Principle and Working Mechanism of Microbial Fuel Cell

Muhammad Farhan Hil Me, Mohd Nur Ikhmal Salehmin, Swee Su Lim, and Hau Seung Jeremy Wong

Abstract As its name implies, a microbial fuel cell (MFC) is a device capable of producing electricity and electrogenesis from the oxidation of substances catalysed by microorganisms. The achievable voltage range from MFC is between 0.3 and 0.7 V. Due to the biological nature of biofilm growth, it is hard to estimate the voltage generation in MFC compared to a chemical fuel cell. One of the ways to estimate the maximum voltage producible by MFC is by determining its maximum electromotive force (E_{emf}). The value obtained theoretically can be established as a ceiling for the producible cell voltage. However, through empirical study, the obtainable potential is much lower due to potential losses attributed to various factors. Due to different substrates and materials used, the combination of different anodic and cathodic potentials will also affect the maximum obtainable power owing to inherent conductivity differences. By disconnecting the resistor in MFC, open-circuit voltage (OCV) with a value approaching the theoretical E_{emf} can be obtained. The difference in value can be used to pinpoint the cause of potential losses, either from the anode or cathode side. Electrogenesis in MFC relies on the electron produced by microorganisms. As of present, three methods of electron migration method have been theorised: through mediators and electron shuttles, C-type cytochromes and nanowires. The migration can be either through electron hopping or electron delocalisation through nanowires, depending on the microorganism species.

M. F. Hil Me · M. N. I. Salehmin (✉) · S. S. Lim
Fuel Cell Institute, Universiti Kebangsaan Malaysia, 43600 Bangi, Selangor, Malaysia
e-mail: ikhmal@ukm.edu.my

M. F. Hil Me
e-mail: p94598@siswa.ukm.edu.my

S. S. Lim
e-mail: limss@ukm.edu.my

H. S. J. Wong
School of Biological Sciences, Universiti Sains Malaysia, 11800 Minden, Penang, Malaysia
e-mail: jeremywong@student.usm.my

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1 Introduction

Microbial fuel cells (MFCs) are devices that oxidise organic and inorganic substances and produce electricity using microorganisms as catalysts. Electrons released by bacteria from various substrates are delivered to the anode (negative terminal) and flow to the cathode (positive terminal) through a conductive substance including a resistor, or the system is operated under a load (i.e., creating energy to power a device) (Fig. 1). Figure 1 shows the operational principle of a microbial fuel cell. A layer of biofilm is grown on the anode surface called bioanode catalysing substrate oxidation reaction. Electrons collected from the reaction are sent to the cathode as driven by electromotive force between anode and cathode through an external circuit. A positive current, by convention, travels from the positive to the negative terminal in the opposite direction of electron transport. The device must be capable of constantly or intermittently replenishing the substrate oxidised at the anode; otherwise, the system is termed as biobattery, which requires further regeneration.

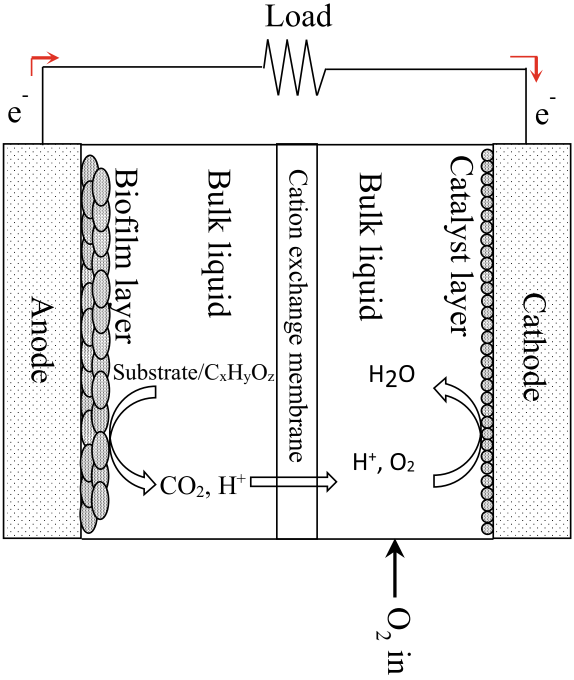

Fig. 1 Principle of microbial fuel cell based on proton transfer and oxygen reduction

