CHAPTER 2

BASIC BACKGROUND AND RELATED TOPIC

This chapter introduces a basic concept and knowledge necessary for understanding the behavior of the BFC such as electrical equivalent circuit, impedance analysis. The simple electrical equivalent circuit of the BFC is proposed based on Thevenin equivalent circuit. Technique of ac-impedance spectroscopy is also briefly provided for analyzing results in chapter 4.

2.1 Biological Mechanism

Metabolism is a chemical process of all living creatures in producing energy for growth, reproduction, maintaining their structures, and responding to environments. Carbohydrates serve as a major source of energy for most creatures. Glucose is the most well known and popular carbohydrate source.

In the first stage of metabolism, glucose is converted to two molecules of pyruvate by glycolysis. This stage occurring in the cytosol of the cell will produce *adenosine triphosphate* (ATP) and *Nicotinamide adenine dinucleotide* (NADH). Pyruvate is subsequently transported into the mitochondria and converted to acetyl-CoA and CO_2 by coenzyme A. The acetyl-CoA is transferred to citric acid cycle. At this state, the carbon dioxide, hydrogen ions and electrons are produced and sent to electron transport system or respiratory chain.

The total metabolism process using glucose and oxygen can be expressed as in Eq. (2.1) [14].

$$C_6H_{12}O_6 + 6O_2 => 6CO_2 + 6H_2O \tag{2.1}$$

The detail of Eq. (2.1) can be expressed by two step reactions. Starting with the decomposition of glucose by enzymatic reactions as shown in Eq. (2.2) [14], following by oxygen reduction as shown in Eq. (2.3) [14]

$$C_6H_{12}O_6 + 6H_2O => 6CO_2 + 24H^+ + 24e^- \tag{2.2}$$

$$6O_2 + 24H^+ + 24e^- \Rightarrow 12H_2O \quad (2.3)$$

It is obvious that the combination of Eq. (2.2) and Eq. (2.3) is Eq. (2.1).

To realize the BFC, it is necessary to draw electron from the microorganism in the absence of oxygen as shown in Eq. (2.2). Hence, the artificial electron mediators such as methylene blue, neutral red were used to mediate electron in the oxidation-reduction reaction. The reduced mediator can shuttle the electrons to an anode as shown in Fig. 1.2. Not only the artificial electron mediator but also many special microorganisms can transfer electrons to electrode by itself. The electrons flow to cathode through an external load. The hydrogen ions diffuse from inner of the cell to outer and pass through the PEM to the cathodic compartment. In the cathodic compartment, electron acceptor, such as oxygen, will combine with electrons and hydrogen ions to produce water.

2.2 Equivalent Circuit of the Bio-Fuel Cell

The BFC behaves like a galvanic cell or battery. It can continuously generate the electricity until the substrate exhausts. Hence, the BFC can be explained using the Thevenin equivalent circuit as shown in Fig. 2.1.

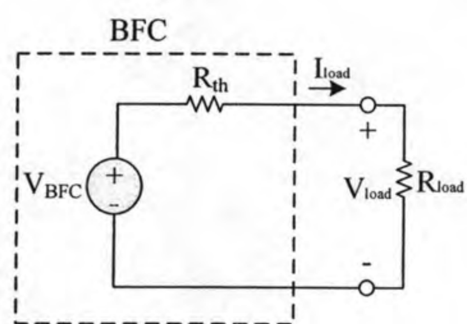


Fig. 2.1 Equivalent circuit of the BFC connecting with the load resistance

where V_{BFC}: BFC voltage (or Thevenin voltage) [V]

R_{th} : Thevenin resistance [Ω]

V_{load}: generated voltage [V]

I_{load}: generated current [A]

R_{load}: load resistance [Ω]

Theoretically, the effective potential V_{BFC}, available for work is resulted from the difference between the cathode and anode half cell potential as indicated in Eq. (2.4)

$$V_{BFC} = E_{cathode} - E_{anode} \quad (2.4)$$

where $E_{cathode}$: half-cell potential at the cathode [V]

E_{anode}: half-cell potential at the anode [V]

