Review article

Models for Microbial Fuel Cells: A critical review

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HIGHLIGHTS

- Mechanisms, advantages, drawbacks, and applications of different MFC models are discussed.
- Mechanism-based and Application-based taxonomy of MFC models is presented.
- Different modeling approaches to the MFC are reviewed.

ABSTRACT

Microbial fuel cells (MFCs) have been widely viewed as one of the most promising alternative sources of renewable energy. A recognition of needs of efficient development methods based on multidisciplinary research becomes crucial for the optimization of MFCs. Modeling of MFCs is an effective way for not only gaining a thorough understanding of the effects of operation conditions on the performance of power generation but also becomes of essential interest to the successful implementation of MFCs. The MFC models encompass the underlying reaction process and limiting factors of the MFC. The models come in various forms, such as the mathematical equations or the equivalent circuits. Different modeling focuses and approaches of the MFC have emerged. In this study, we present a state of the art of MFCs modeling; the past modeling methods are reviewed as well. Models and modeling methods are elaborated on based on the classification provided by Mechanism-based models and Application-based models. Mechanisms, advantages, drawbacks, and application fields of different models are illustrated as well. We exhibit a complete and comprehensive exposition of the different models for MFCs and offer further guidance to promote the performance of MFCs.

1. Introduction

Microbial Fuel Cells (MFCs) have received an extensive attention in the recent years as a novel source of renewable energy. The MFC regarded as a direct bio-electrochemical reactor realizes a conversion of chemical energy in microorganism to electricity, treats the organism as the substrate and utilizes the microbial redox reaction to generate electricity directly [1]. The power generation principle and the application of MFCs have resulted in comprehensive studies [2–6]. Bacteria provide the catalyst to oxidize the substrate in the anaerobic anode and electrons are transferred as the reaction production to the anode electrode, through an external circuit to the aerobic cathode where the reduction reaction is carried out and combines reductant to produce the water molecules, as shown in Fig. 1 [5].

According to the electrons transferred to the anode surface in different ways, the MFCs can be classified into the direct MFCs (conduction based) and indirect MFCs (mediators based). On the basis of the existence of proton exchange membrane (PEM), the MFCs are divided into two-chamber MFCs and single chamber MFCs. As the new biomass power generation energy, MFCs are capable of not only replacing the traditional fossil fuel and reducing the impact on environment but also achieving the sustainability of water resources with the wastewater as substrate used and simultaneous electricity power generation [7,8]. However, there are several hurdles remaining for MFCs to be widely adopted. The main drawback in the MFCs operation is the low power output, which limits the performance of MFCs to drive electronic devices. The power output of MFCs cannot reach the high-power level as well as the industrial application occasions of the other renewable

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Nomenclature

a, b	The coefficient of Tafel equation
$\mu_{a/m}$	Growth rate for anodophilic/methanogenic biomass
η_a	Anode overpotential
S_{d0}	Influent substrate concentration
η	Overpotential
$S_{a/d}$	Concentration of electron acceptor/donor
α	Charge transfer coefficient of anodic reaction
K_{sa}	Half velocity rate constant for electron acceptor
$\alpha_{a/m}$	Biomass retention parameter
K_{sd}	Half velocity rate constant for electron donor
V_a	Volume of anode chamber
$K_{d,a/m}$	Decay rate for anodophilic/methanogenic biomass
U	The local potential
K_{dec}	Decay constant for acetate utilisers
D	Dilution rate
$\phi_{a/i}$	Volumetric fraction of active/inactive biomass
A_m	Cross-section area of membrane
v	Advective velocity of biofilm matrix
A_F	Surface area of the biofilm
r_{res}	The rate of endogenous respiration
R	Ideal gas constant
r_{ina}	The rate of inactivation of active biomass
T	Temperature
k_{bio}	Biofilm conductivity
$D_{ED,f}$	Diffusion constant for electron donor
M_{total}	Mediator fraction
$X_{f,a/i}$	Density of active/inactive biomass
M_{red}	Reduced mediator fraction
n	Number of electrons transferred
$S_{E/B}$	Concentrations at electrode surface/bulk liquid
F	Faraday constant
I	Current
Y	Bacterial yield
i	Current density
q_{max}	Maximum substrate consumption rate
i_0	Exchange current density
$q_{a/m}$	Substrate consumption rate by anodophilic/methanogenic biomass
i_l	Limiting current density
$q_{s,B/F}$	Net reaction rates of reaction in bulk/biofilm
$R_{solution}$	Resistance of solution
$q_{s,E}$	Electrochemical rates of solute component
$R_{membrane}$	Resistance of membrane
x	Concentration of biomass
$R_{A/B}$	Resistance of anode/cathode
$x_{a/m}$	Concentration of anodophilic/methanogenic biomass
$R_{min/max}$	Lowest/Highest observed internal resistance

energy, such as solar power, wind power, nuclear power, and others. Furthermore, the costly materials of electrode and catalyst result in reducing the economic competitive abilities compared with other sources of energy [9]. Therefore, how to improve the power generation performance and find inexpensive electrode and catalyst materials are the pronounced challenges present in the applications of MFCs.

The MFC is a complex and hybrid system that involves a number of bio-electrochemical coupling reactions, which leads to the strong non-linear characteristics and significant hysteresis properties and makes it difficult to control and optimize the power generation of MFCs directly. Furthermore, bacteria inoculation and performance measurement completed through experiments are time-consuming and uneconomic. Hence, considering mathematical models to understand the major influence factors of the whole system to distinguish the main bottlenecks and improve the power generation performance of MFCs arises as an efficient alternative to follow. The influential variables of the MFCs power generation performance can be obtained based on mathematical modeling. In general, the models primarily represent the chemical reaction process, mass transport process and electricity generation process of the cell. MFCs models have also been developed by considering the successfully implemented models for other fuel cells, such as the Direct Methane Fuel Cell (DMFC) [10], the Solid Oxide Fuel Cell (SOFC), the Anaerobic Digest Model No.1 (ADM1) [11], and others. MFCs models are applied to the online or offline mode on basis of different real-time data, which means these two models have independent application areas. However, both models exhibit the same key objectives of providing sound prediction abilities as well as robustness. Adhering to different modeling objectives, the models for MFCs can be divided into the full-cell models discussing reactions of both the anodic and cathodic compartment, and the half-cell models focusing on a specific compartment considering the anode or cathode as the limiting factor of MFCs [12]. With the development of MFC modeling, conflicting aspects between the exhaustive expressing degree and practical application have appeared in different models. Many efforts have been directed to the fields related with MFCs modeling.

Zhang and Halme [13] proposed a dynamic mathematical model for an MFC with added-mediator to transfer electrons. The process of modeling ignored the cathodic reactions and incorporated the classical electrochemical reactions in the anode chamber, including the consumption of substrate, the potential, and the current calculation and so on. With the novel understanding of the electron transfer mechanism, Kato Marcus et al. [14] modeled the conduction-based MFC that applied the biofilm to transferring the electrons to the anode without mediator, that is biofilm-anode, for the first time and evaluated, the limitation element caused by biofilm in MFCs. Based on the mediator-less MFCs, the biofilm models have been added to MFCs models. Picioreanu et al. [15] developed the first computational biofilm model of an MFC to investigate that the bacteria accumulated at the anode surface to form the biofilm and the variation of thickness of biofilm. The
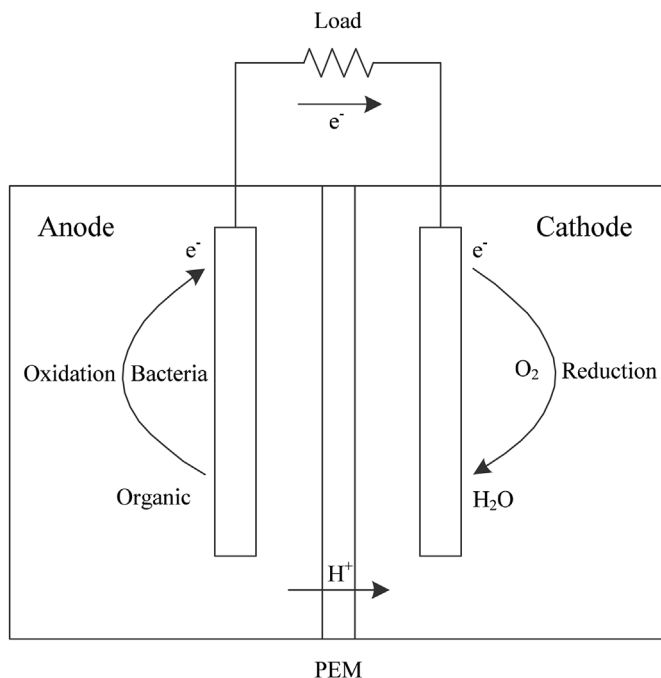

Fig. 1. Schematic diagram of MFCs (shown are two-chamber MFCs).

model can be used in different ways according to the requirements of modeling under consideration. Being differing from the previous half-cell models for the anode chamber, Zeng, et al. [16] presented a two-chamber MFC model by taking into account the anodic reactions as well as the cathodic to characterize the MFCs in continuously stirred tank reactor (CSTR) operating mode. After the series of reactions in anode chamber had been paid close attention to, it gradually appeared the models aimed at the cathode reaction process [17]. For example, Ou, et al. [18] established a model for cathode biofilm formation and considered its influence to MFC output.

