Influence of pH and Carbonate Buffering on the Performance of a Lactate Microbial Fuel Cell

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Abstract: Microbial Fuel Cells (MFC's) contain complex environments where electrochemical, physical and biological events are tightly linked. In this work we present a 1D model partially describing a *Shewanella oneidensis* MFC that consumes sodium lactate [lactate → acetate + CO_2 + $2H^+$ + $2e^-$]. The model focuses on the effects of pH on the output of the MFC. Release of protons during lactate consumption is critical for fuel cell performance because they are needed to reduce O_2 to water at the cathode. Simultaneously, proton transport affects the pH of the anode compartment and this in turn can affect bacterial metabolic key processes. Often in MFC experiments, a pH buffer is used to protect the biological species, but this affects H^+ transport across the membrane and its availability at the cathode.

In our model we consider anodic, proton exchange membrane (PEM) and cathodic subdomains to study pH changes and their effects on different chemical species in their protonated and dissociated forms [lactate and acetate, CO_2 buffering system {CO_3^{2-}, CO_2^-, H_2CO_3 and HCO_3^-}, OH^-, H^+, O_2 and Na^+]. CO_2, which is present as a by-product of the lactate oxidation, also have pH buffering activity.

The rate of lactate consumption used is taken from experiments carried out under aerobic conditions (1).

The model predicts significant media acidification during operation of the MFC, which can affect the availability of lactate, pH and proton transport.

Keywords: Microbial Fuel Cell, Modeling, pH Buffering

1. Introduction

Fuel cell technology is receiving increasing attention recently (2, 3). One of the most challenging types are microbiological fuel cells (MFC), where bacteria and other microorganisms can be used to oxidize several organic compounds at the anode, releasing electrons to the anode and protons (H^+) to the solution. These protons then diffuse through a proton exchange membrane, to the cathode chamber where the electrical circuit is closed. MFC's are potentially able to work with organic-rich media, such as wastewater and other organic residues (3, 4).

This capability of electrical generation may also be the basis for different sensors on a wide range of applications (5, 6, 7).

Fuel cells are already complex and interdisciplinary electrochemical systems where both charge transfer and mass transport (sometimes including convection) must be closely watched. Moreover, bacteria in MFC's introduce an additional source of complexity in MFCs so the overall operation is even more complicated. In that case, simulations turn into a fundamental tool and can help to afford that complexity by a) weighting the influence of the multiple factors that affect the overall system operation and b) focusing the experimental effort to optimize the system (8, 9, 10).

In this study we present an MFC model that accounts for pH effects in the solution.

1.1 pH buffers

The microbial anaerobic degradation of organic compounds yields the electrons and protons necessary for the fuel cell to work. The electrons are directly released to the anode metal but the protons remain in the solution. This causes an increasing proton concentration in the anodic chamber, leading to a general acidification of the medium. This acidification can lower the metabolic performance of the biological agents in the fuel cell, making the overall performance of the MFC worse. Therefore, to avoid that effect it is common practice to introduce excess pH buffers in the solution. However, at that point, it is interesting to study the effect of such a huge buffer concentration in the proton transport from the

anode to the cathode (buffering effect). These buffers may reduce the number of "free protons" from the solution which are able to reach the cathode. This "kidnapping" of protons by the buffer might reduce the overall efficiency of the system.

1.2 Biological considerations

The Gamma Proteobacteria *Shewanella oneidensis* was chosen as microorganism for two main reasons.

a) This organism lives directly attached to the electrode surface and has the ability to exchange electrons with it through transmembranal citocromes, so electron mediators are neither present nor needed (11).

b) *Shewamella spp.* is able to degrade lactate to acetate, but it cannot further degrade acetate on anaerobic conditions. This clearly simplifies the biochemical aspects (12, 13).

Both aspects simplify the model and the analysis of experimental results by reducing the number of chemical species and biochemical reactions need to be considered (see figure 1) (12).

2. Methods

2.1 Model definition

We built a one-dimension model with 3 subdomains and 4 boundaries (see figure 2).

Each domains represents 1) the anodic chamber [5mm], 2) a proton exchange membrane (PEM) [1mm] and 3) the cathodic chamber [5mm], and the boundaries are 1) Anode, 2 & 3) Chamber/PEM interface and 4) Cathode.