1.1 Fundamentals of Electrogenesis in MFC

1.1.1 Maximum Voltages Defined by Thermodynamic Correlation

The achievable voltage from microbial fuel cells is typically in the range between 0.3 and 0.7 V. Voltage (E) is a product of external resistance (R_{ext}) and current (I), which is simply expressed as follows:

$$E = IR_{\text{ext}} \tag{1}$$

Given that the current produced in a single MFC (lab scale) is tiny, the current is estimated through the voltage drop across the resistor defined as $I = E/R$. The maximum achievable voltage generated by an MFC is the open-circuit voltage, or OCV, which can be quantified by disconnecting the circuit yielding zero current and infinite resistance. In this case, voltage drops as resistances are decreased. At any time, power is measurable using the following function:

$$P = E.I$$

Because of sluggish bacterial growth for biofilm formation on bioelectrode (bioanode), the voltage generation in MFC is more challenging to comprehend or anticipate than the voltage generated in a chemical fuel cell. Even voltage generated from a pure culture in MFC cannot be predicted, not to mention the voltage generated from a mixed culture. Relying on the thermodynamic relation between the substrate as electron donor and electron acceptor on the cathode, there are limits to the maximum achievable voltage in MFC.

To prove that statement, [19] learned an equation used for determining the maximum electromotive force (E_{emf}) in any type of battery or fuel cell and modified it to accommodate MFC systems which will be explained in detail in the next section. The original equation is given by

$$E_{\text{emf}} = E^{o} - \frac{\text{RT}}{\text{nF}}\ln(\Pi) \tag{2}$$

where E^{o} is the standard potential calculated from Gibbs free energy data provided by [44], $R = 8.31447$ J/mol K denotes the gas constant, T represents the absolute temperature (298 K), n signifies the number of transported electrons, F is Faraday's constant = 96,485 C/mol and π is the ratio of [product] and [reactant] to the power of respective mol derived from the stoichiometric equation as shown below:

$$\Pi = \frac{[\text{products}]^{p}}{[\text{reactant}]^{r}} \tag{3}$$

The benefit of Eq. 2 is that it is positive for a favourable reaction and generates an E_{emf} value directly. This estimated E_{emf} establishes a ceiling for the cell voltage; the exact potential obtained through the empirical study of MFC is lower due to a variety of potential losses.

1.1.2 Theoretical Potential Based on Standard Electrode Potentials

Reactions that take place at the anode and cathode of MFC are classified as half-cell reactions. Under standard potential at 298 K, 1 M for liquid and 1 bar for gasses, the half-cell reaction is expressed in the form of scavenging electrons [1]. In the case of microbial acetate oxidation at the anode, the stoichiometric equation is as given below:

$$2\mathrm{HCO}_3^- + 9\mathrm{H}^+ + 8\mathrm{e}^- \rightarrow \mathrm{CH_3COO}^- + 4\mathrm{H_2O} \tag{4}$$

Standard potentials determined in terms of the normal hydrogen electrode (NHE) under standard conditions have zero potential. Taking acetate oxidation for an example, considering $E^o = 0.187$ V, at pH 7, with reactant [$\mathrm{HCO_3}^-$] and product [$\mathrm{CH_3COO}^-$] concentration to be 5 mM and 16.9 mM, respectively, the theoretical potential of E_{An} is as indicated in Eqs. 5 and 6:

$$E_{\mathrm{An}} = E^0_{\mathrm{An}} - \frac{\mathrm{RT}}{8F}\ln\left(\frac{[\mathrm{CH_3COO}^-]}{[\mathrm{HCO_3}^-]^2[\mathrm{H}^+]^9}\right) \tag{5}$$

$$E_{\mathrm{An}} = 0.187 - \frac{(8.31\,J/\mathrm{molK})(298.15K)}{(8)(9.65\times 10^4\mathrm{C/mol})}\ln\frac{[0.0169]}{[0.005]^2[10^{-7}\mathrm{M}]^9} = -0.300\mathrm{V} \tag{6}$$

Under specific conditions, the theoretical anode potential (E_{An}) of different species with varied activities assuming equal concentration can be calculated by applying Eq. 2 (Table 1).