Additionally, an equivalent circuit (EC) model with some basic electronic elements was presented based on analyzing the electrical performance of MFCs like the dynamic characteristics of output voltage and current. It provides an alternative way to detect the electrical characteristic of MFCs and expand the application to the energy storage system [19]. In recent years, with the increasingly development of methods of artificial intelligence and control theory, the methods that employed machine learning (e.g. Ref. [20]), experimental design (e.g. Ref. [21]) and methods of parameter estimation of state equations have started emerging [22]. These models require determining the input and output variables and learning on basis of a large number of experimental data. Simultaneously they could produce the optimal output power density.

In this paper, MFCs' models discussed in the literature have been classified into the two main groups, namely Mechanism-based models and Application-based models. Mechanism-based models focus on the key reactions processes including the rate of substrate utilization, the expression of voltage and current, the biofilm formation and decline, among others. These models with the purpose of presenting the MFC's reaction mechanism in detail can be used to optimize the MFCs configuration and power generation performance. Application-based models focus on electrical models along with various aspects of learning and controlling completed for such models. The electrical models are likely to be applied to configure the circuit components parameters and analyze the response (voltage) of the cells. The learning and controlling

aspects are mainly used to optimize the output power and coulombic efficiency without considering in overall reaction processes. The model parameters can be obtained via learning on a basis of experimental data; the pertinent state equations are built by involving several important reactions. Fig. 2 displays the classification of the MFC models to be presented in the following sections.

This paper delivers an overview of the various models for MFCs. The conventional classification methods for constructing MFCs models engage various reacting chambers of the MFCs. Accordingly, the half-cell models and full-cell models were involved in the previous study; most of them belong to the models explaining the ensuing reaction mechanism [13]. Nevertheless, this work not only includes the newly proposed learning models and the models focusing on the electrical application to the models' retrospect, but also employs the general modeling regions to classify into a number of sub models and integrates the various aspects of models systematically, which is the first time to exhibit a more complete and comprehensive exposition of the different models for MFCs. The rest of this paper is organized as follows. Numerous MFCs models are summarized in Section 2. Section 2.1 discusses the Mechanism-based models along with the related modeling equation and characteristics. Some special factors and modeling ways are also involved in this section. The Application-based models with different application purposes and approaches are summarized in Section 2.2. Conclusions are covered in Section 3.

2. MFC models

2.1. Mechanism-based model

The Mechanism-based models are mainly summarized and classified by means of different domains where the bioelectrochemical reactions occur in an MFC. Those include the bulk liquid containing substrate and bacteria, the biofilm attaching to the electrode and several physical and chemical influential factors impacting the performance. The electrochemical characteristics are also discussed in terms of the output
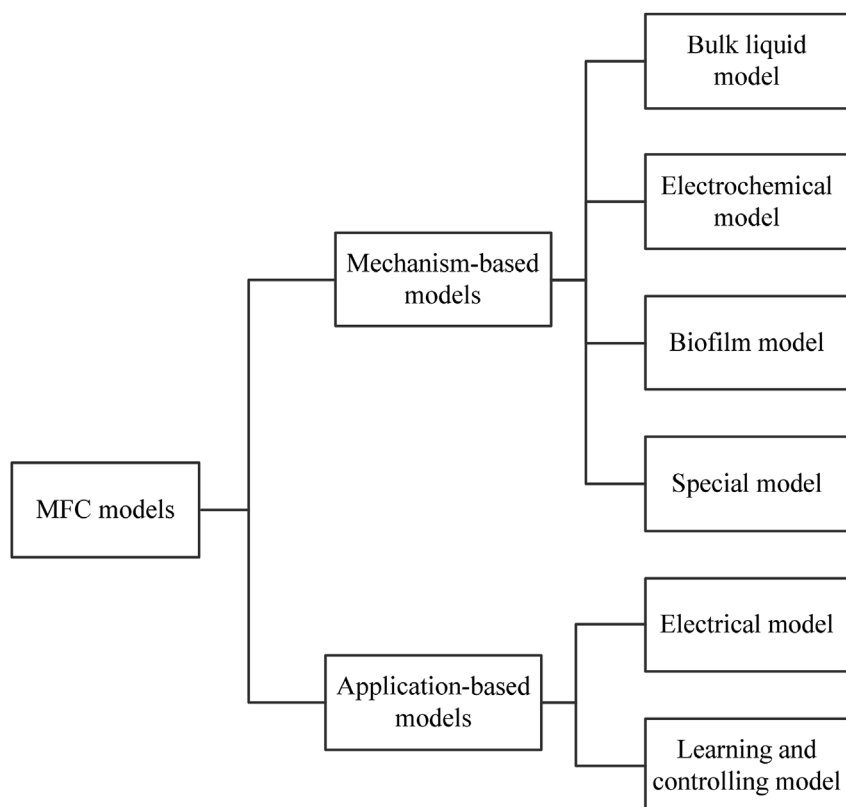
Fig. 2. Classification of MFCs models discussed in the paper.

voltage and current. Consequently, the Mechanism-based models are composed of the following four groups: bulk liquid models, electrochemical models, biofilm models, and special models.

2.1.1. Bulk liquid model

Bulk liquid model involves the basic reactions of electricity generation of MFCs presented at a macroscale aspect. Here we discuss the rate of substrate consumption and mass balances as important variables encountered in the problem.

Substrate is a significant power production element as the electrons donor. The bacteria oxidize the substrate to generate the electrons, and the rate of substrate utilization indicates the rate of reaction in reactors and relates to the way in which the growth rate of bacteria is affected. Esfandyari et al. [23] compared three types of expressions that described the bacteria specific growth rate, namely the Monod, the Blackman, and the Tessier. Experimental results demonstrated that the Monod equation exhibited significant applicability to present the rate of bacterial growth, which was bound up with the consumption of substrate. In this way, the relationship between the concentrate of substrate and other species are described based on the Monod equation. However, under the condition of high substrate concentration, the inadequacy of Monod equation is reflected due to the inhibition effect of the solution. Jafary et al. [24] presented the Tessier, Aiba and Haldane model in terms of the utilization of substrate to investigate the substrate inhibition effect at both low and high levels of substrate concentration. All the proposed models were capable of fitting the experimental data well and discussed with the characteristics in application. The study revealed that the high substrate concentration would cause the decrease in the output power density, thus the model without the inhibition constant was not applicable for calculating the rate of substrate utilization, particularly at the high concentration. For example, the current density of the MFC decreases with the increase of the substrate concentrate because of the substrate inhibition. While in the Monod equation, the bacteria growth rate is going to maintain a constant value when the concentration is higher than a certain threshold. Hence, the Monod equation without the inhibition term exhibits limitations when substrate concentrate is high.

Picioreanu et al. [15] noted that the substrate consumption was affected both by the concentrate of electron donor (ED) and electron acceptor (EA). For example, in case of an acetate-based MFC, the acetate acted as the ED and the mediator as the EA during the oxidation reaction occurred in anode chamber. The double-limited Monod equation was therefore established to model this process. The equation is applied in a situation where the add-mediators are employed to transfer the electrons, when the ED and EA are both solute components and the rate of substrate utilization is limited by their concentrations. Pinto et al. [25] used this expression in the case of the competition of two microbial groups, viz. the electrogenesis and methanogenic. With the competition of the same substrate, the rate of electrogenesis consumed the substrate and its growth rate were both expressed by the double-limited Monod equation, while the consumption along with the growth

of methanogenic were both determined with the use of the Monod equation. This approach was widely used in later works with the same consideration regarding the different microbial populations competing for the same substrate [26–28]. Zeng et al. [16] developed a model for a dual-chamber MFC and regarded the process of consuming substrate as an electrochemical reaction that was affected by the anode potential in an electrochemical cell. Then the Monod equation was combined with Bulter-Volmer/Tafel equation (fundamental electrochemical equations) to establish an equation of substrate consumption rate while the cathodic reaction rate referenced this form as well. The equation considered not only the consumption but also the influence of potential, which was generally applied with the similar expression form of the anodic reaction and cathodic in modeling a two-chamber MFC [23,29,30]. In the model of conductive mechanism in the biofilm, Kato Marcus et al. [14] mentioned a double-limited Monod equation, considering that the electrons were transferred through biofilm as the EA rather than the extra mediators. The expression of specific consumption rate was determined by the concentration of EA and anode potential calculated with the Nernst equation, recombined the Monod equation into Monod-Nernst equation and was subsequently used in the later models of conduction-based MFCs. For example, Ou, et al. [18] proposed a model of cathode biofilm that involved two microorganisms consuming the oxygen competitively in cathodic compartment that is the autotrophic aerobic biomass (AAB) and heterotrophic aerobic biomass (HAB). The Monod-Nernst equation was applied to show the oxygen consumption by AAB and the double-limited Monod equation was associated with the Nernst equation to establish the rate equation for competition of substrate and oxygen by HAB. Mardanpour et al. [31] considered the suspended biomass and attachment biomass on the biofilm of an MFC. Because electrons generated by the attachment biomass were transferred by biofilm directly and the others produced from suspended biomass were transferred by mediators, the double-limited Monod equation and Monod-Nernst equation were employed to calculate the rate of two types of biomass consumed the substrate respectively. Apart from the single calculation of substrate reaction rate based on Monod equation, Oliveira, et al. [29] and Ismail and Habeeb [32] simulated the anode substrate reaction with both biological degradation and electrochemical reaction being considered. The degradation effect was described by the Monod-type equation that explained the electrons produced at anode chamber, while the Tafel-based equation was used to calculate the electrochemical effect regarding the electrons as the production from the biofilm reaction.