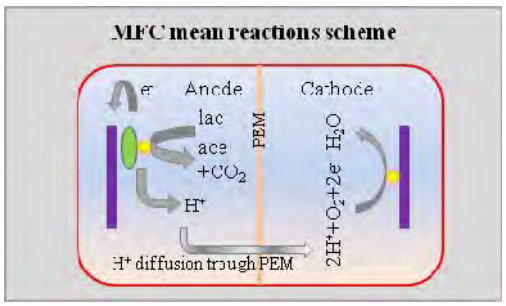

Figure 1. Schematic representation of the microbial fuel cell (MFC).

Moreover, we have taken the following assumptions:

• The chemical species considered in the model are: lactate (lac^-) lactic acid (Hlac), acetate (ace^-), acetic acid (Hace) protons (H^+), hydroxide ion (oh^-), sodium (Na^+), carbon dioxide and the hydrolysis product carbonic acid (CO_2 and H_2CO_3), bicarbonate (HCO_3^-) and carbonate (CO_3^{2-})

• All bacteria live attached to the anode and no degradation of lactate occurs in the solution bulk.

• The fuel cell is based in two main chemical processes: the oxidation of lactate by *Shewanella spp*.at the anode:

$$Lac^- + Na^+ \rightarrow ace^- + Na^+ + CO_2 + 2H^+ + 2e^- \quad [1]$$

And the oxygen reduction at the cathode:

$$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O \quad [2]$$

• We consider that no other buffer is added than the carbon dioxide resulting of lactate degradation. Usually in experiments an external buffer is added (i.e. phosphate buffer) but this will be a next step for the model.

• We consider a closed system where al CO_2 generated by lactate degradation is dissolved in the water medium and cannot escape to the gas phase. On the other hand, given that CO_2 is in equilibrium with H_2CO_3 and that neither has a charge, we will treat CO_2 as the sum of both CO_2 an H_2CO_3.

• We assume that the fuel cell runs on a batch mode. It means it is a closed reactor where all substrates and biological agents are placed at the beginning and there is not further feeding.

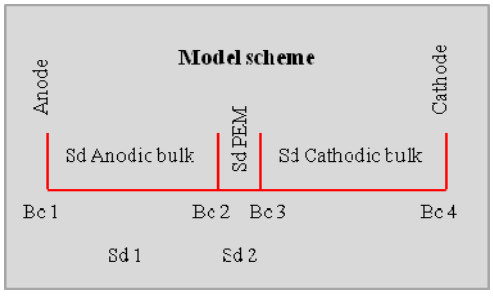

Figure 2. Schematic representation of the model. Subdomains are labelled "Sd" and boundaries "Bc".

2.2 Kinetic model

The model is build based on four main processes: the consumption of lactate at the anode, the consumption of oxygen and protons at the cathode, pH equilibria and mass transport (across the PEM and the anodic and cathodic chambers).

a. Consumption of reactants

The consumption of reactants is described by first order chemical reactions at the electrode surfaces:

1) At the anode (boundary #1) the lactate degradation mediated by *Shewanella spp* is defined by:

$$\frac{d_{lac}}{dt} = -k_{1_{lac}} \cdot [\mathrm{lac}] \qquad [3]$$

Where $k_{1_{lac}}$ is a constant reaction term (1/m) and lac is is the concentration of lactate.

2) At the cathode (boundary #4) oxygen is reduced to water by:

$$\frac{d_{ox}}{dt} = -k_{2ox} \cdot [H^+] \cdot 4 \cdot [O_2] \qquad [4]$$

Where k_{2ox} is a constant reaction term (1/m) and H^+ and $O_2$are t he concentrations of protons and oxygen respectively.

b. Buffering system (pH equilibria)

pH is calculated in each subdomain considering the following equilibria:

$H_2O \Leftrightarrow H^+ + OH^-$ [5]
$Hlac \Leftrightarrow lac^- + H^+$ [6]
$Hace \Leftrightarrow ace^- + H^+$ [7]
$CO_2 + H_2O \Leftrightarrow H^+ + HCO_3^-$ [8]
$HCO_3^- \Leftrightarrow H^+ + CO_3^{2-}$ [9]

