CHAPTER 1

INTRODUCTION

In the past, energy consumption from fossil fuel such as coal, oil and natural gas played a vital role in human life. Due to being the finite resources and taking millions of years to form, the alternative energy sources have been developed for replacing fossil fuel at the present time. One such alternative energy source is the fuel cell that is increasingly interested by many researchers around the world.

1.1 Fuel Cell

A fuel cell is an electrochemical device that converts the chemical energy of a fuel into electricity by electrochemical reactions. The first fuel cell was developed by Sir William Grove (Father of the Fuel Cell) since 1839 [1]. He discovered the principle of the fuel cell by accident during an electrolysis experiment. It was found that the electricity can decompose water into hydrogen and oxygen. This brings him to believe that if it was possible to split water into hydrogen and oxygen with electricity, the reverse of the electrolysis process should generate electricity from the reaction of oxygen with hydrogen as shown in Eq. (1.1).

$$2H_2 + O_2 \leftrightarrow 2H_2O \tag{1.1}$$

This is a principle of hydrogen-oxygen fuel cell. The basic physical structure consists of an electrolyte layer in contact with an anodic compartment and a cathodic compartment as shown in Fig. 1.1.

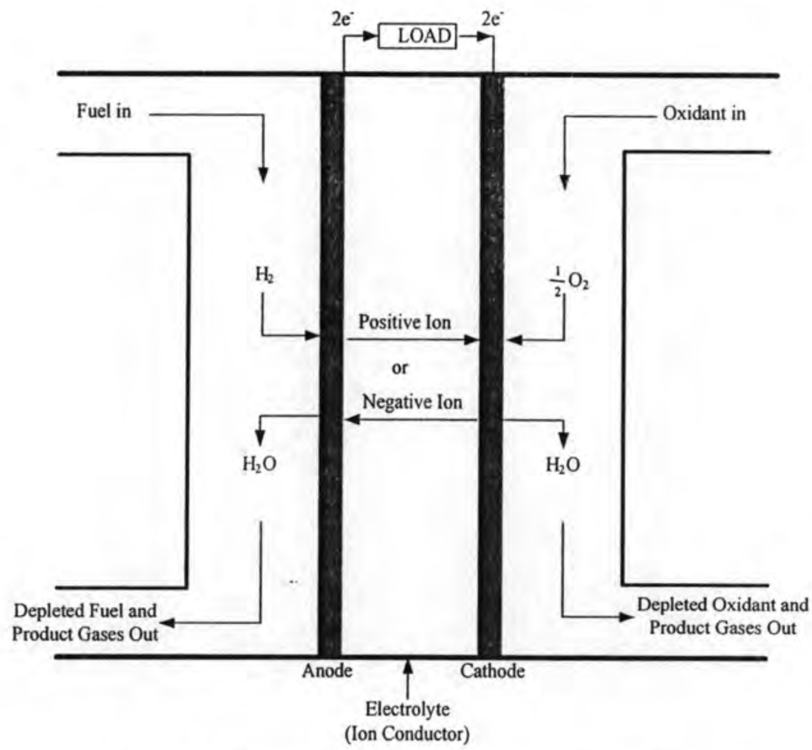

Fig. 1.1 Schematic of an individual fuel cell [2]

Fuel source (i.e., hydrogen) and an oxidant (i.e., oxygen from air) are continuously supplied to the anodic compartment (negative electrode) and the cathodic compartment (positive electrode), respectively. Electron (e^-) and hydrogen ions (H^+) are produced from decomposition of the hydrogen molecule (H_2). The hydrogen ions diffuse through the electrolyte layer such as a proton exchange membrane (PEM) while the electrons transfer through external load. Afterward, the hydrogen ions and electrons combine with oxygen to form water in the cathodic compartment. The hydrogen fuel cell is much more efficient than other types of energy converters. The energy conversion efficiency of 40-80% has been achieved [2]. Furthermore, this energy conversion produces less emissions and low noise pollution, etc. During the phase of development, different types of fuel cell such as polymer electrolyte fuel cell (PEFC), alkaline fuel cell (AFC), phosphoric acid fuel cell (PAFC), molten carbonate fuel cell (MCFC), and solid oxide fuel cell (SOFC) have been developed. Moreover, there are also some other types of fuel cells, such as direct methanol fuel cell (DMFC), zinc air fuel cell (ZAFC), regenerative fuel cell (RFC) and bio-fuel cell (BFC). Various types of fuel cells are summarized in Table 1.1.

