A framework for modeling electroactive microbial biofilms performing direct electron transfer

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A B S T R A C T

A modeling platform for microbial electrodes based on electroactive microbial biofilms performing direct electron transfer (DET) is presented. Microbial catabolism and anabolism were coupled with intracellular and extracellular electron transfer, leading to biofilm growth and current generation. The model includes homogeneous electron transfer from cells to a conductive biofilm component, biofilm matrix conduction, and heterogeneous electron transfer to the electrode. Model results for Geobacter based anodes, both at constant electrode potential and in voltammetric (dynamic electrode potential) conditions, were compared to experimental data from different sources. The model can satisfactorily describe microscale (concentration, pH and redox gradients) and macroscale (electric currents, biofilm thickness) properties of Geobacter biofilms. The concentration of electrochemically accessible redox centers, here denominated as cytochromes, involved in the extracellular electron transfer, plays the key role and may differ between constant potential (300 mM) and dynamic potential (3 mM) conditions. Model results also indicate that the homogeneous and heterogeneous electron transfer rates have to be within the same order of magnitude (1.2 s⁻¹) for reversible extracellular electron transfer.

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1. Introduction

Microbial extracellular electron transfer (EET) describes the ability of microorganisms to connect their cellular metabolism with the flow of electrons in their surroundings [1–3]. EET is now believed to play a key role for natural redox-cycles [3,4], but it has also attracted ever increasing attention for its technical exploitation [5]. This interest and the associated progress in research and development during the last decade led to the foundation of the emerging field of microbial electrochemical technologies (MET) [6]. MET now cover different concepts of applications ranging from its archetype the microbial fuel cells (MFCs) [7,8] via bioelectrochemical resource recovery [9,10] and microbial electrosynthesis [11] to biocomputing [12].

In line with the technological advancement, the discovery of the underlying fundamentals of EET has made significant progress, resulting in detailed knowledge on different hierarchical levels from biofilms via cells to organelles and molecules [2]. However, there are still largely untapped areas and one future key to success will be the continuing standardization, cross-validation and benchmarking of the individual results [13]. This also holds true for the central elements of all bioelectrochemical systems (BESs), the microbial electrodes. These electrodes are comprised of electroactive microorganisms (also referred to as electricigens [14] on anodes and electrotophils on cathodes [15]) able to perform EET and thereby creating the link between microbial physiology and the flow of electric current. Different modes of EET are now known including most prominently the direct electron transfer (DET) [16,17]. DET requires a physical contact between the microorganism and the electrode, usually in a biofilm on the electrode surface. DET is not only restricted to microorganisms at the electrode surface transferring electrons with trans-membrane cytochrome complexes [18,19], as “long-range” DET can also be performed from more distant locations of the biofilm. One possible mode of long-range DET occurs via so-called nanowires or conductive pili [20–22] or other cellular appendages [23]. The most common model system for DET-based microbial electrocatalysis is the anodic oxidation of acetate by Geobacter. Even for this model system, comprising pure culture studies (e.g. [24–26]) as well as Geobacter dominated mixed cultures generated by electrochemically driven selection [27,28], different and sometimes contradictory EET results [29–31] have been shown, leading to the proposal of different mechanisms of electron transfer.

So far, different numerical models have been proposed for microbial fuel cells (e.g. [34–36]) or for electroactive microbial biofilms (e.g. [37–39]). For the latter, the existing models represent either the electron transfer at the electrode by voltammetry (i.e. voltage−current polarization experiments, [25,40,41]) or during biofilm growth [34].

We propose here a unifying modeling framework for DET-based electrodes possessing a metal-like conductive matrix: i) connecting
2. Model description

2.1. Biological, electrochemical and chemical reactions

2.1.1. Substrate conversion

For modeling purposes, the metabolism of electroactive microorganisms can be separated into several steps: the energy-yielding catabolic reaction, the biomass-producing anabolism and the electron transfer from the intracellular reduction equivalent NADH to c-type outer surface cytochromes, which deliver the electrons to a biofilm conductive matrix and finally to the anode [42–44] (Scheme 1A). For example, acetate, \( \text{Ac}^- \), is considered here both the microbial carbon and electron source. If the redox couple \( \text{NAD}^+ / \text{NADH} \) is the intracellular electron acceptor [45], then the overall catabolic reaction of acetate oxidation (Eq. (1)) can be assumed to occur with a double Michaelis–Menten reaction rate, \( r_{\text{bio}} \) (mol Ac\(^-\) m\(^-3\) s\(^{-1}\)) (Eq. (2)): \[ \text{Ac}^- + 4\text{H}_2\text{O} + 4\text{NAD}^+ \rightarrow 4\text{NADH} + 2\text{HCO}_3^- + 5\text{H}^+ \] (1)

\[ r_{\text{bio}} = q_{\text{Ac}^-} \cdot C_{\text{FX}} = q_{\text{Ac}^-} \cdot C_{\text{Ac}^-} \frac{C_{\text{NAD}^-}}{C_{\text{NAD}^-} + K_{\text{Ac}^-}} \frac{C_{\text{FX}}}{C_{\text{FX}}} \] (2)

\( K_{\text{Ac}^-} \) and \( K_{\text{NAD}^-} \) are the half-rate coefficients for acetate and NAD\(^+\), \( q_{\text{Ac}^-}^{\text{max}} \) is the maximum biomass specific substrate uptake rate (mol Ac\(^-\) C-mol X\(^{-1}\) s\(^{-1}\)) and the biomass concentration in the biofilm is \( C_{\text{FX}} \). Further, \( q_{\text{Ac}^-} \) (mol Ac\(^-\) C-mol X\(^{-1}\) s\(^{-1}\)) is the acetate uptake rate per biomass.

