Studying the Effective Mathematical Concepts in the Performance of Microbial Fuel Cells

Abstract

Microbial fuel cells (MFC) are considered one of the important potentials in the supply of clean and renewable energy in the future. In addition to the supply of electrical energy, which is the most extensively used and flexible among other types of energy, MFCs do not cause the slightest pollution to the environment and purify and play a significant role in eliminating environmental pollution such as urban wastewater and leachate from urban solid wastes. At present, MFC technology has not yet been produced in mass and commercially due to low efficiency. With the commercialization of this industry, the issue of urban wastewater will be raised not only as a problem but also as a source of clean energy supply, since urban wastewater is a rich source of microorganisms used in microbial fuel cells. Mathematical modeling of microbial fuel cells makes it possible for researchers to predict the resulting changes in the generated power and modify their design by changing the parameters affecting the efficiency of microbial fuel cells without performing numerous and time-consuming tests.

Keywords: *Microbial Fuel Cells, Mathematical Modeling, Energy Supply Source, Hydrogen Electrode*

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Introduction

The increasing use of fossil fuels has caused an energy crisis in the world. Biological renewable energy is one of the appropriate options for compensating for a part of human societies' need for energy. Several studies have been conducted in recent years to develop different methods of energy production. In this regard, the production of electricity from renewable sources that do not emit carbon dioxide into the environment has been considered more than any other method (Lovely, 2006, Davis and Hingson, 2007).

The technology of microbial fuel cells (MFCs), which convert the energy stored in the bonds of organic compounds into electrical energy through catalytic reactions by microorganisms, has recently attracted a lot of interest, according to Allen and Bennetto (1993), Gil et al. (2003), Moon et al. (2006), and Choi et al. (2003). In the last few years, there have been substantial and quick advancements in MFC research. Logan et al. (2006) examined the design of MFCs and their characteristics and performance of MFCs. Rabaey and Verstraete (2005) examined the metabolism in MFCs. Lovely (2006) examined BUG (Benthic Unattended Generators) systems to supply the power of remote-sensing equipment or graph display devices from the microbial physiology perspective. The advantages and disadvantages of MFCs and anaerobic digestion technology for the creation of biogas as a sustainable energy source were compared by Pham et al. (2006).

When marine sediments or anaerobic sludge is used in an MFC, there will be a mixture of cultured microbes inside the anode chamber. Most MFCs that use a mixture of microbes perform very well. Using a mixture of microbes facilitates the digestion of the substrate in the chamber. This indicates the special characteristics of this type of MFC compared to MFCs in which only one type of pure microbe is used. Both electrophiles and anodophiles are present in MFCs, which use a variety of microbes, and both use the same electron transport intermediates.

According to Ieropoulos et al., power output and the quantity of sulphur compounds accessible are related. Since sulfur-containing substances are always found in the sludge, Ieropoulos et al showed that 70% to 80% of the production power is due to the presence of sulfide or sulfate intermediate system and only 20% to 30% is due to the presence of electrophiles. A tube with an outer cathode and an interior anode that uses carbon granules is an MFC system. (Rabaey et al., b2005). The catalyst is applied to the graphite surface drop by drop in the absence of a cathode chamber to avoid complete drying. Rabaey et al. (b2005) stated that the continuous use of a cathode in the vicinity of air is essential in the practical application of such MFCs. Given what was stated, the present study aims to study the effective mathematical concepts in the performance of microbial fuel cells.

Theoretical foundations of research
Cell voltage and electrode potential

Consider an everyday galvanic battery. (Figure 1). A quantity that can be measured and is equal to the potential difference of the cell is called the electromotive force (EMF) of the cell. The potential differential results from four variables because the cell has four phase boundaries—two metal-solution boundaries and two metal-metal boundaries. The graphic representation of the cell in Figure 1 is as follows:

Pt/M'/S/M/Pt

(1)

Starting at the right electrode in Figure (1) and moving clockwise while keeping the previously mentioned schematic symbol for the cell, the following equation is found:

$\mathcal{E} = \Delta\Phi(Pt,M) + \Delta\Phi(M,S) + \Delta\Phi(S,M') + \Delta\Phi(M',Pt)$