The varieties of different expressions of the substrate consumption rate based on the Monod equation were given in Table 1. From this table, one can conclude that the Monod-type and the Nernst-Monod equation both remake the double-limited Monod equation. The double-limited Monod equation is applicable for both solute electron donor and acceptor, thus it is necessary to combine the ED concentration with electrode potential rather than EA concentration when the mechanism of electron transferred has changed. The part of potential can substitute the function of electron acceptor in the equation with a relatively

Table 1
The equation of the rate of substrate consumption.

Name	Mechanism Equation	Characters	Applicable object	References
Monod equation	$q = q_{max} \frac{S_d}{K_{sd} + S_d}$	Express the limitation by the concen-tration of ED.	Biochemical system;	[13,33,34]
Double-limited Monod equation	$q = q_{max} \phi_a \frac{S_a}{K_{sa} + S_a} \frac{S_d}{K_{sd} + S_d}$	Express the limitation by the concen-tration of ED and EA.	Add-mediator; Soluble donor and acceptor;	[15,25,31,35,36]
Monod-type equation	$q = q_{max} \phi_a \frac{S_d}{K_{sd} + S_d} \exp\left(\frac{\alpha F}{RT} \eta_a\right)$	Similar to Nernst-Monod equation; Base on the similar manner to ADM1;	Full-cell simulation	[16,29,30,32,37]
Nernst-Monod equation	$q = q_{max} \phi_a \frac{S_d}{K_{sd} + S_d}\left(\frac{1}{1 + \exp\left(-\frac{F}{RT}\eta_a\right)}\right)$	Express the limitation by the concentra-tion of ED and electrical potential.	Conduction-based	[14,17,18,23,28,31,37–39]

comprehensive consideration of substrate consumption process.

The utilization rate of substrate represents the basic efficiency of electricity generation effect, while the expressing dynamic mass balance equation for the main biological and chemical material in the MFCs is of importance in the model likewise. Mass balances equations represent the variation of primary components in MFCs. Mass balances in the bulk liquid normally contain all solute chemical species as well as biomass and are commonly represented by the ordinary differential equations. The solution to solute mass balances equations could be regarded as the set of bulk liquid concentrations needed at each time moment as boundary conditions for solute mass balance in the biofilm [15]. It can also be used to calculate the specific reaction rate, i.e. the rate of substrate consumption. Similarly, the biomass dynamic balances can be employed to calculate the variation of biofilm thickness as well. The form of equation is generally different depending upon the operation modes of the MFC and the emphasis of simulation models. Table 2 shows the expressions of MFCs mass balances presented in different situations.

A model that focuses on the full-cell simulation comprehensively considers the changes in important chemical components of anode and cathode chamber and the exchange through proton membrane, but the diffusion between the biofilm and substrate are usually ignored. The full-cell model proposed by Zeng et al. [16] consisted of the mass balances for substrate concentration, hydrogen ion concentration, dissolved carbon dioxide, and biomass (determined by the requirements of different types of bacteria) for a CSTR MFC. In the cathode chamber, it involved the dissolved oxygen, hydroxyl ion, and cation. All the chemical components variation was mainly influenced by the feed flow rate. This modeling process is generally considered to offer a large-scale aspect method and normally applied to other full-cell models.

On the other hand, some models aimed at the half-cell simulation mainly discussed the mass balance equations in specific chamber (most in anode chamber). Picioreanu et al. [15] employed ordinary differential equations both in batch and continuous MFCs and established the mass balances for solute and biomass components in the anode chamber. These equations included the electrochemical reaction rate in the bulk liquid as well as biofilm. Next, Picioreanu, et al. [36] used the equation in batch mode and expressed the electrochemical reactions separately in the whole process, established mass balances for each relevant chemical composition (the redox production) and an expression equation for current density. While in conduction-based models, Kato Marcus et al. [14] proposed a one-dimensional and multi-species model for biofilm anode of an MFC, correlated mass balances with reactions occurred in the biofilm, including the substrate mass balance in biofilm and biomass mass balance. All these models assumed that the biofilm as a porous solid conductor and the mass balances expression

commonly took into account the substrate that diffused from bulk liquid to biofilm. This diffusion process was regarded as the limitation of the reaction rate. For biomass, the mass balances for active and inert biomass represent the growth, decay and conservation of two species as well as their influence on biofilm thickness (will be discussed in 2.1.3). The following conduction-based models used the analogous approach to the modeling process. Karimi Alavijeh et al. [43] considered more species biomass and expanded the mass balances expression to different types of substrate conditions [14]. Ismail and Habeeb [32] added the diffusion process to full-cell simulation, established the diffused substrate mass balances in biofilm, and other balance equations also accounted for the dynamic process of carbon dioxide and substrate concentration in bulk liquid. Kazemi et al. [38] presented a model for a reverse-MFC aimed at the cathodic compartment, considered the diffusion to the biofilm cathode and the mass balances were employed for the variation of the chemical component in catholyte. Zeng et al. [16] focused on the competition behavior between the two microbial populations and proposed relatively simple mass balances equations for an MFC working in continuous mode, calculated the change of two microorganisms and substrate concentration. Karimi et al. [28] and Alavijeh et al. [39] developed the mass balances for the wastewater treatment application of MFCs, combined the diffusion effect of substrate to biofilm and competition in the same substrate.

2.1.2. Electrochemical model

Electrochemical models characterize and evaluate the electrical parameters of MFCs, and the relevant electrical performance of MFCs is presented through the basic theory of electrochemistry. Here we discuss the models and specific formulas for the output voltage, current density and electrons balance in MFCs.

Current density is the current flowing through the area or volume of unit electrode and links to the rate of electrochemical reaction. Some models require expressing the current density of MFCs to describe the polarization curve (e.g. Ref. [45]). Table 3 is the different equations of current density in the literature. For modeling two chambers of an MFC, one can relate the current density to the flux of ions via membrane [47]. Zeng et al. [16] determined the current density through multiplying the species' flux of ions via the membrane by charge number of species, actually only the cations are assumed to be transferred through the membrane. The current density can also be calculated with the use of the Ohm's law with the known output voltage and external resistance.

Kazemi et al. [44] studied the influence of separator on the performance of a passive air-breathing flat-plate MFC. The Bulter-Volmer equation was used in this model to describe the relationship between the current density and activation overpotential in case of anode ethanol oxidation and cathode oxygen reduction reactions. Pinto et al.

Table 2
The equations of mass balances.

Mechanism Equation	Characters	Reference
$\frac{dS_d}{dt} = -q_a x_a - q_m x_m + D(S_{d0} - S_d)$ $\frac{dx_{a/m}}{dt} = \mu_{a/m} x_{a/m} - k_{d,a/m} x_{a/m} - \alpha_{a/m} D x_{a/m}$	Considering two microorganisms compete for the substrate;	[22,25–27,35,40]
$\frac{dS_d}{dt} = D(S_{d0} - S_d) - \frac{A_m}{V_a} q$ $\frac{dx}{dt} = D(x_0 - x) + \frac{A_m}{V_a} Y q - K_{dec} x$	MFCs operating in CSTR; Full-cell simulation;	[10,16,29,30]
$\frac{dS_d}{dt} = \frac{\phi}{V_a}(S_{d0} - S_d) + q_{s,B} + \frac{1}{V_a}\int_{V_F} q_{s,F} dV + \frac{1}{V_a}\int_{A_F} q_{s,E} dA$ $\frac{dx}{dt} = \frac{\phi}{V_a}(x_0 - x) + q_{x,B} + q_{det}\frac{A_F}{V_a} + q_{ata}\frac{A_F}{V_a}$	Continuous and batch mode ($\phi = 0$) for MFCs; Considering the reaction rate of biofilm;	[11,15,34,41]
$0 = D_{ED,l}\frac{\partial^2 S_d}{\partial z^2} - X_{f,a} q$ $\frac{\partial \phi_a}{\partial t} + \frac{\partial(v\phi_a)}{\partial z} = Y q - r_{res} - r_{ina} = \mu_a$ $\frac{\partial \phi_i}{\partial t} + \frac{\partial(v\phi_i)}{\partial z} = \frac{X_{f,a}}{X_{f,i}} r_{ina} = \mu_a$	Conduction-based MFCs; Considering the conversion between two microorganisms.	[14,31,33,38,42,43]

Table 3
The equations describing current density.