Where [5] is the water equilibria, [6] and [7] are the equilibria between the protonated and unprotonated forms of lactate and acetate and [8] to [9] are the equilibria between the considered carbon species.

c. Diffusive and convective transport

The mass transport of the different species is defined by the diffusion-convection equation as:

$$\frac{\partial C_i}{\partial t} = -D_i \cdot \nabla^2 C_i + R_i + u\nabla C_i \qquad [10]$$

Where: c_i is the concentration of specie i (mol/m^3)
D_i is the diffusion coefficient (mol/(m^3*s))
R_i is the reaction rate for specie i (W/m^3)
u is the velocity factor (in our case we use a dimensionless factor Udl)

For the diffusion coefficients of each species we have used known values for diffusion in water (14) at infinite dilution and ionic effects have not been considered. Inside the PEM, and because of the lack of diffusion rates for most species we have used reduction factors considering the size of chemical species 1/1.5 for H^+, 1/100 for O_2, CO_3^{2-}, HCO_3^- and CO_2- H_2CO_3 and finally, 1/1000 for lac, Hlac, ace, Hace.

d. Initial conditions

The model simulates a batch reactor, so the anodic chamber is loaded with sodium lactate (20.0 mol/m^3) at t_0. At the cathodic chamber an initial load of 12 mg/l of oxygen (0.75mol/m^3) is considered.

2.3 Use of COMSOL Multiphysics

The model was defined using the Chemical Engineering module of COMSOL Multiphysics software 3.5a.

The pH equilibria and value of pH calculation are introduced as Global Expressions (one for each specie), while the electrode reactions (lactate degradation and oxygen reduction) are implemented as Boundary Expressions.

We use a transient analysis with a direct linear system solver (UMFPACK) and relative and absolute tolerances of 10^{-6} and 10^{-7}, respectively.

Stabilization techniques:

The solver cannot easily reach a stable solution due to the fast and labile changes of several species with slight pH changes.

Several steps were followed to overcome this issue:

a) Use of BDF method (Backward differentiation formula) instead of 'Generalized alpha' (max. 5, min. 1).
b) Activated 'Consistent initialization of DAE systems' (differential-algebraic equation) with backward Euler method.
c) The chemical species where introduced sequentially, first the model is solved just considering lac, Hlac, H^+, OH^-, ace, Hace, O_2 and Na^+ for a period of 1s. After, it is solved for for the mentioned species together with CO_3^{2-}, HCO_3^- and CO_2 for 1s again and finally, for all the species defined in the model together for a period of 24 hours (86,400 s).
We chose this sequence to first stabilize the model before the pH buffer equilibria, which were found to be the most unstabilizing factor in the model.

3. Results

The model is run for a period of 24 hours (86,400 seconds). Figure 3 (a and b) shows the pH for both subdomains (anodic and cathodic chambers) at different times, each line in the figure (a) is a pH measurement every 30 minutes. As expected, pH decreases with time. At 24 hours the model shows a value for both the anodic and cathodic chamber of about 2.06 pH. Figure (b) shows the same results for the first period of 3 hours (with 10 minutes per line). We can theoretically consider that a pH with values under pH=4 might affect the metabolic rate of *Shewanella spp.*, this value is completely achieved in the cathodic solution after a period of 1 hour and 10 minutes.

Regarding the different species concentrations at time 24h, table 1 shows the anodic and cathodic solutions concentrations of several relevant species.

Specie	Anolite (mol/m^3)	Catholite (mol/m^3)
Lactate	9.43×10^{-3}	3.26×10^{-4}
Lactic acid	2.51×10^{-1}	8.64×10^{-3}
Acetate	3.81×10^{-2}	4.78×10^{-5}
Acetic acid	18.29	2.29×10^{-2}
Oxygen	2.71×10^{-2}	6.71×10^{-5}
CO_2-H_2CO_3	14.65	3.06
HCO_3^-	7.54×10^{-4}	1.61×10^{-4}
CO_3^{2-}	4.20×10^{-12}	9.03×10^{-13}

Table 1. mol/m3 of main species at time 24h. Anolite corresponds to subdomain 1 and catoliote to subdomain3

A strong displacement to the protonated forms can be seen across the board, with the predominant species being acetic acid, lactic acid and carbonic acid. Oxygen presents, due to diffusion, higher concentration values at the anolyte than at catholyte, where it is close to being fully depleted.