(2)

Were,

$\Delta\Phi(Pt,M)$= The potential difference between the right electrode and platinum

$\Delta\Phi(M,S)$= The potential difference between the right electrode and the solution

$\Delta\Phi(S,M')$= The potential difference between the solution and the left electrode

$\Delta\Phi(M',Pt)$= The potential difference between the left electrode and platinum

Considering that $\Delta\Phi(S,M') = -\Delta\Phi(M',S)$ and $\Delta\Phi(M',Pt) = -\Delta\Phi(Pt,M')$, the previous equation can be written as the potential difference between two electrodes as follows:

$\mathcal{E} = \{ \Delta\Phi(Pt,M) + \Delta\Phi(M,S) \} - \{ \Delta\Phi(M',S) + \Delta\Phi(Pt,M') \}$

(3)

Simply,

$\mathcal{E} = E_r - E_l$

(4)

where, the potential of the right electrode is equal to:
$E_r = \Delta\Phi(Pt,M) + \Delta\Phi(M,S)$

(5)

and the potential of the left electrode:
$E_l = \Delta\Phi(Pt,M') + \Delta\Phi(M',S)$

(6)

If we consider E_l as the reference electrode and optionally assume its potential to be zero, El=0, so $\mathcal{E}=Er$.
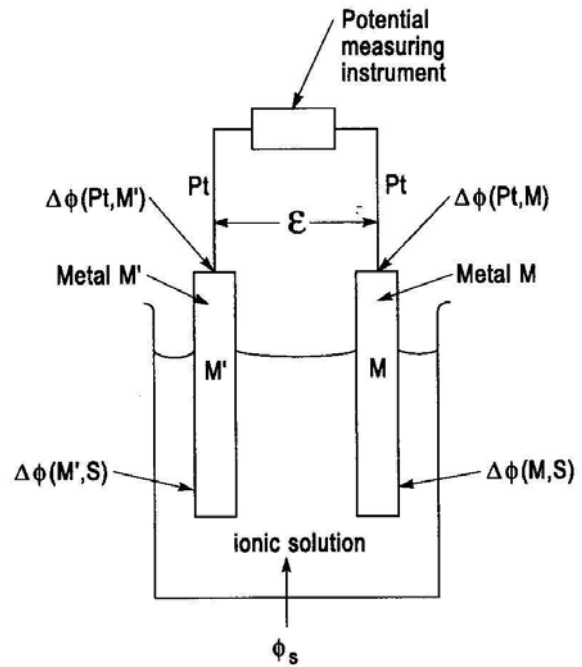

Figure 1: An electrochemical cell is depicted schematically. In the relative potential scale, where El=0 is assumed, the electrode potential Er will therefore be equal to the calculated voltage of the cell, and the following equation will be found:
$\mathcal{E} = E_r = \Delta\Phi(Pt,M) + \Delta\Phi(M,S)$

(7)

Since $\mathcal{E}=E_r-E_l$ و E_l=0.

The term $\Delta\Phi$ (Pt,M) appears in all calculations, so it will not affect the order of electrode potential calculationContact between two non-homogeneous conductors causes the potential differential to be visible. Electrons flow in such a way that their Fermi energies reach equilibrium because the Fermi energies of two distinct metals vary. (i.e., their chemical potential). The Fermi energy is either (1) the boundary between filled energy levels and empty electron bond levels in a solid or (2) the highest filled energy level in a partly filled valence electron bond. There is a potential difference as a consequence of the electron flow charging one conductor to another (Figure 2).
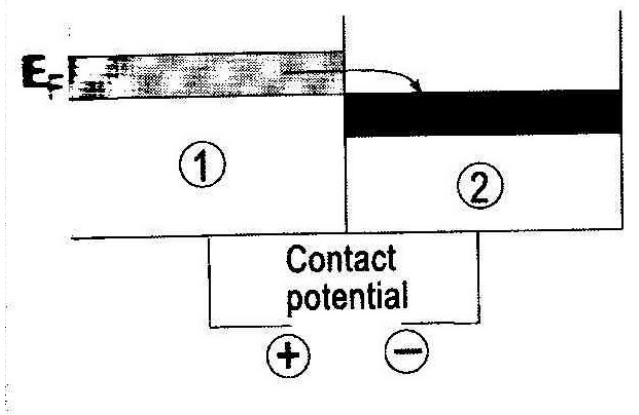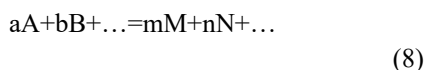
Figure 2: EF Fermi level; contact potential differential between two non-homogeneous conductors