Name	Mechanism Equation	Reference
Bulter-Volmer equation	$i = i_0\left(\exp\left(\frac{\alpha nF}{RT}\eta_a\right) - \exp\left(\frac{-(1-\alpha)nF}{RT}\eta_a\right)\right)$	[11,15,34,36,44]
Bulter-Volmer-Monod equation	$i = i_l\left(\frac{1 - e^{-f\cdot\eta}}{K_1\cdot e^{-(1-\alpha)f\cdot\eta} + K_2\cdot e^{-f\cdot\eta} + 1}\right)\cdot\left(\frac{S_d}{\frac{K_M}{K_1\cdot e^{-(1-\alpha)f\cdot\eta}} + K_2\cdot e^{-f\cdot\eta} + 1 + S_d}\right)$	[45,46]
Ohm's law	$i = -k_{bio}\frac{\partial U}{\partial z}$	conduction-based model
Tafel-Monod	$i = \frac{8F}{3600}\frac{S_d}{K_{sd} + S_d}xq_{max}\exp\left(\frac{\alpha F}{RT}\eta_a\right)$	[10]

[27] employed the mass balances and the current expression to discuss the effect of operation current in MFCs on the existence of two species microorganisms, proposed a theoretical operation current under optimal production and extended the method to the Microbial Electrolysis Cell (MEC). Hamelers et al. [45] introduced a Bulter-Volmer-Monod (B-V-M) equation to describe the anode polarization curve and applied this equation to calculate the current density. Compared with the Nernst-Monod equation, the B-V-M equation exhibited a better fit with experimental data as well as showed better abilities to predict the zero current and describe the polarization curve. On this basis, Stein, et al. [46] established a model for a biosensor based on an MFC and took into account the effect of the presence of toxic component. For representing the influence of inhibition at the high concentration substrate, this work modified the B-V-M model with enzyme inhibition kinetics for four types of toxicity. According to the different detecting purposes of biosensors, different expressions were used to calculate the current density and describe the polarization curves. Furthermore, the current density was expressed by another method when the electron transfer mechanism changed. In a conduction-based MFC, the biofilm was regarded as a bio-conductor and the current density was driven by the biofilm gradient in the local potential. The model presented in Ref. [14] referenced to Ohm's law and Fick's law to combine the biofilm conductivity, the diffusion coefficient, the information of gradient in local potential and chemical potential to calculate the current density. Besides the conventional expression of current density related to the activation overpotential based on Bulter-Volmer equation, Ou, et al. [18] also developed a cathode chamber model and characterized the current density of cathodic biofilm and cathode catalyst layer. A model proposed by Yao et al. [10] involved the electrochemical kinetic effect to represent the current density generation. Not only the oxygen reduction reaction was mentioned to calculate the cathodic current density with the Tafel-type based, but the anodic current density was also expressed based on the Tafel-Monod equation in the model.

The output voltage of MFCs can be calculated through the external resistance multiplied by the current and is determined by the cathode and anode potential. In view of the fact that the effect of polarization leads to the overpotential which results in the voltage losses in a cell, there is no apparent discrimination among the different output voltage models but differs from the ways ignoring the overpotential merely. Hence, the stress of this part will focus on the different expression of related overpotential. A basic output voltage calculation equation is expressed as (1). The overpotential consists of three parts: activation overpotential, concentration overpotential, ohm overpotential. The Butler-Volmer equation explains the relationship between the activation overpotential and current density. The equation is used both in the anode and cathode chamber to characterize the activation loss. The current multiplies by the MFC's internal resistance that depends on the materials of solution and exchange membrane, which is adopted to calculate the ohm overpotential with the Ohm's law. The Nernst equation is mainly used to calculate the concentration overpotential as well as the electrode voltage.

$$V_{cell} = V_c - V_a - \eta_{ohm} = V^0 - \eta_{act} - \eta_{con} - \eta_{ohm} \qquad (1)$$

where V_a is the anode potential; V_c is the cathode potential; V^0 is the theoretical thermodynamic potential; η_{act} is the activation overpotential; η_{con} is the concentration overpotential; η_{ohm} is the ohm overpotential;

In the work of Picioreanu et al. [15], the cathode potential was assumed as constant (the assumption was usually proposed in anode-based simulation). The model considered the concentration loss and regarded the equilibrium potential including concentration loss as a new electrical potential, which was a function of concentrations of reacting chemical species in bulk liquid. It calculated the activation overpotential with the ohm's law (for ohm losses calculation) and the standard reduction potential, internal, external resistances and value of pH known. Pinto et al. [25] notes that the activation loss mainly occurs at the low value of current but considers that the activation loss is lower when an MFC operates under the optimal electrical load, resembles the Bulter-Volmer equation to calculate the activation loss. The model replaced the thermodynamic potential with the operating voltage in experiments and referred to a more accurate concentration loss that was expressed by additional boundary conditions at high current density. Moreover, combined with the Monod term, the current calculation was limited when the value of the reduction concentration was low, then the activation loss was ignored to deduce a simple current expression of an MFC. The two known dependent relationships between the internal resistance and open circuit voltage to the concentration of electrogenesis bacterial were employed to calculate the value of internal resistance and cell voltage more accurately during start-up period. The same resistance and voltage expressions were used in Li and He [26] and Recio-Garrido et al. [35]. Besides that the anode activation and anode voltage were characterized by the Bulter-Volmer and Nernst equation respectively, the half-cell model for a continuous MFC anode of [34] considered that the concentration overpotential appeared at the interface of bulk liquid-electrode. It neglected the concentration overpotential and variation of cathode potential to reduce the complexity of the model. On the other hand, the electrons balances equation was used in the full-cell models and normally calculated the activation and concentration losses. In Zeng et al. [16], the ohm loss followed the Ohm's law and the internal resistance was only represented by two parts, the resistance of membrane and solution. Oliveira et al. [29] modeled the cathode electrochemical reaction with using Tafel equation to link the cathode overpotential to the current density and solely considered the membrane resistance as internal resistance of an MFC. While the Ismail and Jaeel [30] calculated the anode activation and cathode activation based on the respective reaction rate equations (Butler-Volmer equation). A membraneless single chamber model Sirinutsomboon [37] used the Nernst equation to calculate the cathode voltage and proposed a half-max-rate anode voltage when the substrate consumption rate reached the maximum value. This voltage and the local voltage in biofilm were both applied to the calculation of anode voltage. The output voltage equaled to the cathode voltage minus the anode voltage. The model of [17] derived by Ou et al. aimed at cathode chamber expressed the anode concentration overpotential through anodic limiting current density, proton concentration and initial proton

concentration based on the Nernst form, and calculated the activation overpotential of anode subsequently. An analogous model of Ou et al. [18] assumed anode potential at a constant value to simplify the complexity of calculation, regarded the electronic resistance of the anode, the ionic resistance of bulk liquid and the electronic resistance of cathode as the entire cell resistance to calculate the Ohm loss. For the ignorance of overpotential, the activation overpotential dominates the polarization losses when current density is low. With the current density increasing, the concentration overpotential increases and gradually becomes dominant. Therefore, some researchers consider that the MFC operates near the optimal current and the activation overpotential thus being ignored. Generally, a more precise model contains more expressions of variables in terms of the overpotential. Nevertheless, different models' focuses enable the different degree of overpotential ignorance. For most anode-based models, to reduce the complexity of the models, the cathode potential is regularly considered as the constant and mainly the anodic variation is modeled. Similarly, the cathode-based models thoroughly discuss the cathode overpotential.

When the polarization curve is known, the activation overpotential could be expressed by a Tafel equation. Wen et al. [48] introduced a simple electrochemical model for an MFC as the continuous beer brewery wastewater treatment. The natural logarithm form of the Tafel equation was used to represent the activation overpotential, which combined the ohm loss and concentration loss to elucidate a relationship equation between the current density and voltage. Furthermore, the model involved a more comprehensive consideration of the current density in the equation and another current loss term was added to the model, reflecting the actual voltage of the MFC rather than theoretical voltage equation. The current leakage, gas crossover and unwanted side reaction were all likely to lead to the parasitic loss, which was represented by additional current density loss. The gross current density produced at electrode, equated the measured current density plus additional current density loss. To analyze the anode dynamic response, Katuri and Scott [49] applied the basic Butler-Volmer equation to calculate the current density and expressed the anode overpotential in hyperbolic sine function with the value of microbial cells concentration and Tafel slope, a relatively simple expression of anode steady state overpotential was derived by combining with the substrate mass balance. The corresponding conclusion was used in other models as well [23,31].