Most of the lactate (lac+Hlac) is consumed with the period of 24 hours (98.65%), with less than 0.270 mol/m^3 remaining in the sum of all three subdomains.

Figure 4 (a) shows the speed of the two main reactions, degradation of lactate at the anode (rate_lac) and reduction of oxygen to water at the cathode (rate_ox). For all the simulation, rate_lac is about 1 to two orders of magnitude higher than

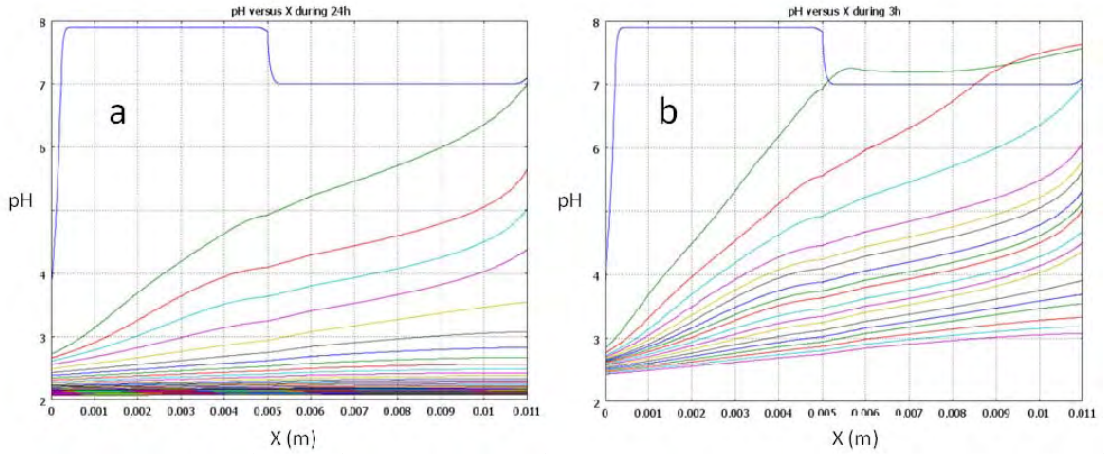

Figure 3. pH change for all 3 subdomains. a) Change during 24 hours (each line represents 30 minutes) and b) Change during the first three hours (each line represents 10 minutes.

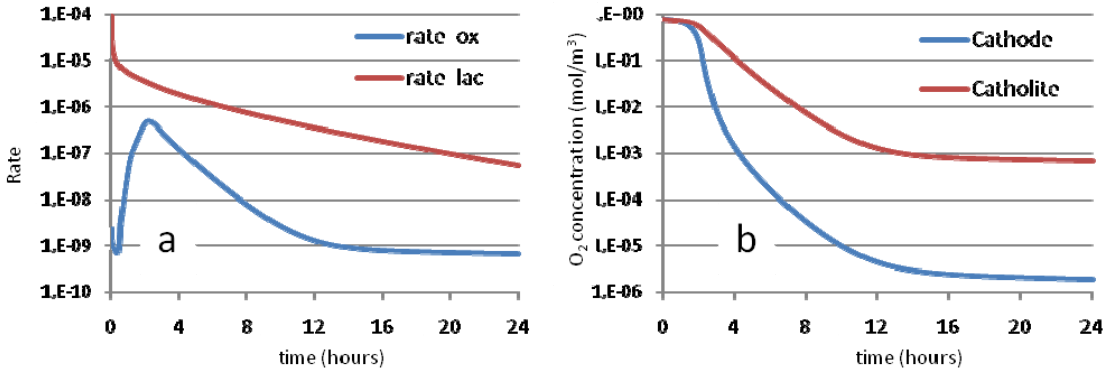

Figure 4. a) Change during 24 hours in lactate degradation rate(rate_lac, red color in mol/(m³·s)) and oxygen reduction (rate_ox, blue color, in mol²/(m⁶·s)). b) Change during 24 hours in oxygen concentration at cathode (blue line, x=0.011m) and in the middle of the cathodic chamber (x= 0.0085m; red line)

rate_ox and shows a deceleration pattern as lactate concentration goes down, while rate_ox after a first deceleration (due to depletion of present H^+), then rate speeds up as new protons generated by lactate degradation reach the cathode. After 3.5 hours the rate of oxidation slows down due to the lack of oxygen, as can be seen at figure 4 (b) where the concentration of oxygen at the cathode is less than 10^{-2} mol/m^3. Catholyte represents the concentration of oxygen at x = 8.5 mm, the middle of cathode solution subdomain.

