Sensors and Materials, Vol. 29, No. 7 (2017) 1055–1060
MYU Tokyo

S & M 1398

2D Numerical Physical Model Settings for Three Electron Transfer Pathways in Microbial Fuel Cells

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(Received April 19, 2016; accepted May 17, 2017)

Keywords: microbial fuel cell, 2D numerical simulation, electron transport mechanism, substrate concentration

Microbial fuel cells (MFCs) are bio-electrochemical transducers that produce electrical energy by the decomposition of organic matter with the aid of microorganisms. Through the transfer of electrons, energy can be delivered to an electrode surface, and understanding the electron transport mechanisms has become very crucial. Although significant research has been carried out in this field, relatively few reports have been based on numerical simulations. Therefore, this study was initiated to design a computational model through numerical simulation and apply it to the betterment of MFCs. Three important biochemical mechanisms of MFCs such as direct electron transport, transport through electron shuttles, and transport through nanowires were considered for simulation. The results showed that the function of the thickness of the active biofilm (j_{max}) was obtained at a substrate concentration of 1.1 M with a current of 0.16 mA. The direct electron transport mechanism was reported to produce the maximum current density of 15.14 mA/m^2. The direct transport also used a higher concentration of substrate to generate power than the nanowire transport and electron shuttle processes. These findings provide useful information on the enhancement of the performance of MFCs and especially on the application of numerical simulations for their scale-up process.

1. Introduction

Numerical simulation is a well-known technology, which can be very beneficial and cost effective for the construction and operation of microbial fuel cells (MFCs). Simulations can computationally predict the processes of biochemical reactions and moreover optimize the parameters in MFCs for their efficient performance.(1) Zhang *et al.*(2) reported that the numerical simulations can provide a design for MFC models as a preliminary result to evaluate the effects of substrate concentrations on microorganism uptake and current output. The model reported by Wen *et al.*(3) combined the electron transport mechanism and kinetics in MFCs to achieve a maximum current of 25 mA. According to these findings, the numerical simulation of MFCs could be transformed into an effective technology, which could help to upgrade the MFCs.

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http://dx.doi.org/10.18494/SAM.2017.1593

The microbes in MFCs oxidize the organics in the substrate to produce energy in the form of electrons and transfer them to the electrode surface by various electron transport mechanisms such as nanowire transport, direct electron transport, and electron shuttle (see Table 1). The nanowire transport mechanism employs electrically conductive fibers to connect the microbial cell with the anode surface.[4] Reguera *et al*.[5] reported that the pili of *Geobacter sulfurreducens* were highly conductive and facilitated the reduction of Fe(III) oxide as the pili directed electrical connections between the cell and the surface of Fe(III) oxides. In addition, Merkey and Chopp[6] developed a model that utilized a conductive extracellular polymer substance (EPS) called matrix to transfer electrons to the anode. The electron shuttles used soluble compounds as mediators to accept electrons from the microbial cell wall and transfer electrons to the anode surface.[7] From these studies, it was obvious that there were different kinds of electron transport mechanisms.

In this research study, we focused on the simulation and selection of the best electron transport mechanism for MFCs through numerical simulation analysis. A 2D kinetic model was designed to better undestand the relationship between these three electron transport mechanisms and electrodes. The findings provided useful information on scaling up and the performance enhancement of MFCs, which could bring about a pronounced breakthrough in the field of bio-electrochemical systems.

2. Materials and Methods

2.1 Computational model

This computational modeling study was based on dual-chamber MFCs in order to simplify the biochemical reactions in the anode chamber. Figure 1 shows the 2D model of the membrane layer and the electrode layer in an anode chamber.[15] In this study, we used a numerical simulation to address some assumptions as follows: (i) Mass electron transport processes were steady-state and two-dimensional. Mass transport was assumed to be a diffusion-controlled process, and the convection effect was negligible, neglecting the impedance of each layer. (ii) The electron transport mechanism on the anode side can be described by the Monod equation, the Nernst–Monod equation, Ohm's laws, and the Butler–Volmer equation. (iii) The microorganism was assumed to be in the logarithmic phase, with uniform distribution on the anodic electrode's surface.

Table 1
Microbes and their mode of electron transport.

