Prediction of Electricity Generation in a Duel Chamber Microbial Fuel Cell

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Abstract

Electricity generation in a duel chamber microbial fuel cell (MFC) consisting of graphite anode electrode, platinum cathode electrode and Nafion 117 membrane was investigated. Anaerobic sludge was used as the source of microorganisms in the anode chamber. Acetic acid as the sole carbon source along with other nutrients was added to the anode chamber in a batch or repeated-batch modes. System curves and polarization curves were obtained in different operational conditions and the internal resistance of the system was calculated. Electricity generation by MFC in both batch and repeated-batch modes was modeled using a biofilm based hypothesis and the results were compared with experimental data.

Keywords: *Microbial Fuel Cell, Biofilm Based Model, Electricity Generation*

1. Introduction

The forecast of the world's population reveals that by 2050 it will reach 9.4 billion and therefore there is an urgent need to increase energy production by that time [1,2,3]. In past centuries, fossil fuels have been a key factor for industrial and economic development. Obviously, this energy resource cannot retain global economy unlimitedly and some day its production will end. Oil cannot be consumed for more than at most, 100 years [4,5]. Microbial fuel cells (MFC) have recently attracted significant interest, as a renewable source of electricity generation [6,7,8]. Generating microbial electricity in MFCs relies on the movement of bacteria to achieve the highest amount of energy [9]. Contrary to natural environmental systems, the anode element in microbial fuel cells is an engineered ambience where access to electron solution receivers is limited. The main electron receiver enables bacteria to use breathing processes. A high amount of released metabolic energy through electrons to electrodes rather than other electron receivers causes bacteria to form an electrode colony and promote electron transfer strategies. The result is a process in which

bacteria as a biocatalyst operate to convert a rich electron substrate to electrons (which are then transferred to electrodes), protons (which move toward the cathode), and oxidized products (which leave the reactor). Through an external electrical circuit, electrons flow in the cathode electron where the final receiver is reduced by a microbial or chemical catalyst [10]. Because of the potential difference between anode and cathode, the electrons current leads into electricity generation.

Several mechanisms for electron transmissions have so far been investigated and discovered [11]. However, the complicated interaction of bacterial electron transmission in biofilm is not yet known [12]. Mechanisms for electron transmission, which are so far founded in microbial fuel cells, have a close relationship with the studied mechanisms for dissimilar microorganisms.

Electricity generation in MFCs have been modeled by a few researchers. Complexity of the system and involvement of many model parameters causes poor accuracies in the suggested model. The model suggested by Picioreanu et al estimates electricity generation according to a biofilm based hypothesis in the anode chamber and considering an imaginary mediator [12-14].

The objective of this study was to estimate electricity generation in the MFC. A dual chamber MFC was made and the above mentioned model with some simplifications was used. Model constants were either calculated according to the reactions stoichiometry or obtained from other works. The experimental results have been compared with the model.

2. Materials and methods
2-1. MFC description

To examine electricity generation by microorganisms, a duel fuel cell chamber was built. The cell consisted of two 250 ml anode and cathode chambers separated by a cationic Nafion 117 membrane. Graphite (5cm × 3.6cm × 3.6cm) and platinum plate (0.01cm × 2cm × 2cm) were used as cathode and anode electrodes, respectively. As for microorganisms, anaerobic sludge was provided from a laboratory scale moving bed biofilm reactor and was applied in the anode chamber. Previous studies indicated that the optimum pH value for the sludge was around 8.4 and contained the following microorganisms: *Nitrosolobus* sp., *Nitrososoccus* sp., *Nitrosoribrio* sp., *Nitrosospira* sp., *Nitrococcus* sp. and *Disulfobulbus* sp. The sludge was fed into using acetate as the carbon source. The feed solution contained variable acetate concentrations (equivalent to 100 to 400 mgCOD/l) and the following nutrients: NH_4OH, 0.19; $FeCl_3$, 0.4, $MgSO_4$, 3.0; $CuSO_4.5H_2O$, 0.11; $NaCl$, 0.7; $ZnCl_2$, 0.015; $Na_2S_2O_5$, 4.0; $MnSO_4.H_2O$, 0.25; $FeSO_4.7H_2O$, 2.1 mg/l. Each time, as much as 5ml of the feed solution was added to the anode chamber. A gentle circulation by magnetic mixer was applied in the anode compartment. The cathode chamber was filled with a buffer solution with pH 7.0 and aerated by a small air pump. Cathode and anode electrodes were attached to two multi-meters for the measurement voltage and current.

