Model based evaluation of the effect of pH and electrode geometry on microbial fuel cell performance

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A B S T R A C T
A mathematical model for microbial fuel cells (MFC) which integrates macro-scale time-dependent mass balances for solutes and biomass in the anodic liquid with a micro-scale individual-based two-dimensional biofilm model is developed. Computational fluid dynamics and Nernst–Plank mass and charge balances with diffusion, electromigration, convection and electroneutrality in the biofilm are combined to calculate spatial pH distribution and solutes speciation. Soluble redox mediators are the electron shuttle between microbial cells and the electrode. The model describes the generally observed variations of pH, solute concentrations and electrical current produced over time from electroactive biofilms. Numerical simulations also show the effect of bicarbonate buffer and mass transfer through the proton exchange membrane on the microbial population within a mixed anaerobic digestion sludge consortium of methanogenic and electrogenic microorganisms. In addition, the new modeling approach opens the way to study the influence of fluid flow and any two- or three-dimensional biofilm and electrode geometry on the MFC output parameters. Hydrodynamic calculations show that porous bio-electrodes with greater specific surface area do not necessarily produce more current, as long as convection through the pores is absent. An innovative model solution strategy combines in a very efficient and flexible way MATLAB, COMSOL finite element and Java codes.

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1. Introduction

Microbial fuel cells (MFC) are a type of fuel cell that converts the chemical energy contained in organic matter to electricity using microorganisms as a biocatalyst. In MFC, bacteria do not transfer their electrons directly to their characteristic terminal electron acceptor, but rather to a solid electrode [1,2]. Although MFCs are not a new discovery [3], the interest in their study and development has been increasing extraordinarily in recent years. This is mainly because it is believed that MFCs offer the possibility of directly harvesting electricity from organic waste and renewable biomass [4]. Potentially, microbial fuel cells add the diversity of microbial catalytic abilities to the high-efficiency design of fuel cells, allowing the energy of mixed organic compounds to be converted into electricity [5]. Driving factors are not only harvesting small amounts of electricity while polishing wastewater. Other applications seem even more interesting such as: conversion of residual glycerol from biodiesel into ethanol [8], bio-catalyzed H2 production [9,10], or biosensors [11,12]. We believe that the modeling framework presented here can be extended to describe also these related bio-electrochemical systems.

A few options exist currently for design of MFC, and these are outlined in a number of reviews dedicated both to the understanding of the microbiology of MFC processes [4,13,14] and to advances in the technological aspects [15,15,16]. Although MFCs promise sustainable energy generation in the future, many major bottlenecks still exist [17]. Identification of the rate-limiting steps allows the development of strategies to enhance the MFC output. The performance of a MFC can be influenced by several physical, chemical and biological factors such as the rates of [18]: (1) mass transfer of substrates to and into biofilm, (2) microbial oxidation of substrate, (3) electron transfer from the microbial cells to the electrode, (4) electric load in the circuit, (5) proton transfer to the cathode compartment, and (6) oxygen supply and reduction at the cathode. The mechanism of electron transfer in step (3) is one of the most disputed areas in current MFC research. First, direct electron transfer involves either cytochromes (contact conduc-

tion) or proposed conducting structures termed “nano-wires” [19,20]. The second mechanism involves diffusible electron transfer relays (mediators) that can shuttle electrons between the microbial biocatalytic system and the electrode [21]. The biocatalytic process performed by the microorganisms differs from the natural situation because the electron flow goes (partly) to the anode instead of to a natural electron
acceptor. Fuel cells with externally supplied mediators tend to be inefficient and expensive [12]. However, it has been demonstrated that electrochemically active bacteria (EAB) from a biofilm enriched in a MFC can produce mediator compounds in-situ [22,23]. Therefore, in spite of a present tendency of the scientific community to focus on the direct electron transfer, we believe that the study of MFCs with soluble redox mediators is also very significant. In addition, besides MFCs, other bio-electrochemical systems using mediators have been reported for which the present model could be adapted [8].

A suitable method to integrate information gathered from several disciplines ranging from biology to engineering is by mathematical modeling. Essentially, the rigor of modeling provides a framework for testing hypotheses. Most recent MFC studies are experimental, and focus either on a detailed understanding of the microbiology of bacteria involved in MFC or on engineering aspects with reports of incremental increases in MFC performance from MFCs with increasingly advanced designs. A breakthrough that will propel MFC into a large-scale feasible technology can come only from a multidisciplinary approach integrating both microbiology and engineering. This is precisely the bridge computational models can make and it is our aim to promote this approach through the present study. Only a handful of modeling studies have been yet dedicated to microbial fuel cells. More than a decade ago preliminary work attempted to simulate the currents produced by MFC with suspended cells and an added mediator [24]. This line of research has not been pursued further until in 2007 when we introduced a model for the biofilm-based microbial fuel cells with mediated electron transfer [25]. The model realistically described many experimental observations, including the influence of operational parameters on the current/power-voltage characteristics and the current development in time. A further extension of this model included methanogenic processes, with preliminary results presented in [26]. Based on a different hypothesis, Kato–Markus et al. interestingly explained the functioning of biofilm-based MFCs based on a hypothetical biofilm electrical conduction property instead of diffusible mediators [27]. This approach combined in the microbial growth kinetics limitations by the electron donor substrate and by electrical potential, introducing a rate equation dubbed “Monod–Nernst”.

This study’s main aim is to extend the MFC modeling framework presented in [25] in order to include pH calculations. The acidification of the anodic electrolyte is a primordial limitation hampering the use of MFCs. Because the electrons are collected by the anode, an equivalent amount of protons is released into the solution and must be eventually transferred away from the anode surface to reach the cathode, where $\mathcal{H}^+$ can be consumed. Important limiting steps in the proton transport from anode to cathode are the transport in the biofilm [28] and through the proton exchange membrane (PEM, [29]). There are at least two effects of anolyte acidification. First, the reversible electrochemical oxidation of the soluble electron mediator is negatively influenced by the protons. SecoTD, the activity of neutrophilic biofilm microorganisms would be decreased if the pH drops too suddenly. However, on the long term, the second effect may not be the main problem because acidophilic organisms with similar activities will be naturally selected. The mathematical model of the anodic compartment of a MFC introduced in this study is more general, versatile and rigorous because: (i) in order to calculate pH, Nernst–Planck fluxes of ions (electromigration and diffusion) together with an ionic charge balance are introduced instead of molecular diffusion only; (ii) mass transport by convection and liquid flow over the irregular biofilm and electrode surface are considered; (iii) any two- or three-dimensional geometry of the electrode/biofilm can be accommodated in the model, not only the planar electrode system. Three case studies are presented here to exemplify the use of the model for pH calculations, for mixed species electroactive biofilms with methanogenic and fermentative microorganisms and for flow/mass/charge transport with biofilm growth in geometrically complex electrodes. Including other electron transfer mechanisms such as by direct contact or connection to the anode via proposed conducting structures termed “nano-wires” (e.g., [19]) in the model framework is possible, and shall be presented in further studies. In this model we aim to describe in detail only the dynamic behavior of the anodic compartment, having in mind that a description of the cathode chamber can follow the same approach. The mediator was assumed in this study to diffuse freely in the biofilm and bulk liquid. Retention mechanisms of a produced electrochemical mediator in the biofilm must be further identified and introduced in an improved model.

2. Model description

The model accounts for two spatial scales: a macrofor the bulk liquid anolyte and a microscale for the biofilm on the electrode and its close environment. These two scales are linked via the fluxes integrated over the open boundaries of the microscale domain. It is implicitly assumed that the microscale domain chosen is representative for the whole biofilm developed on the electrode. A schematic representation of the model domains, links and fluxes is presented in Fig. 1.

