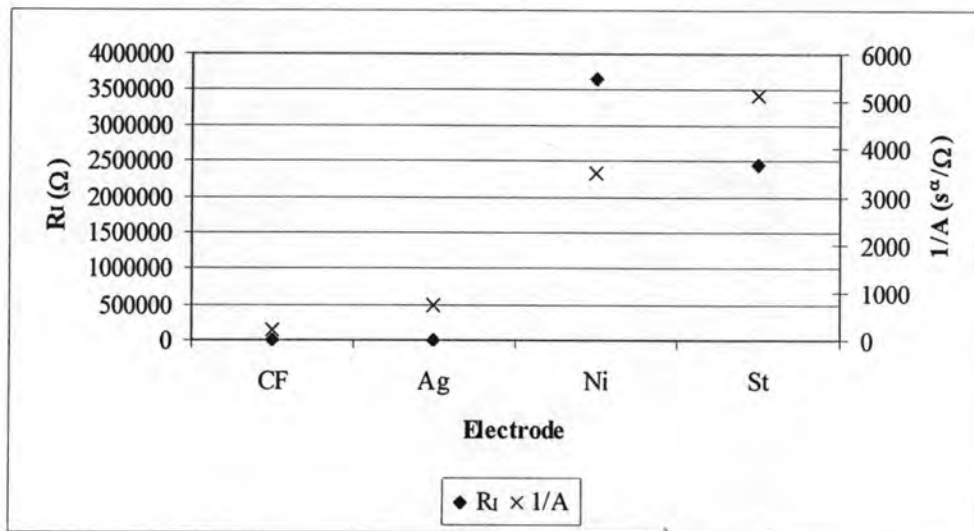


Fig. 4.7 A comparison of R_i and $1/A$ for various electrodes

It is obvious that the R_i and $1/A$ of the carbon fiber, and silver were low comparing to nickel, aluminum and stainless steel. This indicates that electrons could transfer through electrode-solution interface of the carbon fiber, and silver electrode better than nickel, stainless steel and aluminum electrodes. The better electron transfer in the system means there is less loss and smaller loading effect when the electrode was connected to external load. Loading effect could be determined from the voltage obtained at external load and the open circuit voltage (V_{BFC}). The obtained voltage at load (V_{load}) is equal to $Z_{load} * V_{BFC} / (Z_T + Z_{load})$. Generally if the Z_{load} is much higher than the Z_T , the V_{load} is nearly equal to the V_{BFC} , however, the V_{load} will decrease as the Z_T increase. Since the R_i and $1/A$ of the carbon fiber, and silver were low then the loading effect due to these electrodes were less than the nickel, aluminum and stainless steel

electrodes. These results clearly support the results of the BFC performance as mentioned above that carbon fiber and silver distribute higher power and current than nickel, stainless steel and aluminum. It should be noted that the magnitude of the Z_{CPE} impedance depends on frequency. Eq. (2.22) indicates that the magnitude of the Z_{CPE} impedance decreases as the frequency increases implying that at low frequency the electron will flow through the R_f , while at higher frequency the electron will flow through Z_{CPE} .

As shown in the Fig. 4.3, the response of the BFC was not fast indicating that the electron transfer in the system should be slow. Then to investigate the conduction pathway for the BFC, we could evaluate the impedance at low frequency. Table 4.3 shows the estimated resistance (Z_{re}), reactance (Z_{im}) and magnitude ($|Z_{CPE}|$) of the Z_{CPE} for all electrodes at a frequency of 1Hz.

Table 4.3 Resistance (Z_{re}), reactance (Z_{im}) and magnitude ($|Z_{CPE}|$) of the Z_{CPE} for all electrodes when the frequency was set at 1 Hz

Electrode	CF	Ag	Ni	St	Al
$Z_{re} (\Omega)$	27	166	215	317	5229
$Z_{im} (\Omega)$	-55	-201	-741	-1092	-13209
$ Z_{CPE} (\Omega)$	61	261	771	1137	14206
$ Z_T (\Omega)$	96	291	805	1169	14236
% Loading Effect at $1k\Omega$ (calculation results)	9	22	45	54	93
% Loading Effect at $1k\Omega$ (experimental results)	83	87	97	98	99

It was found that, for all electrodes, $|Z_{CPE}|$ are $1/10 \sim 1/4750$ of the R_f , this implies that the electron will flow through the Z_{CPE} more easily than the R_f . In other word, the R_f is a limiting factor for the electron transfer at low frequency or Z_{CPE} is a conduction pathway

for the system. Since Z_T is the series connection of R_{SE} and Z_I , it could be summarized that the conduction pathway of the BFC is the route from R_{SE} through Z_{CPE} not the route from R_{SE} through R_I .

