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PII: S1385-8947(15)00285-5
DOI: http://dx.doi.org/10.1016/j.cej.2015.02.076
Reference: CEJ 13329

To appear in: *Chemical Engineering Journal*

Received Date: 22 October 2014
Revised Date: 6 February 2015
Accepted Date: 10 February 2015

Please cite this article as: V.M. Ortiz-Martínez, M.J. Salar-García, A.P. de los Ríos, F.J. Hernández-Fernández, J.A. Egea, L.J. Lozano, Developments in Microbial Fuel Cell Modeling, *Chemical Engineering Journal* (2015), doi: http://dx.doi.org/10.1016/j.cej.2015.02.076

DEVELOPMENTS IN MICROBIAL FUEL CELL MODELING

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ABSTRACT:

Microbial Fuel Cells (MFCs) offer promising prospects in the field of renewable energy since green electrical power is produced by the microbial activity and wastewater is treated simultaneously. MFCs are complex devices whose study requires an interdisciplinary approach as many processes of a diverse nature are involved. Interest in MFC has significantly increased in recent decades, and much scientific effort has been dedicated to making this technology more efficient. However, the focus has been on experimental work, and MFC modeling has tended to be neglected, and only recently has it received more attention with a consequent rise in the number of new MFC models available. Modeling is an effective tool for gaining a better understanding of MFCs, since it has many advantages in terms of cost and time savings. The present article looks at the state of modeling and simulation of MFCs and outlines and classifies the most prominent models described in the literature. Since modeling approaches can vary greatly from case to case, this work will summarize the advantages and drawbacks of each approach, including not only models based on classic approaches but also those using mathematical optimization techniques.

Keywords: Microbial Fuel Cell, Renewable Energy Sources, Modeling, Simulation, Optimization.

1. INTRODUCTION.

Microbial Fuel Cells (hereafter MFCs) are devices in which a substrate is degraded and electrons are released by the action of microbes. The oxidation of organic matter takes place in the anode, and if the electrons are led to the cathode through an external circuit, a voltage drop and an electrical current are produced [1], thus transforming chemical energy into electrical power. In addition, if wastewater is used as fuel, the benefits are twofold: water purification and electricity production [2, 3]. However, the large-scale application of this technology has been unfeasible to date since the power densities reached are still low and the material and design costs are too high [4]. MFC research tries to make this technology technically and economically viable, but while most of the work described in the literature are based on experimental work [5], MFC modeling has been left behind. It is only in the two last decades that interest has grown in focusing research effort on MFC modeling and simulation.

The phenomena that take place in a MFC are complex as many biological, physical-chemical and electro-chemical processes are involved [6]. Figure 1 shows a typical configuration of a two-chamber MFC. Both MFC configurations and the range of materials used in MFC set-ups have evolved considerably. For instance, in the late 1990s, a series of discoveries showed that certain bacteria could be used directly to produce electricity in fuel cells and thus early studies (e.g. [7]) included a chemical or redox mediator to allow the transfer of electrons from the anode to the cathode, while in more recent works (e.g. [8]), it is omitted and the transfer mechanism occurs through the action of electroactive microbes. Modeling is a powerful tool for the in-depth study and optimization of MFCs. A model is basically aimed at describing MFC performance based on certain

laws and equations. The complexity of any model depends on different factors such as the dimension selected, the assumptions made and the level of detail used in describing the processes involved. Study of the phenomena that take place in an MFC covers a wide range of processes, from mass transport through the cell, the phases of matter considered and the boundary conditions, to microbial growth, the anode and cathode reaction kinetics and the electrochemical behavior of the system. The robustness of a model will be judged by its predictive capacity and the balance between the computation time needed and the precision of the results [9].

[INSERT FIGURE 1]

Modeling efforts have also been directed to fields related with MFCs. Biofilm growth has a critical role in these devices and other engineering applications and scientific research has focused on modeling its behavior to make predictions. Biofilm models have evolved in recent years from using simple to following complex approaches, such as multi-species, multi-dimensional or multi-scale models. Wang et al. [10] classified such models into four classes: low-dimensional continuum models [11], diffusion limited aggregation models [12], continuum-discrete models [13] and fully coupled biofilm-fluid models [14]. Also in the field of fuel cells, scientific effort has been devoted to modeling these devices. Such models are key factors for optimizing their design and performance. For instance, in the case of direct methanol fuel cells (DMFC), analytical [15, 16], semi-empirical [17, 18] and mechanistic models [19, 20] have been developed describing the main phenomena that take place in these systems. In the case of direct ethanol fuel cells (DEFC), these modeling studies are still in their initial steps: Although there are zero [21], one [22, 23], two [24, 25] and three [26] dimensional models, most of them are not able to describe these systems as a whole, and do not consider all the main components that affect the process, meaning that they cannot predict their real behavior. Other fuel cells are solid oxide fuel cells (SOFC) whose

advantages, such as the possibility to operate at high temperatures, long lifetimes, and insensitivity to several contaminants make them interesting power systems to be modeled. In recent years, significant progress has been made in developing new models based on this type of cells [27].

In this work, MFCs models in the literature have been classified into two main groups according to the approach followed by the authors in each case: (a) global models, whose purpose is to study the overall behavior of MFCs from a comprehensive point of view and (b) specific models for the study of key components, processes or variables in MFCs. Most of the models in the literature fall into the first group and can be further subdivided depending on the limiting factor of the system considered. Several of the most recent MFC models are based on previous works or are an extension of them. Figure 2 shows the classification of the MFC models that will be discussed in the following sections.

[INSERT FIGURE 2]

Table I presents the most widely used equations and laws, and their applications in MFC models, for describing the phenomena that occur in MFCs. The use of a given equation depends on the configuration as well as the chemical species involved.

Name	Equation	Applications in MFC models
Monod equation	$\mu = \mu_{max}\frac{S}{K_s + S}$ μ: specific growth rate of the microorganisms; μ_{max}: maximum specific growth rate of the microorganisms; S: concentration of the limiting substrate for growth; Ks: value of S when $\mu/\mu_{max} = 0.5$.	• Describe substrate oxidation and microorganism growth (anode). • Adapted to oxygen reduction reaction (cathode). • Combined with Nernst equation to describe bacterial metabolism in response to electron release or electrical potential.
Tafel equation	$E - E_{eq} = \frac{RT}{(1-\alpha)nF}.ln\frac{i}{i_0}$ E: electrode potential; E_{eq}: equilibrium potential; i: current density; i_0: exchange current density; T: temperature; n: number of electros involved in the electrode reaction; F: Faraday constant; R: universal gas constant; α: charge transfer coefficient.	• Combined with Monod equations to describe anode reaction kinetics. • Describe cathode kinetics.

Bulter-Volmer equation	$i = i_0 exp\left[\frac{(1-\alpha)nF}{RT}\left(E - E_{eq}\right)\right] - i_0 exp\left[-\frac{\alpha nF}{RT}\left(E - E_{eq}\right)\right]$ i: current density; i_0: exchange current density; E: electrode potential; E_{eq}: equilibrium potential; T: temperature; n: number of electrons involved in the electrode reaction; F: Faraday constant; R:universal gas constant; α: charge transfer coefficient.	• Calculate current density from oxidation reactions (anode). • Combined with Monod equation to describe electrochemical anode and/or cathode reactions.
Nernst equation	$E = E^0 - \frac{RT}{nF}\ln(Q)$ E: electrode potential under non-standard conditions; E^o: standard electrode potential; R: universal gas constant; T: temperature; n: number of electrons involved in the electrode reaction; F: Faraday constant; Q: reaction quotient (Example: aA + bB → cC + dD, then Q= $[C]^c[D]^d[A]^{-a}[B]^{-b}$).	• Description of electrochemical behavior. Combined with Monod equation to describe electrochemical anode and/or cathode reactions. • Focus on extra-cellular activity.
Nernst-Planck equation	$\frac{\partial c}{\partial t} = \nabla \cdot \left[D\nabla c - uc + \frac{Dze}{k_B T} c(\nabla\Phi + \frac{\partial A}{\partial t}\right]$ t: time; D: diffusivity of chemical species; c: concentration of the chemical species; *u*: velocity of the fluid; z: valence of ionic species; e: elementary charge; k_B: Boltzmann constant; T: temperature; A: magnetic vector potential; Φ: potential	• Describe mass, momentum and charge balances for ion fluxes. • Describe ion transport across the MFC separator (membrane).
Fick's first law	$j = -D \cdot \frac{\partial \varphi}{\partial X}$ (*) $\quad j = -D \cdot \nabla c$ (**) j: diffusion flux; D: diffusion coefficient or diffusivity; c: concentration; φ: concentration; x: position; *one-dimension, **two or more dimensions.	• Calculate gradient concentrations for chemical species (anode).
Fick's second law	$\frac{\partial \varphi}{\partial t} = D\frac{\partial^2 \varphi}{\partial x^2}$ φ: concentration; t: time; D: diffusion coefficient or diffusivity; x: position.	• Calculate gradient concentrations for chemical species (cathode).
Ohm's law	$V = IR$ V: potential difference; I: current intensity; R: resistance value.	• Calculate cell output voltage and current.