2-1) Equilibrium of cell voltage dependence on concentration: General Nernst equation

The general cell reaction with reactants A, B,... and products M, N, and can be used to compute the Nernst equation:...

$$aA+bB+\ldots=mM+nN+\ldots \qquad (8)$$

The Gibbs free energy change equation, ΔG, can be calculated by using the two formulae below:

The first equation: Gibbs free energy as a function of cell voltage (ε):

$$\Delta G=-zF\varepsilon \qquad (9)$$

Where, respectively, z, F, and are the cell voltage, the Faraday number (96500 Coulombs), and the number of involved electrons in the operation. Equation represents the job finished in the cell. (6). In other words, $W = qV$, where q = electric charge (zF), V = voltage (ε), and W = work done (ΔG).

Free energy shift as a function of reactant concentration (activity) is represented by the second equation.

$$\Delta G= \Delta G^0+RT\ln Q \qquad (10)$$

Where:

$$Q=(a_M{}^m \; a_N{}^n\ldots)/(a_A{}^a \; a_B{}^b\ldots)=\prod(\text{Products})/ \; \prod(\text{Reactants}) \qquad (11)$$

R is gas constant, T is absolute temperature, Ln is the natural logarithm, $\prod$ and represents the multiplication of concentrations (activities, a) by their squared stoichiometric coefficients.

When the activities of the reactants and products are equal to 1, normal states, the following equation is obtained from equations (6) and (7) ($\Delta G=\Delta G0$ when $Q=1$):

$$\Delta G^0=-zF\varepsilon^0 \qquad (12)$$

where the cell voltage for the standard condition of the reactants and products is $\varepsilon0$ and $\Delta G0$ is the free energy standard.

By integrating equations (6) and (9), the following equation is obtained:

$$-zF\varepsilon=- zF\varepsilon^0+RT\ln Q \qquad (13)$$

By dividing the both sides by -zF:
$$\varepsilon=\varepsilon^0-(RT/zF).\ln Q \qquad (14)$$

Or:
$$\varepsilon=\varepsilon^0+(RT/zF).\ln(1/Q) \qquad (15)$$

By inserting the value of Q (equation 8) in equation (15):
$$\varepsilon=\varepsilon^0+(RT/zF).\ln(\prod[\text{Reactants}]/\prod[\text{Products}]) \qquad (16)$$

The basic Nernst equation (16) illustrates how concentrations affect the equilibrium cell voltage. This equation is used to determine the electrode equilibrium potential for metal/metal ion and reduction electrodes. (redox).

Metal/Metal Ion Potentials (M/Mz+)

The metal/metal ion anode contains a metal in an ionic fluid. The electrode potential is determined by the activity of the $Mz+$ metal ions in the solution, or more precisely by their abundance. For example, Cu can be found in solutions of $CuSO4$ or $Cu/Cu2+$.

Depending on quantity, the metal/metal ion potential: Equation of Nernst The general state of a metal/metal ion electrode shows that Metal M in an ionic solution is in equilibrium as shown below:

$$M^{z+}+ze \; \underset{\longleftarrow}{\overset{M}{\longrightarrow}} \qquad (17)$$
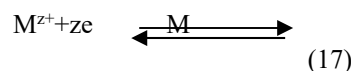
A left-to-right, electron-consumption process is referred to as a reduction. The procedure that discharges electrons from right to left is known as an oxidation reaction.

The potential of this electrode is defined as the voltage of a $Pt\,|\,H2(1atm)\quad|\,H+(a=1)\,|\,Mz+\,|\,M$ cell, where the left electrode, El=0, is the normal hydrogen electrode as a reference electrode.