2.1.2. Intracellular electron transfer

Following the catabolic reduction of \( \text{NAD}^+ \) to \( \text{NADH} \) (Eq. (1)) the electrons are transferred via multiple redox carriers, like cytochromes and the quinone pool, to the terminal immobile redox centers that are as c-type outer surface cytochromes. Here this entire redox chain is modeled as cytochromes possessing two oxidation states, \( R \) and \( RH \) [37] (Eq. (3) and Scheme 1A). The redox centers are assumed to be transmembrane cytochromes and therefore using a 1H\(^+\)/1e\(^-\) transfer mechanism [46,47].

\[ \text{NADH} + \text{H}^+ + 2R \rightarrow 2\text{RH} + 2\text{NAD}^+ + 2\text{H}^+ \] r_{m} \] (3)

The reversible reaction rate \( r_{m} \) is here simply expressed as function of concentrations of involved chemical species and rate coefficients \( k_{r,m} \) and \( k_{r,m}^{-1} \):

\[ r_{m} = k_{r,m} C_{\text{NADH}} C_{R}^{-2} + k_{r,m}^{-1} C_{\text{RH}} C_{NAD}^{-2} \] (4)

In this model, tuned for anodic biofilms, the forward reaction rate has been assumed to be much faster than the reverse one.
2.1.3. Extracellular electron transfer to the conductive matrix

The cytochromes can change redox states by electron transfer with the biofilm conductive matrix (Scheme 1A, B):

\[ R + e^- + H^+ \xrightarrow{k_e} RH \]

(5)

The Butler–Volmer equation is assumed for \( r_e \) (mol R m\(^{-3}\) s\(^{-1}\)) and derived as a single electron transfer process between the two redox states of the cytochromes:

\[ r_e = k_f e C_e C_{HI} - k_r e C_{RH} \]

(6)

The rate coefficients are a function of the electrical potential in the conductive matrix, \( E_{BM} \), such that:

\[ k_{f e} = k^0_f e \exp \left[ -\alpha \frac{F}{RT} (E_M - E^0_R) \right] \]
\[ k_{r e} = k^0_r e \exp \left[ (1 - \alpha) \frac{F}{RT} (E_M - E^0_R) \right] \]

(7)

where \( k^0_f e \) is a standard rate for the electron transfer from the cytochromes to the biofilm matrix [48], \( \alpha \) is the transfer coefficient and \( E^0_R \) is the standard redox potential of the redox centers. The equation was developed similarly to [50]. This model assumes the cytochromes are in full contact with the conductive matrix, i.e. there is no resistance in this electron transfer.

So far, two main approaches exist for modeling the electron transfer rate of electroactive microbial anodes: Nerst–Monod (N–M) equation (e.g. [39,50]) and Butler–Volmer (B–V) equation (e.g. [37,49]). Due to the advantage of a more general approach, in the present model we chose to use B–V equation for modeling electron transfer. In contrast, N–M can be considered as a limiting case of B–V and it is useful if the terminal (heterogeneous) electron transfer is not rate limiting [51]. A detailed discussion on this can be found in SI 1.4.

2.1.4. Electrical conduction in the biofilm

It was assumed that the microbial cells transfer electrons via cytochromes to a conductive biofilm matrix. The “wires” of the conductive matrix conducting electrons from cells to the electrode (here an anode, Scheme 1B) are insulated from the electrolyte contained in the matrix conducting electrons from cells to the electrode (here an anode). The Butler–Volmer equation is assumed for \( r_e \) (mol m\(^{-3}\) s\(^{-1}\)) and derived as a single electron transfer process between the two redox states of the cytochromes:

\[ r_e = k_{f e} C_e C_{HI} - k_{r e} C_{RH} \]

(8)

The transfer of electrons by microbial redox centers to the conductive matrix with rate \( r_e \) (Scheme 1B) provides the current over the biofilm length, \( dJ/dx = r_e F \). With the current source defined by the Butler–Volmer Eqs. (6) and (7) the electron balance in the conductive matrix takes the form of Eq. (9):

\[ \sigma M \frac{d^2 E_M}{dx^2} + r_e F = 0. \]

(9)

The conductive matrix is electrically insulated (\( dE_M/dx = 0 \)) at the biofilm surface (biofilm/liquid interface, \( x = L_e \)).

Finally, the conductive matrix transfers electrons to the electrode with a rate \( r_e \) (mol-e m\(^{-3}\) s\(^{-1}\)) being a function of the electrode/matrix overpotential \( (E_k - E_{M}) \) and an standard electron transfer rate \( k^0_\text{e} \), different from the cell-matrix transfer rate coefficient \( k^0_e \). The homogeneous electron transport between cell and biofilm matrix and within the biofilm is achieved by similar redox species — in contrast to the heterogeneous electron transfer occurring between the redox centers and the anode [48]:

\[ r_e = k^0_e C_e \left\{ C_R \exp \left[ -\frac{F}{RT} (E_k - E_{M}) \right] - C_{RH} \exp \left[ (1 - \alpha) \frac{F}{RT} (E_k - E_{M}) \right] \right\}. \]

(10)

The current continuity condition at the electrode (\( x = 0 \)) is therefore \( r_e F = -\sigma_M dE_M/dx \) and the anodic current density is calculated as \( J_A = r_F = J \).

2.1.5. Anabolism and microbial growth

The microbial growth stoichiometry was derived using the thermodynamic principles described by Heijnen and Kleerebezem [52]. The energy released by the catabolic reaction (Eq. (1)) is utilized by the microbial anabolism (Scheme 1A, Eq. (12)):

\[ \text{Ac}^- + 4\text{H}_2\text{O} + 4\text{NAD}^+ \rightarrow 2\text{HCO}_3^- + 5\text{H}^+ + 4\text{NADH} \quad \Delta G^\text{cat}^\text{w} \]

(1)

The Gibbs energies \( \Delta G^\text{cat}^\text{w} \) and \( \Delta G^\text{cat}^\text{an} \) at pH 7 and 298 K were calculated with values of \( \Delta G^\text{cat}^\text{w} \) from Heijnen and Kleerebezem [52], then corrected for the local reaction conditions (e.g. concentration, temperature) (see Supplementary information 1.2), while the Gibbs energy of NAD\(^+\)/NADH couple was estimated from the respective standard potential (SI 1.1). \( \Delta G^\text{cat}^\text{w} \) is positive for standard conditions but after correction for local reaction conditions it becomes negative, therefore making biomass growth possible. To produce biomass, part of the gained catalytic energy released by the catabolic reaction (Eq.(1)) is utilized by the microbial anabolism (Scheme 1A, Eq. (12)):

\[ \text{f}_{\text{cat}} = \frac{(\Delta G^\text{cat}^\text{w} + \Delta G^\text{cat}^\text{an})}{\Delta G^\text{cat}^\text{w}} \]

(13)

The overall growth stoichiometry then becomes:

\[ -(f_{\text{cat}} + 0.525)\text{Ac}^- - 0.2\text{NAD}^+ - 4f_{\text{cat}}\text{NADH} - (4f_{\text{cat}} - 0.4)\text{H}_2\text{O} + \text{CH}_3\text{C}_0=\text{C}_2\text{H}_4 + (2f_{\text{cat}} + 0.05)\text{HCO}_3^- + 4f_{\text{cat}}\text{NADH} + (5f_{\text{cat}} - 0.275)\text{H}^+ = 0. \]