Table I. Most commonly used equations and laws in MFC modeling.

2. MICROBIAL FUEL CELL MODELS.

2.1. Comprehensive models.

This section includes those works which model the performance of MFCs by covering all the crucial processes, according to the criteria, established by the authors, which determine and explain the overall performance of MFCs. Two tendencies are identifiable in the literature: models based on the anode chamber (considered as the limiting factor of the system) and models comprising both anode and cathode.

2.1.1. Anode-based models.

Those models that consider the anode as the limiting factor of an MFC are rooted in the principle that, theoretically, all the protons and electrons generated at the anode are consumed in the oxygen reduction reaction at the cathode. According to this assumption, the energy output of an MFC depends entirely on the anode activity.

The first model in the literature belongs to Zhang and Halme [7], a one-dimensional model based on a double-chamber configuration extended to three cathodes in parallel and three respective separators operating in batch mode (V_{anode}=30 ml). The organic matter source consists of fermented sediment marine with a buffer solution in both chambers. A chemical mediator, HNQ (2-hydroxy-1,4-naphtboquinone), is added to the anode. When substrate oxidation takes places, the electrons are released and captured by the chemical mediator, which is reduced to $HNQH_2$. The mediator transfers the electrons to the anode and returns to its original form. For the sake of simplicity, several assumptions are made - which is also very common in later models. For example, all mass transfer processes in the anode and cathode (diffusion of species exclusive to each compartment, proton transport through the separator or diffusion of the oxygen in the cathode solution) are sufficiently fast with respect to the biochemical and redox reactions for the concentration to be considered uniform for all the species [43].

The main equations used in the model are (a) mass balance for the substrate oxidation and the chemical redox reactions of the chemical mediator in the anode, including the Monod equations (b) equation for calculating the current produced in the cell by Faraday's law and (c) electrochemical behavior modeled by the Nernst's equation. In order to validate the model, both experimental and simulated current output values are compared under different loading conditions (40 and 400 Ω), obtaining very good agreement. Simulated and experimental data follow the same trend (≈10 mA and ≈1.65 mA for respective loading conditions). Once validated, the work focuses on the study of the relationship between the current produced and the main variables of the process: chemical

reactor concentration (from 3 to 20 mM) and initial substrate concentration (from 3.89 to 11.11 mM). The high cost and toxicity of the chemical reactor means that its use needs to be optimized (≈6 mM). As regards the substrate concentration, although similar current values are obtained for all concentrations (≈9 mA), the current output sharply decreases after 16 h for the lowest values. This first MFC model can be regarded as a start point in MFC modeling, but the number of variables and processes covered are limited and the approach is very simple as compared with later, more advanced works.

In 2007, Picioreanu et al. [28] presented a far more complex approach that included two and three-dimensional simulations. Their model focused on the anode microbial activity to understand the performance of mediator-based MFCs. In a further step, Picioreanu et al. [29] completed this model with the IWA Anaerobic Digestion Model N^{o} 1 (ADM1) [44], which allows the steady state behavior of anaerobic semi-continuous digesters to be simulated. In this way, the competition between methanogenic and anodophilic bacteria was included in the model.

[INSERT FIGURE 3]

The first model presented by Picioreanu et al. [28] described the performance of the anode chamber (bulk liquid volume $2.5 \cdot 10^{-4}$ m^3) in a double-chamber MFC that uses acetate as substrate and the bacteria *G. sulfurreducens*, with the system operating in batch mode. The model mainly consists of an electrochemical sub-model and a biofilm growth sub-model. Figure 3 illustrates the basis for this approach. Within the electrochemical sub-model, Butler-Volmer is used to calculate the current density in the electrochemical mediator oxidation, taking into account the concentration of the species involved on the electrode surface. Current density at the electrode is obtained by integrating local current density over the electrode surface. The voltage output is obtained by balancing the cell

equilibrium potential (E_{cell}) with voltage losses (polarization and overpotential losses) and combining them by means of Ohm's law. The biofilm sub-model includes the kinetics of the oxidation reaction of the substrate (Monod equation), biofilm growth and respective mass balances in the state phases considered for bulk liquid and biofilm, which is dominated by molecular diffusion. The anode reaction is given by:

$$aC_2H_3O_2^- + fM + bNH_4^+ + dH_2O \rightarrow 1CH_{1.8}O_{0.5}N_{0.2} + f\,MH_2 + eHCO_3^- + cH^+ \quad (1)$$

This reaction involves acetate, the chemical mediator species (M is the oxidized form, MH_2 the reduced form) and biomass (typically formulated by $CH_{1.8}O_{0.5}N_{0.2}$), among other compounds. The biomass can bound to the biofilm or be in suspension. Given its importance, this sub-model also introduces the pH variable (calculated by local charge balance) since, if protons accumulate at the anode, the consequent acidification may severely affect the overall yield of the MFC.

For model assessment, experimental and simulated data are compared for a given case using the above mentioned configuration. The system is set up with an initial inoculum with an acetate concentration of 1 mM, followed by two pulses of acetate of the same concentration after 4 and 5 days. For the current output, the model shows good correlation between experimental and simulated data until the second pulse, after which the deviation is more pronounced, although still acceptable (for the charge generated, Q, the correlation is even suitable after 5 days). After 5 days, the thickness of the biofilm is such that it limits the diffusion of the mediator species. When simulating another set of experimental data from a different case with an initial acetate concentration of 2 mM and two media replacements (acetate 0.5 and 1 mM) that involve removing the growth medium and replacing it with anaerobic medium, the discrepancy between the experimental and simulated data is greater probably due to the mechanism assumed for the electron transfer based on a redox mediator

(rather than direct transfer to the anode by the bacteria). This mechanism is better explained by conduction-based models [30-33] and, in this respect, the model poses some limitations.

The results obtained for a standard case first offer a one-dimensional analysis (over time) of the operating variables (current output, biofilm growth, biomass in suspension, substrate concentration, electrochemical mediator, among others). From this analysis, it can be seen that the current output reaches its maximum value for the highest substrate oxidation rate and decreases after 8 days, coinciding with the maximum biofilm thickness (≈15 μm). In a further step, two and three-dimensional simulations of the biofilm growth (over the electrode surface) are carried out. These simulations make it possible to study the biofilm formation over the anode dynamically, and it can be seen that local current density increases at those points where the electrochemically active bacteria are present. Other key factors are studied, such as the competition between suspended and biofilm cells and the effect of the internal and external resistance on MFC performance (low values of external resistance ensure optimal cell performance). Finally, it should be noted that the model is built in a flexible way, making it adaptable to other bacteria species.

Picioreanu et al. [29] completed their own model with the integration of the IWA Anaerobic Digestion Biochemical Model (ADM1) [44]. This work is aimed at shedding light on the competition between anodophilic and methanogenic bacteria, due the important role that both species play in MFCs. Anodophilic bacteria degrade the organic matter by releasing protons and electrons that favor the energy output, whilst methanogenic bacteria degrade the organic matter by producing methane, which is detrimental to the overall efficiency of the cell. Again, the results show that low external resistance values boost the growth of anodophilic bacteria rather than methanogenic bacteria, improving the current output obtained. Compared with the former model, this model studies the biological performance of the cell in a deeper and more complete way and broadens the range of phenomena in MFCs that can be included. In a final step, Picioreanu et al.

[30] proposed an extended model with a twofold macro and micro perspective: an overall mass balance (macro) for the bulk liquid anolyte, and mass, charge and momentum balances for ion fluxes and charges using the Nernst-Planck equation (micro) for the biofilm. The model includes mass transport by convection, leading to a more realistic approach. The pH value is also considered as a key factor, being estimated over the geometry of the cell and regarded as the limiting factor of the system (acidification). The model is applied to the study of three cases in which acetate is used as pure fuel, focusing on pH influence, competition between electroactive species and methanogenic and fermentative bacteria, and mass and charge transport in electrodes for different geometries in the biofilm domain, respectively.

In the first case, the effect of anolyte buffering (CO_2/HCO_3^-) is analyzed in a range of concentrations (from 2 mM to 100 mM) in terms of proton transfer rates through the membrane, pH value in the cell and output current. If the proton transfer rate to the cathode is low, the oxidation of acetate (1.65 mM) releases H^+ that can accumulate and produce the acidification of the anode, with consequent adverse effects on the current obtained. Relatively high concentrations of buffering solution (≈100 mM) are needed to maintain the pH at around 7. Two-dimensional spatial distributions are obtained for ionic current (locally up to 1 $A.m^{-2}$), solution potential, pH, diffusion, electromigration and convection fluxes for H^+. Case 2 involves the use of a complex substrate (wastewater) that contains a heterogeneous microbial community in order to model the competition between electroactive and non-electroactive bacteria. When the substrate is depleted, pH decreases and methanogens microbes transform the H_2 obtained into CH_4. Although this type of substrate is closer to real scenarios, the major limitation lies in the determination of realistic parameters to fit the model. The work also lacks an accurate comparison between experimental and simulated data. Finally, case 3 is dedicated to compare the influence of a porous electrode (porosity of ε=0.6) *vs.* a homogenous electrode on the MFC performance. Although higher porosity means that there is more surface available for biomass attachment, the results show that this increase in the area of the

electrode does not necessarily implies more biomass and current output (provided that convention through the pores does not exist) if other factors are not changed at the same time (influent flow, energy input, anode arrangement, etc.).