The electrons as the fundamental elements of current generation are sometimes represented by a balance equation in the model. Besides that the electron balance was proposed to calculate dynamic anode and cathode overpotential with the electrode capacitor known in the full-cell model [16], the most electrons balance appeared in the biofilm simulation. Kato Marcus et al. [14] described the electron balance process that the electron conduction biofilm transferred electrons to the anode, combined the ohm's law into a new expression that resembled the diffusion-utilization equation of ED, and a new equation also represented a mass balance for an EA with two boundary conditions attached to. Others biofilm simulations employed this expression to a certain degree, see e.g. Refs. [42,50]. Table 4 gives the general forms of overpotential calculation expression.

From the above discussion, it becomes obvious that the models are basically established by considering several known electrochemical formulas, such as the Bulter-Volmer, Tafel, Nernst, and Ohm's law, among others. All the mentioned formulas play an important role in elucidating the biochemical and electrochemical reaction processes of MFCs. For the conventional Bulter-Volmer equation, it can characterize the electrons transfer process and build the relationship between the current density and overpotential. Although the equation has been widely used to calculate the activation overpotential, the simple calculation form is also deduced simultaneously to reduce the calculation complexity. The Monod equation expresses the impact of the substrate to the bacterial growth and reaction rate. Due to the description of substrate dependency, which is the fundamental element of reactions, the Monod term combines with other equation in general to completely characterize the related reaction process. For example, the Monod term is added to Bulter-Volmer equation to express the polarization curve of anode [45]. The Bulter-Volmer-Monod equation offers a better ability in fitting the experimental data, especially under the equilibrium potential to predict zero current. However, the comparatively complex parameters to be estimated, limit the usage of this equation. The Tafel equation can be applied to the activation losses calculation with only two coefficients identified. But the known polarization curve is the premise to obtain the activation losses, which increase the steps of experiment. The Nernst equation is used to determine the electrode potential and calculate the concentration potential. The form of expression generally depends on the chemical material's concentration expressed in the relevant mass balances equations. The reduced mediator fraction, the bulk liquid concentration and the limited current all emerge to deduce the calculation equation of concentration losses based on Nernst equation [15,17,25]. Although the basic form of overpotential has been determined to a large extent, the more extensive adaptability still needs to be promoted, for instance, at the high current density [25]. Moreover, different models have different degrees of expression. The variation of concentration losses or activation losses is ignored and assumed as constant to decrease the computing time of models and employ the calculation result of Nernst equation as the electrode voltage directly. In view of the same purpose, the composition expressions of the MFC's internal resistance used in Ohm losses calculation are also decreased in some models. It is noted that the simpler the model's expression is, the worse dynamic adaptability and robustness of the model become.

Table 4
The equations of overpotential.

Overpotential losses	Form	Basic equation	Reference
Activation overpotential	$a + b \ln i$	Tafel equation; Butler-Volmer equation	[48]
	$\frac{RT}{nF} \ln\left(\frac{i}{i_0}\right)$		[30,34]
	$\frac{b}{2.303} \sinh^{-1}\left(\frac{i}{2i_0 S_d}\right)$		[23,31,49]
Concentration overpotential	$\frac{RT}{nF} \ln \frac{M_{total}}{M_{red}}$	Nernst equation	[25,27,31,36,40]
	$\frac{RT}{nF} \ln \frac{S_E}{S_B}$		[15]
	$\frac{RT}{nF} \ln\left(\frac{i_l}{i_l - i}\right)$		[17,18,23,26,48]
Ohm overpotential	$I(R_{solution} + R_{membrane}) I(R_A + R_{solution} + R_B) I(R_{min} + (R_{max} - R_{min}) \times e^{-K_r \cdot x_a})$	Ohm's law	[16,23,30,34] [18] [25,26,35,40]

2.1.3. Biofilm model

Except for electron shuttles (i.e. mediators) were used to transfer the electrons from bacteria to anode, the conduction through biofilm was recognized as another mechanism [3]. The existing researches have demonstrated that the conduction mechanisms were dominant in MFCs (particularly operating in continuous mode) [51,52]. Bacteria accumulate at anode and derive a conductive solid as the biofilm matrix, which is a significant portion of MFCs. For conduction-based MFCs, models need to consider the biofilm formation and establish the biofilm model to estimate the thickness of biofilm and boundary conditions of entire system. Hence, the biofilm model is normally considered in a half-cell simulation with mainly focusing on the biomass distribution and variation of thickness; gradually extend from modeling of anode biofilm to cathode biofilm.

Kato Marcus et al. [14] presented a model based on conduction mechanism of MFCs and defined two species microorganisms: the active biomass and inactive biomass, the former oxidized the substrate and converted into the power for its growth and the latter formed the conductive materials to transfer the electrons directly. The biofilm matrix was characterized by the biofilm conductivity k_{bio} and renamed to biofilm anode, which was the result of the accumulation of the inactive microorganisms and extracellular polymeric substances (EPS) that contained nanowires. The sum of the respective volume fraction of the two types of microorganisms was one. Adopting the net growth rate of each type and the rate of conversion from active to inactive biomass (i.e. inactivation rate), the advective velocity of biofilm matrix was defined and then employed with the biomass losses due to detach microorganisms, to calculate the change of biofilm thickness. Moreover, the model contained a minimum electrical potential equation that the steady-state biofilm formation was guaranteed when the rate of biomass accumulation equaled to the rate of losses under this minimum voltage. The model of [14] contributed to the conduction-based mechanism modeling approach, particularly established a biofilm model, which related to the essential element in power output, considered that the growth of biomass result in the increase in biofilm matrix as well as the biomass losses lead to the decrease, which was the reason of biofilm change. Such main idea was referenced to and expanded in the later work [33,42,43,50]. Jayasinghe et al. [33] modified the biofilm model with integrating the extracellular and intracellular components, which was different from conventional expression, and evaluated the influence of spatial heterogeneity on metabolism through the genome-scale metabolic model for *G. sulfurreducens*. The model expanded the microbial population in biofilm of [14] into defining the three kinds of microorganisms: the active, the inert, and the respiring microorganisms, the conversion from active biomass to respiring biomass was added as well. Pointing out the respiring biomass utilized endogenous respiration to help conserve energy, and the active and respiring biomass were both metabolically active to promote producing energy. In addition, the death and lysis of bacteria were used to characterize the variation of biofilm, which made the modeling process more exhaustive. Sedaqatvand et al. [42] presented a model for a single-chamber MFC treating the dairy wastewater as substrate and operating in batch mode. Whereas the model ignored the effect of detachment biomass and merely considered the advection velocity to express the biofilm thickness change. Besides, the procedure used the genetic algorithm to determine optimal parameters of the model. A two-dimensional biofilm model based on [14] was proposed in Merkey and Chopp [50]. They figured out the relationship between the power output and electrode geometry through computing in three regions: the bulk, the biofilm and anode electrode. Compared with previous models, one interface between a biofilm layer and a bulk liquid layer and another one between a biofilm layer and the electrode were both developed in this model. The location of interface between the liquid and biofilm is altered because the biomass increased. To present the evolution of interface, the normal interface velocity was defined along with the shear stress, which was used to represent the erosion process. For another situation that the biomass colonies grew into the surface between anode and biofilm and made two interfaces intersected so that the ordinary interface velocity was not suitable due to the artificial computing error. The model therefore redefined velocity to apply to the intersection zone and used the piecewise function to calculate interface velocity in entire area.

Unlike the biofilm model based on conduction mechanism to show the biofilm thickness variation, the concentration gradient also characterizes the biofilm domain in MFCs, which involves the electrons shuttles mechanism [15,32,41]. Picioreanu et al. [15] established a model for an MFC operating in the batch mode and the electrons transferred by extra diffusible mediator. The attached biomass related to the biofilm as well as the suspended biomass was discussed in terms of their kinetic reactions and mass balances. The mass balances for both solute and biomass compounds was included in the biofilm model whose main framework referenced the [53], and proposed a modified version that defined the spatial concentration gradients for two chemical species (biomass and solutes) to calculate the variation of concentration in biofilm. The three-dimensional biofilm model could be employed in the rectangular area which was filled with the biofilm and other boundary layer region, and it was also applied to low-dimensional calculation like one- or two-dimension on basis of the requirement of computing time and details. To solve the equation, boundary conditions were proposed to ensure the integrity of calculation over time and space. Ismail and Habeeb [32] presented a pharmaceutical wastewater treatment based on a two-chamber MFC and modeled it with two-dimensional biofilm model in microscale. Assuming concentration of solutes and biomass varying over time and positon in biofilm, and gradient information was applied to the acetate mass balance equation to represent the concentration in biofilm region. Mardanpour et al. [31] introduced a model developed from Ref. [14] for microfluidic MFCs. The model utilized the quantification of bacteria transport to figure out the mechanism of biofilm formation instead of an assumption that the initial distribution of bacteria either on the electrode or the bulk liquid and explained how the bacteria accumulated to form a biofilm and proposed a principle of sensing molecules motion process. To represent the bacterial distribution in microfluidic MFCs, the mass balance for concentration of sensing molecules and suspended bacteria was derived. Considering the random motion and chemotaxis process of bacteria, a generalized Keller-Segel model ([54]) was also used to describe the attached bacteria accumulation as biofilm. Besides the mass balance for bacteria distribution, the thickness of biofilm was calculated by the attached bacteria growth as well as the thickness of inactivated bacteria and suspended bacteria, which was regarded as the affix on the electrode from environment.