(14)

The maximum specific biomass growth rate \( \mu_{\text{max}} \) (h\(^{-1}\)) and the maintenance coefficient on acetate, \( m_{\text{Ac}^-} \) (mol Ac\(^-\) C-mol X\(^{-1}\) h\(^{-1}\)), can also be estimated [52]:

\[ \mu_{\text{max}} = \frac{3 \Delta G^\text{cat}^\text{w}/8 + 4.5 \Delta G^\text{cat}^\text{an}}{\Delta G^\text{cat}^\text{w} - 69000 \text{ (R)} \left( \frac{1}{T} \right)^2 \text{ (298)} \text{mol X}^{-1}} \]

(15)

\[ m_{\text{Ac}^-} = \frac{4.5 \Delta G^\text{cat}^\text{w} - 69000 \text{ (R)} \left( \frac{1}{T} \right)^2 \text{ (298)}}{\Delta G^\text{cat}^\text{w}} \text{mol X}^{-1} \text{ C-mol X}^{-1} \text{ h}^{-1} \]

(16)

The maximum specific biomass growth rate \( \mu_{\text{max}} \) (h\(^{-1}\)) and the maintenance coefficient on acetate, \( m_{\text{Ac}^-} \) (mol Ac\(^-\) C-mol X\(^{-1}\) h\(^{-1}\)), can also be estimated [52]:

\[ \text{f}_{\text{cat}} = \frac{(\Delta G^\text{cat}^\text{w} + \Delta G^\text{cat}^\text{an})}{\Delta G^\text{cat}^\text{w}} \]

(13)

Using a Herbert–Pirt relationship and the growth stoichiometry (Eq. (14)), the \( q^\text{max}_{\text{Ac}^-} \) takes the form of Eq. (17), which can be further used in Eq. (2):

\[ q^\text{max}_{\text{Ac}^-} = -(f_{\text{cat}} + 0.525)\mu_{\text{max}} + m_{\text{Ac}^-} \]

(17)
Finally, the biomass specific conversion rate in any point in the biofilm follows:

$$\mu = \frac{1}{-J_{\text{cat}} + 0.525q_{\text{Ac}} - m_{\text{Ac}}}.$$  \hspace{1cm} (18)

The biological conversion rates of compounds $y = \text{NADH}, \text{NAD}^+$, $\text{HCO}_3^-$, $\text{H}^+$ are $r_{\text{bio,}x} = q_y C_{\text{F,}x}$, with $q_{\text{NADH}} = 4f_{\text{cat}}(\mu - m_{\text{Ac}}) = -q_{\text{NAD}}^-$, $q_{\text{HCO}_3^-} = (2f_{\text{cat}} + 0.05)\mu - 2m_{\text{Ac}}$, and $q_{\text{H}^+} = (5f_{\text{cat}} - 0.275)\mu - 5m_{\text{Ac}}$.

2.1.6. Chemical reactions

Several acid–base equilibria (water, acetate, phosphate and carbonate) were accounted for within the biofilm and bulk electrolyte with most importantly allowing to estimate pH-values. These fast equilibria were mathematically described by using rate expressions, as described in Supplementary information, SI 2.1.

2.2. Mass balances

2.2.1. Biomass (biofilm growth)

The biofilm thickness increases in time due to biomass production or decreases as a result of endogenous metabolism or maintenance. The net biomass generation is described by the rate $r_{\text{bio,}x} = \mu C_{\text{F,}x}$ and transport within the biofilm is dominated by convection (velocity $u_F$), so that the biomass conservation in a one-dimensional biofilm domain becomes [53]:

$$\frac{\partial C_{\text{F,}x}}{\partial t} = \frac{\partial (u_F C_{\text{F,}x})}{\partial x} + r_{\text{bio,}x}.$$ \hspace{1cm} (19)

By assuming a constant biomass density in the biofilm, $C_{\text{F,}x}$, and a zero-velocity condition at the electrode surface ($u_F = 0$ at $x = 0$), Eq. (19) can be integrated to obtain the speed of the biofilm surface advancement due to net biomass generation ($u_F = u_{\text{fl}}$ at $x = L_F$, Scheme 1B):

$$u_{\text{fl}} = \frac{L_F}{\int_0^{L_F} C_{\text{F,}x} \, dx}.$$ \hspace{1cm} (20)

With $u_{\text{fl}}$ calculated at each time step, the change of biofilm thickness results from integrating Eq. (21) from an initial thickness $L_{F,0}$:

$$\frac{dL_F}{dt} = u_{\text{fl}}.$$ \hspace{1cm} (21)

If desired, rates of biomass detachment from and attachment to the biofilm can be added to the right-hand-side of Eq. (21) in the future [53].

2.2.2. Electron mediators and fixed redox centers

The balance equations for cytochromes ($C_{\text{F,R}}$ and $C_{\text{F,RH}}$) and NAD$^+$/NADH ($C_{19\text{F,NAD}}$ and $C_{19\text{F,NADH}}$) in each point $x$ in the biofilm are similar to the biomass balances and consider the relevant rates $r_{\text{F,R}} = -2r_{\text{m,R}} - r_{\text{R,F}}, r_{\text{F,RH}} = 2r_{\text{m,RH}} + r_{\text{R,H}}, r_{\text{F,NAD}} = r_{\text{bio,NAD}} + r_{\text{m,NAD}}$ and $r_{\text{F,NADH}} = r_{\text{bio,NADH}} - r_{\text{m,NADH}}$. Thus, effective rates change within the biofilm depending on the environmental variables, like electric potential and cytochrome concentration.

2.2.3. Solutes in biofilm

Dissolved chemical species in the biofilm, each with a local concentration $C_{y}(x, t)$, are characterized by spatial concentration gradients. The Nernst–Planck equations with diffusion and ion migration, coupled with the electroneutrality condition (see Supplementary information 2.1), were used for transport and reaction of ions and neutral molecules in the biofilm, as detailed in Supplementary information, SI 2.2. At the biofilm surface all concentrations are equal with those in bulk liquid, while at the electrode surface zero-flux is set.