When oxygen is employed as the electron acceptor at the cathode, the half-cell reaction for oxygen reduction is

$$\tfrac{1}{2}O_2 + 2H^+ + 2e^- \rightarrow H_2O \tag{7}$$

Thus, the theoretical cathode potential for E_{Cat} is calculated by considering E^o ($\mathrm{O_2}$) = 1.229 V and adjusted to pH = 7, as shown below:

$$E_{Cat} = E^o_{Cat} - \frac{RT}{nF}ln\left(\frac{1}{[O_2]^{1/2}[H^+]^2}\right) \tag{8}$$

$$E_{Cat} = 1.229 - \frac{(8.31\,J/molK)(298.15K)}{(2)(9.65\,x\,10^4\,C/mol)}ln\frac{1}{[0.2]^{1/2}[10^{-7}\,M]^2} = 0.\ 805\,V \tag{9}$$

Various catholyte have been utilised, generating different cell voltages. For instance, ferricyanide and manganese oxide have been employed as substitutes for oxygen. Over time, the pH of the catholyte might change, influencing the cathode potential. With the given standard potentials for various electron acceptors (catholyte) tabulated in Table 1 and plugged into Eq. 2, the theoretical cathode potential of different catholyte can be determined, which varied from 0.361 to 1.385 V. Thus, the E_{emf} of the MFC can be determined using the following equation:

$$E_{\text{emf}} = E_{\text{Cat}} - E_{\text{An}} \tag{10}$$

Assuming that oxygen is used as an electron acceptor at the cathode and acetate as an electron donor at the anode, under the set condition of 298 K, 1 bar and pH = 7, the resulted $E_{\text{emf}} = 0.805\text{ V} - (-0.300\text{ V}) = 1.105\text{ V}$. Equation 10 shows that utilising similar anode compound in an MFC system with various catholyte parameters as given in Table 1 results in considerably varied cell voltages (E_{emf}), consequently, the power output levels. Different types of anode and cathode material would also affect the half-cell potential due to the magnitude of conductivity the material offers. The

Table 1 Reported standard anode and cathode potential (E_0) and respective theoretical potentials of MFC (E_{emf}) under specific conditions determined using Eq. 2. Both potentials are shown against the normal hydrogen electrode (NHE)

Reaction	E_o (V)	Conditions	E_{emf} (V)
Anode			
$2HCO_3^- + 9H^+ + 8e^- \rightarrow CH_3COO^- + 4H_2O$ [19]	1.23	$HCO_3^- = 5$ mM; $CH_3COO^- = 16.9$ mM; pH = 7	−0.300
		$HCO_3^- = 5$ mM; $CH_3COO^- = 5$ mM; pH = 7	−0.296
$6CO_2 + 24H^+ + 24e^- \rightarrow C_6H_{12}O_6 + 6H_2O$ [35]	−0.014	pH = 7	−0.428
$CO_2 + HCO^-{}_3 + 8H^+ + 8e^- \rightarrow CH3COO^- + 3H_2O$ [35]	0.130	pH = 7	−0.284
Cathode			
$O_2^- + 4H^+ + 4e^- \rightarrow 2H_2O$ [19]	0.187	$pO_2 = 0.2$; mM; pH = 7	0.805
		$pO_2 = 0.2$; mM; pH = 10	0.627
$MnO_2(s) + 4H^+ + 2e^- \rightarrow Mn^{2+} + 2H_2O$ [19]	1.229	$[Mn^{2+}] = 5$ mM; pH = 7	0.470
$MnO_4^- + 4H^+ + 3e^- \rightarrow MnO_2 + 2H_2O$ [50]	1.70	$MnO_4^- = 10$ mM; pH 3.5	1.385
$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2$ [19]	0.695	$pO_2 = 0.2$; $[H_2O_2] = 5$ mM; pH = 7	0.328
$Fe(CN)_6^{3-} + e^- \rightarrow Fe(CN)\ _6^{4-}$ [19]	0.361	$Fe(CN)_6^{3-} = Fe(CN)\ _6^{4-}$	0.361