Apart from modeling the anode biofilm, some models focused on cathode reactions especially the biofilm formation [18,38]. Experimental work validated that the electrons were accepted by cathode biofilm and such process affected the reaction of cathode [55]. Cathodic biofilm is a transition from an aerobic environment to an anaerobic environment. An one-dimensional transient model in Ref. [18] was established for an air-cathode single chamber MFC with the purpose of detecting the limitation factor in cathode chamber on the MFC performance. The model did not involve the variation of cathode biofilm thickness or the concentration distribution in biofilm region, but rather the reaction of oxygen consumption that partly occurred in biofilm, which was regarded as a complex region containing different microorganisms. Moreover, based on [14], the model for a reverse MFC of Kazemi et al. [38] took into account the biofilm formed in cathode and its thickness change. From the point of view of biofilm models mentioned above, it is concluded that most of work resembled the model of [14] and expanded the application occasion in the later work.

2.1.4. Special models

Apart from the model based on the fundamental reaction mechanism, some special factors were less mentioned in the literature and

were not considered as the main influencing elements in the system. Therefore, the models proposed in this section for influential variables emerged to a lesser extent in the previous literature. The classification for these elements is no longer based on the reacting regions or MFC's characteristic. They are summarized as another sub-model to provide another point of view at the models. However, more exhaustive models require the inclusion of more variables for MFCs to fully describe the system. Now we discuss some models involving special factors that affect the performance of MFCs and special modeling methods.

Actually, the pH has been considered as one of the significant influential factors on the performances of the MFC [56]. The value of pH determines the ambient conditions for bacteria survival and indirectly affect the overpotential thus influencing the MFC's performance [57]. The pH of anode chamber higher than neutrality leads to the optimal reacting conditions and the relevant range is given in Ref. [58]. Instead of considering anodic pH merely, the effect of pH in anode and cathode were separately investigated in Ref. [57], to figure out the optimal pH value of two chambers and obtain the maximum power density. It concluded that the alkaline pH 8 of anodic and acidic pH 2 of cathodic normally led to a maximum output. However, less model mention the pH influence and establish the effect of the pH variation. The vast majority models assumed that the pH of liquid in the reactor chamber is kept steady and ignored the effect of pH. While the model of Picioreanu et al. [41] developed from Ref. [15] characterized the added-mediator MFCs in different scales including pH calculation and investigated the effect of electrode geometry. The reaction occurred in anolyte was modeled at the macroscale aspect and a two-dimensional biofilm model was used at a microscale level. The biofilm model based on concentration gradient information was derived by the Individual-based Modeling Approach (IbM) in Ref. [53] to characterize the mass balance and surrounding environment of biofilm domain. Mass and charge balances both for solutes and biomass components were considered in the two systems: the single microbial consumed the substrate (acetate) and mixed microbial organism competitively consumed the substrate (from anaerobic sludge). The model established the water dissociation reaction as well as acid–base equilibria for other types of acid (carbonic, acetic, propionic and butyric acids) to calculate the pH distribution. It was noticeable that the modeling approach not only expanded the methodology both for experiments and modeling but also investigated the impact on electrode geometry to the MFCs. Similarly, regarding to effect of pH value on the biochemical reaction, the PerazaBaeza et al. [59] presented a mathematical model to predict the anode biofilm formation (based on [14]) and the influence of oscillatory of the pH. The model referenced the performance of LRC electrical circuit to regard the pH of anode chamber as an underdamping second-order oscillatory system, which changed over time. The model suggested that the consumption rate of substrate was related to the pH value thus obtaining the relationship between the rate and pH through the combination of Monod-type equation with bacterial concentration. In accordance with a function of pH, the model utilized the genetic algorithm to seek the best-fit parameters of model and the optimal pH value with corresponded substrate consumption rate. Additionally, Oliveira, et al. [29] established a model for a two-chamber MFC based on [16] with ignoring the biofilm growth due to the short computation time, added the heat conduction process model consisting of fundamental heat balance equations to the previous model. The model assumed that the heat generated from anode chamber, biofilm, anode electrode and cathode electrode was the overall heat of the MFC, which was equal to the sum of the heat losses from the transfer of the electrode to surrounding environment and the heat took away by the fuel flow in the reacting chambers. To calculate the heat in different species, the model also used the Fourier's law and Newtown's law to represent the heat of anode, cathode end plate, heat flux in cathode chamber and biofilm, related the heat to the temperature gradient in varied layer.

Based on the models successfully applied to other fuel cells, Yao, et al. [10] referenced to the agglomerate model, which was used to characterize the DMFC to studied the mass transport process of MFCs. The work revealed that the previous models only considered the single-phase reactions occurred in anode biofilm with the assumption of fix cathodic potential. The proposed mass transport model was established by the two-phase reactions that the proton transport and electrons transport occurred at the liquid phase and solid phase respectively. According to the combination of the proton and electron transport process, the current vector calculation equation was derived at liquid and solid phase. Moreover, the liquid and gas pressure gradient were also employed to establish the liquid saturation relationship and the mass conversation equation for these two phases. Explaining the electrochemical effect with relevant kinetics and balance equation, the model was applicable for describing the distribution of components of MFCs and revealing the transport mechanism of internal components possibly.

Oyetunde et al. [60] established a relatively simple model, which can be applied to carry out prediction with a comparatively rapid computing. The model aimed at reducing the complexity of the application without losing detailed illustration of mechanism, described the reactions occurred in multiple electrodes and defined the effect of different chemical or biological species on the consumption and production of the current. The loss factor model was used to calculate the activation overpotential around the electrode, which reduced the computational complication compared to the conventional calculation based on the Butler-Volmer equation. The biofilm was not considered as the variation of space anymore, while the biomass retention and solids retention time were applied to the biofilm description of MFCs. Through the definition of algebraic state variables, the temperature, the pH value, the substrate concentration and the hydraulic retention times were discussed in four areas of MFCs with using ordinary differential equations. The model also referenced by several general models used for other bioelectrochemical process, like the IWA ADM1 model, the generalized physical-chemical framework and the ASM2d-activated sludge model, considered the competition of different microbial population, which offered the favorable data fit ability.

2.2. Application-based model

As an energy supply device, an MFC are normally expected to output the maximum power density to achieve the effective utilization of energy. Although the mechanism-based models of MFCs are likely to optimize the operation conditions and configuration to improve the magnitude of power generation from basic principles, the long computation time and multidisciplinary complexity continuously limit the

Table 5
Summary of the Application-base modeling methods.

Method	Advantages	Disadvantages
Equivalent Circuit	Helpful to the application at electrical level	Dynamic process expression is not enough thorough
System Identification	The steps are determined and simple; Short computation time	Relatively poor accuracy and applicability
Intelligence Approach	Great accuracy of the model reflecting the relationship between the input and output variables; Less information of MFC's reacting principles is needed	Plenty of experimental samples are required; Complex procedure and long computation time;
State Space Equations	Basically coherent with the mechanism of MFC reaction; Relatively simple structure	Limited predictive ability and applicability

practical application occasions of these models. Hence, for actual engineering designers, some application-based models are proposed to satisfy the requirements of the shorter calculation time and specific application occasion. Several models based on the electrical characteristics of MFCs are described by an equivalent circuit model with basic electrical components [61–65]. Furthermore, there are some models developed from the perspective of several typical reactions and a number of experimental data of MFCs to acquire the best parameters and maximum output power through the optimization algorithm as well as machine learning approaches [20–22,40,66,67]. Learning and control aspects of the models are discussed here as well. Table 5 shows a brief summary of modeling methods for Application-based model.