2.2.4. Solutes in bulk electrolyte

Concentrations of solutes in the bulk liquid, $C_y(t)$, change in time. The balance equations in the bulk volume ($V_B$) include contributions from acid–base reactions in the bulk liquid, ion flux exchanged with the biofilm ($J_{y,i}$) through the area exposed to the bulk ($A_B$), the flux through the membrane ($J_{y,\text{M}}$) with the membrane surface area ($A_M$) and, possibly, new medium additions or substitutions, all detailed in SI 2.3.

3. Results and discussion

The presented modeling framework has been applied on experimental data from various studies by different research groups. Thereby, for each study case specific input parameters were considered, such as electrode size, buffer composition, and acetate concentration. These parameters are listed in the respective supplementary information sections.

3.1. Macroscopic level: biofilm growth and current production

This first model application demonstrates how the modeling framework allows describing two of the most important performance parameters of microbial anodes: current density ($j$) and coulombic efficiency ($CE$). Fig. 1A shows the current production in time measured for a Geobacter biofilm by Bond and Lovley [54] as well as the best fit model results (details on fitting see below). The measured and modeled current curves are very similar and, in terms of maximum current density, almost identical (36 $\mu$A cm$^{-2}$). When considering a complete digestion of the initially provided substrate (acetate) as well as the two substrate additions at day 4 and day 5, the achieved coulombic efficiency ($CE$) can be calculated. The experimental values ($CE = 86.6\%$ and $CE = 90.3\%$ for the first and second cycle, respectively) are also very close to the modeled ones ($CE = 90.4\%$ and $CE = 89.8\%$).

Furthermore, the biofilm thickness is calculated, a parameter usually not easy to measure in vivo and in real time (Fig. 1B). In non-limiting substrate supply the biofilm grows, but it starts to shrink when the substrate is depleted. This is due to biomass maintenance, a process implemented in the model by considering the energy consumption for sustaining the biofilm and its activity. In the presence of acetate the maintenance also slows down the biofilm growth, but this biomass-consuming process becomes clearly visible after the complete substrate oxidation, when the biofilm thickness decreases. The model-derived maximum growth rate of anode respiring Geobacter biofilms of 0.022–0.029 h$^{-1}$ (Fig. 1B) is in the range of other reported anaerobic growth rates based on acetate, e.g. of 0.010–0.018 h$^{-1}$ [55,56]. Another interesting result is the calculated metabolic efficiency of biomass build-up, $f_{\text{cat}}$, i.e. the moles of acetate needed to generate 1 C-mol of biomass. Expectedly, the metabolic efficiency remained nearly constant ($f_{\text{cat}} = 2.2$–2.3) during the course of the experiment (Fig. 1B), since the biofilm was relatively thin and thus no external factors were limiting (e.g. acetate diffusion, pH, redox potential and biofilm matrix conductivity). However, when acetate is depleted, the maintenance requirements dominate the metabolism, leading to a remarkable increase in $f_{\text{cat}}$ and biofilm shrinkage (Fig. 1B).

When fitting the model to the measured current–time curve in an iterative approach a number of available input parameters were varied. Thereby the fitting of maximum current density and duration of the current production in a certain fed-cycle were main fitting criteria. Generally, the following parameters could play a role in the metabolic activity and thus current production of electroactive microbial biofilms: (i) concentration of cytochromes (i.e. redox centers) in the biofilm.
(C_{R,RI}), (ii) substrate affinity constant \( (K_{S}^-) \), (iii) electron transfer kinetics \( (k_{1}^0, k_{2}^0) \), (iv) biofilm conductivity \( (\sigma) \) and (v) intracellular electron transfer kinetics \( (k_{r,m}, k_{r,m}) \).

The cytochrome concentration in the biofilm is clearly a critical and sensitive model parameter. Low cytochrome concentrations slow down the biofilm growth and subsequently lower also the current production (Fig. 1C–D). For a detailed discussion about cytochrome concentration, see Section 3.3: concentration of redox active centers. Furthermore, cytochrome concentration is directly linked to the biomass concentration within the biofilm and thus influences the resulting biofilm thickness and the current production (SI Fig. S2E–F). Biomass concentration in electroactive microbial biofilms shows strong variability among cultivation conditions [57,58] and therefore we used an accepted standard value for anaerobic biofilms [53]. From the qualitative estimation based on the model results compared with current data (see Fig. 1A and C–D), the cytochrome concentration used in the following was 300 mM. This obtained value is in the same order of magnitude compared to values calculated and derived from Esteve-Núñez et al. [59] (for details, please see SI 1.3). Other parameters show only a minor impact on the biofilm growth and current production. Alterations of the heterogeneous electron transfer rate \( (k_{0}^0) \) by several orders of magnitude compared to the literature values [48] show no remarkable change in the biofilm growth and current production (Fig. 1E–F). Only if the heterogeneous electron transfer rate was unrealistically decreased to \( 10^{-7} \) s\(^{-1} \) it would become growth limiting (Fig. 1F). In contrast, alterations in the heterogeneous electron transfer rate \( k_{0}^0 \) have a considerable effect during cyclic voltammetry, as it is shown in Section 3.3. Likewise, the homogeneous electron transfer rate \( (\text{cell/biofilm}, k_{0}^0) \)
and the biofilm conductivity do not reveal a significant effect on the biofilm growth (SI Fig. S1) within the studied range of value. The metabolic parameters remained untapped in the calibration of the model due to the lack of input parameters. So far, the metabolism of *Geobacter* is not comprehensively described and no data about enzyme turnover rates and Michaelis–Menten constants of enzymes are available. Hence, the model focused on electrochemical parameters to help in the interpretation of recent experimental data. Nevertheless, the parameter testing on several metabolic properties (intracellular electron transfer \( k_{f,m} \), half-saturation coefficient for acetate \( K_{Ac} \)), biomass concentration \( C_{f,X} \) revealed also a great influence on the model calculation (SI Fig. S2). A faster intracellular electron transfer increased the biofilm growth (SI Fig. S2A–D) but an increased half-saturation coefficient for acetate slowed down growth and current production (SI Fig. S2E–F).