The maximum voltage occurs when there is no load to the BFC. It means that, the BFC voltage (V_{BFC}) equals the load voltage (V_{load}) and the load current equals zero. When the BFC was connected to the external load, the V_{BFC} was divided by the Thevenin resistance and load resistance. Therefore, the V_{load} can be expressed as Eq. (2.5).

$$V_{load} = (R_{load}/(R_{load}+R_{th}))*V_{BFC}. \quad (2.5)$$

The I_{load} can be calculated from the V_{load} and R_{load} as shown in Eq. (2.6).

$$I_{load} = V_{load}/R_{load} \quad (2.6)$$

The current density (i_{load}, A/m^2) is then given by

$$i_{load} = I_{load}/A \quad (2.7)$$

where A is the electrode surface area [m^2].

Eq. (2.5) implies that the Thevenin resistance (R_{th}) has an effect on the current of BFC. This is called the loading effect or ohmic loss. The highest current obtained from the BFC occurs when the load impedance is minimized.

The power consumed by R_{load} is shown as Eq. (2.8)

$$P_{load} = I_{load} * V_{load} = R_{load}*(V_{BFC}/(R_{load}+R_{th}))^2 \quad (2.8)$$

The power density is then,

$$p_{load} = P_{load} / A \tag{2.9}$$

Considering Eq. (2.8), if V_{BFC} and R_{th} are fixed, P_{load} is the function of R_{load}. The maximum power will be generated when R_{load} is equal to the Thevenin resistance (R_{th}). This is known as maximum power transfer theorem.

The theoretical voltage generation when using glucose as organic substrate can be estimated from Eq. (2.10).

Anodic : $C_6H_{12}O_6 + 6H_2O \rightarrow 6CO_2 + 24H^+ + 24e^-$ $E^0 = -0.42$ V (at pH 7.0, 25°c) [41]

Cathodic : O_2 (g) + $4H^+ + 4e^- \rightarrow 2H_2O$ $E^0 = +0.82$ V (at pH 7.0, 25°c) [41]

$$V_{BFC} = 0.82-(-0.42) = 1.24 \text{ V} \tag{2.10}$$

Practically, the BFC operates in the solution and electron acceptor such as ferricyanide was used. Half-cell reaction of ferricyanide is shown in Eq. (2.11).

$$\mathrm{Fe(CN)_6^{3-}} + e^- \leftrightarrow \mathrm{Fe(CN)_6^{4-}} \qquad E^0 = +0.36 \text{ V [42]} \tag{2.11}$$

Hence, the BFC voltage when using ferricyanide as electron acceptor is approximately 0.78 V as shown in Eq. (2.12).

$$V_{BFC} = 0.36-(-0.42) = 0.78 \text{ V} \tag{2.12}$$

The ideal characteristic of BFC is a straight line as shown in Fig. 2.2 however the actual BFC voltage drops from the ideal one due to irreversible losses occur in the system. They are activation loss, ohmic loss and concentration loss [2].

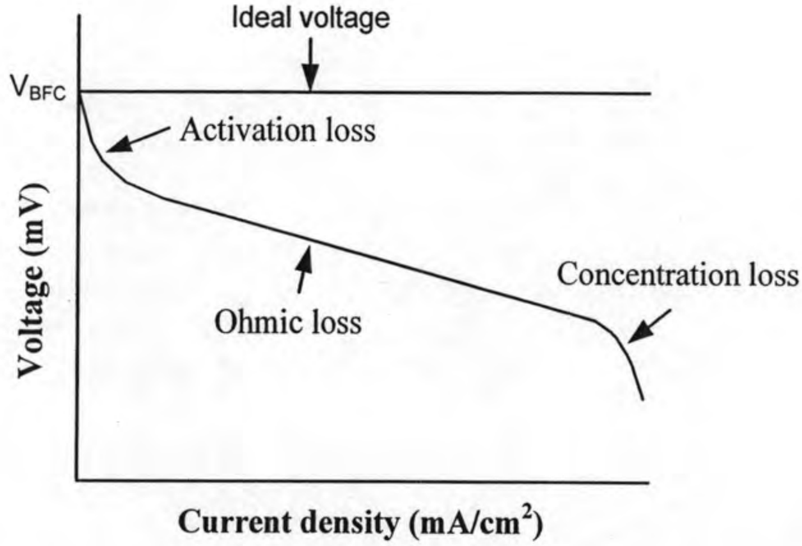


Fig. 2.2 Ideal and actual BFC voltage vs. current density characteristics [2]