Marcus et al. [8] proposed a significant one-dimensional and dynamic conduction-based model. In this case, the electrons are transferred directly from substrate to anode - through the biofilm - by the action of electroactive microorganisms such as *G. sulfurreducens* bacteria [45]. The model describes electron transfer based on both electron donor oxidation and endogenous respiration. This biofilm, which grows over the anode surface, has a conductive zone and an inactive zone. The model is built with: (a) electron production rate, which is related to substrate degradation rate through a combination of the Monod and Nernst equations, (b) mass balances that embrace the diffusion phenomena of the active zone of the substrate, the inactive zone of the biomass and the flow of electrons, (c) Ohm's law to calculate the current density and (d) the minimum local potential to maintain the biofilm steady. With this model, the biofilm can be characterized as a biological conductor, which is defined by a k_{bio} parameter-matrix, whose maximum value is estimated. The main finding is that the conductivity of the biofilm is one of the major limiting factors of the system. The model of Marcus et al. [8] can be considered of great interest for its contribution to the understanding of the electron transfer mechanism, since this factor is directly related to the energy output. It allows its value to be analyzed depending on parameters such as the concentration of the substrate, local potential values, biofilm conductivity and the concentration gradient of the species involved in the process.

The results from a simulation analysis (for 250 and 400 days) offer the possibility to study biofilm thickness, current density, electro-donor flux, current flux and Coulombic yield (for a V_{anode} =0.5 V). The variation of the anode voltage is also studied (from 0.1 to 1 V). When the anode voltage increases, a thicker biofilm is obtained (with a consequent fall in the current). With a biofilm

conductivity of 10^{-4} mS.cm^{-1}, current density increases until the biofilm thickness is around 12 mm (max. 1.24 A.m^{-2}). With the removal of inert biomass, the current intensity can reach higher values (up to 1.92 A.m^{-2}). The most interesting conclusions are related to the effects of the dual limitation posed by biofilm thickness and inert biomass, which must be alleviated. The work does not offer an accurate comparison between experimental and simulated data, although the data follow the trends observed by other works [46].

Both Marcus [8] and Picioreanu et al.'s works [28-30] are key studies for understanding how the anode performs in MFCs, which, in turn, is crucial for obtaining high power yields, and can be regarded as valuable complementary contributions to experimental lab-work. Microbial activity is regarded the engine of MFCs and, therefore, one of the most important factors in this technology. The models of these authors consider that the anode is the limiting factor in the whole system, although this is questioned by other models (see section 2.1.2). Comparing both models, Marcus et al. [8] do not account for the pH value across the biofilm as Picioreanu et al. [30] do, so their model is incomplete as this regard, and, as explained above, the pH can play a critical role in MFC performance. In addition, Picioreanu et al. [30] carry out a more complex multi-dimensional analysis (spatial distribution over time) of some operating variables that help better understand MFC technology (micro-scale perspective).

Other models in the literature have been developed based on previously published work. This is the case of the following two models. Merkey and Chopp [31] created a two-dimensional model to explain the relationship between the power output and some operating parameters, especially the geometry of the cell. Based on Marcus et al.'s biofilm approach [8], the model considers three regions in the anode to be modeled - bulk liquid, solid electrode and biofilm with conductivity defined by the matrix parameter k_{bio}. The inclusion of the liquid-biofilm and biofilm-solid interfaces adds complexity to the model. Both interfaces are affected by the growth rate of the biofilm and the

erosion of the anode caused by biomass diffusion to the liquid solution. From a mathematical point of view, this is one of the most complete works in the MCF modeling field. Among other purposes, the model is simulated to find out the optimal number of bristle anodes, the way they must be placed in a grid and how these two aspects affect biofilm growth and energy output. The model is validated by comparing the simulated data for current output with previously reported data [46], which runs an MFC for 7 days with substrate replacement (acetate with an inoculum of *G. sulfurreducens*) after days 4 and 5. The current production yield (maximum of 2.25 mA) closely fits experimental data, supporting the suitability of this conduction-based biofilm model.

Regarding the results, the work first studies the effect of the number of anodes (from 1 to 6 single anodes with total surface area constant) around which biofilm grows (2D) with a constant total anode surface. The spatial distribution of the biofilm shows how the total biofilm colony (thickness of ≈200 μm) is formed (in 30 days) by the biofilm colonies growing around the single anodes. Non-significant differences are observed in terms of output current, which is favored by the total anode surface available and the biofilm conductivity. The same conclusions are valid for the spatial position of the single anodes, which is also simulated. For wider spacing arrangement and when biofilm starts to grow, a higher current value is obtained as acetate can easily diffuse into the biofilm layer. But for longer periods, current production follows a similar trend in all cases. Other parameters such as the flow speed are analyzed, with a balance being found between nutrient inflow and erosion of the biofilm layer (caused by the flow speed). These results represent the highlights of this model, whose complexity and detailed approach allows precise geometrical parameters to be studied in order to improve the MFC yield.

Sedaqatvand et al. [32] published an extended version of Marcus et al.'s [8] model combined with a Genetic Algorithm for an annular single-chamber MFC. With the integration of this algorithm, the authors sought to minimize the difference between simulated and experimental data, which is the

objective function, through the calculation of some model parameters related to biofilm conductivity or cell potential. As mentioned above, most of the modeling approach (kinetics of anode reaction, potential equation, biofilm conductivity defined by the matrix parameter k_{bio}, mass balance and biofilm growth) is mainly based on Marcus et al.'s work [8]. The model is adapted to simulate a single-chamber MFC operating in batch mode with daily replacements of wastewater corresponding to one third of the anode volume (1 mg COD.cm^{-3}) and with mixed microbial community (active and inert biomass). Experimental data for an external resistance load of 100 Ω, as well as data from the literature, are used to estimate parameters of the MFC system. Three unknown parameters are selected as best-fit parameters ($X_{bio,a}$ or active bacteria density, mg.VS^{-1}.cm^{-3}, k_{bio} or biofilm conductivity, mS.cm^{-1}, and E_{KEA} or half maximum rate potential, V) and calculated by Genetic Algorithm. This algorithm calculates the optimal point for an objective function in a randomly created populated generation and evolves toward better solutions by searching in new generations based on techniques inspired by natural evolution. A final model fitting is carried out comparing experimental data with simulations for the current output within a time horizon of 3 days. The great discrepancy shown for the interval from ≈0 to 1 days can be explained by the initial biofilm thickness and the microbial distribution predicted by the model, as it has non-linear nature. These differences are corrected by a trial and error procedure. As seen, different fitting steps and methods are needed before the model can be validated.

The parameter k_{bio}, which plays an important role in the model, is estimated at $8.76 \cdot 10^{-4}$ mS.cm^{-1}. For biofilms based on *G. sulfurreducens* a conductivity of at least 0.5 mS.cm^{-1} has been reported [47]. Low biofilm conductivity is typical of extracellular polymeric substances (EPS). This fact allows the authors conclude that the nature of the biofilm may be dominated by this kind of compounds.

Finally, the model is used to study the MFC system under consideration by plotting profiles of wastewater concentration and electrical potential across the biofilm layer for a substrate

concentration of 1 mgCOD.cm^{-3} and an external resistance value of 50 Ω (dimensionless profiles). A sharp fall in the potential can be observed as the distance from the anode increases (from 0.04 to -0.05 at 0.2 across the biofilm, dimensionless variables). Wastewater concentration also follows a downward trend as the distance from the biofilm/bulk-liquid interface increases, which explains the high contribution (≈ 99.8 %) of the concentration of the boundary layer to the mass transfer resistance. As in Marcus et al [8], the work concludes that biofilm growth is due to active and inactive biomass, and the total thickness make more difficult the diffusion of the substrate into the biofilm layer as it increases. From the polarization curve (power density *vs.* current density) a maximum value of ≈0.22 W.m^{-2} at ≈1 A.m^{-2} is obtained.