### 3.2. Spatial resolution on the biofilm level

In addition to macroscopic variables, i.e. current production, coulombic efficiency and biofilm thickness, the model also reveals biofilm properties at the micro scale, i.e. concentration profiles, pH and redox potential along the biofilm depth. The microscale properties, however, are often more difficult to be obtained experimentally. Fig. 2A, C shows experimental results reported by Franks et al. [60] on the pH profile in *Geobacter* biofilms of a given thickness (70 μm) during anodic respiration, conditions in which a current density of 2.2 A m\(^{-2}\) was reached. The pH profile was calculated with the model for the same current density, but at different buffer compositions (detailed parameters in Table S2), mimicking the flow chamber experiments from [60]. While the pH remains almost constant in the bulk liquid, a pH gradient builds up in the biofilm, which increases with a lower buffer capacity (Fig. 2A). Furthermore, an important factor determining solute profiles in the biofilm is the attenuation of diffusion coefficients within the biofilm compared with those in water (i.e. an “effective” diffusion coefficient in the biofilm). Simulations presented in Fig. 2C show how decreased diffusivities of all chemical species can lead to substantial acidification at the electrode surface, for the same bulk electrolyte solution. However, a comparison between modeled and measured pH can only remain here at a qualitative level, because: (i) the effective diffusion coefficient is likely to change as a function of biofilm density [61], (ii) the solution speciation depends in reality on dissociation equilibria of many other chemical species present in the medium, as well as (iii) on the buffering capacity of the biofilm cells and its polymeric matrix. All these phenomena can presently not be included in the model.

The redox gradient, i.e. ratio of oxidized and reduced cytochromes, for which contradictory experimental data exist [62–66], is of special interest for microbial electrodes. The mode of electron transfer, e.g. soluble mediators, electron hopping or metal-like conductivity, is assumed to play a major role in the formation of redox gradients, i.e. indicates if redox gradients will arise. A few model approaches already focused on soluble electron mediators using Fick’s diffusion and Nernst–Planck’s electromigration for these solutes and therefore for electron transport and reported electron mediator gradients of concentration [34,41]. For direct electron transfer two hypotheses exist: electron hopping and metal-like conductivity. An electron hopping

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**Fig. 2.** Modeled and experimental pH profiles and the respective redox profiles for the modeled biofilms. (A–B) Calculated (solid lines) and experimental (dotted line) pH profiles and the corresponding redox profiles (concentration of oxidized \( C_{O,C} \), solid lines) and reduced cytochromes \( C_{R,H} \), dashed lines) for biofilms with a constant diffusion attenuation factor \( \varepsilon_D = 0.5 \) and different bicarbonate buffer composition \( C_{HCO_3} = 1–50 \text{ mM} \), 1 mM (orange lines), 5 mM (red lines), 10 mM (green lines), and 50 mM (blue lines). (C–D) Calculated (solid lines) and experimental (dotted line) pH profiles and the corresponding redox profiles (profiles of oxidized \( C_{O,C} \), solid lines) and reduced cytochromes \( C_{R,H} \), dashed lines) for modeled biofilms with a constant bicarbonate buffer composition \( C_{HCO_3} = 5 \text{ mM} \) and different diffusion attenuation factors \( \varepsilon_D = 0.1–0.8 \), 0.1 (blue), 0.2 (red), 0.5 (green), and 0.8 (blue). Experimental data are taken from Franks et al. [60,85]. The model parameters are listed in Tables 1 and S2.
### Table 1
Summary of all parameters their symbols, values and units used throughout the model.