Table 1.1 Summary of various types of fuel cells

Fuel Cell Type	Fuel	Electrolyte	Operating Temperature	Applications
PEFC	hydrogen gas	ion exchange membrane	< 80 °C	vehicle, mobile, and portable applications
AFC	hydrogen gas	mobilized or immobilized potassium hydroxide	65-220 °C	NASA space missions
PAFC	hydrogen gas	Immobilized liquid phosphoric acid	150-220 °C	many 200 kW power plant
MCFC	gaseous hydrocarbon gas	Immobilized liquid molten carbonate	600-700 °C	medium to large scale power plant, up to MW capacity
SOFC	gaseous hydrocarbon gas	Ceramic	800-1000 °C	power plant (2 kW to multi MW)
DMFC	Methanol	ion exchange membrane	< 80 °C	portable applications
ZAFC	Zinc	Ceramic	700 °C	industrial and commercial applications
RFC	hydrogen gas	ion exchange membrane	< 80 °C	NASA space missions
BFC	organic substances	wastewater or phosphate buffer or other solutions	Ambient temperature	low power sources for micro sensors, portable applications

As indicated in Table 1.1, although the power output of the BFC is relatively low, it offers the advantages over other types of fuel cells in that it can operate at room temperature and using less corrosive electrolyte. Additional advantage of the BFC is that microorganisms and crude organic substrates can be utilized for production of electrical energy which is able to reduce the cost of energy conversion comparing to the other types of fuels such as hydrogen or methanol. Hence, the BFC has been drawn attention from many researchers.

1.2 Bio-Fuel Cell (BFC)

A bio-fuel cell (BFC) is a bio-electrochemical device that utilizes the metabolism of microorganisms in generating electricity from organic substrates. Electricity accompanied the fermentation process of *Saccharomyces cerevisiae* using glucose as fuel was firstly reported by Potter since 1911 [3]. However, not many reports on the BFC were reported until early 1960s when it was discovered that the addition of electron mediators such as methylene blue, thionine etc. can enhance the performance of the BFC.

The conventional BFC consists of an anodic and a cathodic compartments which are separated by a PEM. In the anodic compartment, the microorganism oxidizes organic substrates and generates electrons (e^-) and hydrogen ions (H^+). The electrons are transferred from the anode to the cathode through an external load, while the hydrogen ions are transported from the anodic compartment through the PEM into the cathodic compartment. Since the electron transfer from the microorganism to the electrodes occurs at a very low efficiency, then two redox couples such as an electron mediator and an electron acceptor have been used in many reports. An electron mediator was used for coupling oxidation at the anode while an electron acceptor was used for coupling reduction at the cathode surface. The electron acceptor such as oxygen is combined with the electrons and the hydrogen ions to produce water as shown in Fig. 1.2.