Kind of microorganism	Surface transport-microorganism	Mediator	Nanowire	Reference
Pelotomaculum thermopropionicum	○	×	×	Ref. 9
Methanothermobacter thermautotrophicus	○	×	×	Ref. 9
Shewanella oneidensis	○	×	○	Ref. 8
Escherichia coli	×	○	×	Ref. 11
Pseudomonas aeruginosa	×	○	×	Ref. 12
Shewanella oneidensis MR-1	×	○	○	Ref. 9
Saccharomyces cerevisiae	×	○	○	Ref. 10
G. sulfurreducens	×	×	○	Ref. 14
Rhodopseudomonas palustris	×	×	○	Ref. 13

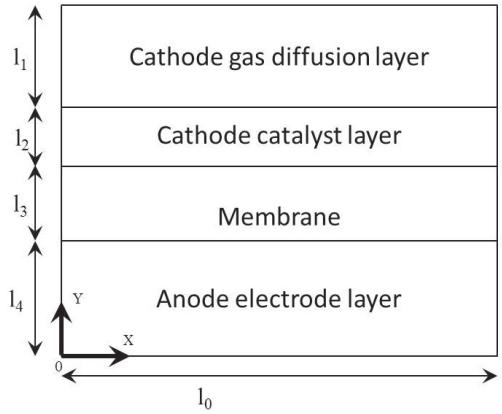

Fig. 1. Schematic representation of the MFC model.

2.2 Numerical methods

In this study, the numerical simulation of MFCs was carried out using MATLAB 2013(a) and this software greatly helped us to analyze the biochemical reactions. Sodium acetate was used as a substrate, and it was assumed to produce a current density of about 20 mA m^{-2}. The electron transport mechanisms between the microorganisms and the electrode surface included direct electron transport, electron shuttle, and nanowire transport mechanisms. Equation (1) represents the energy produced by direct electron transport.[16] Equation (2) represents the energy produced by electron shuttle.[16] Equation (3) represents the energy produced by the nanowire transport mechanism.[16] All parameters are listed in Table 2.

$$Q = Q_0 - j_{max}\frac{S}{K_{sp}+S} - j_{max}\left(\frac{1}{1+\exp\left[-\frac{F}{RT}\eta\right]}\right) - \left[-j_0\exp\left[\frac{nF(1-\alpha)(E_{anode}-E_0)}{RT}\right]\right] \quad (1)$$

$$Q = Q_0 - j_{max}\frac{S}{K_{sp}+S} - j_{max}\left(\frac{1}{1+\exp\left[-\frac{F}{RT}\eta\right]}\right) - \left[nF\left(\frac{D_{shuttle}\Delta C_{shuttle}}{\Delta z}\right)\right] - \left[-j_0\exp\left[\frac{nF(1-\alpha)(E_{anode}-E_0)}{RT}\right]\right] \quad (2)$$

$$Q = Q_0 - j_{max}\frac{S}{K_{sp}+S} - j_{max}\left(\frac{1}{1+\exp\left[-\frac{F}{RT}\eta\right]}\right) - \left[-\frac{k_{bio}\left(E_{OM}-E_{interface}\right)}{\Delta z}\right] - \left[-j_0\exp\left[\frac{nF(1-\alpha)(E_{anode}-E_0)}{RT}\right]\right] \quad (3)$$

Table 2
Numerical analysis of electron transport mechanism and parameters.

Parameter	Symbol	Unit	Value
Conversion factor from mass of substrate to coulombs	γ_s	A h mol^{-1}	0–10
Maximum specific rate of substrate utilization in biofilm with active concentration	$q_{max} X_f$	mol e^{-1} m^{-3} h^{-1}	4500
Biofilm thickness	L_{fa}	m	3×10^{-4}
Substrate concentration at apparent half-saturation	K_{app}	mole	0.5
Ideal gas constant	R	J mol^{-1} K^{-1}	8.314
Faraday constant	F	C mol^{-1} e^{-1}	96485
Temperature	T	K	298
Conductivity of the solid matrix	k_{bio}	R^{-1} L^{-1}	0.5
Electron-transport coefficient	α	V	1×10^{-5}
Transport distance	Δz	m	3×10^{-5}
Diffusion coefficient of the electron shuttle	$D_{shuttle}$	m^2 s^{-1}	6.7×10^{-10}
Exchange current density	Jo	mA m^{-2}	8000
Substrate concentration	S	Mole	0–8
Shuttle concentration	$\Delta C_{shuttle}$	mole	1
Voltage difference	η	V	0–2
Voltage (anode side)	E_{anode}	V	0–2
Open circuit voltage	E_0	V	0–2
Voltage	E_{OM}	V	0–2