2.1. Macroscale mass balances in the anodic bulk liquid domain

The bulk liquid in the anodic compartment of a MFC is assumed completely mixed so that the concentrations $C_B$ of all soluble chemical and microbial species are uniform in the whole volume $V_B$. The system (1) of $n_B$ ordinary differential equations representing mass balances of each model component $i$ (chemical or microbial) in the bulk liquid $(B)$ will be solved:

$$\frac{dC_{B,i}}{dt} = \frac{\Phi}{V_B} (C_{in,i} - C_{B,i}) + r_{B,i} + \frac{A_F}{V_B} N_{F,i} + \frac{A_M}{V_B} N_{M,i}$$

(1)

with a set of specified initial conditions $C_{B,i}(t=0) = C_{i,0}$. Molar units are used for each component. Batch operation is assumed in the first two cases of this paper, therefore the rate of exchange with the exterior (first term in the right hand side of Eq. (1)) is zero. $r_{B,i}$ is the net rate of reaction in the bulk for a component $i$, and it is made up of contributions from rates of all individual reactions multiplied by the corresponding stoichiometric coefficients. The third term in Eq. (1) is the rate of mass transfer with the biofilm on the electrode with area $A_F$. Finally, the last term is the rate of mass transfer through the membrane (area $A_M$) that separates the anodic and cathodic compartments. Fluxes $N_{F,i}$ and $N_{M,i}$ are given by Eqs. (12) and (13), respectively. Although Eq. (1) is general and can be applied to solutes and biomass as well, we choose for the illustration cases here not to account for the biomass in the bulk liquid. The effect of the biomass concentration in the bulk liquid on the MFC performance was analyzed in [25], and found that suspended microorganisms contribute much less to the current production than the biofilm cells. The solution of Eq. (1) is a set of bulk liquid concentrations $C_{B,i}$ needed at each moment in time as the boundary condition for solute mass balances in the biofilm domain (see Fig. 1).

2.2. Microscale mass, charge and momentum balances in the microscale domain

The biofilm domain is characterized by concentration gradients both for solutes and for biomass components [Fig. 1]. We present here for illustration only two-dimensional model simulations because of the good balance between calculation time and model realism, but one-dimensional reduction or three-dimensional extensions are perfectly possible (as shown in [25,26] for MFC diffusion/reaction systems only). The concentrations $C_{i_B}(x,y)$ are also time dependent as the biofilm structure continuously changes.
2.2.1. Solute components

For any soluble component $i$, a mass balance is set up by assuming transport by diffusion $N_{di} = -D_i \nabla C_{i,F}$, convection $N_{ci} = u_i C_{i,F}$, and electromigration $N_{ei} = -z_i u_{mi} F C_{i,F} \nabla V$ fluxes (the gradient operator is $\nabla = \hat{i} \partial / \partial x + \hat{j} \partial / \partial y$, with $i$ and $j$ the unit vectors in the $x$ and $y$ directions). Soluble components can be produced or consumed in several biotic or abiotic transformation processes with net rate $r_{i,F}$. Therefore, the $B_{c}$ mass balances written for each soluble component $i$ will form the following system of partial differential equations written in molar units:

$$\frac{\partial C_{i,F}}{\partial t} = D_i \nabla^2 C_{i,F} + z_i u_{mi} F \nabla \cdot \left( C_{i,F} \nabla V \right) - u \cdot \nabla C_{i,F} + r_{i,F}$$  \hspace{1cm} (2)

by assuming constant diffusion coefficients $D_i$ and ion mobilities $u_{mi} = D_i / RT$, and incompressible fluid (see [30] for details on the derivation, and [31] for an application of a similar approach to model microbially influenced corrosion). The present model does not account for potential gradients between anode and cathode, which could lead to an electrokinetic flow of ions. However, the ions will move in the potential gradient $\nabla V$ developed by imposing an electroneutrality condition everywhere in the biofilm domain:

$$\sum_i z_i C_{i,F} = 0$$  \hspace{1cm} (3)

Eqs. (2) and (3) are applied on the microscale rectangular computational domain partially filled with attached microbial cells (the biofilm matrix subdomain) and partially with liquid (the mass transfer boundary layer sub-domain, see Fig. 1). Particular forms of Eq. (2) will apply for different species and sub-domains. For example, neutral species (charge $z_i = 0$) will not have electromigration, no convection will occur in the biofilm matrix (liquid velocity $u = 0$), and, while acid–base equilibria apply everywhere, no microbial reactions will occur in the liquid sub-domain.

The field of liquid velocity $u$ results from the Navier–Stokes equations of momentum balance and liquid continuity for incompressible liquid in laminar flow regime:

$$\frac{\partial u}{\partial t} = -(u \cdot \nabla) u - \frac{1}{\rho} \nabla p + \nu \nabla^2 u$$  \hspace{1cm} (4)

For a complete model setup, the system of Eqs. (2)–(4) needs boundary conditions. At biofilm domain/bulk liquid interface $\Gamma_B$ (e.g., $y = L_y$ for planar electrode) bulk concentrations of all soluble components are assumed, while the potential $V$ is set to zero, as the constant reference value in the bulk liquid. Symmetry boundary is assumed for the flow on $\Gamma_B$ (Eq. (5)):

$$\begin{cases}
C_{i,B} = C_{i,B}(t) \\
V = 0 \\
u_y = 0, \partial u_x / \partial y = 0
\end{cases} \quad \text{on } \Gamma_B$$  \hspace{1cm} (5)
The electrode surface on which the biofilm develops $F_E$ (at $y = 0$) for the planar electrode, but on boundaries with other orientations for the porous electrode, see Fig. 1) is electrochemically active for certain chemical species, e.g. for mediators and protons. The surface-based rate or reaction $r_{EL}$ equals the total flux normal on the surface. For the electrochemically inactive chemical species, zero-flux condition applies (insulation because $r_{EL} = 0$). A current inflow condition applies for the charge balance, with the inward current density $i_i$ given by a Butler–Volmer expression (see Table 1). The electrode is a no-slip wall for the flow:

$$\begin{align*}
\mathbf{n} \cdot \left( D_i \nabla C_i + z_i u_{m,i} F \mathbf{C}_i \nabla V \right) &= r_{i,EL} \\
\mathbf{n} \cdot \mathbf{F} i &= \mathbf{n} \cdot \left( D_i \nabla C_i + z_i u_{m,i} F \mathbf{C}_i \nabla V \right) = i_i \\text{on } F_E
\end{align*}$$

The liquid inlet has a fully developed laminar velocity profile with an average velocity $u_{0,i}$. The inlet concentrations are those from the bulk liquid and electrical insulation applies:

$$\begin{align*}
P \sum_i z_i \left( D_i \frac{\partial C_i}{\partial x} + z_i u_{m,i} F \mathbf{C}_i \frac{\partial V}{\partial x} \right) &= 0 \quad \text{on } F_i \\
u_y = 0, u_x = \frac{3}{2} u_{0,i} \left( 2 - \frac{y}{L} \right)
\end{align*}$$

In the liquid outlet there is a zero pressure (arbitrary reference value), convective flux only for the chemical species and electrical insulation:

$$\begin{align*}
P \sum_i z_i \left( D_i \frac{\partial C_i}{\partial x} + z_i u_{m,i} F \mathbf{C}_i \frac{\partial V}{\partial x} \right) &= 0 \quad \text{on } F_0 \\
p &= 0
\end{align*}$$

The boundary layer/biofilm matrix interface $F_F$ is an internal boundary with flux and current continuity for the mass and charge.