The activation loss is directly related to the rates of electrochemical reactions, involving absorption of reactant species, transfer of electrons across the double layer, desorption of product species and the nature of the electrode surface. It is dominant at low current density and increase as current increases. Ohmic loss varies directly with current because cell resistance remains essentially constant. Concentration loss is the prominent at high limiting currents. It is a loss of potential since a reactant is exhausted at the electrode by electrochemical reaction. That is, the initial concentration of the bulk fluid at the surrounding material cannot be maintained. These losses result in the decrease of the BFC voltage from its ideal potential.

2.3 Ac-Impedance Spectroscopy

An ac-impedance spectroscopy is a useful tool for analyzing the electrochemical system as it is able to provide value of each component in the equivalent circuit of the system. The equivalent circuit model of electrochemical system is usually measured by applying an ac voltage (Eq. (2.13)) and measuring the current (Eq. (2.14)).

$$V(t) = V_m \cos(\omega t + \theta) \tag{2.13}$$

$$I(t) = I_m \cos(\omega t + \phi) \tag{2.14}$$

where V(t): voltage source [V]

$I(t)$: current [A]

V_m: voltage amplitude [V]

I_m: current amplitude [A]

ω: angular frequency [rad/s] while $\omega = 2\pi f$

f: frequency [Hz]

t: time [s]

θ: phase angle of voltage source [rad]

ϕ: phase angle of current [rad]

At a certain frequency, ω, the Eq. (2.13) and (2.14) can be expressed in a complex form called phasor as shown in Eq. (2.15) and (2.16), respectively.

$$V = V_m e^{j\theta} = V_m \angle\theta \qquad (2.15)$$

$$I = I_m e^{j\phi} = I_m \angle\phi \qquad (2.16)$$

where V: phasor voltage [V]

I: phasor current [A]

$e^{jx} = \cos x + j \sin x$ (Euler's formula)

The impedance of a circuit, Z (ohm: Ω), is defined as the ratio of the voltage phasor and the current phasor.

$$Z = \frac{V}{I} = |Z| \angle\theta_Z = |Z| e^{j\theta_Z} = \frac{V_m}{I_m} \angle\theta - \phi \qquad (2.17)$$

where $|Z|$: magnitude of the impedance [Ω]

θ_Z: angle of the impedance [rad]

The impedance in Eq. (2.17) is written in polar form. It may be written also in rectangular form,

$$Z = R + jX = Z_{re} + jZ_{im} \qquad (2.18)$$

The quantities $R = Z_{re}$ and $X = Z_{im}$ represent the resistive component or simply resistance and the reactive component or reactance, respectively. In general, $R = R(\omega)$ and $X = X(\omega)$ are real function of ω while $Z = Z(j\omega)$ is a complex function of $j\omega$. The relations between polar and rectangular forms are illustrated in Fig. 2.3.

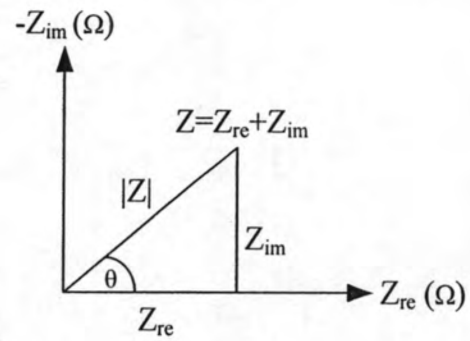


Fig. 2.3 Geometrical representation of impedance

Comparing Eq. (2.17) and Eq. (2.18), it is clearly

$$Z_{re} = |Z| \cos \theta_Z$$

$$Z_{im} = |Z| \sin \theta_Z$$

while the angle and the magnitude of impedance are as follows:

$$\theta_Z = \tan^{-1} \frac{Z_{im}}{Z_{re}}$$

$$|Z| = \sqrt{Z_{re}^{\ 2} + Z_{im}^{\ 2}}$$

The impedance of resistor, capacitor and inductor are denoted as listed in Table 2.1.