2.2.1. Electrical model

There is no doubt that the most direct application of MFCs is as the power supply equipment, namely the source of electricity. For a battery, it is inevitable that the related output electrical parameters of the cell have to be evaluated and are consequently used to imply its practical implementation. In MFCs electrical models, the equivalent model of the circuit and the output power curve would be described by some classical electrical parameters of MFCs, such as current, voltage and internal resistance. Electrical models are able to simulate the variation trend of these relevant electrical parameters, against the actual MFCs electrical dynamic behavior. The dynamic characteristics of the MFCs output voltage and the current reflecting the corresponding internal biological and electrochemical reaction process are studied with several testing approaches. However, the features of time delay and cannot rapidly changing for these dynamic processes are capable of being explained with several electronic elements [68]. For example, the capacitor has the role of the charge store and discharge, which indicates that the voltage of capacitor does not change abruptly. The insistence denotes an impediment on the current flow and caused voltage drop [65]. The DC power source represents the ideal source supply denoting the theoretical voltage of the MFC. Therefore, the equivalent circuit model with electronic elements is likely to describe the characteristics of the MFC effectively. The conventional equivalent circuit model consists of series electronic elements, shown in Fig. 3 [69]. The V_{MFC} is the DC power, representing the direct energy supply. The C_{dl} denotes the capacitor which have the effect of the delayed electrons discharge/charge in an electrochemical cell namely double-layer capacitor. It corresponds to the bacteria aggregation, reaction and electrons transfer and other slow process, indicating that no abrupt voltage changes of the MFC. The R_{ohm} is the ohm loss, which is directly calculated by the ohm's law with current and resistance multiplied. The other resistances R_{act} and R_{con} stand for the activation loss and concentration loss, respectively. Two resistances connect the capacitor in a parallel way. All of the resistances constitute the internal resistance of an MFC and the capacitor represents the bacteria colony reaction process with charges produced. The components of equivalent circuit are capable of explaining the dynamic characteristics of an MFC at the electrical level. It provides another analytical method particularly aims at the application in electronic and electrical way. For example, to promote the output power magnitude of the MFCs to drive the practical electronic devices, some practical energy harvesting schemes and the studies of maximum power tracking for MFCs have been proposed [70]. The dynamic response and analysis obtained through the equivalent circuit are used to design the harvesting electrical circuit to achieve the improvement of power and system scale up, e.g. Refs. [71,72]. Table 6 is the summary of proposed equivalent circuits for MFCs.

To remedy the disadvantages of the conventional equivalent circuit simulating the behavior of the discharge in the double-layer capacitor, Park, et al. [65] introduced a circuit model which had advantages in expressing the dynamic characteristics particularly in electrons flow and the charge store in MFCs. Two resistors put in series were applied to represent the limitation of the transportation of electrons produced by bacteria and current flow into/out the double-layer capacitor, as the

input and output resistance respectively. Combined with the previous analysis of charge store and release behavior of the biofilm, the parallel capacitor was employed to imitate the corresponding electrons movement process. The short and open circuit test techniques were proposed to observe the dynamic change of current flowing and voltage crossing the circuit, and obtained the parameters of the model. From the result, the model was capable of presenting the store and flow of electrons in a reasonable way.

By identifying the limitation factors of MFCs power, the internal resistance influences the output performance of MFC to a large extent has been reported in the literature and the most direct impact is reflected in the ohm loss of MFCs [73,74]. To figure out the effect of internal resistance, electrochemical impedance spectroscopy (EIS) is a general and effective tool to measure the value of internal resistance of an MFC [75]. Some other approaches such as the current interruption and the polarization curve test are also used to determine the parameters of the equivalent circuit with resistance(R), capacitor(C), and constant phase elements to carry out the application of MFCs [76–78]. However, the material of electrode is one of the factors that determine the value of internal resistance. Hernández-Flores et al. [79] proposed a numerical relationship between the volumetric power of MFCs and specific surface area of anode, linked the anode region to the output power as well as internal resistance in a succinct expression based on Tafel equation. Through the experimental work on three types of anode materials (graphite rods, triangles of graphite and graphite flakes), the best-fit model's form and related parameters were figured out and also indicated that the increase of log of anode specific surface area leaded to reduce the value of internal resistance, but the volumetric power kept the opposite trend. It was noticeable that the model was firstly presented as a novel way to analyze the electrical performance of MFCs with anode surface area. Sindhuja et al. [61] established two equivalent circuit models for different materials of electrode for a two-chamber MFC. A lumped equivalent circuit model for activated charcoal electrode and fitting equivalent circuit model for graphite electrode were established both through the EIS measurement for cathode and anode respectively and the calculation of anode overpotential. The experiments validated that the activation overpotential played an important role in the reaction rate of an MFC with activated charcoal electrode but was ignored with graphite electrode. Yin et al. [62] modeled the MFC operating under static magnetic field (MF) that contributed to inducing several biological reactions in a microbial system [80]. It proved that the MFC had shorter start-up period when worked under MF, promoting the rate of electricity generation in anode as well. The EIS was used to investigate the electrochemical reaction of the MFC in the work and presented the equivalent circuit model of anode, cathode and entire system respectively. The result had insight into that the internal resistance of anode was higher than cathodic and the impact of MF did favor of reducing the charge transfer resistance of anode, thereby reducing the overall resistance of cell and activation loss and improving the voltage output. The work of Ha et al. [64] improved the defect of
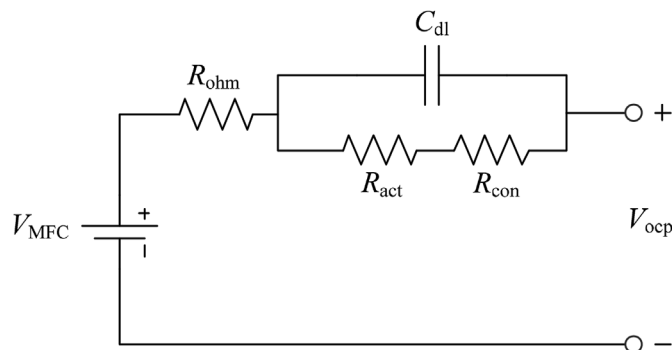

Fig. 3. Basic equivalent circuit model of an MFC.

Table 6
Summary of equivalent circuit for the MFC.

Reference	EC Characteristics	Application Objective
[63,69]	Basic form;	All MFCs
[65]	Advantages in simulating the electrons flow and charge store;	All MFCs
[61]	Two models for two kinds of electrode materials;	A lumped EC for activated charcoal electrode;
		A fitting EC for graphite electrode;
[62]	Connecting the anode and cathode model in series;	For anode, cathode, entire system respectively
[64]	Considering the effect of electrode's capacitor effect;	All MFCs

EIS using so that the fuel cell disconnect to a potentiostat during the measurement, which was a novel method to determine the value of charge transfer resistance and double-layer capacitor in MFCs. An equivalent circuit model was introduced through considering the effect in terms of the capacitor within an electrode. According to the expression between the current and voltage, the dynamic step response of anode could be analyzed and used to determine the parameters of model. Coronado et al. [63] conducted the experiment that the MFC connected to the Pulse Width Modulation external resistance (R-PMW), which meant that the value of external resistance could vary from different duty cycle of PWM. The existence of the fast and slow dynamic component of the MFC was obtained via the analysis of R-PWM experiment, thus utilizing the capacitor and resistance to establish the equivalent circuit model of the MFC. Although the electrochemical reactions were negligible in this model, it provided the dynamic behavior of relevant electrical performance. When the external resistance changed, the output variables of an MFC could be reflected by the dynamic characteristics of the capacitor. The experimental work also operated in different frequency of PWM and demonstrated that the output power of an MFC linking to the PWM resistance was increased compared with connecting to the constant resistance, when the frequency was higher than 100 Hz.
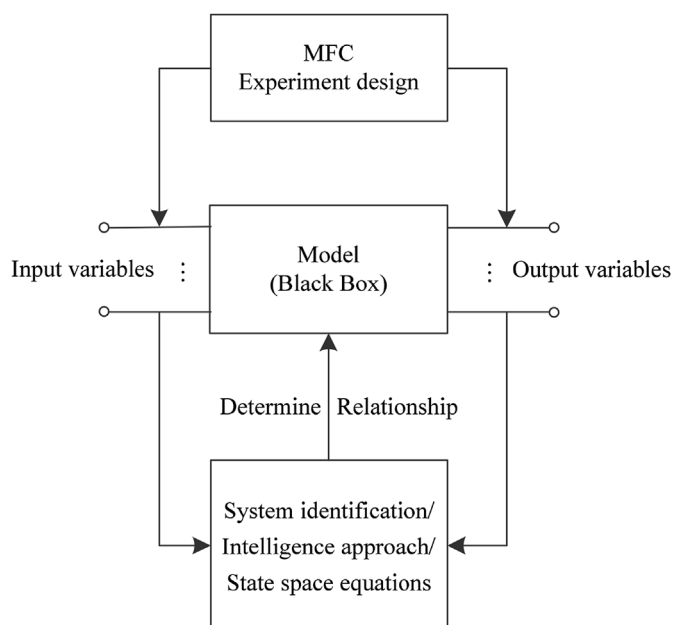
2.2.2. Learning and controlling model

It is generally known that the chemical, biological and electrical phenomenon occurred in MFCs complicate its understanding and application. The multidisciplinary knowledge is required for designers to explore the original limiting problems of system, which seems to be the obstruction for modeling development. However, apart from the model based on the mechanism of the system, the intelligent approach and modern control theory contribute to deriving the model with learning approach and unfolding the control strategy, so called the learning and controlling model. The learning models recognized as the black box are established without in-depth understanding of the MFC; instead, a large amount of experimental data plays an essential role in modeling. Several modeling approaches dedicate to enhancing the accuracy practically in terms of the predictive results and decrease the time consuming of the learning models. This type of nonparametric modeling methods reduces the complexity of modeling but emphasizes the importance of learning sample and methods. So, the derived models are different due to the acquisition methods of experimental data and learning process. Moreover, the controlling models are slightly different that a few significant reactions are considered in the model. Although the established model resembles the mechanism-based one, the different purpose of which makes two categories differentiate, and the model was provided with the feasibility of controlling strategy application to control the related variables. These models create another way for designers to maximum the MFCs output and help some researchers who own more experience of electrical controlling application rather than bio-electrochemical knowledge to configure the MFCs, which contributes to improving the development of MFCs application. Fig. 4

presents the normal modeling process for learning and controlling models.