2-2. Measurements

COD was measured according to open reflux method (standard methods 5220 B). Voltage

and current were measured at least 6 times a day using two multi-meters connected to the electrodes in series or parallel manner, respectively. At the time the highest current density was observed, the open circuit voltage was obtained first and the polarization curve was estimated using variable external resistance ranging from 10 kΩ to 500 kΩ. The internal resistance was calculated considering the constant slope of the polarization curve.

2-3. Model descriptions

A precise model consists of a series of equations that must be solved simultaneously in which mass balance for all interacting components including chemical reactions and their rates of ration, a general charge balance considering electrochemical reactions, and a dynamic for biofilm development are all considered together. This demands a good knowledge of the model constants.

The model presented by Piciorea nu et al. [14] with some simplifications was adopted here. This model is based on redox mediators with populations of suspended and attached biofilm microorganisms and dissolved chemicals involved in electrochemical reactions. Three kinds of materials are considered in the model including (1) materials existing in biofilm and bulk reactions including acetate, ammonia and chemical mediators, (2) inert materials like water, and (3) materials regulating the charge that are introduced in the charge balance like H^+.

The operation environment is divided into three regions including (1) fluid bulk region where the concentration distribution of each fluid is assumed uniform, (2) biofilm region where in a concentration, distribution exists for different material, (3) electrode region where in oxidation or reduction, reactions with anode and charge exchange occur [15].

The following simplifications were applied to the precise model: (1) there is an one dimensional concentration distribution in the biofilm, (2) biofilm thickness is constant, (3) pH value of the bulk is constant, (4) concentrations of mediators and substrate in the biofilm region are constant, (5) there is a uniform concentration distribution in the biofilm region for all components except for the mediators, (6) electron transfer occurring only by mediators.

2-3-1. Electrochemical model

Produced current density in the electrochemical mediator oxidation was obtained using Butler-Volmer equation,

$$i = i_{0,ref} \left(\frac{s_{E,merd}}{s_{ref,merd}}\right)\left(\frac{s_{E,mox}}{s_{ref,mox}}\right)^{-1}\left(\frac{s_{E,H}}{s_{ref,H}}\right)^{-2}$$
$$*[\exp(\frac{2.303}{b}\eta_{act}) - \exp(-\frac{2.303}{b}\eta_{act}))] \quad (1)$$

The current I collected at electrode was calculated by integration of all local current densities:

$$I = \int_{A_f} idA \quad (2)$$

At the anode surface, electrochemical oxidation of the mediator occurs as shown in equation (3).

$$M_{red} \leftrightarrow M_{ox} + 2H^+ + 2e^- \quad (3)$$

Where, the rate of this reaction is expressed as follows:

$$r_{Mred,E} = -\frac{i}{2F} \quad ; \quad r_{Mox,E} = \frac{i}{2F} \qquad (4)$$

Having both the electrolyte and the electrodes obeying Ohm's law, an equation for the MFC's potential can be obtained as equation (5).
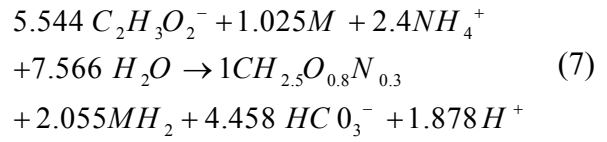
$$V_{CELL} = (E_C - \eta_{C,act}) - (E_A + \eta_{A,act}) - I.R_{int} = I.R_{ext} \qquad (5)$$