Table 2.1 The impedance of electrical element

Component	Impedance	Voltage-current
resistor	$Z = R$	$V=IR$
capacitor	$Z = \frac{1}{j\omega C} = -\frac{j}{\omega C}$	$I= j\omega CV$
inductor	$Z= j\omega L$	$V= j\omega LV$

It should be noted that the impedance of a resistor is a real component and is independent of frequency while the impedance of capacitor and inductor depend on frequency. The impedance of inductor decreases as frequency decreases. On the contrary, the impedance of capacitor increases as frequency decreases.

For a parallel resistor-capacitor (Fig. 2.4), the resistive component and the reactive component can be plotted on the x and the y axes as shown in Fig. 2.5. This plot is called Cole-Cole plot or Nyquist plot.

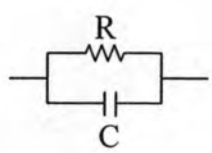


Fig. 2.4 Parallel resistor-capacitor circuit

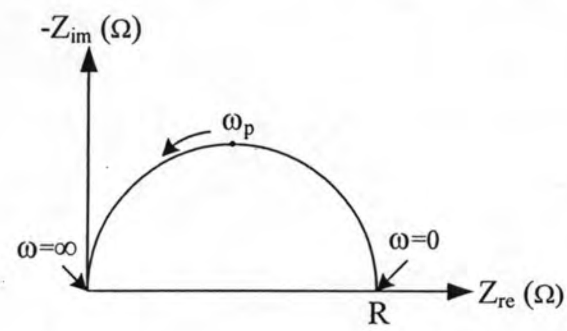


Fig. 2.5 Complex plane impedance plot for equivalent circuit in Fig. 2.4

The impedance of this parallel circuit (Fig 2.4) can be calculated as follows:

$$Z(j\omega) = \frac{R \times \left(\frac{1}{j\omega C}\right)}{R + \left(\frac{1}{j\omega C}\right)} = \frac{R}{1 + j\omega RC} \times \frac{1 - j\omega RC}{1 - j\omega RC} = \frac{R - j\omega R^2 C}{1 + (\omega RC)^2} \qquad (2.19)$$

where $Z_{re}(\omega) = \dfrac{R}{1+(\omega RC)^2}$ and $Z_{im}(\omega) = \dfrac{-\omega R^2 C}{1+(\omega RC)^2}$

Considering the x axis (Z_{re}) in Fig. 2.5, it should be noted that at an extremely low frequency, the impedance is dominated by resistive component and the value approach to R. At the extremely high frequency, the impedance is zero. The maximum capacitance can be estimated from the peak of the semicircle where the frequency (ω_p) can be calculated from the following equation.

$$\omega_p = \frac{1}{RC} \quad \left(\frac{\partial Z_{im}}{\partial \omega} = 0\right)$$

At this frequency, it is found that the magnitude of real part and the imaginary part are equal.

$$Z_{re} = \frac{R}{2} \text{ and } Z_{im} = -\frac{R}{2}$$

A simulation example of equivalent circuit in Fig. 2.4 is shown in Fig. 2.6 when R = 10 kΩ, C = 0.01 μF in the frequency range from 0.05Hz to 10MHz.

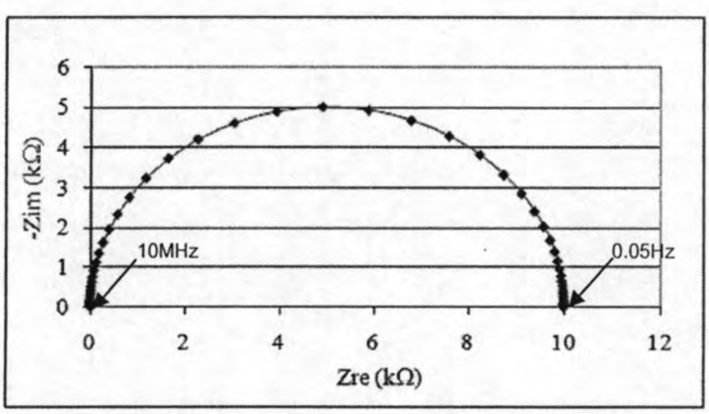
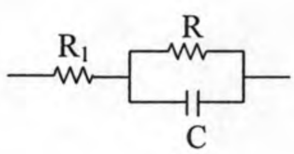