<table>
<thead>
<tr>
<th>Reaction name</th>
<th>Reaction equation$^a$</th>
<th>Reaction rate</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acid–base equilibrium</td>
<td>$\ce{H2O + OH^- + H+} \rightarrow \ce{H3O+}$</td>
<td>$r_{\text{HOH}} = k_{\text{HOH}} \left( 1 - \frac{[\text{H}_2\text{O}]}{[\text{H}_3\text{O}^+]} \right)$</td>
</tr>
<tr>
<td>b. Glucose fermentation</td>
<td>$\ce{C6H12O6 + H2O + \text{H}+} \rightarrow \ce{PrH + \text{Pr}+ + \text{H}2O}$</td>
<td>$r_{\text{GlFer}} = k_{\text{GlFer}} \frac{\text{GlFer}}{[\text{Gl}]} \frac{\text{PrH}}{[\text{Pr}]} \frac{\text{H2O}}{[\text{H}_2\text{O}]}$</td>
</tr>
<tr>
<td>b. Butyrate fermentation</td>
<td>$\ce{C2H5COO^- + \text{H}2O + \text{H}+} \rightarrow \ce{BuH + \text{Bu}+ + \text{H}2O}$</td>
<td>$r_{\text{BuFer}} = k_{\text{BuFer}} \frac{\text{BuFer}}{[\text{Bu}]} \frac{\text{H2O}}{[\text{H}_2\text{O}]} \frac{\text{BaH}}{[\text{Ba}]} \frac{\text{Bu}+}{[\text{Bu}]}$</td>
</tr>
<tr>
<td>a. Oxidation single protonated mediator</td>
<td>$\ce{1/2 \text{MH}_2 + \text{H}+ + \text{e}^-}$</td>
<td>$r_{a,1} = i_1 / F; i_1 = \Phi_{\text{MH}_2} \frac{[\text{MH}]}{[\text{MH}_2]} \frac{[\text{H}]}{[\text{H}+]} \frac{[\text{e}]}{[\text{e}^-]}$</td>
</tr>
</tbody>
</table>

Table 1

Molar stoichiometry and reaction rates for the chemical, microbial and electrochemical conversions included in model. All reactions are used in Case 2, whereas only reactions a1–a5, b1 and e1–e3 are used in Case 1 and Case 3.

---

$^a$ Abbreviations used for chemical and microbial species names: $\text{Ac} \equiv \ce{CH3COO^-}$, $\text{AcH} \equiv \ce{CH3COOH}$, $\text{Pr} \equiv \ce{C2H5OH}$, $\text{PrH} \equiv \ce{C2H5OH}$, $\text{BuH} \equiv \ce{C3H7COO^-}$, $\text{BuH} \equiv \ce{C3H7COOH}$, $\text{Gl} \equiv \ce{C4H6O6}$, $\text{MH}2$ \equiv \ce{C4H4O4}$^2+$, $\text{MH}3$ \equiv \ce{C4H4O4}$^3+$, protonated and neutral forms of the reduced thionine mediator, $\text{MH}^+$ \equiv \ce{C4H4O4}$^2+$, protonated form of the oxidized thionine mediator. $\text{Xo}$ \equiv acetate consumer both electrochemically and by methanogenic fermentation. $\text{Xo}$ \equiv acetate consumer, $\text{XoH}$ \equiv $\text{CH}_3\text{COOH}$ (butyrate) consumer, $\text{Xo}$ \equiv acetate consumer, $\text{Xo}$ \equiv acetate consumer, $\text{XoH}$ \equiv $\text{CH}_3\text{COOH}$ (butyrate) consumer.

$^b$ The potential and current dependency of the electrochemical rates is $f(e_{\text{eq}}) = \exp \left( \frac{2 F A}{R T} \left( \frac{e_{\text{eq}}}{e_{\text{eq}}} - 1 \right) \right)$ with the equilibrium potential $e_{\text{eq}}$ calculated as: $e_{\text{eq}} = e_{0,i} + 0.0295 \log \left( \frac{\text{M}}{\text{M}} \right) + 0.0592 \log \left( \frac{\text{M}}{\text{M}} \right)$.
2.2.2. Biomass balances

The model for biomass production/consumption and transport within the biofilm matrix closely follows the individual-based modeling approach (iBm) described and applied in [32,33]. Multiple microbial species (metabolic groups) can be easily considered with this approach. The relevant parameters are: \( n_{\text{ini}} \), initial number of biomass particles, \( \rho_b \), density of biomass particles, \( m_0 \), initial mass of biomass particles and \( m_{X,\text{max}} \), critical biomass for biomass particle division. The biomass particles grow with the rates expressed in Table 1, as a function of solute concentrations at the position of the spherical particle center. Then, the biomass particles divide and a hard collisions shoving algorithm are applied to avoid particle overlapping [34]. The position of the moving boundary \( f_t \) is the result of this algorithm.

2.3. Model components and reactions

A choice of the set of chemical and biological model components (“species”) together with the set of chemical, biological and electrochemical reactions (conversions) must be made. The microbial metabolism needs a reduced substrate (electron donor) to be oxidized with an electron donor in order to gain the energy needed by the cells for growth and maintenance. A series of metabolic products can be formed during the biological conversions performed by the cells. The present model is based on the mediated electron transfer between microbial cells and electrode. In this simple model it is therefore assumed that the organic substrate is converted by the oxidized mediator into more oxidized products, while the mediator is reduced. The reduced mediator diffuses to the anode where it is electrochemically oxidized and can be re-used by the cells (Fig. 1).

2.3.1. Electron mediator

Given this simple mechanism for electron transfer, a diffusible mediator species must be chosen. There are exogenous mediators naturally present or just added in the medium and there are also endogenous mediators produced by the microbes. Among the many choices that can be made, we opted here (like in [25]) for thionine as an exogenous mediator because this is a well known electron shuttle, studied and used before in MFCs, and for which kinetic and thermodynamic data exist. Most of the rate parameters listed in Table 2 were obtained by Benetto’s group on MFCs with added thionine and suspended Proteus cells [2135–371].

Thionine exists in two forms: an oxidized purple dye and reduced colorless one, called also leuco-thionine. The reduced leuco-thionine can have several protonated states present around the neutral and slightly acidic pH, which must be considered in this study that focuses on pH effects on the MFC performance. These states are denoted: \( MH_x \), \( MH_x^+ \) and \( MH_x^{2+} \). The two acid–base equilibria with \( pK_a \) 4.4 and 5.3 ([38,39]) are shown in Table 1 (reactions a4 and a5). The oxidized thionine exists in a single protonated form \( MH^+ \) between pH 2 and 10 (\( pK_a \approx 11 \), from [39]). It is assumed that at the anode surface all forms of the reduced mediator can be electrochemically oxidized (reactions e1–e3 in Table 1), with production of protons. The reaction rates are of Butler–Volmer reversible type, dependent on the concentrations of participant species at the electrode surface and on the anodic activation overpotential \( \eta_a \) (see footnotes of Table 1). The activation overpotential depends on the ohmic losses of potential (due to internal and external electrical resistance \( R_e \) and current \( I \)), on the cathodic potential \( V_c \) and equilibrium redox potential of the mediator oxidation reaction, \( E_m \). The derivation of \( \eta_a \) was presented in [25].

2.3.2. Substrates and products

In this study we investigated two reaction systems. In the first, one simple substrate — acetate — is converted by a single microbial species \( (X_{ac}) \) into CO\(_2\). In this conversion the oxidized mediator is the electron acceptor. The reaction stoichiometry (b1 in Table 1) was derived in [25] based on elemental and charge balances and thermodynamic considerations [40].