Oxidation/reduction potentials (RED/OX)

The general reaction of the RedOx electrode will be as follows if we designate the oxidised ions with Ox and the reduced ions with Red:

$$Ox+ze \; \underset{\longleftarrow}{\overset{Red}{\longrightarrow}} \qquad (18)$$
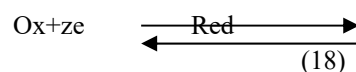
This reaction is referred to as a reduction reaction because electrons are burned in it from left to right. The process is referred to as oxidation if it occurs from right to left because electrons are released.

$H+$ ions are also involved in complex RedOx reactions. For example:

$$MnO_4^- + 5e + 8H^+ \rightleftharpoons Mn^{2+} + 4H_2O \tag{19}$$
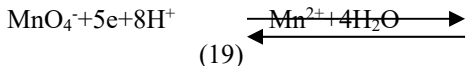
Application of Nernst equation in dependence of RedOx potential on concentration:

Using equation (16) for the RedOx electrode in the general state, the following equation is obtained:

$$E = E^0 + (RT/zF).Ln([Ox]/[Red]) \tag{20}$$

and with log (10), it is as follows:

$$E = E^0 + 2.303.(RT/zF).Log([Ox]/[Red]) \tag{21}$$

When the activities of reactant (Ox) and product (Red) are equal to 1:

$$E = E^0 , [Ox]=1 , [Red]=1 \tag{22}$$

Where, E0 is the standard potential of the RedOx electrode.

Calculation of electrode equilibrium potentials

The equilibrium potential of an electrode (eg $M/Mz+$) is determined by the cell voltage, $Pt\,|\,H2(1atm)\,|\,H+(a=1)\,|\,|\,Mz+\,|\,M$, where a represents the activity.

Hydrogen electrode

The hydrogen electrode is composed of a platinum wire in contact with hydrogen gas and a solution holding hydrogen ions. (Figure 3). Because hydrogen gas and hydrogen ions are present on the contact surface of the electrode and the solution, this electrode can be represented as $Pt\,|\,H+\,|\,H2$, and the electrode reaction is as follows.
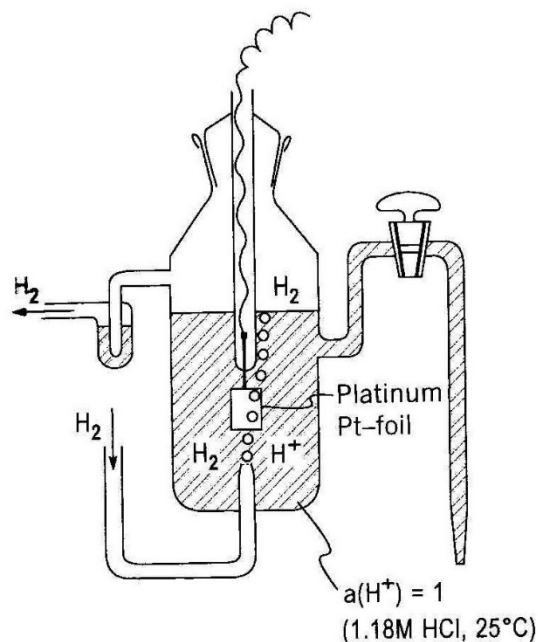
$$2H^+ + 2e \leftrightarrow H_2 \tag{23}$$

Figure 3: Schematic view of hydrogen electrode

Equation (16) can be used to determine the hydrogen electrode's electrode potential:

$$E = E^0 + (RT/2F).Ln([H^+]^2/p(H_2)) \tag{24}$$

The hydrogen electrode potential is dependent on hydrogen-ion activity and partial pressure of hydrogen gas, as can be seen.(H_2).

Metal/insoluble salt/ion electrodes

expression (16) yields the following electrode potential expression for this general reaction:

$$E = E^0 + (RT/zF).Ln([MA][e^Z]/[M][A^{z-}]) \tag{25}$$

Equation (2-34) is simplified as follows because the insoluble salt MA and the metal M are both pure solids in this standard condition (a=1).:

$$E = E^0 - (RT/zF).Ln(1/[A^{z-}]) \tag{26}$$

And/or

$$E = E^0 - (RT/zF).Ln[A^{z-}] \tag{27}$$

As a result, the activity of the anions in the minimally soluble substance of the metal electrode determines the potential of the $M\,|\,MA\,|\,Az$-typ electrode.