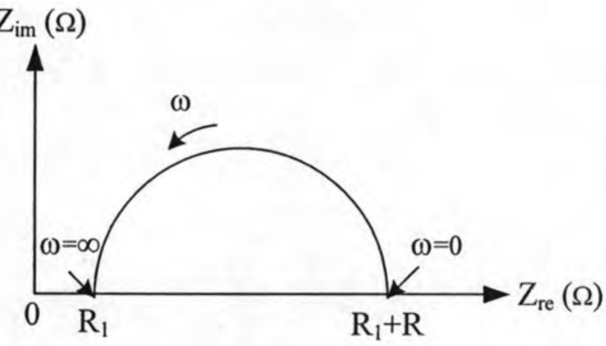
Fig. 2.6 Simulation of equivalent circuit in Fig. 2.4 when R = 10kΩ, C = 0.01 μF and f = 0.05Hz-10MHz

It is shown that at low and high frequencies, Z_{re} converge to 10kΩ and zero, respectively. The peak frequency occurs at f_p=1.59 kHz, where Z_{re} = 5kΩ and Z_{im}=-5kΩ. According to this simulation, the equivalent circuit of electrochemical system can be predicted if the impedance curve is similar to Fig. 2.6. At low frequency, the value of impedance represents the resistance value of the system. The capacitance value can be estimated using R value and the frequency value where the maximum reactance is obtained ($C = \frac{1}{R\omega_p} = \frac{1}{2\pi R f_p}$).

If the equivalent circuit in Fig. 2.4 is connected to another resistor (R_1) as shown in Fig. 2.7 (a), complex plane impedance plot of this equivalent can be shown as in Fig. 2.7 (b).



(a) Randles Cell



(b) Cole-Cole plot of Randles Cell

Fig. 2.7 Randles Cell and its Cole-Cole plot

This equivalent circuit is one of the simplest model for electrochemical system including a solution and electrode. R_1 is a solution resistance while C and R are a double layer capacitance and a polarization resistance, respectively. This model is sometimes called Randles Cell [43].

The impedance of Fig. 2.7 (a) equivalent circuit can be determined as follows.

$$Z(j\omega) = R_1 + \frac{R - j\omega R^2 C}{1 + (\omega RC)^2} \tag{2.20}$$

where $Z_{re}(\omega) = R_1 + \frac{R}{1 + (\omega RC)^2}$ and $Z_{im}(\omega) = \frac{-j\omega R^2 C}{1 + (\omega RC)^2}$

It is clear that R_1 affects only Z_{re}. The value of Z_{re} is shifted from zero to R_1 at high frequency while it becomes $R+R_1$ at low frequency. The peak frequency occurs at $\omega_p = \frac{1}{RC}$ ($\frac{\partial Z_{im}}{\partial \omega} = 0$) where $Z_{re} = R_1 + \frac{R}{2}$ and $Z_{im} = -\frac{R}{2}$. A simulation of equivalent circuit in Fig. 2.7 (a) is shown in Fig.2.8 when R_1 = 1 kΩ, R = 10 kΩ, C = 0.01 μF and f = 0.05Hz-10MHz.

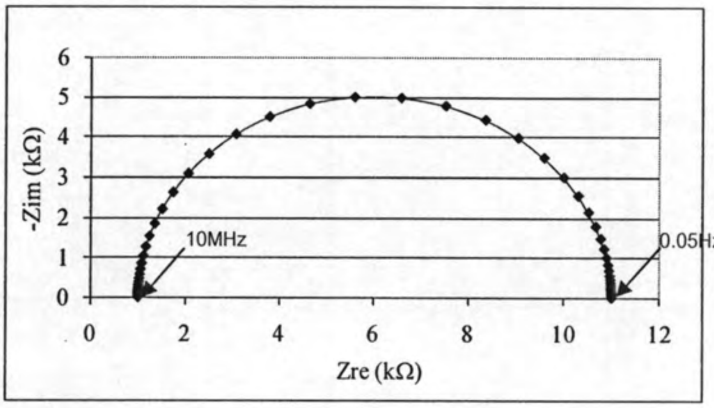


Fig. 2.8 Simulation of equivalent circuit in Fig. 2.8 (a) when R_1= 1kΩ, R = 10kΩ, C = 0.01 μF and f = 0.05Hz-10MHz

It is obvious that at low and high frequency, the Z_{re} values converge to 11kΩ and 1kΩ, respectively. The peak frequency occurs at f_p=1.59 kHz where Z_{re} = 6kΩ and Z_{im}=-5kΩ.