<table>
<thead>
<tr>
<th>Parameter description</th>
<th>Symbol</th>
<th>Value</th>
<th>Units</th>
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<tr>
<td><strong>Microbial kinetic and thermodynamics</strong></td>
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<tr>
<td>Half-saturation coefficient for acetate</td>
<td>$K_{Ac}$</td>
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<td>mol Ac$^-$/m$^3$</td>
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<td>[52]</td>
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<td>[52]</td>
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<td>kJ/mol C-mol$^{-1}$</td>
<td>[52]</td>
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<td><strong>Acid–base reactions</strong></td>
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<td>mol$^2$/L$^2$</td>
<td>[86]</td>
</tr>
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<td>mol/L</td>
<td>[86]</td>
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<td>$10^{-4.756}$</td>
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<td>- Water dissociation</td>
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<td>$10^5$</td>
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<td>Arbitrarily large value</td>
</tr>
<tr>
<td>- CO$$_2$$, acetate and H$$_2$$PO$$_4$$ dissociation</td>
<td>$k_{w}$</td>
<td>$10^7$</td>
<td>1/s</td>
<td>Arbitrarily large values</td>
</tr>
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<td><strong>Electrochemical kinetics and electrical properties</strong></td>
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<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Standard (homogeneous) electron transfer rate (cell/biofilm conductive matrix)</td>
<td>$\theta$</td>
<td>1.2</td>
<td>1/s</td>
<td>[48]</td>
</tr>
<tr>
<td>Standard (heterogeneous) electron transfer rate (biofilm/electrode)</td>
<td>$\theta$</td>
<td>0.03</td>
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<td>[48]</td>
</tr>
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<td>m$^2$/mol$^3$ s</td>
<td>Chosen</td>
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<td>Reverse rate constant for the intracellular electron transfer from redox centers to NAD$^+$</td>
<td>$\theta$</td>
<td>$1 \times 10^{-10}$</td>
<td>m$^2$/mol$^2$ s</td>
<td>Chosen</td>
</tr>
<tr>
<td>Standard redox potential of the redox centers</td>
<td>$E_a$</td>
<td>–0.136</td>
<td>V (SHE)</td>
<td>[70]</td>
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<td>Transfer coefficient for redox rate</td>
<td>$\alpha$</td>
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</tr>
<tr>
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<td>$\mu$m</td>
<td>Chosen length of a typical microbial cell</td>
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<tr>
<td>Electrode potential</td>
<td>$E_{eq}$</td>
<td>b</td>
<td>V (SHE)</td>
<td>Variable by case$^b$</td>
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<td>Biofilm matrix conductivity</td>
<td>$\sigma_{lm}$</td>
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<td>S/m</td>
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<td><strong>Biofilm properties</strong></td>
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<tr>
<td>Initial biofilm thickness</td>
<td>$L_{bi}$</td>
<td>b</td>
<td>$\mu$m</td>
<td>Variable by case$^b$</td>
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<td>Biomass concentration in the biofilm</td>
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<td>2000</td>
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<td>Chosen</td>
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<td>Concentration oxidized/reduced redox centers</td>
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<td>300</td>
<td>mol/m$^3$</td>
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<tr>
<td></td>
<td></td>
<td>1.3</td>
<td>mol/m$^3$</td>
<td>Chosen for cyclic voltammetry</td>
</tr>
<tr>
<td>Concentration NAD$^+$/NADH</td>
<td>$C_{NAD^+/NADH}$</td>
<td>20</td>
<td>mol/m$^3$</td>
<td>Adapted from [87]</td>
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<tr>
<td>Biofilm area and electrode area</td>
<td>$A_a$</td>
<td>b</td>
<td>cm$^2$</td>
<td>Variable by case$^b$</td>
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<td><strong>Diffusion coefficients in water</strong></td>
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<td>- Acetate</td>
<td>$D_{Ac}$</td>
<td>$1.1 \times 10^{-9}$</td>
<td>m$^2$/s</td>
<td>[88,89]</td>
</tr>
<tr>
<td>- Acetic acid</td>
<td>$D_{Ac}$</td>
<td>$1.3 \times 10^{-9}$</td>
<td>m$^2$/s</td>
<td>[88,89]</td>
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<td>- CO$$_2$$</td>
<td>$D_{CO_2}$</td>
<td>$2.0 \times 10^{-9}$</td>
<td>m$^2$/s</td>
<td>[88,89]</td>
</tr>
<tr>
<td>- H$$^+$$</td>
<td>$D_{H^+}$</td>
<td>$1.3 \times 10^{-9}$</td>
<td>m$^2$/s</td>
<td>[88,89]</td>
</tr>
<tr>
<td>- Na$$^+$$</td>
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<td>$9.3 \times 10^{-9}$</td>
<td>m$^2$/s</td>
<td>[88,89]</td>
</tr>
<tr>
<td>- OH$$^-$$</td>
<td>$D_{OH^-}$</td>
<td>$5.3 \times 10^{-9}$</td>
<td>m$^2$/s</td>
<td>[88,89]</td>
</tr>
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<td>- CO$$_2$$</td>
<td>$D_{CO_2}$</td>
<td>$1.9 \times 10^{-9}$</td>
<td>m$^2$/s</td>
<td>[88,89]</td>
</tr>
<tr>
<td>- HCO$_3$</td>
<td>$D_{HCO_3^-}$</td>
<td>$1.2 \times 10^{-9}$</td>
<td>m$^2$/s</td>
<td>[88,89]</td>
</tr>
<tr>
<td>- H$_2$PO$_4$</td>
<td>$D_{H_2PO_4^-}$</td>
<td>$1.2 \times 10^{-9}$</td>
<td>m$^2$/s</td>
<td>[88,89]</td>
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<tr>
<td>- HPO$_4$$^2-$</td>
<td>$D_{HPO_4^{2-}}$</td>
<td>$1.0 \times 10^{-9}$</td>
<td>m$^2$/s</td>
<td>[88,89]</td>
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<td>Reduction factor for diffusion coefficient in the biofilm</td>
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<td>0.5</td>
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<td>[90]</td>
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<td>Bulk liquid volume</td>
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<td>b</td>
<td>L</td>
<td>Variable by case$^b$</td>
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<td>Initial concentrations in bulk liquid and biofilm$^a$</td>
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<tr>
<td>- Total acetate</td>
<td>$C_{b,Ac^-}$</td>
<td>b</td>
<td>mol/m$^3$</td>
<td>Variable by case$^b$</td>
</tr>
<tr>
<td>- Total carbonate</td>
<td>$C_{b,CO_3^-}$</td>
<td>b</td>
<td>mol/m$^3$</td>
<td>Variable by case$^b$</td>
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<td>- Total phosphate</td>
<td>$C_{b,PO_4^{2-}}$</td>
<td>b</td>
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<td>Variable by case$^b$</td>
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<td>$C_{b,Cl^-}$</td>
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<td>$C_{b,H^+}$</td>
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<td>If not stated otherwise$^b$</td>
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<td>cm$^2$</td>
<td>Chosen</td>
</tr>
<tr>
<td>Diffusion coefficients in membrane</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>- H$^+$</td>
<td>$D_{M,H^+}$</td>
<td>$5.3 \times 10^{-10}$</td>
<td>m$^2$/s</td>
<td>[91]</td>
</tr>
<tr>
<td>- Na$^+$</td>
<td>$D_{M,Na^+}$</td>
<td>$2.1 \times 10^{-10}$</td>
<td>m$^2$/s</td>
<td>[91]</td>
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<td>Membrane thickness</td>
<td>$L_M$</td>
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<td>$\mu$m</td>
<td>[91]</td>
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<tr>
<td>Membrane electric permittivity</td>
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<tr>
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<td>$\varepsilon_M$</td>
<td>$1.8 \times 10^{-10}$</td>
<td>F/m</td>
<td>[91]</td>
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<tr>
<td>- Na$^+$</td>
<td>$\varepsilon_M$</td>
<td></td>
<td></td>
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<td>C/mol</td>
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<td>Universal gas constant</td>
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<td>J/mol K</td>
<td></td>
</tr>
<tr>
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<td>$T$</td>
<td>298</td>
<td>K</td>
<td>If not stated otherwise$^b$</td>
</tr>
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</table>
approach with fixed electron mediators (e.g., similar to a redox-polymer [67,68]) and a respective electron diffusion coefficient was used by Strycharz et al. and resulted in the occurrence of redox gradients due to limiting electron transfer between the bound mediators [40]. Experimental and modeling results from Richter et al. support this modeling approach, but these studies also suggest that the homogeneous electron transfer is limited by the diffusion of counter ions within the biofilm [25,40]. An alternative to Fick’s law for modeling “diffusive” electron transport is Ohm’s law of conductivity. Only Marcus et al. and Fischer et al. used this approach for modeling the electron transfer performing electric conduction within the biofilm but did it also not comment on the evolution of redox gradients [39,49]. In the model presented here, based on metal-like conductivity, the electron transfer is driven by an electric field and with the parameters derived from literature (Table 1) no redox gradients arise, i.e., gradients of the ratio of oxidized and reduced cytochromes (Figs. 2B, D, S3, and S4). In the following, several model parameters were tested to reveal potential factors influencing the redox gradient. For instance, the standard heterogeneous electron transfer rate (\(k^0\)) of the “electron gates” at the electrode surface is supposed to play a key role, as this may limit the electron flow in the biofilm layers more distant to the electrode surface. Within the wide range of values tested, the heterogeneous electron transfer rate to the electrode limited the biofilm growth and microbial metabolism only, if drastically decreased (Fig. 1E-F). Even then, almost no redox gradients arise (SI Fig. S4A–B) across a 12 μm thick biofilm. Only if the biofilm becomes remarkably thicker and the heterogeneous electron transfer rate is slower than experimentally measured [48], reduced cytochromes accumulate near the electrode and a redox gradient evolves (SI Fig. S3A–B). Certainly, other parameters could impact the formation of redox profiles in reality. For instance, buffer conditions and the diffusion of ions within the biofilm (especially protons) and consequently the pH profile inside the biofilm influences slightly the ratio of oxidized and reduced cytochromes (Fig. 2B, D). Therefore, not the electron, but the counter ion (mainly H\(^+\)) transport may govern the overall activity, which is in line with indications from several experimental studies [69]. One also may speculate that the biofilm conductivity is crucial for the formation of a redox gradient. However, even a decrease of the biofilm matrix conductivity to semiconductor-like values led to only a minor redox gradient (SI Fig. S3C). These model results support recent experiments, which also did not lead to observable redox gradients and subsequently assumed other bottlenecks for current production in Geobacter based biofilms, i.e., metabolic constraints or different control mechanisms for electron flow between pure and mixed Geobacter cultures [62]. Nevertheless, it is still subject of investigation whether electron hopping or metal-like conductivity is the mechanism for electron transfer within a specific biofilm. Although the proposed biofilm model is based on metal-like conductivity and as such it shows no redox gradients, other models based on different electron transfer modes may lead to redox gradients. Thus, a coupling of the presented metabolic calculations with electron hopping as alternative mode of EET could help clarifying this open question in future.