The term j_{max} was a function of the thickness of the active biofilm according to Torres *et al.*[16]

$$j_{max} = \gamma_s q_{max} X_f L_{fa} \tag{4}$$

Equation (4) represents the kinetics of the electron transport mechanism between microorganisms and electrode.

3. Results and Discussion

3.1 Comparison of three electron transfer mechanisms

The three important electron transport mechanisms were compared for their effects on the MFC performance. For that, sodium acetate was employed as the carbon source, and concentrations ranging from 0.1 to 2 M were prepared. The results showed that a substrate concentration of 1.1 M used in Eq. (1) could produce a current of 0.16 mA (Fig. 2). Equation (4) described the kinetics of the electron transport mechanism, and the results obtained were in terms of the function of concentration value on the anode electrode surface. The results were similar to the experimental case value previously reported.[16] Figure 3 shows that nanowire transport, direct electron transport, and the electron shuttle had limiting current densities of 14, 15.14, and 9 mA/m^2, respectively. Obviously, direct electron transport demonstrated the best performance in terms of limiting current density. The results can be explained by Eqs. (1) and (3) in which the potential losses in the direct electron transport mechanism were less than that in the electron shuttle and

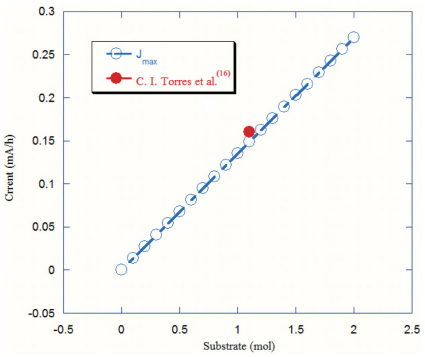

Fig. 2. (Color online) Numerical simulations compared with other studies.

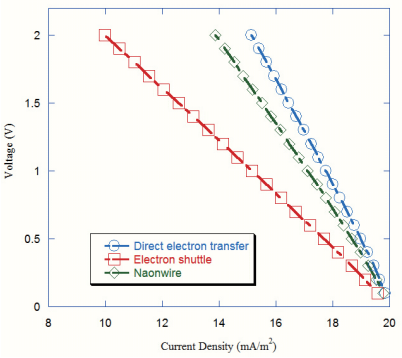

Fig. 3. (Color online) *I–V* curves of the three transport mechanisms.

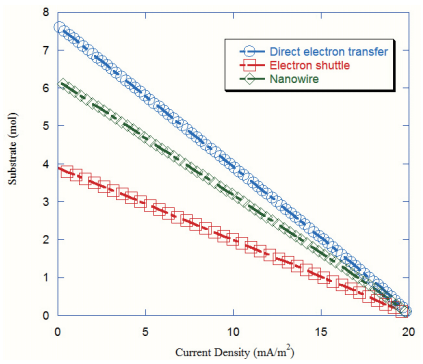

Fig. 4. (Color online) Current density production with respect to substrate concentration.

nanowire transports. In addition, Torres *et al.*[16] have suggested that the diffusion coefficients of organic molecules were relatively less in value, which indicated that diffusion is an inherently slow process. Therefore, direct electron transport was considered to be advantageous in enhancing the MFC performance.