For more complex electrochemical system with two electrode-solution interfaces, the equivalent circuit can be expressed as a series of parallel RC as shown in Fig. 2.9 (a). The Cole-Cole plot of this system is shown in Fig. 2.9 (b).

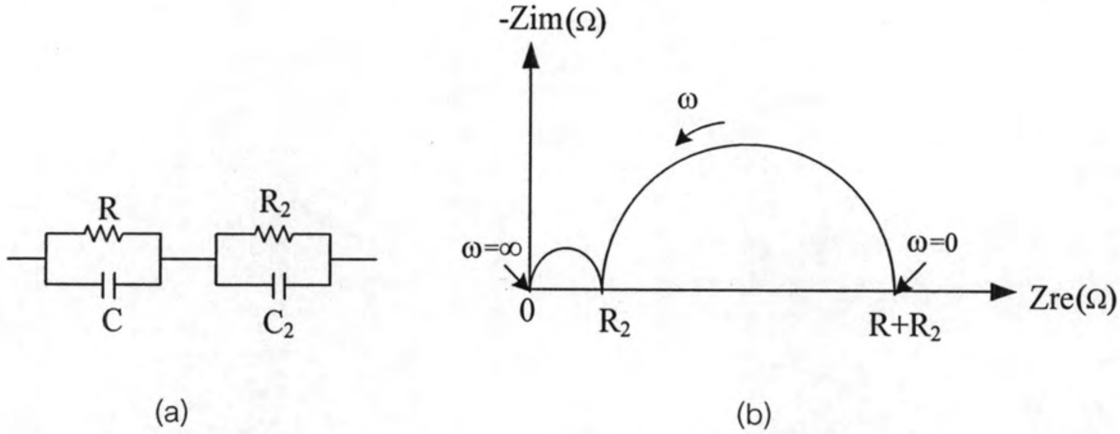


Fig. 2.9 Series connection of RC equivalent circuit and its Cole-Cole plot

(a) Series connection of RC equivalent circuit

(b) Cole-Cole plot of series connection of RC equivalent circuit

The impedance can be derived as follows:

$$Z(j\omega) = \frac{R - j\omega R^2 C}{1+(\omega RC)^2} + \frac{R_2 - j\omega R_2{}^2 C_2}{1+(\omega R_2 C_2)^2} \tag{2.21}$$

where

$$Z_{re}(\omega) = \frac{R}{1+(\omega RC)^2} + \frac{R_2}{1+(\omega R_2 C_2)^2}$$

and $$Z_{im}(\omega) = \frac{-j\omega R^2 C}{1+(\omega RC)^2} + \frac{-j\omega R_2{}^2 C_2}{1+(\omega R_2 C_2)^2}$$

Numerical simulation of the equivalent circuit in Fig. 2.19 (a), with different R and C value, are shown in Fig. 2.10 where f = 0.05Hz-10MHz.