Assuming a constant value for cathode potential as $V_C = E_C - \eta_{C,act}$, the anode overpotential can be obtained:

$$\eta_{act} = V_C - I.(R_{int} + R_{ext}) - (E_M^0 - 0.059\text{pH} + \frac{0.059}{2}\log\frac{S_{E,Mox}}{S_{E,Mred)}}) \qquad (6)$$

2-3-2. Bulk liquid model

The following overall biochemical reaction was considered in the anode chamber:

$$5.544\ C_2H_3O_2^- + 1.025M + 2.4NH_4^+$$
$$+7.566\ H_2O \rightarrow 1CH_{2.5}O_{0.8}N_{0.3} \qquad (7)$$
$$+2.055MH_2 + 4.458\ HCO_3^- + 1.878H^+$$

Constants of the above equation were obtained according to the mass balance, charge balance and Gibbs free energy balance over the involved components and solving the relevant linear equations (data not shown).

It was assumed that microbial growth was due to assimilation of acetate with the oxidized mediator as indicated in equation (8).

$$\rho = q_{Ac,max} x \frac{S_{Ac}}{k_{Ac} + s_{Ac}} \frac{S_{Mx}}{k_{Mx} + s_{Mx}} \qquad (8)$$

$$r_{Ac} = -\rho \ , r_x = Y_x\rho \ , r_{Mred} = Y_M\rho$$
$$r_{Mox} = -Y_M\ \rho \ , r_{car} = Y_{car}\rho \ , r_H = Y_H\rho \qquad (9)$$

Values for the relative yield constants are shown in Table 1.

Table 1. Model parameters for simulation of current production in MFC

Parameter	Description	Value
b	Tafel coefficient	0.12 $L^2MT^{-3}I^{-1}$
$i_{0,ref}$	Exchange current density for mediators	2×10^{-4} A m^2
E^0_M	Standard reduction potential	0.477 V
V_C	Cathode potential	0.68 V
$R_{int} + R_{ext}$	Total cell resitance	100 Ω
$q_{Ac,max}$	Maximum specific rate constant for microbial acetate consumption	10 g COD acetate /g COD biomass.day
K_{Ac}	Monod coefficient for acetate substrate	100 gCOD/m^3
K_{Mox}	Monod coefficient for oxidized mediator	0.1 mM
Y_X	Yield of biomass on substrate	0.1 g COD biomass/ g COD acetate
Y_{car}	Yield of bicarbonate from substrate	0.024 mol HCO$_3^-$/g COD acetate
Y_M	Yield of mediator versus substrate	0.0473 mol mediator/g COD acetate
Y_H	Yield of protons from substrate	0.0098 mol H$^+$/g COD acetate

Mass balance for five components including acetate, ammonia, carbonate, proton and mediators in the bulk region is:

$$\frac{dS_{B,i}}{dt} = r_{S,i,B} + \frac{1}{V_B}\int_{V_f} r_{S,i,F}\,dv + \frac{1}{V_B}\int_{A_f} r_{S,i,E}\,dA$$

(10)

$$\frac{dX_{B,i}}{dt} = r_{X,i,B} \quad,\text{ where } i=1,2,3,4,5.$$ (11)

2-3-3. Biofilm model

A quasi – steady condition and one dimensional concentration distribution was assumed in the biofilm region.

$$D_i \frac{d^2 S_{F,i}}{dz^2} + r_{S,F,i} = 0$$ (12)

Boundary conditions for the above equations were as follws:

$S_F=S_B$; at the interface with the bulk region,

and $\dfrac{dS_{F,i}}{dz} + r_{S,F,i} = 0$; near the electrode surface.

where, $r_{S,F,i}$ was zero for non-reacting compounds with the anode electrode.

Initial conditions used in differential equations are indicated in Table 1.

These equations were simultaneously solved using numerical method by MATLAB 8.1 software.