Finally, Jayasinghe et al. [33] developed a work that looks more deeply into the biofilm approach by Marcus et al. [8] where electroactive bacteria *G. sulfurreducens* act as electron mediator. However, the basis for the model is founded on a broader point of view. According to this approach, MFC models based on Nernst and Monod equations focus on extra-cellular mechanisms while neglecting the intracellular metabolism of the bacteria. To solve this problem, Jayasinghe et al. [33] combine a genome-scale metabolic model based on flux balance analysis and a modified version of the biofilm model by Marcus et al. [8]. The former provides a highly mathematical, structured platform to understand the metabolic pathways within *G. sulfurreducens* bacteria. In this sense, the resulting model introduces the effects of spatial heterogeneity on metabolism in competition with Marcus et al.'s [8] model. In addition, while the latter differences only two biofilm regions (active and inactive), Jayasinghe et al. [33] consider a new type of biofilm zone called respiring biofilm. Whilst active biofilm invests the energy arising from the oxidization of the substrate for its growth, the respiring zone is in charge of energy conservation at the anode surface. Many more considerations are settled and the approach deserves further study. The model also offers a valuable analysis of the biofilm from a biological point of view.

The simulations first focus on analyzing the electrical current response and the thickness of the biofilm in the presence and absence of ammonium conditions (NH_4^+) in the bulk liquid of the anode, since a mix of nutrients is often added to anode solutions in MFCs. According to the simulated results, the presence of such compound has little impact on biofilm growth and MFC yield, and consequently NH_4^+ can be removed. The work also studies the sensitivity of some parameters such as biofilm conductivity and cell density (number of cells per biofilm volume), concluding that biofilm conductivity is not the limiting factor of the system as Marcus et al. [8] suggested. As regard the cell density, as it increases, the production of current also increases and the biofilm thickness becomes thinner.

The model opens up new possibilities for further studies to provide better understanding of the mechanism by which active biofilm (active cells) transforms into respiring biomass, which could be crucial for enhancing current production. This kind of models requires broad biological and microbial knowledge and demonstrates that MFC modeling requires a multi-disciplinary approach.

Pinto et al. [34] published a one-dimensional model for an air-cathode single-chamber (V=50 ml) MFC with acetate operating in continuous mode. A single-chamber configuration offers easy design and financial savings [48]. Thus, modeling of this type of configuration appears very convenient. The system does not use a chemical mediator, but electroactive microorganisms. The model considers the oxidized and reduced species of the bacteria for the balances. The anode output flow is partially recirculated to the entrance of the anode chamber, which improves stirring. As in Picioreanu et al. [29], the model deals with methanogenesis and its adverse effects on MFC performance. The model mainly consists of (a) mass balance for the substrate, considering anodophilic and methanogenic competition and biofilm retention rate, (b) intracellular mass balance for the oxidized/reduced bacteria that transport the electrons, (c) the kinetics described by Monod's equations and (d) an electrochemical model based on Ohm's law, Nernst's equation and voltage loss

balance. Figure 4 is a schematic representation of the competition between anodophilic and methanogenic bacteria.

[INSERT FIGURE 4]

Regarding experimental data, the work collects information from a set of experimental MFCs according to the configuration described above (MFC-1 and MFC-2 to calculate the best-fit parameters and MFC-2 and MFC-3 for model validation). In these experiments, inoculum heat treatment (yes/no), experiment length (from 35 to 60 days), influent acetate concentration (from 275 to 2550 $mg.L^{-1}$) for each experiment and external resistance load (above and below the internal resistance, up to 60 Ω) are varied.

The model shows robustness when comparing experimental and simulated data for predicted output voltage (up to 0.5 V), but the discrepancy is higher regarding the evolution of the acetate effluent over time due to the difficulty in measuring the methane produced in the anode chamber as consequence of the activity of methanogenic bacteria. Among other results, it is interesting to point out the influence of external resistance on the current output. Once the model is validated, it is run for 200 days, with an external resistance (R_{ext}) load ranging from 10 to 800 Ω in order to study this parameter. Optimal values, in terms of anodophilic bacteria growth, are obtained for R_{ext} values that equal to or are below the internal resistance (R_{int}). The concentration of the acetate influent is also a key factor and is studied in the same range (from 10 to 800 $mg.L^{-1}$). This parameter must be balanced as if the influent acetate concentration is too low there would not be enough fuel available, but if it is too high, the growth of methanogenic bacteria would greatly increase and the power output could be severely affected.

Although based on the modeling of the anode chamber, Pinto et al.'s approach [34] is more general than approaches intended to look at the biofilm growth and study the electron transfer mechanism in detail [8, 31-33].

2.1.2 Models based on both anode and cathode.

Those models that study both the anode and the cathode chambers are included in this section. They simulate the performance of MFCs without assuming that the anode reaction is the limiting factor of the system. Such models are scarce in the literature compared with the previous group.

The first to be discussed is that of Zeng et al. [35], which models a double-chamber MFC ($V_{chambers}$=5.5 mL) using acetate as fuel along with a buffer solution in the anode, platinum in the cathode as catalyst and a commercial Nafion-based membrane as separator. The anode and cathode reactions are modeled by the Monod and Bulter-Volmer equations, which describe them kinetically and electrochemically. For the sake of simplicity, this model does not consider the participation of protons or cations M^+ in the cathode reaction. Although they pass through the membrane, only oxygen, electrons and water are involved in the cathode reaction. The anode and cathode chambers are modeled as continuous stirred tank reactors (CSTRs). The current density of the cells is calculated by relation to the flow of M^+ ions that are transferred to the cathode through the membrane, and the voltage by taking into account charge balances for the anode and cathode and their respective overpotentials. This approach includes a set of parameters, among which there are constants that describe the properties and geometry of the cell, operating variables and six fitting parameters obtained from experimental results to minimize the difference between the experimental and simulated data (kinetic parameters for the reactions and charge transfer coefficients). To estimate these six parameters, the data are collected from cells operating with an initial acetate concentration of 1.56 mM and a 0.375 $ml.min^{-1}$ influent rate. The external resistance between the

anode and the cathode was varied from 10 to 10,000 Ω. The model is validated by matching experimental and simulated data for voltage *vs.* current density, with excellent agreement once the above mentioned best-fit parameters have been estimated ($V_{max} \approx 0.7$ V, $I_{max} \approx 11.5$ A.m^{-2}).

The work includes a sensitivity study of many operating, model and design variables for the stationary state, from which it is concluded that the power produced by the cell is more sensitive to the variation of fuel influent, the charge transfer coefficient of the cathode reaction (β) and the kinetic constant of the anode reaction (k_1^0). The influence of both fuel flow rate and fuel concentration on power output and current density is very significant as can be observed when their values are changed by a multiplication factor of 0.8 and 1.2. On the other hand, the cathode reaction is regarded as one of the major limiting factors of the system according to the sensitivity analysis. This finding contrasts greatly with the models of the previous section, which consider the anode reaction as the limiting factor of MFCs. By simulating the performance of the cell for the steady state, the optimal relationship between some parameters can be inferred; for instance, the proportionality between the anode and cathode rates and the current density obtained ($r_{anode}=450i_{cell}/F$, $r_{cathode}=-900i_{cell}/F$, where i_{cell} is the cell density current and F is Faraday's constant) or the flow of M^+ cations through the membrane and the current density (M^+ concentration linearly increases with current density).

In a final step, the model is applied to an MFC working with a complex substrate (artificial wastewater that mainly consists of a mix of glucose, glutamic and other inorganic compounds), in which more than one oxidation reaction take place:

$$C_6H_{12}O_6 + 6H_2O \rightarrow 6CO_2 + 24H^+ + 24e^- \quad (2)$$

$$C_5H_9NO_4 + 6H_2O \rightarrow 5CO_2 + NH_4^+ + 17H^+ + 18e^- \quad (3)$$

Simulated results reproduce the overall trends of experimental results (voltage *vs.* intensity curves, $V_{max} \approx 0.8$ V, $i_{max} \approx 4$ A.m^{-2}) when wastewater concentration (from 100 to 300 COD mg.l^{-1}) and fuel flowrate (from 0.15 to 0.53 ml.min^{-1}) are varied. However discrepancies are more pronounced with

this second type of substrate, especially for low values of both variables, which can be explained by the inconsistency of experimental results according to the criteria of the authors.

Further studies based on complex substrates are necessary to optimize MFC technology for real applications that use wastewater as fuel. The main limitation of this model is that the biofilm growth cannot be deeply studied, while in models based on the anode chamber this is the focus.

Oliveira et al. [36] studied heat transport in a one-dimensional model for a double-chamber MFC, which also covered the usual aspects dealt with by the rest of models discussed above: charge and mass balances, biofilm growth and redox reactions. The modeling of heat transport relies on the assumption that this phenomenon is caused by diffusion processes while the effect of convection force is negligible. The heat transfer study involves the heat balances for both the anode and cathode chambers and includes energy from electrochemical reactions, activation energy, mass transfer overpotential, heat streams in the anode and the cathode chambers, and heat losses. This approach makes it possible to calculate the temperature profile across the cell (anode electrode, biofilm, anode bulk liquid, membrane, cathode bulk liquid, cathode electrode). Oliveira et al.'s model is more complete, realistic and precise than that of Zeng et al. [35]. As regards the rest of the model, the approach is similar to previous models in which (1) the anode is considered as CSTR for the mass balance, which, in turn is related to the concentration gradient by Fick's law, and (2) the current density is obtained from the substrate (acetate) oxidation rate (Monod and Tafel equations). Modeling of the cathode chamber is based on the oxygen reduction reaction.