As an alternative, the $M\,|\,MA\,|\,Az$- electrode can be considered as follows:

$$M^{z+} + ze \leftrightarrow M \tag{28}$$

where the standard equation for metal/metal ion is used to determine this electrode's potential. (Equation 14). The

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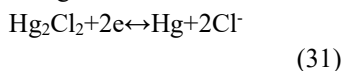solubility of product S of MA salt, which is as follows, is used to determine the activity of Mz+ metal ions:

$$[M^{z+}]=S/[A^{z-}]$$
(29)

Calomel electrode

Mercury coated with mercuric chloride (calomel) and in touch with a KCl solution make up the calomel electrode:

$$Hg \mid Hg_2Cl_2 \mid Cl^-$$
(30)
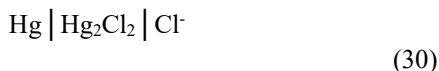
The general reaction in the calomel electrode is as follows:

$$Hg_2Cl_2 + 2e \leftrightarrow Hg + 2Cl^-$$
(31)

And its potential can be calculated in this way:

$$E=E^0-(RT/2F).Ln[Cl^-]$$
(32)

Silver electrode/silver chloride

The reference electrode, a pure silver wire, is immersed in a KCl solution, which has been severely diluted with solid silver chloride. The electrical response is as follows:

Silver chloride and silver anode

This reference electrode consists of a pure silver filament immersed in a KCl solution permeated with solid silver chloride. The electronic response is shown here:

$$AgCl+e \leftrightarrow Ag^+ +Cl^-$$
(33)

And using the following equation, the potential can be determined at 25 °C as a function of the activity of Cl- ions:

$$E=0.222-0.0592 \log[Cl^-]$$
(34)

If KCl saturated solution is used, the potential of this electrode at 25 °C is equal to 0.19 V compared to NHE or 0.045 V compared to SCE.

Mercury-mercury sulfate electrode

In this reference electrode, the element is mercury, which is a slightly soluble form of mercury sulphate (Hg_2SO_4), and sulfuric acid or potassium sulphate are the sources of the SO_4^{2-} ions. Its electrode is displayed as follows and is manufactured identically to the calomel electrode:

$$Hg \mid Hg_2SO_4 \mid SO_4^{2-}$$
(35)
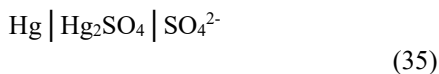
Its potential is a function of the activity of SO_4^{2-} ions:

$$E=0.6156-0.0296 \log[SO_4^{2-}]$$
(36)

The potential of potassium sulphate saturated solution is 0.64 V for NHE and 0.40 V for SCE.

Potential of standard electrodes

When several electrodes are connected, the hydrogen standard electrode is selected as the reference electrode. This electrode's normal potential is generally thought to be zero. By coupling this reference electrode to other electrodes in a cell, it is possible to calculate the relative potential values of multiple electrodes. (Potential difference on the contact surface of the electrodes). Take a look at the cell in Figure, for example. (4). The following is a diagram of this cell:

$$Pt, H_2(p=1) \mid H^+(a=1) \mid \mid Cu^{2+}(a=1) \mid Cu \mid Pt$$
(37)
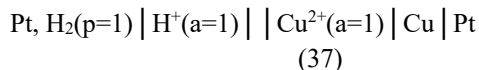
where p denotes hydrogen dioxide pressure and a denotes action. The calculated potential differential for this cell at 25 °C is +0.337 V. The calculated difference in the cell's potential is known as the relative standard potential of the Cu electrode, and it is denoted by the symbol E°.
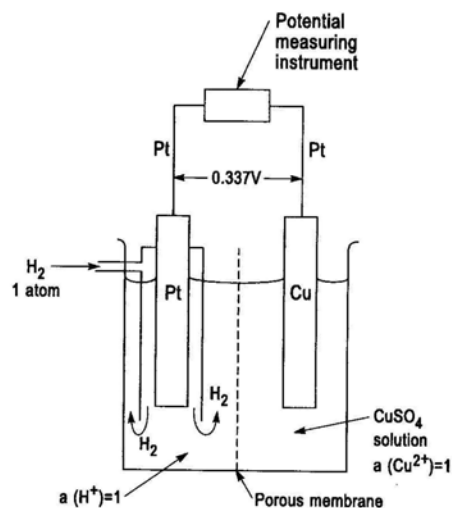