3. Results and discussion
3-1. Current-Time curve

Behavior of the MFC in the batch fed mode is indicated in Fig.1 and Fig. 2 for the feed concentration of 100 and 400 mg/l, respectively. Other feed concentrations (100, 200 and 300 mg/l) were also examined (data not shown). It was observed that by increasing the concentration of feed, there was slower dynamic in the substrate digestion by microorganisms. There was also a slight increase in the produced current density when higher feed concentrations were used.
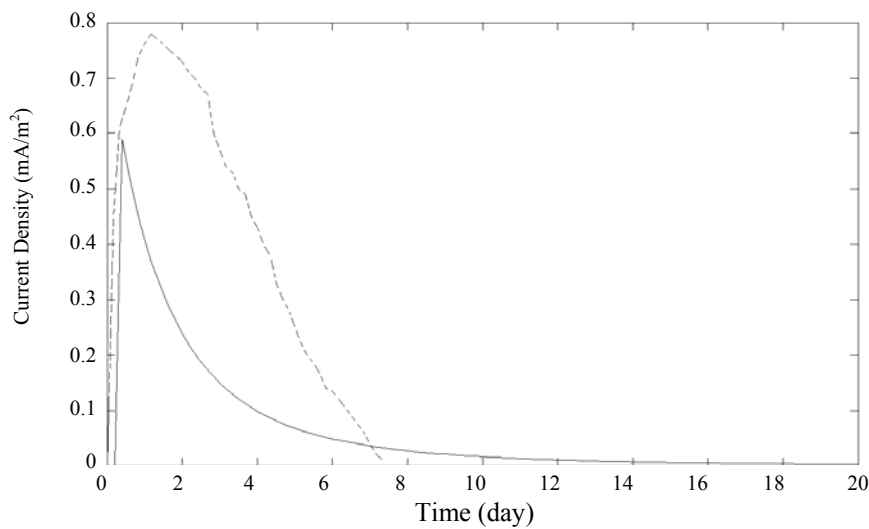
Figure 1. Current density production in a batch MFC; feed concentration: 100 mg COD /l; Experimental (dashed line), Model (bold line).
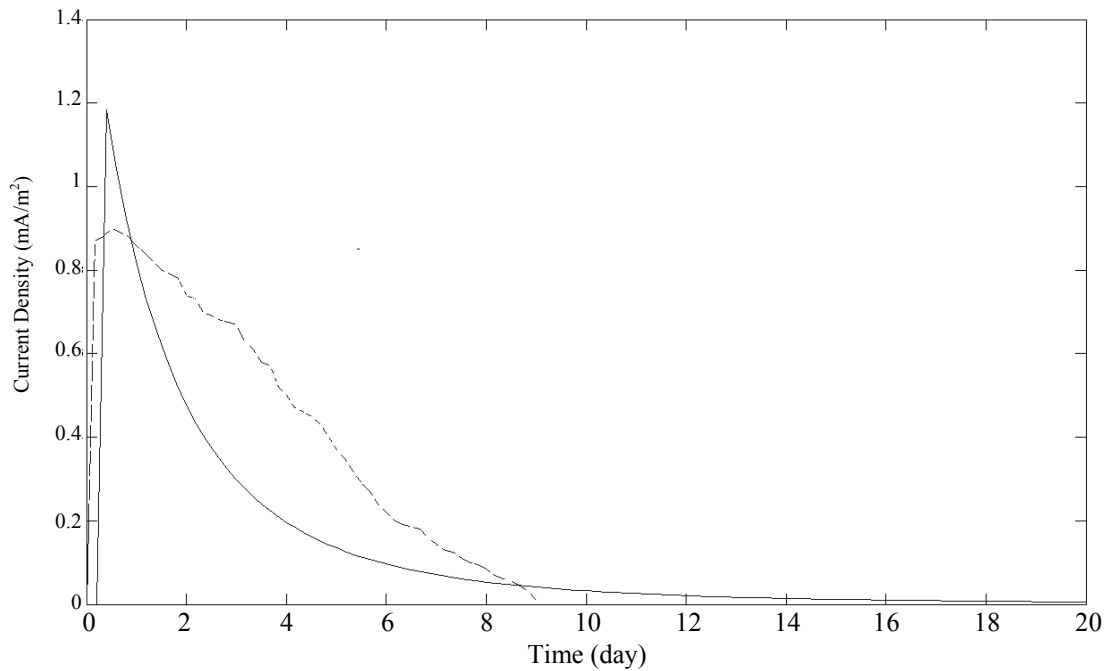
Figure 2. Current density production in a batch MFC; feed concentration: 400 mgCOD /l; Experimental (dashed line), Model (bold line).