3.3. Biofilm electron transfer

One frequently used method to study the mechanisms of microbial extracellular electron transfer is cyclic voltammetry (CV) [70]. CV has been applied in several studies to Geobacter based biofilms [31,70,71] and models to interpret cyclic voltammograms have been developed [25,40,41], for both turnover and non-turnover conditions (i.e., voltammograms obtained in the presence and absence of the microbial substrate, respectively). The introduced modeling framework can also be used for modeling cyclic voltammograms and to study microbial electron transfer properties. In the following the results of its application on a set of non-turnover CV curves from the recent study of Jana et al. [72] harboring a comprehensive data set for thin (5 μm) and thick (50 μm) biofilms (Fig. 3A and B respectively), and turnover CV data from Fricke et al. [70] (Fig. 4A–B) are shown. These studies were chosen in order to fulfill the criteria of comparability with the model set-up, because for planar electrodes the geometric area can be easily used as an input parameter. Most other studies used 3D electrodes (foam, fiber brush) for the experiments (e.g., [73–75]), which cannot be directly used because it leads to the question, how bacterial accessible surface area is defined.

The fitting criteria used to calibrate the model parameters using these sets of data included: (i) peak current densities, (ii) formal potential (in turnover CV), or the oxidation and reduction peak potentials (in non-turnover CV), (iii) the area of the respective oxidation and/or reduction peak in turnover CVs (this area is directly related to the number of cytochromes involved in the dynamic electron transfer process in non-turnover conditions) and (iv) the peak separation from the formal potential (\(E_0–E^\text{f}\)) for non-turnover CVs as function of the scan rate (\(v\)), which reflects the electron transfer kinetics.

Based on these fitting criteria a comprehensive parameter testing was performed. The parameters found to be most important for the correct model description of turnover as well as non-turnover CVs were: (i) the concentration of cytochromes, i.e., redox centers, in the biofilm (\(C_{\text{C,R}}\), Figs. 3E–F and 4C) and (ii) the heterogeneous electron transfer rate (\(k^0\), Figs. 3G–H and 4D).

3.3.1. Concentration of redox active centers

Interestingly, to obtain a reasonable representation of both the voltammetric peak areas and peak current densities for the modeled CVs (Figs. 3A–B, 4A), the concentration of cytochromes had to be lowered to 3 mM (non-turnover) and 1 mM (turnover), compared to the necessary 300 mM when modeling biofilm growth (see Section 3.1). This indicates that only a certain “share” of the redox centers participate in the electron transfer during CV measurements, i.e., they are available for fast responses when using voltammetry. In turnover CVs the concentration of cytochromes does not change considerably the peak currents, but has a significant impact on the formal potential (Fig. 4C) and promotes the occurrence of a peak pair centered at ~0 V (vs. SHE) superimposed to the turnover CV-curve (Fig. 4C). This phenomenon also appears with faster scan rates for a constant cytochrome concentration (Fig. 4F). As previously reported [40], this peak pair may be associated to slow acetate oxidation that is limiting catalytic current production. In this context Strycharz et al. also speculate that rather other intracellular processes, i.e., reduction of the cytochrome pool, may limit current generation and that substrate oxidation is comparable fast [40]. Within the current model the electron transfer limitation related to the peak formation was caused by substrate oxidation rather than by internal electron transfer (SI Fig. S7). Further, one may speculate that the periplasmic pool of redox compounds, e.g., quinones, acts as a redox buffer between the cell and the terminal transfer proteins to the electrode [76].

The fact that differing cytochrome concentrations are needed to represent biofilm growth, turnover CVs and non-turnover CVs – while all other intrinsic parameters are constant – leads to another important question:

*What are the “active” redox centers, i.e., these that can exchange electrons with the electrode, during a certain electrochemical measurement?*
For simplicity reasons this modeling platform considered only one species of a c-type cytochrome possessing one mid-point potential, and transferring one electron per molecule at a time, as cellular redox centers. In reality, Geobacteraceae are known for producing more than 100 different types of cytochromes (with most cytochromes possessing more than one electron binding haem domains) [77] and different electron transfer mechanisms, e.g. \( \text{1H}^+ / \text{1e}^- \) mechanism or \( \text{1H}^+ / \text{2e}^- \) mechanism. Recent experimental data suggest that several respiratory pathways with different cytochromes exist in parallel. Each pathway is able to transfer electrons to an external electron acceptor in accordance to the applied anode potential [78,79]. Furthermore, the amount of cytochromes may change with biofilm age and vary over the biofilm.

Fig. 4. Comparison between simulation results of microbial anodes and results obtained from Fricke et al. [70] in cyclic voltammetry experiments under turnover conditions. (A) Modeled (solid line) and experimental (dashed line) cyclic voltammogram recorded at 5 mVS\(^{-1}\) from −0.5 to 0.5 V vs. SHE. Experimental data is taken from [49]. (B) Corresponding first derivative of the modeled (solid line) and experimental (dashed line) CV. (C) Modeled current density with several values for the total cytochrome concentration \((C_{\text{tot}})\). (D) Modeled current density with several values for the standard heterogeneous electron transfer rate \((k^c)\). (E) Modeled current density with several values for the standard homogeneous electron transfer rate \((k^v)\). (F) Modeled current density with various scan rates \((v)\). A solid line in the parameter analysis indicates the voltammogram obtained with the best fitting set of parameters compared to Fricke et al. One parameter at the time was varied in the simulations. Model parameters are listed in Tables 1 and S4.