Figure 4: Relative standard potential, E°, of Cu/Cu^{2+} electrode

Concentration and activity

The equilibrium potential of the metal electrode/metal ion (M/Mz+) should be linearly related to the logarithm of the abundance of Mz+ ions, according to the Nernst equation. Experimentally, this linear association was found at low MA solute concentrations, such as 0.01 mol/L or less. The equation departs from the linear state at greater concentrations. Ion-ion reactions are the cause of this deviation. The equilibrium potential E and the logarithm of the content are found to be linearly related. The equation below displays the action of component i:

$$a_i=c_i\gamma_i$$
(38)

Where, c_i is the concentration of component i in units of M/l and γ_i is the activity coefficient of component i. The activity coefficient γ is a dimensionless value that depends on the concentration of all ions in the solution (ionic strength I, which

will be explained later). The activity coefficient of individual ions cannot be calculated experimentally, but they can be obtained by calculation.

The following equation can be used to determine the activity value of component i according to the Debye-Hückel model for ion-ion interaction:

$$RTLn\gamma_i = -N(z_ie)^2/(2\varepsilon k^{-1})$$

$$(39)$$

Z_i is the electric charge of the ionic component, and N is Avogadro's constant. A reference ion's electron cloud has a thickness or average radius of k-1, where i, e is the electron's charge, ε is the medium's dielectric constant (aqueous solution), and k is the cloud's thickness.

The value that can be calculated experimentally is the value of the average ion activity coefficient $\gamma\pm$:

$$\gamma_\pm = \sqrt{(\gamma_+ \gamma_-)}$$

$$(40)$$

Where, it is the geometric average of the activity coefficients of ionic components $\gamma+$ and $\gamma-\neg$.

Point-charge model for the Debye-Hückel activity coefficient theory.

The Debye-Hückel ion-ion interaction theory provides the following experimental expression, which is the relationship between activity coefficient and ionic strength I for water at 25°C and dielectric constant 78.54:

$$\log \gamma_\pm = -0.509 \left| z_+ z_- \right| \sqrt{I}$$

$$(41)$$

where I denote the medium's ionic intensity. The given equation calculates the ionic strength, I:

$$I = \frac{1}{2}(c_1z_1^2 + c_2z_2^2 + c_3z_3^2 + \ldots)$$

$$(42)$$

or

$$I = \frac{1}{2}\Sigma c_iz_i^2$$

$$(43)$$

where z_1, z_2, z_3, and z_i are the electrical charges of the various ions in the fluid, and c_1, c_2, c_3, and c_i are their concentrations.

Debye-Hückel activity coefficient theory: finite ion size model If we ignore the point charge approximation, the expanded form of the Debye-Hückel law will be obtained in this way:

$$\log \gamma_\pm = -\{A/(1+r/r_D)\} z_+ z_- \sqrt{I}$$

$$(44)$$

Where, r is the ion radius and r_D is the Debye length.

The size of the ions can be viewed as concentration-dependent parameters for this model's further development, and novel expressions for the activity coefficients can be obtained.

Conclusion

Despite more than one decade of serious research and development in the area of development and commercialization of microbial fuel cell technology, optimization of operating conditions and conversion efficiency of these cells is still progressing slowly. The slow metabolism of microbes and the slow transfer of electrons from the substrate to the surface of the anode and protons from the electrolyte of the anode to the cathode compartment (through membrane penetration or salt bridge) are among the most important barriers to the progress and commercialization of the mass production of microbial fuel cells. The amount of power produced by microbial fuel cells should be optimized to the extent that it can be used on a commercial level. With the development of microbial fuel cell technology, mathematical models are also corrected by other researchers and adapted to the new conditions of these cells. The model presented in this research is not considered a complete model and with new developments in MFC technology, it will undergo changes and corrections in the parameters and assumptions used in the model presentation.

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