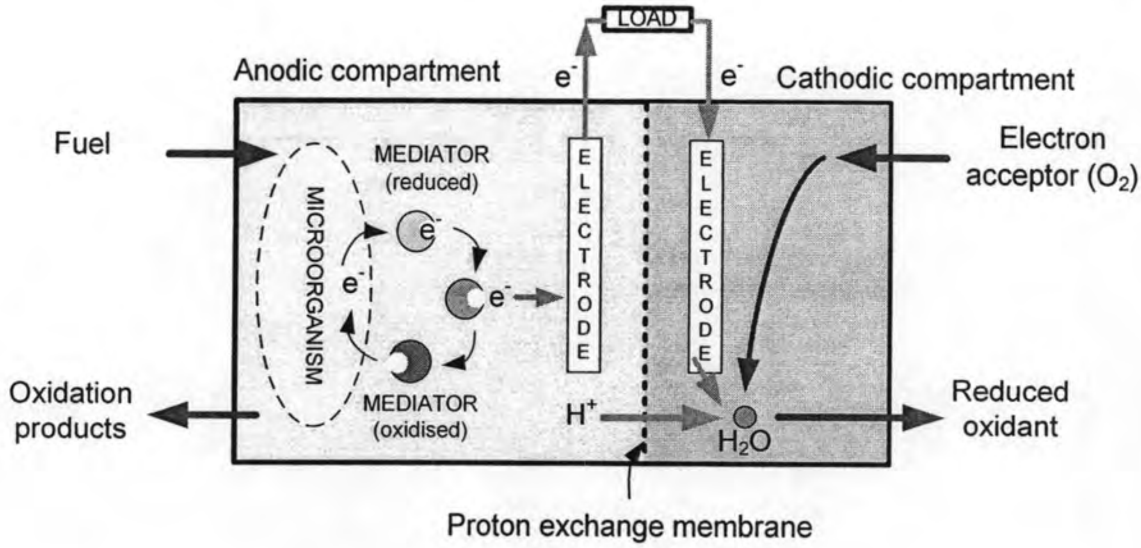

Fig. 1.2 Schematic of a bio-fuel cell

Based on the operating principle of the BFC, there are many parameters which play important roles in its characteristics. There were many reports attempted to increase the performance of the BFC using the following parameters;

i) the species, concentration of microorganism used and type of fuel [4, 5]

ii) the types and/or size of PEM [6, 7]

iii) the types of electron mediator and/or its concentration [8-10]

iv) the types of electron acceptor and/or its concentration [11]

v) the types and/or size of electrodes [7]

A number of investigators have reported utilization of various kind of microorganisms in the construction of the BFC such as *Saccharomyces cerevisiae* [3, 12], *Staphylococcus aureus oxford* [13], *Escherichia coli* [8-10, 14, 15], *Enterobacter aerogenes* [16] and *Actinobacillus succinogenes* [10]. These microorganisms were studied together with the electron mediator in the electrical generation. Various types of electron mediators, including methylene blue [13, 14], ferric chelate [8, 9] and neutral red [10] have been reported. Glucose [3, 5, 10, 12, 14, 16-22], sucrose [4, 23-25], acetate [4, 26-28], butyrate [29, 30] starch [22, 30] and wastewater [31] were used as fuel in several reports. Apart from the mediator, a number of researchers have proposed the use of particular bacterial such as *Clostridium butyricum* [32], *Shewanella putrefaciens* [5, 33], *Geobacter sulfurrenducens* [26], *Geobacter metallireducens* [26, 34], *Rhodoferax ferrireducens* [19] and *Aeromonas hydrophila* [35] which enables the transfer of the electron directly to the electrode without using mediators. Moreover, many researchers have tried to develop a single chamber BFC [27, 28, 30, 33, 36, 37].

The BFC needs two electrodes, anode and cathode to release and receive electrons with an external load, respectively. There are also reports on using various materials as an electrode such as carbon paper, carbon felt, graphite and stainless steel [16, 19, 38]. In addition, there is a report on incorporating the electron mediator (i.e., Mn^{4+} or neutral red) into the electrode to enhance the current [39].

The electrical characteristics such as voltage (V), current (I) or current density (i) and power (P) or power density (p) were investigated by using the above mentioned parameters. The results are summarized in Table 1.2 and 1.3.

Table 1.2 The performances of different types of two compartment bio-fuel cells

Microbes	Fuel	Electron mediator	Electron acceptor	Voltage	Current or current density	Power or power density	Anode	Reference	Year
E. coli	Glucose	Neutral red	ferricyanide	0.85V (oc)	17.7 mA (sc)	-	Graphite felt 12g ($0.47\ m^2/g$)	[10]	2000
Shewanella putrefaciens	Lactate	None	-	0.8V (oc)	0.04 mA (at 1kΩ)	-	Woven graphite	[5]	2002
Geobacter sulfurreducens	Acetate	None	Fe(III) oxide	0.48V (oc)	$65\ mA/m^2$ (at 500Ω)	-	Plain graphite	[26]	2003
Rhodoferax ferrireducens	Glucose	None	ferricyanide	-	$31\ mA/m^2$ (at 1kΩ)	-	Graphite	[19]	2003
Sewage sludge	Glucose	Fe^{3+} graphite cathode	oxygen	0.45 V	$1750\ mA/m^2$	$788\ mW/m^2$	Mn^{4+} graphite anode	[39]	2003
Escherichia coli	Glucose		oxygen	0.28 V	$325\ mA/m^2$	$91\ mW/m^2$			
Mixed consortium, batch	Glucose	None	ferricyanide	-	$6000\ mA/m^2$	$3600 mW/m^2$	Plain graphite (Four cells)	[20]	2003