amount of power generated by an MFC is consequently dependent on the catholyte selection; this should be considered when cross-comparison with the power densities generated from other MFCs in the literature.

1.2 Open Circuit Voltage (OCV) and Potential Losses

As explained earlier, the highest achievable potential of MFC is in the state of open-circuit voltage (OCV). OCV is measurable by disconnecting MFC from the circuit until no current flows across the circuit after a significant time. Removing the resistor should give MFC its OCV approaching the theoretical E_{emf} value of the cell. However, in most cases, the OCV is much lower than the E_{emf} value due to many possible reasons, indicating energy losses. In fact, E_{emf} is a thermodynamic parameter that does not take the internal resistance of cells into account. This energy loss is known as overpotential.

Knowing that the theoretical value of oxygen reduction at the cathode and pH 7 is 0.805 V, but because of the overpotential, the measured potential is typically around 0.2–0.3 V. The energy loss or overpotential value is simply determined by subtracting the theoretical and exact potential value (i.e., 0.805–0.2 V). In this case, 0.605 V has been lost, implying poor catalytic activity on the cathode, which demands the cell's catalytic improvement. One significant advantage of thermodynamic analysis through theoretical calculations is mainly to know how big and what type of energy losses are taking place in the cell.

2 Methods of Electron Transfer

2.1 Electron Shuttles or Mediators

Some microorganisms perform electron transfer with the aid of exogenous substances. Humic substances with quinone/hydroquinone groups are abundant in nature and act as electron acceptors for microbial respiration and oxidation of organic substrates, hydrogen and metals under anaerobic conditions [21, 39, 51]. Besides, they also act as electron donors for microbial respiration and reduce sulfides, nitrate and iron oxides [5, 27, 51]. Humic substances could also act as electron acceptors and donors; they are bacterially reduced along with microbial reductive dehalogenation of pentachlorophenol and iron oxides, which causes the humic substances to be re-oxidised [17]. The presence of humic substances accelerates electron transfer from bacteria to insoluble terminal electron acceptors [16]. They also facilitate the electron transfer of both in vivo and in vitro cytochrome C by promoting NADP generation [15, 43]. Apart from humic substances, iron-bearing minerals such as iron oxide and carbon-based conductive materials also promote electron transfer by enhancing the connection of diverse microbial species. As electrons are loosely bound to their surfaces and are freely moving, they are widely employed as the electrode in a microbial fuel cell [47–49].

Anaerobic respiration of microorganisms produces small molecules as endogenous electron shuttles for interspecies electron transfer. Microorganisms synthesise primary metabolites such as H_2 and intermediary metabolites such as formate from oxidisable organic substrates such as ethanol, leaving the microbial cells in their reduced state to transfer electrons to distant extracellular oxidants interspecies electron transfer to its syntrophic partner. Ethanol is oxidised to acetate, and substrate-utilising bacteria or hydrogenotrophic bacteria liberate H_2. Syntrophic methanogenic bacteria then utilise H_2 to reduce carbon dioxide to methane [3, 9, 45]. The electron transfer by either H_2 or/and formate differs for different co-cultures as it relies on its syntrophic partner, either an H_2 using methanogen or a formate-utilising methanogen [9]. In microbial fuel cells, these metabolites can convey electrons towards iron oxides or electrodes [38].