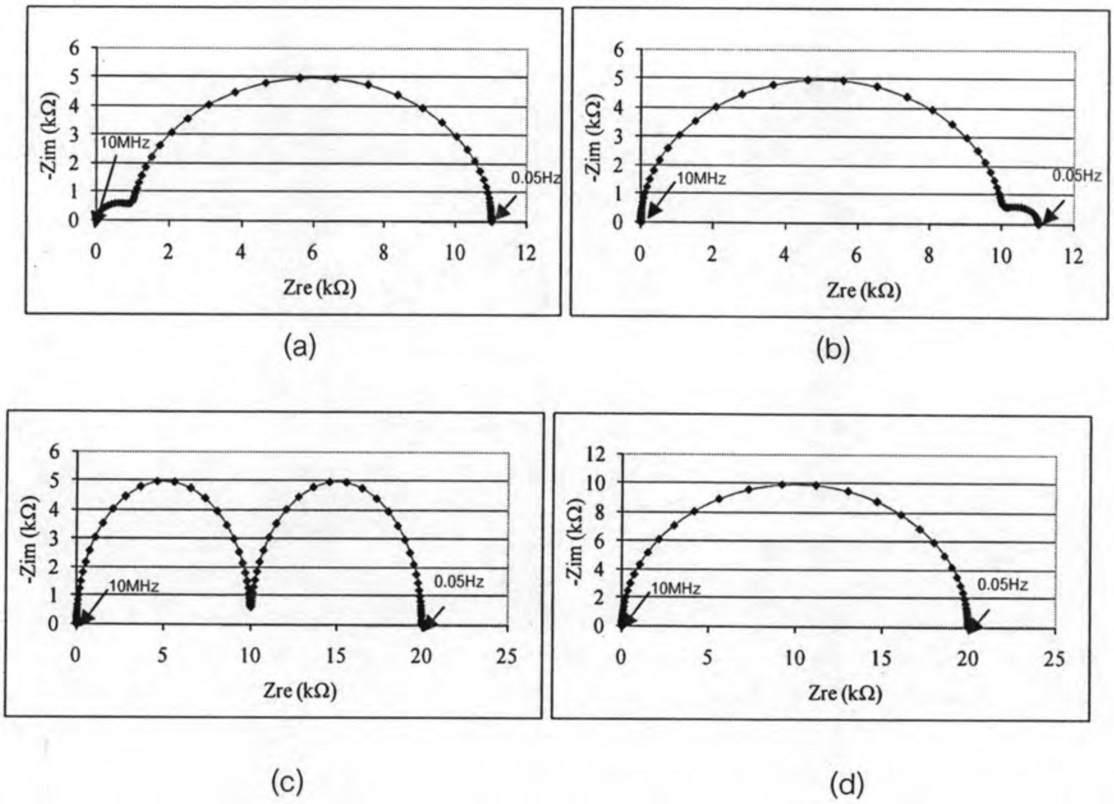


Fig. 2.10 Simulation of equivalent circuit in Fig. 2.10 (a) when

(a) R = 10kΩ, C = 0.01 μF and R_2 = 1kΩ, C_2 = 0.001 μF

(b) R = 10kΩ, C = 0.01 μF and R_2 = 1kΩ, C_2 = 10 μF

(c) R = 10kΩ, C = 0.01 μF and R_2 = 10kΩ, C_2 = 10 μF

(d) R = 10kΩ, C = 0.01 μF and R_2 = 10kΩ, C_2 = 0.01 μF

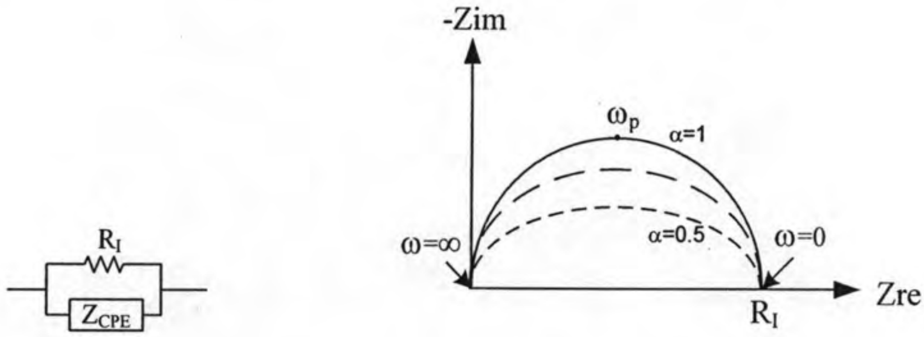
It is obvious that if $R \neq R_2$ or/and $C \neq C_2$, there are two semicircles. In a contrary, if $R=R_2$ and $C=C_2$, there is only one semicircle which occurs from the summation of the series of RC equivalent circuit as shown in Fig. 2.10 (d).