Table 1.3 The performances of different types of single compartment bio-fuel cells

Microbes	Fuel	Open circuit voltage	Current or current density	Power or power density	Anode	Cathode	Reference	Year
Shewanella putrefaciens	Lactate	0.6 mV	2.5 mA	10 mW/m^2	Mn^{4+} graphite	Fe^{3+} graphite	[33]	2002
Geobacter metallireducens	Waste water	0.58 mV	125 mA/m^2 (at 69 Ω)	26 mW/m^2	Eight graphite rods	Carbon cloth/Pt	[27]	2004
Mixed cultures	Acetate	-	1.8 A/m^2 (at 218Ω)	506 mW/m^2	Carbon paper	Carbon paper/Pt	[29]	2005
Mixed cultures	Butyrate	-	0.65 A/m^2 (at 1kΩ)	305 mW/m^2	Carbon paper	Carbon paper/Pt	[29]	2005
Domestic wastewater	Complex	-	-	766 mW/m^2	Carbon cloth	Carbon/polytetrafluoroethylene	[40]	2006
E. Coli	Glucose	0.62V	-	760mW/m^2	Graphite/PTFE	Pt	[15]	2007

1.3 Purposes and Outline of this Study

Since the BFC operates using biological and chemical components, it is a complex system. Moreover, there are still many questions which are not clearly understood such as electron transfer in the system. Since efficiency of electron transfer is related directly to power distribution to external load, then the understanding of mechanism related to the electron transfer in the BFC will lead to the improvement of the efficiency of the BFC.

Hence, the purpose of this dissertation is to investigate parameters that affect the electron transfer in the BFC system. Firstly, the effect of electron transfer by using five different electrodes such as carbon fiber (CF), silver (Ag), nickel (Ni), stainless steel (St) and aluminum (Al) was investigated. The voltage, current density and power density were explored in all conditions. The BFC characteristics of different electrodes were studied by ac-impedance analysis to understand and explain the electron transfer in an electrical equivalent circuit model. In addition, the effect of the physical parameters (i.e., electrode surface area, distance between electrodes, compartment volume), of biological and chemical components (i.e., glucose, baker's yeast, electron mediator and electron acceptor) were also investigated. The performances of these parameters were investigated for understanding the effect of internal resistance of the BFC.

This dissertation consists of seven chapters. In chapter 1, a brief outline about the fuel cells and bio-fuel cell are described.

Chapter 2 will describe the principle of bio-fuel cell. The basic of biological mechanism related to the BFC will be explained. Description of a simple electrical equivalent circuit of the BFC is also proposed in this chapter. Ac-impedance spectroscopy technique will also explain. Materials and method used in this dissertation will be reported in detail in Chapter 3.

In chapter 4, study on the effect of five electrode materials such as CF, Ag, Ni, St and Al on the BFC performances will be shown. An electrical equivalent circuit model will also be proposed for the explanation of the BFC characteristics. The effect of physical parameters such as electrode surface area, distance between electrodes and compartment volume on electrical performance will be described in chapter 5.

Chapter 6 will demonstrate results on the electrical generation from different combination of biological and chemical components in the BFC. The concentration effect of glucose, microorganism, methylene blue and ferricyanide were investigated. Three types of electron mediator such as methylene blue, neutral red and rhodamine B were compared in the BFC performances. Moreover, the effect of two electron acceptors, ferricyanide and oxygen, were also studied.

Finally a summary of the BFC analysis in the present dissertation will be reported and provided suggestions for future works.