The second case study presents a more complex system with a mixed microbial community of electroactive \( (X_{ac}) \) organisms competing with fermentative organisms (see Table 1, reactions b2–b6). The scheme of reactions and the stoichiometric and rate coefficients follow closely the IWA Anaerobic Digestion Model described in [41]. In conjunction with biofilm modeling, the kinetic model from [41] was already applied to methanogenic granular sludge in [42,43] and in a preliminary MFC study [26]. The initial substrate is glucose \( (G) \). This is converted into several low-chain fatty acids (butyrate, Bu, propionate, Pr, and acetate Ac) together with hydrogen and CO\(_2\) production by the glucose fermentative microorganisms \( X_{di} \) (reaction b2). This acidification step is followed by acetogenesis (reactions b3 and b4) performed by microorganisms \( X_{aa} \) and \( X_{a} \), which produce acetate and \( H_2 \) from the C4 and C3 organic acids. These reactions are thermodynamically inhibited by the \( H_2 \). In the last step, methanogenesis, acetate is transformed into methane and CO\(_2\) (\( X_{ac} \) in reaction b5), while \( H_2 \) and \( CO_2 \) are converted into methane by hydrogenotrophs \( (X_{ht}) \) in reaction b6).

The pH changes due to all these biological conversions. For pH calculations, together with the water dissociation (reaction a1), several acid–base equilibria must be taken into account for the carbonic, acetic, propionic and butyric acids (reactions a2, a3, a6 and a7 in Table 1). To maintain electroneutrality and to directly change the ionic conductivity of the solution, inert cations \( (\text{Na}^+) \) and anions \( (\text{Cl}^-) \) can also be added.

2.3.3. Net reaction rates and fluxes

Having the system of reactions defined as in Table 1, the net rates for each chemical or microbial component at each model scale, in each sub-domain and on each reactive boundary can be calculated by the algebraic sum of individual reaction rates \( r_j \) multiplied by the stoichiometric coefficient \( n_{ij} \) of species \( i \) in reaction \( j \). In the bulk liquid there are only the acid–base equilibria, needed in Eq. (1):

\[
r_{iB} = \sum_j r_{aj} n_{ij}
\]

In the biofilm domain there are in addition the biological conversions, needed in Eq. (2), as well as for the biomass growth in the biofilm biomass balances:

\[
r_{iE} = \sum_j r_{aj} n_{ij} + \sum_j r_{bj} n_{ij}
\]

On the electrode surface \( f_E \) the net rates used in Eq. (6) are:

\[
r_{iE} = \sum_j r_{ej} n_{ij}
\]
### Dissolved components

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Description</th>
<th>Value</th>
<th>Units</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>$C_{AL,0}$</td>
<td>Initial concentration total acetate</td>
<td>1.56</td>
<td>mmol L$^{-1}$</td>
<td>[36]</td>
</tr>
<tr>
<td>$C_{CL,0}$</td>
<td>Initial concentration total carbonate</td>
<td>2, 20 and 100</td>
<td>mmol L$^{-1}$</td>
<td>Chosen</td>
</tr>
<tr>
<td>$C_{MM,1,2,0}$</td>
<td>Initial concentration total reduced mediator</td>
<td>0.001</td>
<td>mmol L$^{-1}$</td>
<td>Chosen</td>
</tr>
<tr>
<td>$C_{BuH,0}$</td>
<td>Initial concentration total butyrate</td>
<td>–</td>
<td>mmol L$^{-1}$</td>
<td>Chosen</td>
</tr>
<tr>
<td>$C_{Pr,0}$</td>
<td>Initial concentration total propionate</td>
<td>–</td>
<td>mmol L$^{-1}$</td>
<td>Chosen</td>
</tr>
<tr>
<td>$C_{Bu,L}$</td>
<td>Initial concentration oxidized mediator</td>
<td>1</td>
<td>mmol L$^{-1}$</td>
<td>[36]</td>
</tr>
<tr>
<td>$C_{H,L}$</td>
<td>Initial concentration protons</td>
<td>$10^{-7}$</td>
<td>mol L$^{-1}$</td>
<td>pH 7</td>
</tr>
<tr>
<td>$C_{L,L}$</td>
<td>Initial concentration glucose</td>
<td>–</td>
<td>mmol L$^{-1}$</td>
<td>Chosen</td>
</tr>
<tr>
<td>$C_{H,2}$</td>
<td>Initial concentration $H_2$</td>
<td>–</td>
<td>mmol L$^{-1}$</td>
<td>Chosen</td>
</tr>
<tr>
<td>$C_{Bu,L,0}$</td>
<td>Initial concentration $BuH_4$</td>
<td>0.01</td>
<td>mmol L$^{-1}$</td>
<td>Chosen</td>
</tr>
<tr>
<td>$C_{L,0}$</td>
<td>Initial concentration Cl$^-$</td>
<td>$10^{-5}$</td>
<td>mmol L$^{-1}$</td>
<td>Chosen</td>
</tr>
<tr>
<td>$D_{AC}$</td>
<td>Diffusion coefficient mediator, all forms</td>
<td>$2 \times 10^{-10}$</td>
<td>m$^2$ s$^{-1}$</td>
<td>[25]</td>
</tr>
<tr>
<td>$D_{AC}$</td>
<td>Diffusion coefficient acetate</td>
<td>$1.1 \times 10^{-9}$</td>
<td>m$^2$ s$^{-1}$</td>
<td>[30,44]</td>
</tr>
<tr>
<td>$D_{AC}$</td>
<td>Diffusion coefficient acetic acid</td>
<td>$1.3 \times 10^{-9}$</td>
<td>m$^2$ s$^{-1}$</td>
<td>[30,44]</td>
</tr>
<tr>
<td>$D_{CO,2}$</td>
<td>Diffusion coefficient $CO_2$</td>
<td>$1.9 \times 10^{-9}$</td>
<td>m$^2$ s$^{-1}$</td>
<td>[30,44]</td>
</tr>
<tr>
<td>$D_{HCO,3}$</td>
<td>Diffusion coefficient $HCO_3^-$</td>
<td>$1.2 \times 10^{-9}$</td>
<td>m$^2$ s$^{-1}$</td>
<td>[30,44]</td>
</tr>
<tr>
<td>$D_{H,2}$</td>
<td>Diffusion coefficient $H_2$</td>
<td>$9.3 \times 10^{-9}$</td>
<td>m$^2$ s$^{-1}$</td>
<td>[30,44]</td>
</tr>
<tr>
<td>$D_{OH}$</td>
<td>Diffusion coefficient $OH^-$</td>
<td>$5.3 \times 10^{-9}$</td>
<td>m$^2$ s$^{-1}$</td>
<td>[30,44]</td>
</tr>
<tr>
<td>$D_{Na}$</td>
<td>Diffusion coefficient Na$^+$/Na$^+$</td>
<td>$1.3 \times 10^{-9}$</td>
<td>m$^2$ s$^{-1}$</td>
<td>[30,44]</td>
</tr>
<tr>
<td>$D_{Cl}$</td>
<td>Diffusion coefficient Cl$^-$</td>
<td>$2 \times 10^{-9}$</td>
<td>m$^2$ s$^{-1}$</td>
<td>[30,44]</td>
</tr>
<tr>
<td>$D_{Li}$</td>
<td>Diffusion coefficient Li$^+$</td>
<td>–</td>
<td>m$^2$ s$^{-1}$</td>
<td>[44]</td>
</tr>
<tr>
<td>$D_{BuH,0}$</td>
<td>Diffusion coefficient butyrate and butyric acid</td>
<td>$0.5 \times 10^{-9}$</td>
<td>m$^2$ s$^{-1}$</td>
<td>[44]</td>
</tr>
<tr>
<td>$D_{BuH,0}$</td>
<td>Diffusion coefficient propionate and propionic acid</td>
<td>$0.7 \times 10^{-9}$</td>
<td>m$^2$ s$^{-1}$</td>
<td>[44]</td>
</tr>
<tr>
<td>$D_{BuH,0}$</td>
<td>Diffusion coefficient $H_2$</td>
<td>$0.9 \times 10^{-9}$</td>
<td>m$^2$ s$^{-1}$</td>
<td>[44]</td>
</tr>
<tr>
<td>$D_{BuH,0}$</td>
<td>Diffusion coefficient $BuH_4$</td>
<td>$5 \times 10^{-9}$</td>
<td>m$^2$ s$^{-1}$</td>
<td>[44]</td>
</tr>
<tr>
<td>$R$</td>
<td>Universal gas constant</td>
<td>8.314</td>
<td>J mol$^{-1}$ K$^{-1}$</td>
<td></td>
</tr>
<tr>
<td>$T$</td>
<td>Temperature</td>
<td>300</td>
<td>K</td>
<td></td>
</tr>
<tr>
<td>$F$</td>
<td>Faraday's constant</td>
<td>96,480</td>
<td>C mol$^{-1}$ e$^{-1}$</td>
<td></td>
</tr>
<tr>
<td>$k_{m,1,1}$</td>
<td>Mass transfer coefficient for protons across the PEM</td>
<td>$10^{-7}$ and $10^{-6}$</td>
<td>m s$^{-1}$</td>
<td>Chosen</td>
</tr>
<tr>
<td>$K_{H,H}$</td>
<td>Water dissociation equilibrium constant</td>
<td>$10^{-14}$</td>
<td>mol L$^{-2}$</td>
<td>[41]</td>
</tr>
<tr>
<td>$K_{AC}$</td>
<td>Acetic acid dissociation equilibrium constant</td>
<td>$10^{-4.795}$</td>
<td>mol L$^{-1}$</td>
<td>[41]</td>
</tr>
<tr>
<td>$K_{MM,1}$</td>
<td>Equilibrium constant for dissociation of thionine $MMH_2^+$</td>
<td>$10^{-5.1}$</td>
<td>mol L$^{-1}$</td>
<td>[38,39]</td>
</tr>
<tr>
<td>$K_{MM,1}$</td>
<td>Equilibrium constant for dissociation of thionine $MMH_2^+$</td>
<td>$10^{-4.376}$</td>
<td>mol L$^{-1}$</td>
<td>[38,39]</td>
</tr>
<tr>
<td>$K_{CO,2}$</td>
<td>Carbonic acid dissociation equilibrium constant</td>
<td>$10^{-6.6}$</td>
<td>mol L$^{-1}$</td>
<td>[41]</td>
</tr>
<tr>
<td>$K_{Pr,1}$</td>
<td>Propionic acid dissociation equilibrium constant</td>
<td>–</td>
<td>mol L$^{-1}$</td>
<td>[41]</td>
</tr>
<tr>
<td>$K_{BuH,4}$</td>
<td>Butyric acid dissociation equilibrium constant</td>
<td>–</td>
<td>mol L$^{-1}$</td>
<td>[41]</td>
</tr>
<tr>
<td>$k_i$</td>
<td>Rate constants for the dissociation equilibria ($i=$ HOM, CO2, AcH, PrH, BuH, BuH3, MMH1, MMH4)</td>
<td>$10^7$ ($k_{HOM}$)</td>
<td>mol m$^{-3}$ s$^{-1}$</td>
<td>Large values</td>
</tr>
</tbody>
</table>