The model is validated by comparing simulation results with experimental and simulation data from Zeng et al. [35] (voltage *vs.* current density, $V_{max}\approx 0.7$ V, $i_{max}\approx 11.8$ A.m^{-2}, acetate concentration of 1.56 mol.m^{-3}), showing a higher correlation in this case due to the inclusion of the heat transfer analysis. The simulations show that the cathode is the limiting factor of the system because the cathode overpotential is higher compared with the anode and increases as the current density rises.

Anode and cathode overpotentials range from ≈-0.25 V to 0.2 V and from ≈0.3 V to 0.6 V respectively (in a range of density current from 0 to 12 $A.m^{-2}$). The temperature profile in the cell is simulated at a current density of 5 $A.m^{-2}$ and initial operating temperature of 30 ºC. An increase of around 2 ºC is observed in the cathode chamber due to the exothermal nature of the cathode reaction. Other operating variables such as the effect of the acetate concentration (from 1 to 2 $mol.m^{-3}$) on the current density and voltage are studied. According to the results, the higher the acetate concentration, the higher the resulting power and current outputs. However, this conclusion contradicts the results for some of the models described in section 2.1.1 [28, 29] that take into account the methanogenesis process in the anode and set maximum and minimum limits for fuel concentration.

More recently, Sirinutsomboon [37] presented a comprehensive model for a membraneless single-chamber MFC using molasses (sugar syrup which mainly contains sucrose) as substrate. The separation between the anode chamber and the cathode is given by PTFE. Although a non-pure substrate is used for modeling, the final simplification is near to this kind of approach. As the models mentioned above, the work covers both anode and cathode reactions, the anode reaction being deduced from the extent of acetate oxidation (see figure 5):

$$\text{Anode: } C_{12}H_{22}O_{11} + 25H_2O \rightarrow 12HCO_3^- + 60H^+ + 48e^- \quad (4)$$

$$\text{Cathode: } O_2 + 4H^+ + 4e^- \rightarrow 2H_2O \quad (5)$$

As PTFE is permeable to oxygen, it can reach the anode chamber, reducing the yield of the cell. In the case of the cathode, Fick's second law is used to describe oxygen diffusion, which is a key phenomenon in this approach. This equation is also applied to model sucrose diffusion (from biofilm to bulk liquid) and hydrogen ions in the anode. Both the cathode and the anode reactions are

modeled by the Monod equation combined with the Butler-Volmer and Nernst equations respectively, similarly to the models already discussed. As in Marcus et al. [8], biofilm modeling is based on Nernst-Monod's equation to describe the rate of electrodonor oxidation, differentiating exogenous from endogenous respiration. The former implies the oxidation of sucrose and the latter the oxidation of the cellular mass by the bacteria, which provide an additional amount of energy. The local potential is determined by the combination of Ohm's law and an electron balance (for the steady sate), which, in turns, is used to calculate the local voltage of the biofilm. In this regard, the model is more complete than that of Zeng et al. [35] because it goes deeper into the biofilm activity, without neglecting the involvement of the cathode in MFC performance.

[INSERT FIGURE 5]

Simulations on a flexible interface program (implemented in Visual Basic) are carried out to obtain the profiles of several variables over time. The work lacks a proper comparison and validation of simulations with experimental data.

When profiles of the sucrose concentration in the bulk liquid are obtained over time (up to 300 min) for different initial COD loads (from 1,000 to 20,000 $mg.L^{-1}$), a sharp fall occurs within ≈50 min of simulation. One-dimensional profiles of sucrose concentration and local voltage are also plotted against biofilm location (thickness of 60 μm) for a fixed COD load (10,000 $mg.L^{-1}$) and for different times (from 5 to 400 min). For a longer run (400 min), the sucrose concentration in the biofilm layer increases at the beginning of the simulation because of the diffusion of substrate, after which its remains practically constant (≈0.017 mM). As regard the local voltage, it decreases from the bulk liquid to the anode side until the biofilm thickness reaches a value of ≈30 μm, after which the trend is reversed. It becomes more negative over time as well because of the increase in the rate

of electron production. Simulation of open-circuit voltage values against cathode and biofilm thicknesses (up to 300 μm, respectively) verify that the higher the thickness of the cathode, the lower the efficiency of the cell (oxygen diffusion decreases). In contrast, as the thickness of the biofilm increases, electron release increases, as does the open-circuit voltage. However, the output current of the system is neither simulated nor analyzed and, according to Marcus et al. [8], the thickness of the biofilm is a limiting factor for biofilm conductivity and current output. In addition, some important parameters such as pH are missing compared with other works [30] that describe the influence of this factor on microbial activity (acidification process). In addition, little insight is provided into microbial processes and biofilm development, in line with other models that cover the modeling of both the anode and cathode.

2.2. Specific models.

In this section, models intended for the study of a key factor or component of MFC devices are classified. This type of model remains scarce in the literature but can be very valuable for a better understanding of a given process.

Harnisch et al. [38] model the polarization around a Nafion-based membrane, that is, ionic transport through an ion exchange membrane, and provide valuable information on this mechanism and its limitations when used in MFCs. The MFC set-up modeled in this work has a two-chamber configuration ($V_{chamber}$=250 mL) with two platinum mesh electrodes as anode and cathode, respectively. In order to obtain experimental data, the system also incorporates two electrodes to monitor the pH value in both chambers and two Luggin capillaries to measure the membrane polarization. They, in turn, are connected to two counter-electrodes, Ag/AgCl, both located 1 mm from the membrane.

Using the Nernst-Planck equation for all the species involved, the model describes ion transport across the membrane in terms of flux density. This equation has two terms, corresponding to diffusion and migration transport mechanisms (convection is negligible).Figure 6 shows the ion fluxes that can move from anode to cathode and vice versa, according to Harnisch et al.

[INSERT FIGURE 6]

This one-dimensional model distinguishes three regions in the MFC system: the largest region that covers 95% out of the total volume in the anode and cathode chambers, an intermediate region adjoining the membrane and the membrane itself (thickness), a Nafion-117 membrane. The ion distribution both sides of the membrane produce the build-up of opposite charges around it. The measured polarization allows calculation of the membrane resistance, which hinders ion transport across it and the electric yield of the cell, and also affects the resistance of the electrolyte solution. Values of the potential, plotted across the membrane (for 1 mM KNO3 solution) increase linearly with the distance from the Luggin capillaries to the surface of the membrane.

Due to physical–numerical restrictions, the model cannot be used for long term simulations. Similarly, concentrated electrolytes cannot be simulated as the computation time is very high and their trends can only be estimated by linear extrapolation from results obtained for low concentrations (<100 mM). Finally, the model is reliable for neutral values of electrolyte pH but shows discrepancies for acid media.

The main conclusion concerning this model is that the use of concentrated electrolyte in the anode and cathode increases the pH difference between both chambers, and hence the resistance of the membrane. This is the main limitation related to the application of conventional MFC separators.

Wen et al. [39] created a simple electrochemical model to reproduce the polarization curve of a single-chamber MFC ($V_{reactor}$=100 mL, cathode based on carbon cloth/Pt) using wastewater from a brewery as fuel, rather than a simple substrate, and operating in continuous mode. The use of wastewater in MFC modeling is still scarce but represents a further step toward the practical application of MFCs in wastewater treatment plants [49]. The polarization curve can be plotted as power *vs*. current density or voltage *vs*. current density in a range of load resistances [50]. When voltage *vs.* current density is plotted, the curve can be divided into three regions, corresponding to activation polarization, ohmic losses and concentration polarization. The model attempts to reproduce MFC performance in terms of voltage, which is calculated by balancing this three terms with the thermo-dynamically predicted voltage ($V=E_{thermo}- \eta_{act} - \eta_{ohmic} - \eta_{conc}$). This approach is completed by the addition of a term that fits the experimental and simulation data, the parasitic loss produced by current leakage. The polarization curve gives valuable information on MFC performance, such as the maximum power reached by a cell at which the external and internal resistance are equal. For the case in question, maximum open-circuit voltage and power density are 0.578 V and 9.52 W/m^3, respectively. Validation of the model is based on a single parameter, the ohmic resistance given by the model itself and that calculated by Electrochemical Impedance Spectroscopy (EIS) applied to the physical MFC system (≈7.305 Ω *vs.* 7.160 Ω, respectively). Finally, the work studies the effect of each of the components of the voltage loss independently, finding that kinetics and concentration losses are the most important.