In the real systems, the electrochemical system is more complex than an element, namely the constant phase element (CPE), is introduced for analyzing the system. The CPE is a circuit element which is a combination of a resistor, capacitor or inductor. Mathematical representation of the CPE is given by

$$Z_{CPE} \text{ (Constant-Phase Element impedance)} = \frac{1}{A(j\omega)^{\alpha}} \qquad (2.22)$$

where A: pseudo capacitance [s^{α}/Ω], α: direction of impedance

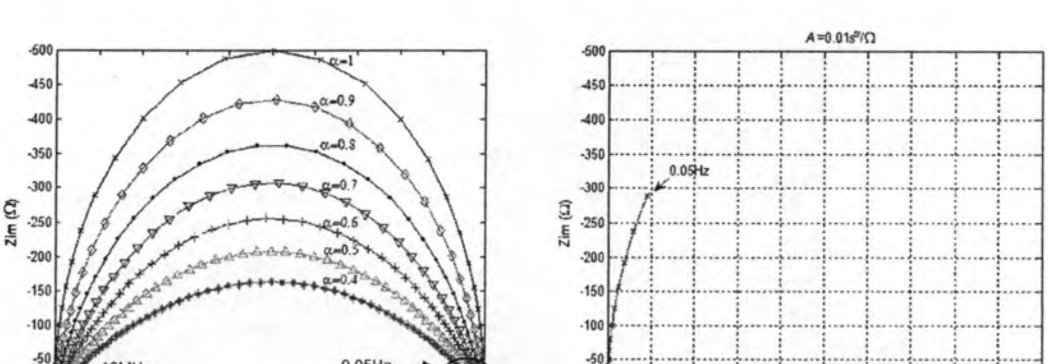
The CPE will represent a pure resistor, capacitor and inductor when $\alpha = 0$, 1 and -1, respectively. If the value of α is in the range of 0 and 1, the CPE is a combination of resistor and capacitor. A simple model of the CPE is shown in Fig. 2.11.



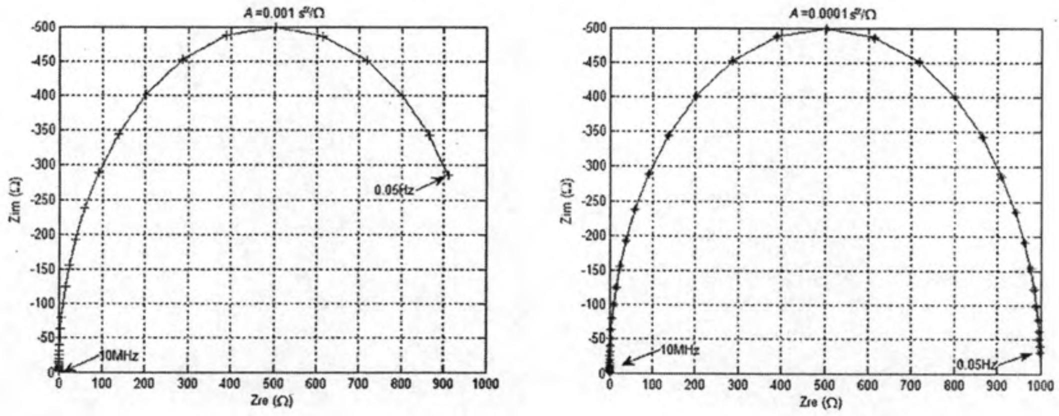
(a) Z_{CPE} model (b) Cole-Cole Plot of Z_{CPE} model

Fig. 2.11 Simple equivalent circuit of Z_{CPE} model

A simulation example of equivalent circuit in Fig. 2.11 (a) is shown in Fig. 2.12 when $R_I = 1k\Omega$ and f = 0.05Hz-10MHz.



(a) A=0.0001 s^{α}/Ω and α = 0.4-1 (b) A = 0.01 s^{α}/Ω and α = 1



(c) $A = 0.001$ $\mathbf{s^{\alpha}/\Omega}$ and $\alpha = 1$ (d) $A = 0.0001$ $\mathbf{s^{\alpha}/\Omega}$ and $\alpha = 1$

Fig. 2.12 Simulation of Z_{CPE} model when $R_l = 1k\Omega$ and f = 0.05Hz-10MHz

From the simulation result in Fig.2.12 (a), it shows that the $|Z_{im}|$ decreases as α decreases. It is obvious that the pattern of the Cole-Cole plot varies as the value of A is varied (Fig.2.12 (b)-(d)).