### Biomass components

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Description</th>
<th>Value</th>
<th>Units</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>$n_{P,0}$</td>
<td>Initial number of biomass particles</td>
<td>2, 25</td>
<td>Chosen</td>
<td></td>
</tr>
<tr>
<td>$n_{P,0}$</td>
<td>Density of biomass particles$^a$</td>
<td>89000</td>
<td>cmol m$^{-3}$</td>
<td>[25]</td>
</tr>
<tr>
<td>$n_{P,0}$</td>
<td>Initial mass of biomass particles</td>
<td>$(4.5 \pm 1.2) \times 10^{-14}$</td>
<td>cmol</td>
<td>[25]</td>
</tr>
<tr>
<td>$C_{MM,1,2,0}$</td>
<td>Critical biomass for biomass particle division</td>
<td>$6 \times 10^{-14}$</td>
<td>cmol</td>
<td>[25]</td>
</tr>
</tbody>
</table>

### System dimensions

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Description</th>
<th>Value</th>
<th>Units</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>$V_B$</td>
<td>Bulk liquid volume</td>
<td>$2.5 \times 10^{-4}$</td>
<td>m$^3$</td>
<td>[36]</td>
</tr>
<tr>
<td>$A_p$</td>
<td>Anode surface area</td>
<td>$10^{-2}$</td>
<td>m$^2$</td>
<td>[36]</td>
</tr>
<tr>
<td>$L_x \times L_y$</td>
<td>Size of biofilm computational domain</td>
<td>(1) $300 \times 100$, (3) $300 \times 400$ and 2300 x 100</td>
<td>cmol</td>
<td>Chosen</td>
</tr>
</tbody>
</table>

### Electrical parameters

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Description</th>
<th>Value</th>
<th>Units</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>$V_C$</td>
<td>Cathode potential</td>
<td>0.68</td>
<td>V (SHE)</td>
<td>[36]</td>
</tr>
<tr>
<td>$R_p$</td>
<td>Total MFC resistance</td>
<td>100</td>
<td>f$ar{t}$</td>
<td>[36]</td>
</tr>
</tbody>
</table>

### Electrochemical rate parameters

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Description</th>
<th>Value</th>
<th>Units</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>$i_0$</td>
<td>Exchange current density for mediator oxidation in reference conditions ($C_{MMH1}=C_{MMH2}=C_{MMH4}$, $C_{BuH}=1$ mM, $C_{H} = 10^{-7}$ M)</td>
<td>$2 \times 10^{-4}$</td>
<td>A m$^{-2}$</td>
<td>[25] based on [36]</td>
</tr>
<tr>
<td>$E_M$</td>
<td>Standard reduction potential for the mediator couple (vs. SHE)</td>
<td>0.477</td>
<td>V (SHE)</td>
<td>[21] at pH 0</td>
</tr>
<tr>
<td>$b_M$</td>
<td>Tafel coefficient for mediator oxidation</td>
<td>0.120</td>
<td>V</td>
<td>For 2 e$^-$</td>
</tr>
</tbody>
</table>

### Microbial rate parameters

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Description</th>
<th>Value</th>
<th>Units</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>$K_{AcM}$</td>
<td>Rate constant for $X_{Ac}$ growth on acetate and mediator</td>
<td>$2.8 \times 10^{-5}$</td>
<td>s$^{-1}$</td>
<td>[25] from [21]</td>
</tr>
<tr>
<td>$K_{AcM}$</td>
<td>Monod half-saturation coefficient for acetate in growth with mediator</td>
<td>1.56</td>
<td>mol Ac m$^{-3}$</td>
<td>[25]</td>
</tr>
</tbody>
</table>

(continued on next page)
The total flux exchanged between the small-scale biofilm domain and the bulk liquid in Eq. (1) is calculated by integrating total fluxes over the inlet, outlet and bulk boundaries:

\[
N_{fl} = \frac{1}{L_h} \int_{s} \left( N_{ID} + N_{IE} + N_{IC} \right) d\Gamma
\]  

The flux of protons through the membrane between anode and cathode solutions is expressed as function of the mass transfer coefficient \(k_{mt}\) and assuming a constant pH in the cathodic solution (a set-point concentration \(C_{IC}\)):

\[
N_{IC} = k_{mt} (C_{IC} - C_{IE})
\]  

Because the anodic activation overpotential is a function of the total current \(I\) (see Table 1), an implicit integral equation must be solved simultaneously with the Eqs. (2) and (3) (see also the model description and solution algorithm from [25]):

\[
I = \int_{V} \sum_{l} I_{i} (E_{i}, I) ds
\]  

2.4. Model solution

The model was implemented in a combination of MATLAB code (MATLAB 2007b, MathWorks, Natick, MA) as the main algorithm script, COMSOL Multiphysics (COMSOL 3.5, Comsol Inc., Burlington, MA) finite element methods for solving the PDEs, ODEs and coupling integral condition, and own Java code for the individual-based biofilm model.