In fact, MFCs have the slow dynamics characteristic due to much electrochemical and biochemical reactions occurred in system, which requires a long period to acquire the experimental data. Therefore, to satisfy the requirement of a great many of data, the experiment design (ED) approach has been proposed in the literature to shorten the time of the experiment. Fang et al. [20] developed a modeling method aimed to optimize the power generation of MFCs with multivariable. The experiment was performed by the uniform design (UD) approach which determined four input variables (the ionic strength, initial pH, nitrogen concentration, temperature) in five levels and regarded the power density and coulombic efficiency as output variables. The model adopted relevance vector machine (RVM) approach of machine learning to acquire a mathematical model between the input and output variables through the result from sixteen experiments. To speed up the rate of optimization of model's parameters, accelerating genetic algorithm was selected in the entire procedure to seek the maximum power density and coulombic efficiency as well as optimal reaction conditions. The model also contrasted to another model conducted by the approach of support vector machine (SVM). The predictive results of model validated the better efficiency and accuracy of proposed model with RVM. Another experimental design approach: the response surface design methodology (RSM), which was also employed to design the experiment of MFCs in Martínez-Conesa et al. [66]. The work of [66] introduced a Box-Behnken design approach (one of RSM) to optimize the operating temperature, external resistance, the concentration of feed fuel and the pH in anode chamber for a two-chamber MFC, maximize output power density simultaneously. The experiment was designed by the Box-Behnken matrix, classified the four influential elements into three levels on basis of their value and determined the maximum and minimum value for every element. The results from 28 times experiments derived a reasonable quadratic mathematical model for an MFC by RSM approach and meanwhile the output power density achieved the maximum.

When the input and output variables are confirmed, system identification approach is of efficiency to elucidate the relationship between the input and output time function and models the nonlinear characteristics of MFCs. Boghani et al. [81] utilized this approach to set a series of linear models and piecewise linearized the system over the whole load operation wide. The electrical load was considered as the

Fig. 4. The modeling process of learning and controlling models.

input variable that caused the variation of the output voltage namely output variable. The author altered the loads of various pseudo-random and input the step signal to test the voltage of the MFC and acquire the experimental data. A first order generic model was established as the process model, which was applicable with piecewise using, and a fourth order Autoregressive with extra inputs (ARX) model was proposed to characterize the system appropriately as well. It is noticeable that the fourth order ARX model offer a better data fit ability especially while the load working near the maximum power point, nevertheless, the low order models were considered representing the system enough. The model that developed from the system identification approach do favor of applying the controlling strategy in MFCs, controllers configured through the system transfer function are capable of optimizing and controlling the output of MFCs. For instance, Boghani, et al. [82] employed the transfer function of the MFC and design the controller by the gain scheduled method to control the output voltage keep constant, conducing to promoting the disturbance rejection of MFCs application.

To improve the shortcoming of mechanism-based model that has long computational time, He and Ma [21] proposed a model based on data-driven Gaussian Process Regression (GPR) for a two-chamber MFC. The GPR model is a non-parametric modeling approach to represent the nonlinear characters of a complicated system based on data-driven modeling which merely required less information of the reaction process but plenty of experimental dataset. The concentration of substrate, anodic feed rate and current density were applied as the input variables while the voltage as the output variable in the model. The experimental design approach was used above all to obtain a series of experiment data as the initial sample. After that, the training procedure was called to update the model and diminish the predictive error. The result of experiment revealed that if appropriate experimental data was selected as the training sample, the model was able to offer the great prediction capacity under the off-line mode. Moreover, under the on-line mode, the model made the judgement between the prediction error generated on each new input and the preset threshold, to decide whether the new input variable was added to the training sample to update the model or not. Hence, it was possible to reduce the amount of initial learning sample apparently and improved the accuracy and reliability of model. The artificial neural network (ANN) is another approach to model the performance characteristics of the MFC. Four input factors (ionic strength, initial pH, medium nitrogen concentration, and temperature) were considered as the more essential influential variables with five levels for each one in Esfandyari et al. [67], indicating that four neurons were selected in the input layer and the power density and coulomb efficiency were in the output layer as the output variables of ANN. There was only one hidden layer in the back-propagation ANN which was trained by the Levenberg Marquardt algorithm. Furthermore, the advanced modeling approach based on ANN namely the adaptive neuro-fuzzy inference system (ANFIS) was also adopted to investigate the performance of MFCs. The hybrid intelligence inference system consisting of fuzzy inference system and ANN was used in the modeling process emphasizing the adaptability of the model. The ANFIS employed the accelerate algorithm in terms of the combination of gradient descent and the least-squares method to improve the speed compared with the back-propagation of ANN. The validation experiment illustrated the correctness and predictability of both the ANN and ANFIS model, but the ANN was provided with the simpler structure and training procedure. Whereas the Garg et al. [83] compared the modeling performance of ANN with the multi-gene genetic programming (MGGP) and support vector regression (SVR). Less input variables are selected in the procedure, i.e. the temperature and ferrous sulfate concentrations. The effect of these input influential factors on output voltage was discussed during the before and after star-up period of an MFC. Evaluated the correlation coefficient of three approaches verification experiments, the superiority of MGGP method offering better generalization ability and less computing time among three methods was described and ANN was validated that had better performance than

the SVM method. Accordingly, the feasibility of predicting and maximizing voltage of the MFC under the off-line mode was proposed with regulating the input variables.

Besides the intelligent approach to determine the parameters of models, the state estimation method was introduced with state space model in control theory as well. Basic form of state equation is shown as (2).

$$\dot{x} = Ax + B \tag{2}$$

where x stands the state vector variable, $\dot{x}$ is the derivative of the variable. A and B represent the matrices of coefficients. The main influential variables are determined as the state variables with their reaction equations. Generally, different kinds of components' concentration are selected as the variables, because the mass balance equations have the similar form and function to describe such dynamic process.

A control-oriented model based on state space equations of an MFC was presented in Ref. [22]. The state space model for the MFC set the substrate concentration, biomass concentration, hydrogen ion concentration and bicarbonate ion concentration as the state variables, and combined the mass balances and voltage equation to establish the state space equations of an MFC. It was worth noting that this approach offered an alternative way to deduce the model, applying the state estimation method (e.g. Kalman filter) to observing the parameters and other optimization control strategy to the on-line mode. However, the biofilm formation, pH, temperature and other influential factors of system were overlooked in the model. Therefore, more equations could be considered to elaborate the MFC's reaction process and modeled it. In view of the more complexity of the MFC model, the more difficult it is for the process controlling and the parameter estimation, the model of Recio-Garrido et al. [40] aimed to propose a model which could be applied to both the fast calculation process and the slow dynamic simulation. The model combined the previous model which mentioned competitive substrate consumption in different microbial population [25] and the equivalent circuit model [61] into a bioelectrochemical-electrical model. From the existed empirical formula, the work also took into account the effect of double-layer capacitor and introduced a control-oriented model. Selecting the voltage and concentration of substrate as the output variables, the proposed model might be applied both to on-line mode and off-line mode. With measuring the voltage of MFC, when the model operated in on-line mode some electrical parameters were assessed and used to predict relevant variables, while the off-line mode required all the parameters knowing in order to have a good predictive capacity.

3. Conclusions

In this paper, different models of MFCs have been carefully analyzed. These models contribute to the detection of various limiting factors of MFCs and offer further guidance to promote the performance of MFCs. The discussed models are divided into two groups. The Mechanism-based models based on the reactions of system are categorized into several sub-models completed on a basis of the normal modeling domains. The taxonomy is based on a thorough analysis; different electrons transfer mechanisms and the requirement of modeling emphasis lead to the difference among the Mechanism-based models. The apparent disadvantages of such models are the long computation time and a tedious and demanding parameter estimation procedure. However, with further developments of biochemical, electrochemical and related disciplines, further deeper insights into reactions and more detailed models could be developed. Moreover, high-performance computing such as the multi-core processor and parallel programming also contribute to addressing the problems of long computing time and help accelerate online optimization of models. For Application-based model, the existing electrical models have been (to some extent) successfully applied to practical circuit designs. The form of equivalent circuit model has been basically determined and was

comparatively less likely to be improved, while the accuracy of learning and controlling model remains requiring continuous advancement. The machine learning, data-driven and advanced Computational Intelligence techniques have been dedicated to the investigation and modeling for MFCs. We may envision that further involvement of Artificial Intelligence in this style of modeling could offer further progress and widen application areas.

Acknowledgements

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