Fig. 3. Comparison between modeled cyclic voltammograms and experimentally obtained by Jana et al. [72] in the absence of acetate (non-turnover conditions). (A) Thin biofilms (5 \(\mu \text{m}\)) and (B) thick biofilms (50 \(\mu \text{m}\)) at different scan rates. Modeled data (solid lines) is compared to experimental data obtained from Jana et al. (dotted lines). 5 mVS\(^{-1}\) (blue), 20 mVS\(^{-1}\) (red), 40 mVS\(^{-1}\) (green), and 60 mVS\(^{-1}\) (black). Respective peak separation analysis for (C) thin and (D) thick biofilms. Modeled data (solid lines) is compared to experimental data obtained from Jana et al. (dotted lines). (E) Modeled current density with several values for the total cytochrome concentration \((C_{\text{tot}})\) for a 5 \(\mu \text{m}\) biofilm. (F) Modeled current density with several values for the total cytochrome concentration \((C_{\text{tot}})\) for a 50 \(\mu \text{m}\) biofilm. (G) Modeled current density with several values for the standard heterogeneous electron transfer rate \((k^c)\) in a 5 \(\mu \text{m}\) biofilm. (H) Modeled current density with several values for the heterogeneous electron transfer rate \((k^c)\) in a 50 \(\mu \text{m}\) biofilm. (I) Modeled current density with various biofilm matrix conductivities \(\sigma_{\text{matrix}}\) for a 5 \(\mu \text{m}\) biofilm. (J) Modeled current density with various biofilm matrix conductivities \(\sigma_{\text{matrix}}\) for a 50 \(\mu \text{m}\) biofilm. The solid line in the parameter analysis indicates the voltammogram obtained with the best fitting set of parameters compared to Jana et al. (scan rate of 60 mVS\(^{-1}\)). One parameter at the time was varied in the simulations. Model parameters are listed in Tables 1 and S3.
thickness [18,80] and cytochromes can have different functions within the microbial cell. Generally, in addition to their role in extracellular electron transfer, cytochromes are involved in further metabolic pathways and there indications for charge storage function within the biofilm [81]. Further on, other redox carriers like the quinone pool are involved, being only in contact with the electrode via a chain of redox carriers. All these redox carriers possess not only individual formal potentials, but also specific electron transfer rates etc. As a consequence a certain species of cytochrome will only exchange electrons with the electrode (i.e. be responsive to the measurement) when the driving force (i.e. the electrode potential) as well as the time needed for electron transfer is sufficient. As more data becomes available, the model could be extended with different numbers and types of cytochromes (with different redox potentials) and additional internal electron transfer processes, so that more complex non-turnover CV shapes can be obtained than those in Fig. 3A–B.

3.3.2. Electron transfer rate

The heterogeneous electron transfer rate (k_C^HET) does, within the range of 0.001 s^{-1} to 10 s^{-1}, not alter the biofilm growth (Fig. 1E–F). The value k_C^HET = 0.03 s^{-1}, reported in [48] and used for modeling biofilm growth and current production (Section 3.1), did not result in good description of the CV experiments. Only using values of about 1.2 s^{-1} for the heterogeneous electron transfer rate (similar to the homogeneous electron transfer rate coefficient) provided a reasonable agreement with the experimental data (Figs. 3A–D and 4A–B). In turnover CV curves the formal potential of the cytochromes is shifted to more positive values the slower the heterogeneous electron transfer rate is set (Fig. 4D). The same observations are made for the homogeneous (cell/biofilm) electron transfer rate (k_C^HET, Fig. 4E). However, k_C^HET and k_C^HET consider considerably change the electrochemical reversibility, expressed in peak separation in non-turnover CV curves (Figs. 3–H and S5A–B).

Most voltammetric studies do only allow to get access to the apparent electron transfer rate [31,70,71] and only a few studies describe kinetic mechanisms that can distinguish between homogeneous and heterogeneous electron transfer [48]. The electron transfer rate depends on other factors as well, including for instance the electrode material [82], its crystallographic orientation, or the different electron tunneling distance between the electrode and the iron center [83]. Therefore, the model should be adapted for a more detailed description of the extracellular electron transfer process.

It was also found that biofilm matrix conductivity (σ_m) could influence the outcome of the modeled voltammetric response, but only when approaching semiconductor-like values [84] (Fig. S1–J and SI Fig. S6C). It is obvious that a thicker biofilm produces more current (Fig. 3 and SI Fig. S6A), but it also shifts the formal potential to more positive values due to the build-up of ohmic resistance in the biofilm (SI Fig. S6B, e.g. [25]).

4. Conclusions

A modeling framework for microbial anodes composed of electroactive microbial biofilms based on direct electron transfer was developed and used for interpretation of experimental observations on Geobacter based biofilms from several independent sources focusing on electrochemical data, as the kinetics of the metabolism of Geobacter is not comprehensively described and metabolic parameters could not be included extensively. The novelty of the proposed model consists in its combined description of biofilm growth and performance at constant electrode potentials with a voltammetric characterization (i.e. dynamic potential conditions). It is shown that during biofilm growth under previously reported experimental conditions no redox gradients and only weak pH gradients should form. Furthermore, while for growth conditions the heterogeneous electron transfer rate is not a sensitive parameter, when modeling CVs this rate has to be within the range of the homogeneous electron transfer rate. In general, the concentration of cellular redox carriers (here denominated as cytochromes) proved to be the most sensitive parameter and therefore the key for data fitting. Thereby the concentration of “active” (i.e. “electrochemically accessible”) redox carriers that participate in the heterogeneous electron transfer to the electrode differs strongly between constant potential and voltammetric conditions. This may imply that an important share of the cellular redox carriers may act solely as “electron pool” that can only release/accept electrons at lower rates than the rate of the extracellular electron transfer. Especially this latter finding has to be assessed further, and raises interesting questions on the microbial physiology.

This modeling framework may be extended with the description of anodes of complex geometries, with biofilms composed of a diverse microbiomes and thus complex food webs, as well as DET-based cathodes, and full bioelectrochemical systems.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.bioelechem.2015.03.010.

References