The main program code is a MATLAB script, which in a first section defines the:

(a) model input parameters — from Table 2;
(b) model geometry (the rectangular biofilm domain and the anode geometry);
(c) initial biomass distribution on the anode surface;
(d) two-dimensional COMSOL application modes (1: momentum transfer — incompressible Navier–Stokes Eq. (4); 2: mass transfer — Nernst–Planck with diffusion, convection, electromigration and electroneutrality condition Eqs. (2) and (3)), with corresponding boundary conditions Eqs. (5)–(8) and equilibrium initial conditions;
(e) integral-algebraic Eq. (14) for the total current;
(f) ODE system of mass balances in bulk liquid Eq. (1);
(g) reaction rates in the bulk liquid (9), in the biofilm domain (10) and on the electrode surface (11), with expressions from Table 1;
(h) integral coupling condition (12) for the biofilm/bulk sub-models; and
(i) 2D mesh for finite element solution of the hydrodynamics and mass balances.

The second section of the script solves the model equations in a time loop (time step \(\Delta t = 1\) hour). The finite element mesh size was 2\(\mu\)m. At any time \(t\) there are successively solved:

(j) biofilm domain hydrodynamics at steady state to get \(u\) and \(p\) (with COMSOL finite element methods), for a given geometry of the biofilm matrix and electrode;
(k) biofilm domain mass balances at steady state to get $C_{lf}$ (with COMSOL finite element methods) by using the calculated velocity field $u$, given 2d biomass distribution $C_{xf}$ and given bulk liquid concentrations $C_{ih}$. All the model state variables at this time $t$, i.e., $u(t,x,y)$, $p(t,x,y)$, $C_{lf}(t,x,y)$, $C_{hf}(t,x,y)$, $C_{ih}(t)$ are saved after this step.

(1) time evolution of bulk liquid concentrations $C_{ih}$ from $t$ to $t+Dt$ using the coupling fluxes with biofilm domain;

(m) biomass balances in the biofilm to get $C_{xf}$ from the previously calculated $C_{ih}$, using own Java algorithms as described in [32–34].

Finally, the biofilm matrix distribution $C_{xf}(t,x,y)$ is updated from the particle-based biomass model. With the new biofilm geometry and biomass distribution so obtained a new time step starts with the hydrodynamic calculations (j).

3. Model results and discussion

Three case studies are presented here to exemplify the use of the model: (1) for pH calculations, (2) for multiple species electroactive biofilms mixed with methanogenic and fermentative microorganisms and (3) for mass/charge transport in electrodes with complex...
geometry (e.g., porous electrodes). Table 2 lists all parameters used in the simulations.

3.1. Case 1 — mono-species electroactive biofilm on planar electrode

This is a relatively simplified model system with one microbial species (X_m) that consumes acetate and oxidized mediator as substrates for growth. We studied the effect of anolyte buffering with CO_2/HCO_3^- in different concentrations (C_CO_2 = C_CO_2 + C_HCO_3^-) and of different mass transfer rates of protons through the PEM (k_m,H) on the anolyte pH and on the current obtained with the MFC. Spatially two-dimensional mass balances in the biofilm domain and time-dependent balances in the ideally mixed bulk anolyte liquid were solved for the following chemical species: H^+, OH^-, MH^+, MH_2, MH_3^+, MH_4^2+, AcH, Ac, CO_2, HCO_3^-, Na^+ and Cl^- (see footnote (a) of Table 1 for abbreviations).

When the rate of proton mass transfer through the PEM is negligible (k_m,H = 10^-6 m/s), the anode compartment is practically a closed system, in which H^+ will accumulate. The consequence is that pH decreases during the microbial conversion of acetate and will then remain constant when the substrate is depleted (Fig. 2A). The more CO_2/HCO_3^- in the solution (from 2 mM to 100 mM) the closer the pH remains to the initial value of 7. How much bicarbonate in the solution is needed to keep the pH constant depends on the initial concentration of acetate. In an ideal electrochemical conversion of acetate into CO_2, 1 mol acetate releases 8 mol H^+ into the solution. With the microbial/electrochemical system, where acetate is also consumed for microbial growth, about 7 mol H^+ will be released (summed eq. b1 and e2 in Table 1). We used 1.56 mM acetate (which means 100 g COD/m^3, with COD = chemical oxygen demand, a measure of reduction equivalents contained in a substrate frequently used in environmental technology), for which it is clear that 2 mM bicarbonate buffer is insufficient. Consequently, in that case the medium acidifies in such extent (pH < 4.5 after 7 days) that the electrochemical oxidation of the mediator — assumed here as a reversible process which produces H^+ — is practically blocked. The result of poor buffering is lower current production (Fig. 2B) and incomplete acetate conversion (Fig. 2G). Obviously, both these effects are negative for the use of MFC technology in wastewater treatment. At pH > 5 the reduced thionine exists in three forms, as shown in Fig. 2C. Although this justifies the need for considering all thionine dissociation equilibria, we did not account for the possibility that only some of these species may be electrochemically active (all three species react at the electrode cf. eq. e1–e3 in Table 1). Another known effect not investigated here is the dependency of microbial metabolism on pH.

In the presence of significant proton transfer to the cathode (k_m,H = 10^-2 m/s), the pH remains above 6 during the acetate conversion even for low bicarbonate content of the feed solution (Fig. 2D). Also, when the rate of acetate consumption and proton production slow down, the pH increases again towards the initial values around 7. The current production is first limited by the biomass attached on the anode (the anodic biofilm). The current increases together with the biofilm biomass (Fig. 2G) as long as there is substrate to sustain microbial activity and growth. After a peak of 0.7–0.8 A/m^2 around day 4, the current decreases again due to the substrate exhaustion (Fig. 2B and E). Low buffering and low proton transfer lead to lower and later (day 5) current peaks. With sufficient buffer in the anode (here, 100 mM), the rate of H^+ transfer matters less for the anodic process and assuming that the cathodic process is not influenced, the same current-time curves are obtained (Fig. 2B and E). For a rather constant pH around 7, the mediator speciation can be neglected. The concentration of reduced mediator in time follows closely the current production and only one chemical species dominates (Fig. 2F). The above simulations clearly indicate that the current model is capable of simulating the effect of anode to cathode proton transfer rate on the functioning of MFCs. Moreover, the model also points to the crucial role of this transfer process in the MFC.
The production of electrons at the anode is accompanied by an ionic current through the solution, defined as:

\[
i = -F \sum_i \left( P_i \nabla u_{i\text{ex}} \cdot \nabla \Phi + z_i D_i \nabla C_i \right).
\]

The intensity and 2d spatial distribution of the ionic current at different moments in time can be seen in Fig. 3A. The ionic current — shown with arrows scaled relative to the maximum current obtained during the whole operation of 15 days — is maximum at day 4 (locally can reach 1 A/m²). Although the general direction of the current is from the electrode towards the bulk liquid (constrained by the insulation condition imposed on the lateral boundaries), it can be clearly seen that the current mainly originates on the anode places covered by the microbial colonies (Fig. 3B).