In the repeated-batch mode, feed with a concentration of 200 mg/l was added to the anode chamber, internally in the 0, 9, 15, 20, 26 and 31st day. Behavior of the system is indicated in Fig. 5. Current densities similar to that for the batch fed mode was produced. However, in the first batch less current density was observed. It gradually increased in successive batches. Substrate assimilation was faster than that for the batch fed mode.

3-2. Potential/Power–Current curves

Obtaining the polarization curve is a time consuming task. For each condition, polarization curve must be obtained at a definite day where the highest current density is achieved. Internal resistance of the system can be estimated from the slope of the curve. Polarization curves for both the batch fed and repeated-batch modes are shown in Fig. 3. Internal resistance for the batch fed and

repeated-batch mode were 32 kΩ and 30kΩ, respectively. Also, the power-current curves for these two conditions are indicated in Fig. 4. The power generated by the repeated-batch mode (in the third cycle) was more than two times higher that of the batch fed mode.

3-3. Model prediction

Current densities predicted by the model are compared with the experimental data and presented in Figs. 1, 2 and 5. It can be seen that with all simplifications assumed in the model, there is an acceptable agreement between the model and experimental data. The trend of variation of the current density with respect to time predicted by the model is similar to the experimental. For the repeated-batch mode, the moment that the feed solution was added into the anode chamber was defined in the modelling, too.
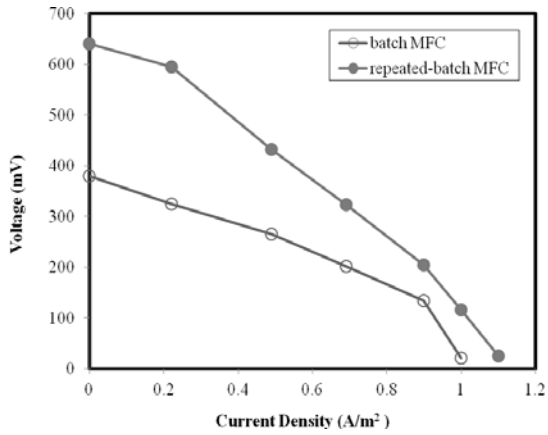
Figure 3. polarization curves of batch and repeated-batch (third cycle) MFCs.