At 1Hz, the Z_{re} was smaller than the Z_{im} by about ~2-3 times for all materials. This indicates that the Z_{im} is a limiting factor in electron transport, in other words, the electrode-solution interfaces behave as a polarized electrode. This can be understood because the electrical double layer occurs at the electrode-solution interface. The impedance characteristics of these polarized interfaces will directly affect the electron transfer in the system. It was found that the $|Z_{CPE}|$ for the nickel, aluminum and stainless steel electrodes were 3-200 times higher than carbon fiber and silver ones. This high interfacial impedance of the nickel, aluminum and stainless steel electrodes indicates that they were more polarized than the carbon fiber and silver electrodes. These results indicate that the voltage drop (loading effect) at the electrode-solution interface of nickel, stainless steel and aluminum are high. Therefore, they could not distribute power to load even though they generated a higher open circuit voltage than the carbon and silver. Considering the carbon electrode, $|Z_{CPE}|$ was only 61Ω then the loading effect will reduce the generated voltage less than 9% if the external load is higher than $1k\Omega$. Compared to the nickel electrode which had $|Z_{CPE}|$ about 771Ω , the loading effect will reduce the generated voltage more than 45%. These estimations support our results in Table 4.1 that carbon fiber electrode could supply voltage, current and power to external load higher than the nickel one even through its open circuit voltage was low. However, from the experimental results shown in Table 4.1, the voltage drops due to the loading effect, when the BFC was connected to the external load, were higher than the theoretical estimation. The generated voltage from the BFC dropped about 83, 87, 97, 98, 99% for carbon fiber, silver, nickel, stainless steel and aluminum electrodes, respectively.

At the frequency close to zero, the Z_{CPE} will be extremely high and could not conduct the current in the system. The conduction path way will be R_{SE} and R_I will be a limiting factor for the electron transfer. Table 4.4 shows the estimation of the total

total resistance (Z_T) and loading effect of the system when considering the frequency at near zero or direct current (DC) condition.

Table 4.4 Total Resistance ($f \rightarrow 0$) when using different electrode materials

Electrode	CF	Ag	Ni	St	Al
$Z_T (\Omega) = R_{SE} + R_i$	4,960	2,610	3,662,560	2,452,870	224,140
% Loading Effect at $1k\Omega$ (calculation results)	83	72	100	100	100
% Loading Effect at $1k\Omega$ (experimental results)	83	87	97	98	99

It was found that at frequency converts to zero, the loading effect of the carbon fiber will reduce the generated voltage $\sim 83\%$ if the external load is higher than $1k\Omega$. It should be noted that the value of loading effect from the calculation and experimental results are nearly the same. Therefore, it can be concluded that the electron transfer in the BFC was limited by the interfacial resistance.

However, the difference between the theoretical estimation and experimental results was due to a difference in the conditions of use. The theoretical estimation had been done under the condition that the electrode was in contact with only PB while many components were added into the experimental setup. Therefore, the impedance of the BFC was affected by the PEM, the anodic solution (with microorganism, methylene blue and glucose in PB) and the cathodic solution (with ferricyanide in PB).

Following the electrode selection requirements as mentioned in the introduction, with a limitation to our experiments, we can say that carbon fiber is the best material for using as a BFC electrode since it is not toxic to microorganisms, physically and chemically stable, has a low impedance and, finally, is relatively cheap in comparison with gold or platinum. Even though the silver electrode also offered good BFC performances, it is known that silver is not stable in many environments so silver was not suitable for using as the BFC electrode.

4.3 Summary

BFCs with different electrode materials were constructed. The nickel, aluminum, and stainless steel electrodes were found to generate a higher open circuit voltage than the carbon fiber and silver electrodes, however, they distributed less power than the later group. To explain the phenomena, an impedance measurement together with a model analysis of the electrodes was performed. The results indicated that the nickel and stainless steel electrodes had high electrode-solution interfacial impedance (Z_i) which resulted in a high loading effect when they were connected to the external load. This was in contrast to the carbon fiber electrode which had low interfacial impedance and could supply higher power than metal electrodes because there was less loss at the electrode-solution interface.