The 2d distributions of reduced mediator concentration (MH₂ as the total of the three leuco-thionine species) are also shown in Fig. 3. The highest concentration of reduced thionine is in the middle of the microbial colonies, as the result of microbial metabolism. The concentration decreases at the anode surface due to MH₂ consumption in the electrochemical reactions and towards the bulk liquid due to diffusive transport.

Fig. 4. Spatial distributions of solution potential, pH, diffusion, electromigration and convection fluxes for H⁺ calculated in Case 1 (k_{diff} = 10^{-5} m/s, 2 mM carbonate). (A) Surface plots of solution potential (V, in mV) and arrow plots of H⁺ electromigration flux vectors. (B) Surface plots of pH and arrow plots of H⁺ diffusion (black) and H⁺ convection (white) flux vectors. The length of the diffusion flux arrows is on the same scale with that from electromigration fluxes in (A), but the convection fluxes are ~100 times scaled down in (B). Microbial cells are shown as small black circles attached to the electrode surface.

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\[
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\]

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The 2d distributions of reduced mediator concentration (MH₂ as the total of the three leuco-thionine species) are also shown in Fig. 3. The highest concentration of reduced thionine is in the middle of the microbial colonies, as the result of microbial metabolism. The concentration decreases at the anode surface due to MH₂ consumption in the electrochemical reactions and towards the bulk liquid due to diffusive transport.

The concentration of protons is slightly higher (lower pH) in the biofilm-covered areas (Fig. 4). However, there is no maximum concentration in the middle of the colonies, but rather near the electrode, where the protons are mainly produced. Protons will be transported out of the biofilm by diffusion and electromigration. Diffusion is driven by concentration gradients, and dominates near the biofilm surface (Fig. 4B). The electromigration is driven only by the potential gradient formed as a result of electroneutrality condition. As a result of the electrode polarization, there is a higher potential near the electrode, relative to the biofilm. This potential gradient leads to more electromigration near the electrode (Fig. 4A), with values comparable with those of molecular diffusion fluxes. In Fig. 4, the maximum diffusion flux is \(N_{H^+,D} = 4 \times 10^{-9} \text{ mol/m}^2\text{s}\), and the maximum electromigration flux is \(N_{H^+,M} = 3 \times 10^{-9} \text{ mol/m}^2\text{s}\). These transport mechanisms are however negligible in the bulk liquid (or anyway, far from the biofilm surface), where the convection clearly dominates (maximum in Fig. 4 is \(N_{H^+,C} = 5 \times 10^{-7} \text{ mol/m}^2\text{s}\)). We did not consider in this model electrophoretic fluxes created due to the potential difference between cathode and anode. Supposedly, the electrophoretic fluxes may also be important either for the proton transfer through the biofilm [28], or for retaining negatively-charged mediator species in the anodic biofilm (such as the phenazines, [2]). Following model extensions will investigate these electrophoretic fluxes too.

Fig. 4. Spatial distributions of solution potential, pH, diffusion, electromigration and convection fluxes for H⁺ calculated in Case 1 (k_{diff} = 10^{-5} m/s, 2 mM carbonate). (A) Surface plots of solution potential (V, in mV) and arrow plots of H⁺ electromigration flux vectors. (B) Surface plots of pH and arrow plots of H⁺ diffusion (black) and H⁺ convection (white) flux vectors. The length of the diffusion flux arrows is on the same scale with that from electromigration fluxes in (A), but the convection fluxes are ~100 times scaled down in (B). Microbial cells are shown as small black circles attached to the electrode surface.

3.2. Case 2 — multi-species electroactive and fermentative biofilm on planar electrode

For wastewater treatment, a mixed microbial community consisting mainly of anaerobic microorganisms will be active in the anode space. Therefore, the electroactive microorganisms will compete for substrate and space in the biofilm with fermentative bacteria. The
model includes for this case several microbial species: \(X_{Gl}, X_{Bu}, X_{Pr}, X_{Ac}\) and \(X_{H2}\), all active in the anaerobic digestion process, but it is assumed that only \(X_{Ac}\) is able to use the mediator to exchange electrons with the anode. In addition to all species from Case 1, solute mass balances are also solved for \(Gl, Bu, Bu^{-}, Pr, Pr^{-}\). Table 1 presents the reaction rates and stoichiometry and Table 2 all the parameters used.

In general, the calculated change in time of concentrations of chemical species in the bulk liquid follows the normal course of the anaerobic digestion process (Fig. 5A). Glucose is first converted in acetic, propionic and butyric acids, with the concomitant production of molecular \(H_2\). When glucose is depleted, the fast growing glucose consumer microorganisms stop accumulating in the biofilm (Fig. 5B). In this acidogenic period the pH decreases (Fig. 5C). Methanogens (\(X_{H2}\)) further convert the \(H_2\) formed by the fermentative organisms into \(CH_4\) and grow as long as \(H_2\) is present in sufficient concentrations. In the methanogenic biofilm there are strong \(H_2\) gradients, clearly visible in Fig. 6B. Especially at day 5, corresponding
Fig. 7 (continued).
to the peak in $H_2$ concentration, high $H_2$ concentrations (3 $\mu$M) are in the $X_{Ac}$ colonies and extremely low in the $X_{H_2}$ populated biofilm areas.

Methane forms also during acetate fermentation. This process competes with the acetate utilization for electricity production by $X_{Ac}$. Current production begins only when sufficient $X_{Ac}$ microorganisms have accumulated in the biofilm (see the 2d microbial distribution in Fig. 6A and biofilm biomass in Fig. 5B), and this can take place only after acetate has been formed by fermentation. With the used model parameters, current production starts only after day 5 and reaches a peak around day 10 (Fig. 5C). After that, the current rapidly decreases because the acetate is consumed and it is not produced at a sufficient rate from propionate and butyrate. However, the small acetate formation from higher organic acids is still able to support a low current production. The current is produced in localized areas on the electrode (Fig. 6C), corresponding to places where the colonies of $X_{Ac}$ form (Fig. 6A). Compared with Case 1, less current (max. 0.3 A/m$^2$) is obtained in this mixed-species biofilm.

The pH evolution in time is shown in Fig. 5C along with the current production. When a low bicarbonate concentration is present in the feed solution (2 mM total $\text{CO}_2/\text{HCO}_3^-$), the pH falls rapidly during acidogenesis, and a visible accentuation of the pH decrease occurs when current production takes place. Due to the proton transfer rate through the PEM ($k_{\text{pem}} = 10^{-2}$ m/s), the pH increases again after the acetate conversion with current production. In the case of a buffered feed solution (20 mM total $\text{CO}_2/\text{HCO}_3^-$) without proton transfer, the pH decreases slower but it does not recover after 15 days. The electrical current is larger due to the more favorable conditions for the electrochemical oxidation of the mediator (higher pH during the current production phase).

This case study clearly shows that the proposed model reflects the general variation over time of pH, solute concentrations and current as experimentally obtained in MFCs operated with anaerobic sludge in the anode ([26] and Katuri et al. 2009, submitted). The main obstacle however would be the realistic identification of model parameters.