The model described by Yan and Fan [40] is an example of a model that combines a classic approach with mathematical algorithms. This work uses Zeng et al.'s [35] model but focuses on the application of fuzzy control (inspired by fuzzy mathematics) combined with PID control to a double-chamber MFC device. PID control *per se* is not sufficient for systems of high non-linearity such as MFCs devices, even when pure substrates are used (acetate in this case). With fuzzy control it is possible to overcome the complexity of these devices. Fuzzy logic allows a controller to be built even when the system

is not fully understood, offering several advantages such as robustness, model-free and universal approximation theorem [51]. These control techniques are implemented (in Matlab/Simulink) to maintain the voltage output constant, which is a realistic approach for practical applications that would need a constant voltage supply. The model is simulated for a period of 100 h, with a current ranging from 3 $A.m^{-2}$ to 6 $A.m^{-2}$. Traditional PID control is compared with fuzzy PID control in term of voltage stability, fixed at 0.44 V. Fuzzy PID control is more precise than conventional PID control since, when the current changes, fuzzy PID is much quicker to correct disturbances in the system in order to maintain the voltage constant.

Other predictive techniques have been applied to MFC modeling. Stratford et al. [41] studied the correlation between some biological indexes for the anode and the output energy of an MFC system in order to analyze their predictive capability. The indexes were Shannon index, which measures the relative abundance of species, Simpson index, which measures the evenness of the microbial species (probability that two randomly selected microorganisms belong to the same species), and richness, which quantifies the number of different types of species present in the anode (community diversity).

To study the influence of these parameters in terms of predictability, four replicas of a single-chamber MFC (V_{anode}=9 cm^3) operating in continuous mode and fed with sucrose (0.1 $g.l^{-1}$ in medium solution) were run for 91 days (cathode based on Pt/carbon cloth). Previously, these MFCs were started-up in batch mode (enrichment period) until the system offered repeatable voltage circles. DNA analysis of the bacteria were carried out for biofilm and bacteria in suspension at different sampling points in order to calculate the above indexes.

Bivariate analysis between power output and the three microbial community indexes points to a higher correlation for the Shannon index (coefficient r=0.65 compared with r=0.5 for the Simpson index and 0.39 for richness). A non-significant correlation between suspension diversities and power output exists (in line with the significant and positive correlation between biofilm diversities and power output). In a further step, lineal regression analysis is also applied by constructing three

regression models, each of them with two predictor variables: biofilm diversity (given by the three indexes) and biofilm DNA (per cm^2). The highest correlation between these models and the power output is observed for the Shannon index (r=0.73). Neither biofilm richness nor the Simpson index reaches significant correlation with power output, within their respective models. As a conclusion, it can be highlighted that the Shannon index is a good predictor of power output, and that the biodiversity of the MFC microbial population is favorable for the output power of the cell, but only the species in the biofilm are involved to any great extent in the electron transfer mechanism compared with those that are present in the anode bulk liquid.

The limitations of this work are posed by the lack of pH and salinity variables, both of which have been shown to affect the biodiversity of the bacterial community with a positive and negative impact on this index, respectively.

Finally, Garg et al. [42] provide an example of the most recent techniques used for MFC modeling: Artificial Intelligence (AI) methods, which are formulated to model the response of the system in term of voltage in the face of two changing input parameters, temperature and concentration of the ferrous sulfate ($FeSO_4$) present in the anode (media solution with substrate). The methods studied are Multigene Genetic Programming (MGGP), an algorithm based on biological evolution, Artificial Neural Networks (ANNs), based on the operation of central nervous systems (brain), and Support Vector Machines or Networks (SVMs), which uses a set of routines of supervised learning for classification and regression data. These methods are complex from a mathematical point of view and their sequences of instructions require in-depth study.

Experimental data are collected from double-chamber MFCs ($V_{chambers}$=1 L) operated in batch mode, in two series of voltage data, one for an interval of temperatures ranging from 15 to 40 ºC and, a another for a ferrous sulfate concentration ranging from 50 to 400 $mg.L^{-1}$.

When the effect of temperature on voltage is modeled, MGGP presents the strongest correlation between experimental and simulated data (R^2=0.98), but ANN and SVR also offer high correlation coefficients (R^2=0.95). Regarding the ferrous sulfate concentration, MGGP performs better (R^2=0.98) than ANN and SVR (with R^2=0.83), the accuracy of MGGP being due to its intrinsic thoroughness.

The great advantage of these techniques is their predictive capability, although they do not offer a detailed insight into internal processes and mechanisms compared with classic approaches.

3. CONCLUSIONS.

This work provides an overview of the modeling and simulation of Microbial Fuel Cells. The most representative models published to date are discussed and classified according to the approach they follow. Few models are described in the literature compared with the number of experimental works available, and even some of the latest ones tend to be extended versions of previous works. However, there has been a significant evolution in complexity and diversity in the MFC modeling field, both in the number of dimensions and the processes covered. MFC modeling allows a better understating of the performance of MFCs and the optimization of control and operating variables. The number of models is expected to increase in coming years as modeling is clearly a powerful tool in the attempt to improve MFC technology. It can be expected that these new models will embrace innovative materials whose application in MFCs are currently being studied, such as nanomaterials or ionic liquids [52, 53]. Complex systems, such as those that include non-pure substrates like wastewater, are of great interest and could offer a more complex and richer approach to MFC technology. There are still many areas in the MFC field that remain unexplored from the point of view of modeling but which could open ups new possibilities.

4. ACKNOWLEDGEMENTS.

The Spanish Science and Innovation Ministry, ref. CICYT ENE2011-25188, the Spanish Economy and Competitiveness Ministry, ref. DPI2011-28112-C04-04 and the Seneca Foundation ref. 18975/JLI/2013 have supported this work. V.M. Ortiz-Martínez (grant FPU AP2012-5444) and M.J. Salar-García (grant FPI BES-2012-055350) thank the Spanish Education Ministry and Economy and Competitiveness Ministry for supporting their doctoral theses.

5. REFERENCES

[1] K. Rabaey and W. Verstraete. Microbial fuel cells: novel biotechnology for energy generation. Trends Biotechnol. 23 (2010) 291-298.

[2] N. Lu, S.-G. Zhou, L. Zhuang, J.T. Zhnag, J.-R. Ni. Electricity generation from starch processing wastewater using microbial fuel cell technology. Biochem. Eng. J. 43 (2009) 246-251.

[3] H. Moon, I.S. Chang, B.H. Kim, B.H. Continuous electricity production from artificial wastewater using a mediator-less microbial fuel cell. Bioresour. Technol. 97 (2006) 621-627.

[4] M. Zhou, H. Wang, D.J. Hassett, T. Gu. Recent advances in microbial fuel cells (MFCs) and microbial electrolysis cells (MECs) for wastewater treatment bioenergy and bioproducts. J. Chem. Technol. Biotechnol. 88 (2013) 508-518.

[5] V.B. Oliveira, M. Simões, L.F. Melo, A.M.F.R. Pinto. Overview on the developments of microbial fuel cells. Biochem. Eng. J. 73 (2013) 53-64.

[6] Z. Du, H. Li, T. Gu. A state of the art review on microbial fuel cells: A promising technology for wastewater treatment and bioenergy. Biotechnol. Adv. 25 (2007) 464-482.

[7] X.-C. Zhang and A. Halme. Modeling of a microbial fuel cell process. Biotechnol. Lett. 17 (1995) 809–814.

[8] A.K. Marcus, C.I. Torres, B.E. Rittmann. Conduction-based modeling of the biofilm anode of a microbial fuel cell. Biotechnol. Bioeng. 98 (2007) 1171-1182.

[9] C. Spiegel. PEM Fuel Cell Modeling and Simulation using Matlab. Elsevier Science & Technology Books, 2008. ISBN: 9780123742599.

[10] Q. Wang and T. Zhang. Review of mathematical for biofilms. Solid State Commun. 150 (2010) 1009-1022.

[11] O. Wanner and P. Reichert. Mathematical modeling of mixed-culture biofilms. Biotechnol. Bioeng. 49 (1996)172–184.

[12] H. Fujikawa. Diversity of the growth patterns of Bacillus subtilis colonies on agar plates. FEMS Microbiol. Ecol. 13 (1994) 159–167.

[13] J.D. Chambless and P.S. Stewart. A three-dimensional computer model analysis of three hypothetical biofilm detachment mechanisms. Biotechnol. Bioeng. 97 (2007) 1573–1584.

[14] E. Alpkvist and I. Klapper. A multidimensional multispecies continuum model for heterogenous biofilm. Bull. Math. Biol. 69 (2007) 765-789.

[15] B.L. García, V.A. Sethuraman, J.W. Weidner, R.E. White Mathematical model of a direct methanol fuel cell. J Fuel Cell Sci. Technol. 1 (2004) 43–48.

[16] H.Gou. C.-F. Ma. 2D analytical model of a direct methanol fuel cell. Electrochem. Commun. 6 (2004) 306–312.

[17] P. Argyropoulos, K. Scott, A.K. Shukla, C. Jackson A semi-empirical model of the direct methanol fuel cell performance Part I. Model development and verification. J. Power Sources. 123 (2003) 190–199.

[18] H. Dohle, K. Wippermann. Experimental evaluation and semi-empirical modeling of U/I characteristics and methanol permeation of a direct methanol fuel cell. J. Power Sources. 135 (2004) 152–164.