4. Discussion

The model shows a fast and strong acidification of the media after a brief period, reaching values under pH=4 after 1h and 10' for the anodic chamber and 2h and 10' for the cathodic one.

The acidification effect of the media, also implies a dominant presence of protonated species, where basically Hlac>>lac and Hace>>ace. This affects the performance of the MFC because the degradation rate for lactate is determined by lactate concentration (equation 1) but not by lactic acid (Hlac). The displacement to the protonated form reduces the present concentration of lactate and this affects the overall rate of the cell. We choose to only considerer lactate degradation because *Shewanalla spp*. has active mechanisms to introduce lactate to the cytoplasm, but not for lactic acid, which can only enter the cell by diffusion (12).

Regarding carbon species, the couple carbon dioxide – carbonic acid clearly dominates over bicarbonate and carbonate.

The fact that CO_2 is generated during the degradation of lactate means that pH has a "natural" tendency to drop in the anolyte.

At this model conditions the initial load of sodium lactate is close to be completely consumed after 24 hours (over 98.65 % of substrate consumption).

The rate of lactate degradation by bacteria is clearly faster than the reduction of oxygen (rate_ox, see figure 4, a) but this is a point to improve in the model.

Also reaction [4] requires electron liberation at the anode to be carried on, thus in a better modeling of the MFC reactions [3] and [4] must be both coupled and reciprocally limited.

Linking and respectively limiting reactions [3] and [4] will lead to a slower lactate degradation, implying a slower acidification of the media too.

In terms of oxygen, (figure 4, b) the model shows a fast depletion of concentration at the cathodic chamber (less than 10^{-3} mol/m^3 at cathode proximity after 4 hours of operation and at the cathodic solution after 12 hours of operation. This model assumes a batch mode, but a continuous feeding with oxygen will permit a higher rate_ox velocity, and in turn a higher proton consumption at the cathode, reducing the pH.

5. Conclusions

This is only a first approximation to model pH effects in a microbial fuel cell, and several aspects need to be better defined in the model.

The main one is the link between the actual lactate degradation rate at the anode (rate_lac), and the oxygen reduction at cathode, because reactions [3] and [4] are coupled, and reaction [4] can work fast without the supply of electrons generated at reaction [3]. This can be done by introducing a suitable Butler-Volmer equation at the cathode for equation [4], which may constrain the lactate degradation speed at the anode.

In terms of taking into account the electrical implications in the model, using the Poisson-Nernst-Plank system of equations will permit the study of electrical migration and better account for internal resistances in the system.

Furthermore better data on the several species considered PEM diffusion will improve the model results and permit to analyze effects as oxygen present in the anolyte.

Another important aspect to clarify is the role of lactic acid in *Shewanella* metabolism, to clarify if it can also be degraded, affecting at the overall lactate and lactic acid degradation rate.

Respect to *Shewanella spp.*, it can be interesting to experimentally analyze the speed of lactate consumption under several pH values, because probably this reaction will be affected as pH reduces. Introducing this data to the lactate degradation rate will change equation [1] from a first order reaction to a Monod type equation.

In another sense, this model can act as a blank test, permitting to optimize the use of other pH buffers as buffer phosphate. This is relevant because buffers play a double effect in the system: if their concentration is low, major pH changes can be observed and lead to a reduction in the efficiency of the MFC. On the other hand, if there is too much of them, then it may be more difficult for protons to participate in the cathode reaction, and the cell yield can be affected.

The model as is defined now can be easily complemented with other chemical species and equilibria, and allows for a refinement that leads to more optimum calculation of the buffering needed.

Another line to improve the model is to expand it to 2 dimensions to better consider aspects as convection, and to consider a pseudo-continuous culture by certain feeding during operation as introducing oxygen at the cathode.

6. Acknowledgements

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