### 3.3. Case 3 — mono-species electroactive biofilm on porous electrode

The model setup allows the definition of any arbitrary geometry of the biofilm domain (not necessarily rectangular) and any electrode shape. To illustrate the model use in such a case, we have chosen here to compare the MFC performance with biofilm developing on a porous anode vs. the planar electrode (Case 1). The porous electrode consists of a granular highly conductive material with inter-granular voids filled by the anodic solution and partially by the biofilm developed on the granules (Fig. 1). In two dimensions the granules are represented by irregular circular shapes, which must be seen actually connected in the third space dimension so that they form a conductive material of uniform electrical potential. The ohmic resistance of the electrode is included in the total resistance ($R_e$). Real equivalents of the modeled porous electrode can be a bed of graphite beads, a carbon sponge or any sintered material. The porous electrode material in this simulation has a porosity $\epsilon = 0.6$, a specific area $a_e = 26000$ m$^2$/m$^3$ and granule diameters in the range of 20–70 $\mu$m. Concentrations of chemical species in the ideally mixed bulk liquid (and thus in the inflow of the biofilm domain) were kept constant in time in this case to simulate a continuous operation of...
the MFC that has reached steady-state in bulk concentrations. This is achievable at high feed flow rates $\Phi$ or small bulk liquid volumes $v_B$ corresponding to a low feed solution residence time (see Eq. (1)). One more process was added as compared to Case 1: biomass attachment on the electrode surface or on the biofilm matrix surface occurred at a rate of one cell per 2 h per biofilm domain area (i.e., $6.5 \times 10^{-6}$ C-mol biomass/m$^2$ h = $4.45 \times 10^{-8}$ g biomass/m$^2$s).

If the electrolyte flows parallel to the top of the porous electrode (see fluid velocity vectors in Fig. 7A) then only a small liquid flow is
entained in the pores (streamlines in Fig. 7A). The contribution of convection to the total mass transfer of substrate or products to or from the inner biofilm is very small compared with the diffusion and electromigration fluxes. Therefore, acetate diffusion gradients develop along the porous electrode depth (y direction). The biofilm cells on the deeper electrode granules will have a lower activity relative to the top ones (Fig. 7A3) and a thinner biofilm will develop on these granules in time. The electron currents collected on each granule are shown in Fig. 7B by normal vectors pointing into the granule. It can be seen that deeper granules (situated at small coordinate y) collect initially as much current as the top ones (Fig. 7B1), but later the currents are much higher on similar granules near the electrode surface (Fig. 7B3). This is the combined effect of mass transfer limitations and biofilm formation. In the first place, acetate and oxidized/reduced mediator gradients form along y. Second, these gradients lead to more biomass (thicker biofilm) near the electrode surface, which means more biological conversion of acetate and oxidized/reduced mediator gradients form along y. Third, acidity accumulates in the inner electrode volume (Fig. 7C), which slows down the reversible electrochemical mediator oxidation. Gradients in the ionic current densities in electrolyte are also evident from Fig. 7C. The ionic currents accumulate from contributions on each granule and due to the insulated lateral boundaries can only escape towards the bulk liquid on top of the electrode. As ions can travel only through the liquid, bottlenecks for the ionic currents form in the narrower inter-granular space (e.g., see ionic currents at y = 200–300 μm).

Simulations with an electroactive biofilm developed on a planar electrode surface with an equivalent surface were also performed. Total concentrations of reduced mediator and the current density obtained on the planar electrode are presented in Fig. 8. When compared with the values from the porous electrode, the mean current density achieved on the planar electrode after 6 days is higher. Apparently, this is correlated with more biomass obtained on the planar electrode (Fig. 9). Mass transfer limitations are easier avoidable on the planar electrode, although per volume electrode the porous electrode offers more surface for biofilm formation. This is why in the first four days of operation, when no transport limitations have yet occurred, the two types of electrode show similar current values. Interestingly, another effect of the mass transport limitations is that although the bulk liquid concentrations are kept constant in time (like in a steady-state continuous MFC operation), the current also reaches a plateau value (Fig. 9). In spite of a still linear biomass accumulation, compared to the exponential biofilm growth phase up to day 4, a saturation level has been reached for the overall current production rate (0.9 A/m² for porous compared with 0.6 A/m² for planar case). This can be both due to a limitation in the biological rate (the deep biofilm layers do not have substrate) or in the electrochemical rate (pH inhibition or mediator limitation).

It is beyond the scope of this paper to analyze in detail all the parameters (thickness, shape, porosity, different flow regimes, etc.) that may influence the performance of porous electrodes. However, for illustration of the model versatility, a simulation was also performed with flow through the electrode pores. We changed the no-flux conditions for flow, mass and charge on the boundaries ΓΩ and ΓΩE, by applying inlet conditions on ΓIE and outlet conditions on ΓOE, similar with those on ΓI and ΓO respectively. In order to make the results comparable, the same liquid flow rate as on ΓI (mean velocity 1 mm/s) was passed through the whole inlet boundary, ΓI U ΓIE. As shown in Fig. 10A, flow through the electrode prevents much of the substrate (acetate) limitation that microorganisms growing in the electrode “depth” experienced, as convection becomes the main mechanism for mass transport. With more active biofilm cells (compare visually the biomass at day 5 on Fig. 10 with Fig. 7, or numerically 1.5 g/m² and 1 g/m² at day 5 in Fig. 9A), about 40% more current is obtained in the “flow-through” system. The current will still become limited when the liquid pores are blocked with biomass and the liquid flows through preferential channels (Fig. 10A2). Nevertheless, the biomass and currents obtained are much closer to those obtained with a planar electrode (Fig. 10B).

Not investigated here but nevertheless important is the effect of hydrodynamics on the biofilm structure. High flow rates generate large shear forces on the biofilm, which should affect the biofilm structure by removing pieces of biofilm and promoting growth of a more compact biofilm [45,46]. However, the experience with biofilm growth in other porous media shows that clogging and preferential flow channeling will still occur, even if after a longer period of time [47,48].

In conclusion, Case 3 shows how to analyze the behavior of porous “bio-electrodes” and in general of electrodes of any shape. It shows also that more area for biomass attachment does not necessarily mean more biomass and more current production, as long as convection through the pores is absent. However, sending the liquid flow through an electrode with the geometrical characteristics chosen here would probably require a greater energy input which must be balanced against any increased power from the MFC. Only the initial calculated pressure drop was ~5600 Pa/cm and this pressure exponentially increased in time, following the pore clogging with biomass. Obviously, the flow regimes chosen here are kind of extremes and reality will be in between the two options: flow over and flow through. The model should however be applied to explore other possibly more favorable configurations, with packed bed anodes [49,50] of larger granules and thus larger pore throat diameters and less pressure drop. The model will be used to explore different geometric configurations (e.g. rectangular vs. cylindrical), flow directions and positioning of current feeds, electrodes of different thickness and material properties (e.g. conductivity).

4. Conclusions

The proposed microbial fuel cell model successfully integrates multi-scale time-dependent mass and charge balances for solutes and biomass in the anodic liquid (at macro-scale) and in a two-dimensional biofilm (at micro-scale). The proposed model reflects the generally observed variations of pH, solute concentrations and current over time in MFCs with mono-species electroactive microorganisms and also in those operated with a mixed methanogenic/electrogenic microbial consortium from anaerobic sludge. In addition, the new modeling approach opens the way for the study of the influence of any two-dimensional biofilm and electrode geometry on the MFC output parameters. By including hydrodynamic calculations it has been shown that porous “bio-electrodes” with greater specific surface area do not necessarily supply more current, as long as convection through the pores is absent. Also an innovative model solution strategy is developed in this study, using a very efficient and flexible combination of MATLAB, COMSOL and Java codes. The modeling framework presented here can be directly extended to describe three-dimensional systems, direct electron transfer and also other related bio-electrochemical systems. We trust that the progress made in this study opens the door to integrated use of experimental and modeling research, which will greatly enhance the speed of developing the MFC technology.

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Appendix A. Supplementary data


References

[3] M.C. Potter, Electrical effects accompanying the decomposition of organic com-

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