[19] A. Kulikovsky. Two-dimensional numerical modeling of a direct methanol fuel cell. J. Appl. Electrochem. 30 (2000) 1005–1014.

[20] E. Birgersson, J. Nordlund, C. Picard, M. Vynnycky, G. Lindbergh. Reduced two-phase model for analysis of the anode of a DMFC. J. Electrochem. Soc. 151 (2004) A2157–A2172.

[21] E. Antolini. An empirical model to evaluate the contribution of alloyed and non-alloyed tin to the ethanol oxidation reaction on Pt-Sn/C catalysts based on the presence of SnO2 and a Pt(1−x) Snx solid solution: Application to DEFC performance Int. J. Hydrogen Energy 36 (2011) 11043-11047.

[22] M. Meyer, J. Melke, D. Gerteisen. Modelling and simulation of a direct ethanol fuel cell considering multistep electrochemical reactions, transport processes and mixed potentials Electrochim. Acta 56 (2011) 4299-4307.

[23] H. Bahrami, A. Faghri, Multi-layer membrane model for mass transport in a direct ethanol fuel cell using an alkaline anion exchange membrane. J. Power Sources 218 (2012) 286-296

[24] R. Sousa, D.M. dos Anjos, G. Tremiliosi-Filho, E.R. Gonzalez, C. Coutanceau, E. Sibert, J.-M. Léger, K.B. Kokoh. Modeling and simulation of the anode in direct ethanol fuels cells J. Power Sources 180 (2008) 283-293.

[25] S. Heysiattalab, M. Shakeri, M. Safari, M.M. Keikha. Investigation of key parameters influence on performance of direct ethanol fuel cell (DEFC). J. Ind. Eng. Chem. 17 (2011) 727-729.

[26] I. Sarris, P. Tsiakaras, S. Song, N. Vlachos. A three-dimensional CFD model of direct ethanol fuel cells: Anode flow bed analysis. Solid State Ionics 177 (2006) 2133-2138.

[27] K. Wang, D. Hissel, M.C. Péra, N. Steiner, D. Marra, M. Sorrentino, C. Pianese, M. Monteverded, P. Cardoned, J. Saarinene. A Review on solid oxide fuel cell models. Int. J. Hydrogen Energ. 36 (2011) 7212–7228.

[28] C. Picioreanu, I.M. Head, K.P. Katuri, M.C.M. Loosdrecht, K. Scott. A computational model for biofilm-based microbial fuel cells. Water Res. 41 (2007) 2921-2940.

[29] C. Picioreanu, K.P. Katuri, I.M. Head, M.C.M. Loosdrecht, K. Scott. Mathematical model for microbial fuel cells with anode biofilms and anaerobic digestion. Water Sci. Technol. 57 (2008) 965-971.

[30] C. Picioreanu, M. van Loosdrecht, T.P. Curtis, K. Scott. Model based evaluation of the effect of pH and electrode geometry on microbial fuel cell performance. Bioelectrochem. 78 (2010) 8-24.

[31] B.V. Merkey and D.L. Chopp. The performance of a microbial fuel cell depends strongly on anode geometry: a multidimensional modeling study. B Math. Biol. 74 (2012) 834-857.

[32] R. Sedaqatvand, M.N. Esfahany, T. Behzad, M. Mohseni, M.M. Mardanpoura. Parameter estimation and characterization of a single-chamber microbial fuel cell for dairy wastewater treatment. Bioresour. Technol. 146 (2013) 247-253.

[33] N. Jayasinghe, A. Franks, K.P. Nevin, R. Mahadevan. Metabolic modeling of spatial heterogeneity of biofilms in microbial fuel cells reveals substrate limitations in electrical current generation. Biotechnol. J. 10 (2014)1350-1361.

[34] R.P. Pinto, B. Srinivasan, M.-F. Manuel, B. Tartakovsky. A two-population bio-electrochemical model of a microbial fuel cell. Bioresour. Technol. 101 (2010) 5256-5265.

[35] Y. Zeng, Y.F. Choo, B.-H. Kim, P. Wu. Modeling and simulation of two-chamber microbial fuel cell. J. Power Sources. 195 (2010) 79-89.

[36] V.B. Oliveira, M. Simões, L.F. Melo, A.M.F.R. Pinto. A 1D mathematical model for a microbial fuel cell. Energy. 61 (2013) 463-471.

[37] B. Sirinutsomboon. Modeling of a membraneless single-chamber microbial fuel cell with molasses as an energy source. Int. J. Energy Environ. Eng. 5 (2014) 1-9.

[38] F. Harnisch, R. Warmbier, R. Schneider, U. Schröder. Modeling the ion transfer and polarization of ion exchange membranes in bioelectrochemical systems. Bioelectrochem. Vol. 75 (2009) 136-141.

[39] Q. Wen, Y. Wu, D. Cao, L. Zhao, Q. Sun. Electricity generation and modeling of microbial fuel cell from continuous beer brewery wastewater. Bioresour. Technol. 100 (2009) 4171-4175.

[40] M. Yan and L. Fan. Constant voltage output in two-chamber microbial fuel cell under fuzzy PID control. Int. J. Electrochem. Sci. 8 (2013) 3321-3332.

[41] J.P. Stratford, N.J. Beecroft, R.T.C Slade, A. Grüning, C. Avignone-Rossa. Anode microbial community diversity as a predictor of the power output of microbial fuel cells. Bioresour. Technol. 156 (2014) 84-91.

[42] A. Garg, V. Vijayaraghavan, S.S. Mahapatra, K. Tai, C.H. Wong. Performance evaluation of microbial fuel cell by artificial intelligence methods. Expert Syst. Appl. 41 (2014) 1389-1399.

[43] A. Halme A, X.-C. Zhang. Research reports of Automation. Technol. Lab. in Helsinki U. of Techno. 12, 1995.

[44] D.J. Batstone, J. Keller, I. Angelidaki, S.V. Kalyuzhnyi, S.G. Pavlostathis, A. Rozzi, W.T.M. Sanders, H. Siegrist, V.A. Vavilin. The IWA Anaerobic Digestion Model No 1 (ADM1). Water Sci. Technol. 45 (2002) 65-73.

[45] L. Mao and W.S. Verwoerd. Model-driven elucidation of the inherent capacity of Geobacter sulfurreducens for electricity generation. J. Biol. Eng. 7 (2013).

[46] D.R. Bond and D.R. Lovley. Electricity production by Geobacter sulfurreducens attached to electrodes. Appl. Environ. Microbiol. 69 (2003) 1548-1555.

[47] C.I. Torres, A.K. Marcus, B.E. P. Parameswaran, B.E. Rittmann. Kinetic experiments for evaluating the Nernst–Monod model for anode-respiring bacteria (ARB) in a biofilm anode. Environ. Sci. Technol. 42 (2008) 6593–6597.

[48] Y.Z. Fan, H.Q. Hu, H. Liu. Enhanced coulombic efficiency and power density of air-cathode microbial fuel cells with an improved cell configuration. J. Power Sources 171 (2007) 348-354.

[49] C. Santoro, Y. Lei, B. Li, P. Cristiani. Power generation from wastewater using single chamber microbial fuel cells (MFCs) with platinum-free cathodes and pre-colonized anodes. Biochem. Eng. J. 62 (2012) 8-16.

[50] B.E. Logan, B. Hamelers, R. Rozendal, U. Schröder, J. Keller, S. Freguia, P. Aelterman, W. Verstraete, K. Rabaey. Microbial fuel cells: methodology and technology. Environ. Sci. Technol. 40 (2006) 5181-5192.

[51] A.H.S. Chan. Advances in industrial engineering and operations research. US, Springer-Verlag New York inc. ISBN 9781441945167

[52] M.J. Earle and K.R. Seddon. Ionic liquids: green solvents for the future. Pure Appl. Chem. 72 (2000) 1391-1398.

[53] L. Feng, Y. Yan, Y. Chen, L. Wang. Nitrogen-doped carbon nanotubes as efficient and durable metal-free cathode catalysts for oxygen reduction in microbial fuel cells. Energy Environ. Sci. 4 (2011) 1892-1899.

FIGURES IN THE MANUSCRIPT

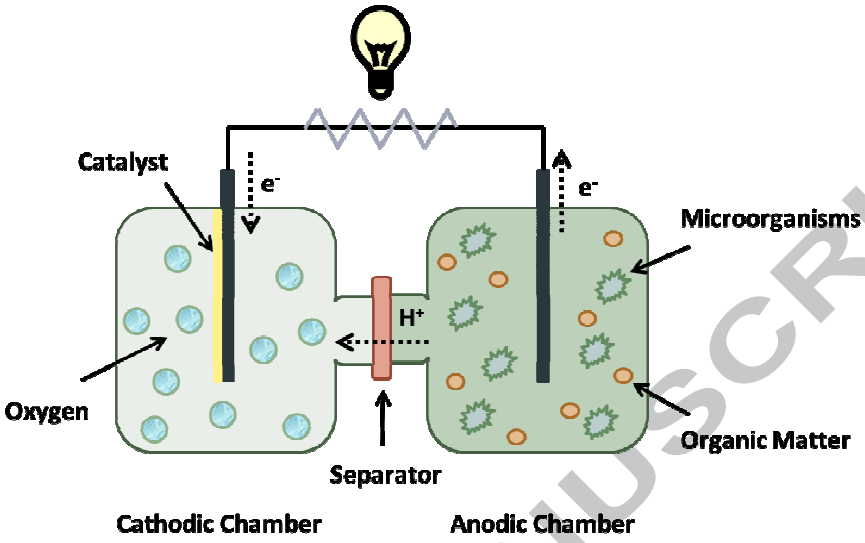

Figure 1. Double-chamber MFC set-up.