Besides, bacteria also produce secondary metabolites such as phenazines and flavins as electron shuttles. Endogenous phenazine antibiotics such as pyocyanin and phenazine-1-carboxamide synthesised by *Pseudomonas aeruginosa* promote anaerobic survival of the bacteria through extracellular electron transfer [37]. The employment of phenazine antibiotics as electron transfer mediators enables the transfer of bacterial electrons towards the anode in a microbial fuel cell [12, 31, 32]. Flavins are another electron shuttling intermediate resulting from riboflavin's employment that promotes anoxic bacterial growth and accelerates the reduction of poorly crystalline Fe(III) oxide with fumarate as the sole electron acceptor [4, 6]. Flavins are also primary cytochrome-bound cofactors. However, its practicality in the microbial fuel cell is inconsistent due to its reliance on bacterial preference [22, 46].

2.2 C-Type Cytochromes

Cytochromes are distributed in the cytoplasm, inner membrane, periplasm and outer membrane, and some are secreted to the extracellular environment. Cytochromes with multiple iron porphyrins or hemes as prosthetic groups were found in diverse prokaryotes where they participated in electron transfer and biochemical cycling of N, S and Fe globally [2]. C-type cytochromes are the main cytochrome group with electron transfer importance. They can be found at the inner membrane (MacA), periplasmic (PpcA, PpcB, PpcC, PpcD and PpcE) and outer membrane (OmcF, OmcS, OmcE, OmcB and OmcZ) [24, 25, 36]. C-type cytochromes mainly accelerate electron transfer from microorganisms to insoluble electron acceptors by coupling with pili [14, 20, 41, 42]. OmcS facilitates electron transfer from pili to Fe(III) oxide, Mn(IV) oxide and humic substances rather than electron transfer along the pili filament [14, 20]. OmcZ promotes electron conductivity of microbial biofilm, whereas

OmcS and OmcE involve in electron transfer to electrodes [10, 11, 26]. Extracellular c-type cytochromes cause the reduction of Fe(III) oxide, Re(III), U(IV) and Cr(IV) due to the utilisation of these metals as terminal electron acceptors for anaerobic respiration [13, 18, 28, 40].

2.3 Nanowires

Microbial pili can act as “nanowires” to facilitate long-range respiration and conduct electrons between microbial cells and electron acceptors. They extend from the outer cell membrane of the microbial cell into the extracellular domain for long-distance extracellular electron transfer or conduction of electrons through biofilms [33, 34]. The electron acceptors can either be reducible substrates or syntrophic partners [20, 33]. There are two electron transfer mechanisms of microbial nanowires. Pili of *Shewanella oneidensis* are electrically conductive filaments that transfer electrons through electron hopping between cytochromes aligned along the filament of pili with inter-cytochrome spacing less than 0.7 nm [30]. In electron hopping, electrons are physically displaced due to diffusion and electron hop from a reduced cytochrome to its adjacent oxidised cytochrome [23]. On the other hand, pili of *Geobacter sulfurreducens* have metallic-like conductivity due to the overlapping of pi–pi orbitals of aromatic amino acids that result in electron delocalisation [8]. As a result, electrons are delocalised and spread across the entire filament of pili [7, 29]. Long-distance electron transfer via pili not only contributes to Fe(III) oxide reduction but is also crucial in interspecies electron exchange between syntrophic microbial partners [20].

3 Concluding Remarks

In MFC technology, obtaining the theoretically calculated potential and power is an endeavouring journey. Due to the added biological nature of the microorganism used, which is yet to be understood fully as to how the interaction between the abiotic and biotic components affects the MFC performance, one could only hope to approach the calculated values obtained through understanding the various equations and physics laws governing electrical generation. A fact to be reminded of is that there are a plethora of microorganisms available in the world, identified or not, with their own intrinsic nature. Thus, understanding how they interact with their surrounding environment could shed some clues and perhaps bring us closer to obtaining the theoretically calculated value. Therefore, there is an absolute must to further study these interactions to enhance knowledge in this field.

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