3.2 Effect of substrate concentration

The effects of substrate (sodium acetate) concentration on the transport mechanisms were also studied for concentrations ranging from 0 to 10 M. Concentrations of 6, 4, and 7.5 M were ascribed to nanowire transport, direct electron transport, and electron shuttle mechanisms, respectively (Fig. 4). The results indicated that a substrate at a high concentration could affect the electron transport mechanism of microorganisms in MFCs. It was possible that direct electron transport required more substrate than nanowire transport and electron shuttle. Mohan *et al.*[17] found that higher power outputs could be attributed to the availability of higher substrate concentrations to sustain metabolic activity. In addition, the enhancement of power generation and substrate degradation indicated that more organic matter was utilized for power generation at higher organic loading rates (OLRs).[18] Thus, direct transport used more organic matter to produce more power than electron shuttle and nanowire transport mechanisms. Thus, these results clearly indicated that substrate concentration had a definite effect on the mechanisms of electron transfer and thereby the MFC performance.

4. Conclusions

On the basis of the computational simulation of three types of electron transport mechanisms and their effects on the MFC performance, the following conclusions can be reported:

(i) The j_{max} used a substrate concentration of 1.1 M to produce a current of 0.16 mA.

(ii) Direct electron transport produced the best current density of 15.14 mA m^{-2}, and it was reported to have less loss than the electron shuttle and nanowire transport mechanisms.

(iii) A high substrate concentration could affect better electron transport between microorganisms and the electrode surface. Moreover, direct transport required higher substrate concentrations to produce power than nanowire and electron shuttle transports.

These findings would surely have an immense potential to deeply understand the biochemical reactions in an MFC, and thereby upgrade it successfully for future applications.

Acknowledgments

The authors acknowledged the generous funding support from NSC Taiwan under contracts MOST 103-2221-E-197-022-MY3 and 105-2623-E-197-001-ET.

References

1 V. B. Oliveira, M. Simões, L. F. Melo, and A. M. F. R. Pinto: Energy **61** (2013) 463.
2 X. C. Zhang and A. Halme: Biotechnol. Lett. **17** (1995) 809.
3 Q. Wen, Y. Wu, D. Cao, L. Zhao, and Q. Sun: Bioresour. Technol. **100** (2009) 4171.
4 K. Rabaey and W. Verstraete: Trends Biotechnol. **23** (2005) 291.
5 G. Reguera, K. D. McCarthy, T. Mehta, J. S. Nicoll, M. T. Tuominen, and D. R. Lovley: Nature **435** (2005) 1098.
6 B. V. Merkey and D. L. Chopp: Bull. Math. Biol. **76** (2014) 1429.
7 S. E. Childers, S. Ciufo, and D. R. Lovley: Nature **416** (2002) 767.
8 G. Reguera, K. D. McCarthy, T. Mehta, J. S. Nicoll, M. T. Tuominen, and D. R. Lovley: Nature **435** (2005) 1098.
9 Y. A. Gorby, S. Yanina, J. S. McLean, K. M. Rosso, D. Moyles, A. Dohnalkova, and D. E. Culley: Proc. Natl. Acad. Sci. U.S.A. **103** (2006) 11358.
10 M. C. Potter: Proc. R. Soc. London, Ser. B, Containing Papers of a Biological Character **84** (1911) p. 260.
11 H. Richter, K. McCarthy, K. P. Nevin, J. P. Johnson, V. M. Rotello, and D. R. Lovley: Langmuir **24** (2008) 4376.
12 K. Rabaey, N. Boon, S. D. Siciliano, M. Verhaege, and W. Verstraete: Appl. Environ. Microbiol. **70** (2004) 5373.
13 C. I. Torres, A. K. Marcus, H. S. Lee, P. Parameswaran, R. Krajmalnik-Brown, and B. E. Rittmann: FEMS Microbiol. Rev. **34** (2010) 3.
14 W. M. Yan, C. Y. Soong, F. Chen, and H. S. Chu: J. Power Sources **125** (2004) 27.
15 T. H. Lan, C. T. Wang, Y. C. Yang, and C. Wen-Tong: Int. J. Green Energy **13** (2016) 1483.
16 C. I. Torres, A. K. Marcus, and B. E. Rittmann: Appl. Microbiol. Biotechnol. **77** (2007) 689.
17 S. V. Mohan, S. V. Raghavulu, D. Peri, and P. N. Sarma: Biosens. Bioelectron. **24** (2009) 2021.
18 V. B. Oliveira, M. Simões, L. F. Melo, and A. M. F. R. Pinto: Biochem. Eng. J. **73** (2013) 53.