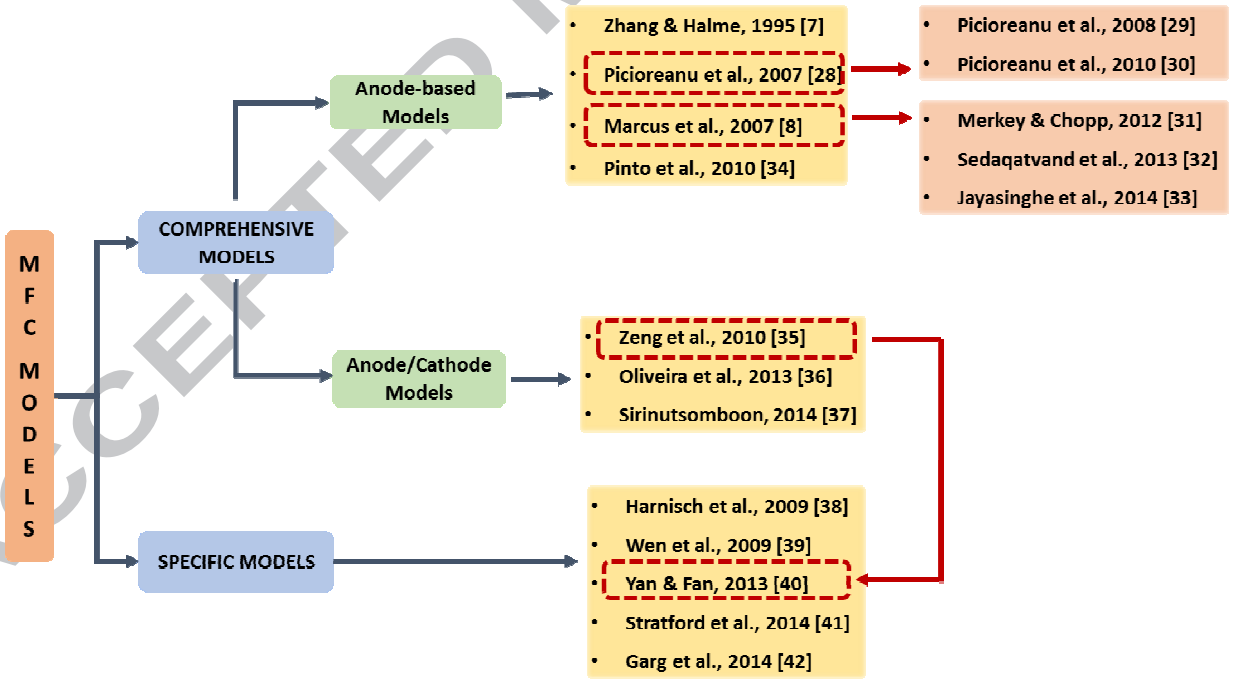

Figure 2. MFC models in the literature.

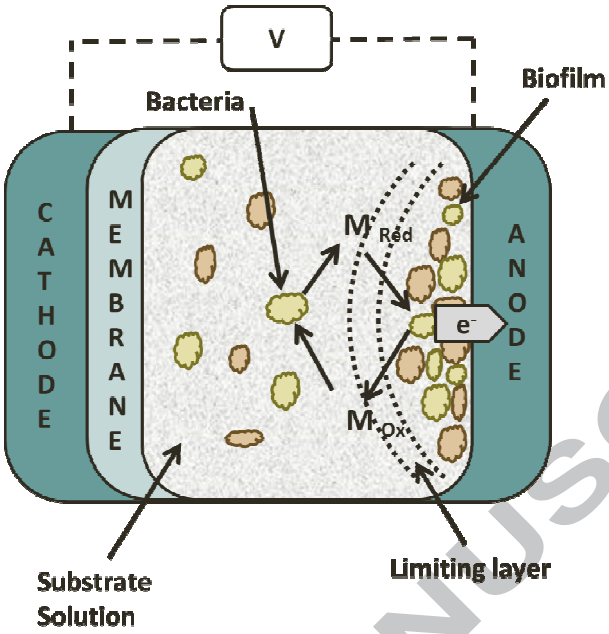

Figure 3. Scheme for anode chamber (based on Picioreanu et al.)

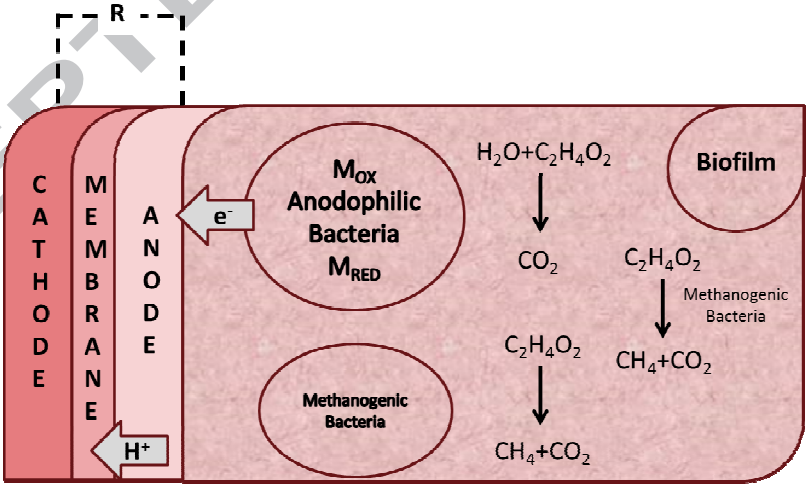

Figure. 4. Chemical reactions for acetate degradation.

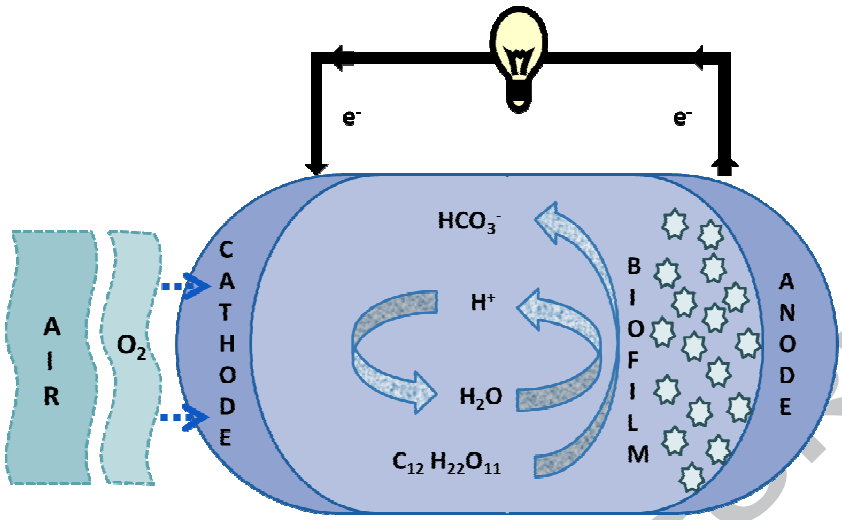

Figure 5. Sucrose digestion.

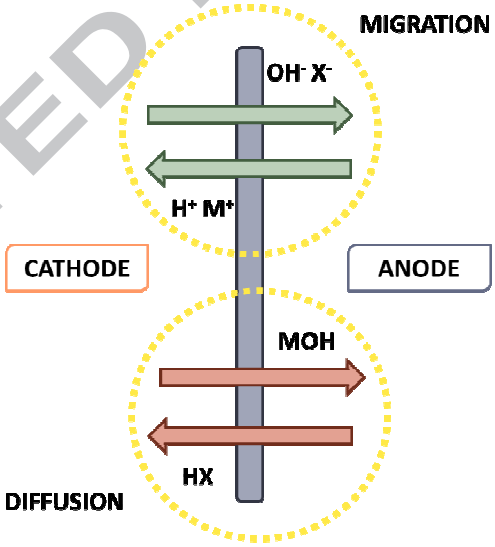

Figure 6. Ionic transport across an MFC separator.

HIGHLIGHTS

- Modeling is a powerful tool for the in-depth study and optimization of MFCs.
- MFC modeling allows valuable data to be collected for decision-making.
- MFC models can be classified according to the approach they follow and their complexity.
- MFC modeling studies remain scarce compared with experimental works.