4. Conclusions

A dual chamber MFC was constructed and the behavior of the system for current production was examined. Microorganisms provided from a laboratory bioreactor were used in the anode chamber and fed with acetate containing solution in either batch or repeated-batch modes. Polarization curve of the system was also obtained in the mentioned conditions and the internal resistance of the system was calculated (30kΩ). A mathemathical model based on biofilm formation on the anode electrode and assumption of mediators was adopted. The model was solved neumerically and the results were compared with the experimental data.
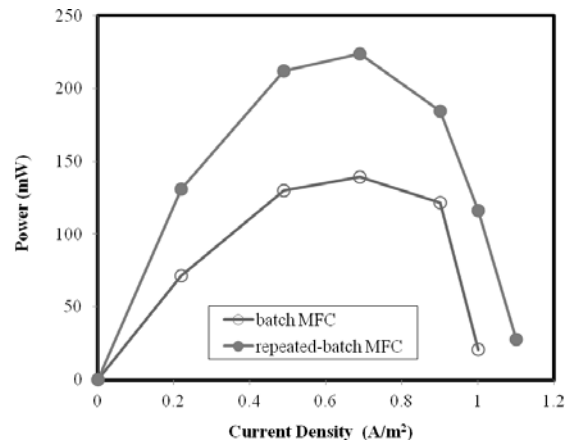
Figure 4. Power-current behavior of batch and repeated-batch (third cycle) MFCs.
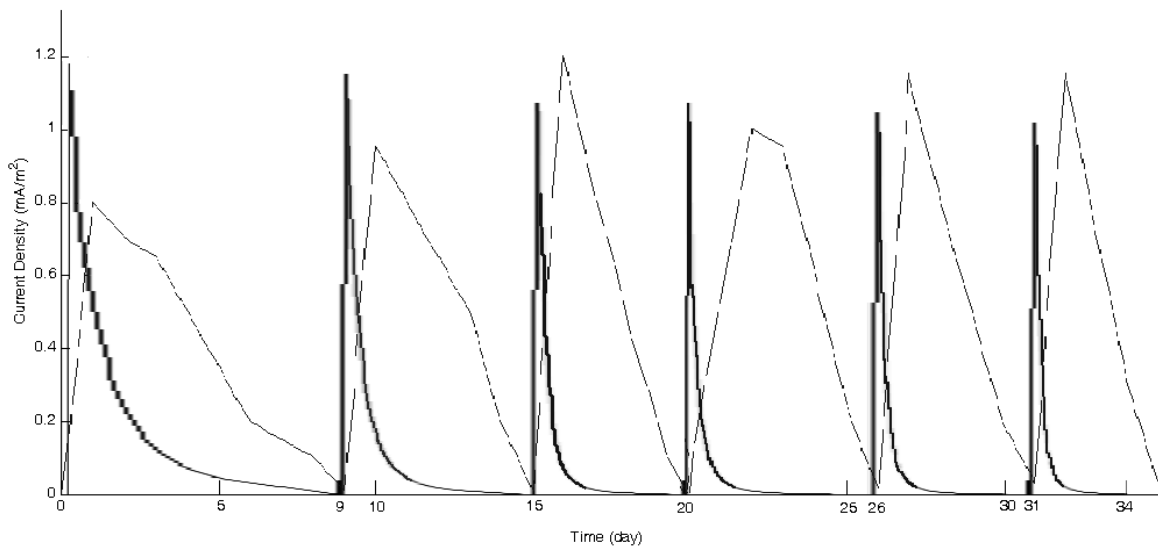
Figure 5. Current density generation in repeated-batch MFC; feed concentration: 400 CODmg/l; Experimental (dashed line), Model (bold line).

Nomenclature

A area, L^2

b Tafel coefficient, $L^2MT^{-3}I^{-1}$ (e.g., V)

d density, ML^{-3}

D diffusion coefficient, L^2T^{-1}

F Faraday's constant (96,480C/mol e⁻)

i current density, IL^{-2}

I total current through the MFC, I

K half-saturation coefficient, NL^{-3} or ML^{-3}

K_a acidity constant

q specific rate, $M\ M^{-1}T^{-1}$

r net reaction rate at electrode, $ML^{-2}T^{-1}$ or $NL^{-2}T^{-1}$ or in bulk or biofilm, $ML^{-3}T^{-1}$ or $NL^{-3}T^{-1}$

S dissolved chemical component (solute) concentration, NL^{-3} or ML^{-3}

t time, T

v volume, L^3

V voltage, V

V_B bulk volume, L^3

X biomass component (particulate) concentration, ML^{-3}

Y yield, N/N or M/M

z coordinate in the biofilm (z perpendicular to electrode surface), L

η over potential (or polarization potential), $L^2MT^{-3}I^{-1}$ (e.g., V)

Subscripts

0 initial

A anode

Ac acetate

act activation

B bulk liquid

C cathode

car carbonate

$Conc$ concentration

E electrode

f biofilm

M mediator (general form)

Mox oxidized mediator (M)

$Mred$ reduced mediator (MH₂)

Ref reference

S soluble component

ρ absolute reaction rate

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