Finite Element Analysis Approach for Optimization of Enzyme Activity for Enzymatic Bio-fuel Cell

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Abstract: Miniaturized enzymatic biofuel cells (EBFCs) are a promising candidant for implantable power sources, which use enzymes as catalysts to perform redox reaction with biological fuels such as glucose. In this study, we optimize the enzyme activity by using COMSOL 3.5 Multiphysics software based on a three dimensional EBFC chip with highly dense micro electrode arrays, fabricated by carbon-microelectromechanical system (C-MEMS) techniques. We mainly focus on two critical parameters related to the biofuel cells efficiency: one is how to optimize the enzyme reaction rate, and another one is how to generate maximum current density or power density. In our 2-D model design, we use the Michaelis–Menten enzyme kinetics theory to work out the relationship between electrode dimensions and enzyme reaction rate as well as output potential by incorporating Nernst potential theory. In the 3-D model design, we study the performance of the bio-fuel cell with relative placement of the electrodes based on our 2-D model.

Keywords: EBFCs, C-MEMS, enzyme kinetics

1. Introduction

Biofuel cell is classified as a special kind of fuel cell where biocatalyst is employed to simply promote the activity of fuels [1, 2, 3], such as hydrogen, methane and sugar. Biocatalyst is directly involved in the redox reaction chain for the generation of electricity.

There are two methods to couple electrode process to enzyme reaction [3]. The first one is based on the utilization of low-molecular weight redox mediators which have an impact on electron transfer between the enzyme and an electrode. Such mediation process is referred to as mediated electron transfer. The other one is to couple the enzymatic and electrode reactions based on direct (mediatorless) electron transfer (DET), in whom the enzyme is, immobilized on a surface in such a way those electronic states in the surface material and an enzyme active center overlap, increasing the probability of electron tunneling across the interface. In our model, we assumed that enzymes are immobilized as a monolayer on the surface of the electrodes via direct electron transfer[5, 6]. Glucose oxidase (GOx) is immobilized on anodes for the oxidation of glucose from blood, and laccase is immobilized on cathodes for the reduction of dissolved oxygen in the body. In this case, the electron is transferred directly from the electrode surface to the substrate molecule through the active site of the enzyme.

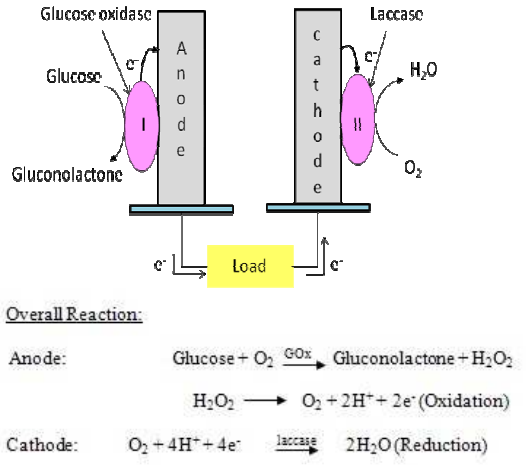


Figure 1 Mechanism of biofuel cell.

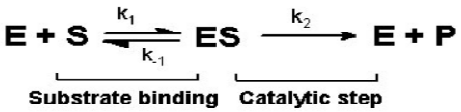
As enzymes are immobilized onto electrodes, interaction of the substrate with electrode hence relates to the enzyme reaction rate. We applied Michaelis-Menten theory [2] in our 2-D design to analyze phenomenon between enzyme kinetics on the electrode surface and glucose diffusion, furthermore find out the design rule of micro array to obtain the maximum enzyme reaction rate.

In order to determine the output potential in developing biofuel cell, we incorporated Nernst equation in 2-D design which was introduced in our previous research [4]. Clearly, the sizes and relative placement of the electrodes determine the output potential of biofuel cell. In order to

achieve the best configuration of electrodes, we optimize the electrode geometry (Height & Well width) of EBFCs based on two critical parameters: enzyme reaction rate and output potential from 2-D design. Based on the 2-D results, we furthered our study by using 3-D model comprised parallel and alternating configuation.

2. 2-D model

2.1 Mechanism/Theory of Michaelis-Menten enzyme kinetics



In the typical enzyme process, there is an initial bimolecular reaction between the enzyme E and substrate S called substrate binding to form the enzyme–substrate complex ES. Next enzymatic step is a typically one rate-determining enzymatic step that allows this reaction to be modeled as a single catalytic step with an apparent unimolecular rate constant k_2. In the catalytic step reaction involves redox reaction[7, 8].

$$v_0 = \frac{V_{\max}[\mathrm{S}]}{K_M + [\mathrm{S}]} \qquad \text{[Eq.1]}$$

V_{max} is the enzyme's maximum rate defined as $V_{max} = k_2\,[E]$; $[E]$ is concentration of active enzyme after immobilization of electrode surface [2];

The Michaelis-Menten equation[Eq.1] describes how the reaction rate v_0 depends on the substrate[S] equilibrium and the rate constant k_M. In other word, we can determine the reaction rate by examining the diffusion process of the substrate based on the electrode geometry of the biofuel cell.

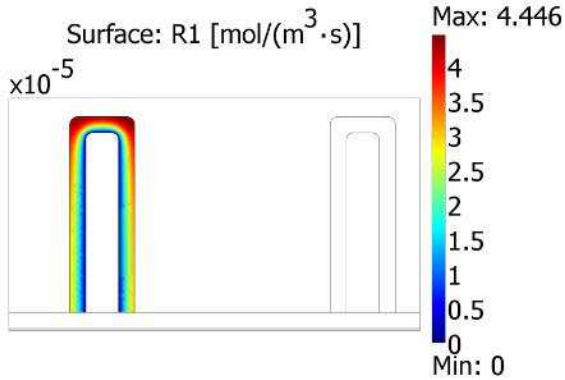
2.2 Simulation

In our 2-D model design, we used the convection and diffusion module in mass transfer to show the reaction rate within the enzyme layer subdomain. As the effective substrates for the anode and cathode are glucose and oxygen respectively, we must consider the reaction rate of both electrodes separately.

Assumptions:

- The steady state response is achieved without considering forced convection due to heart pumping.
- All the reactions are considered at pH 7 and at body temperature of 37^{o}C.
- Many other interfering reactions such as hydrogen peroxide inhibition can take place other than ideal redox reaction in fuel cell but for simplicity they are neglected.
- It is assumed that the enzyme is uniformly distributed in the enzyme layer.
- We assume negligible change in conductivity between enzyme layer and electrode interface.

Anode:(a)



(b)

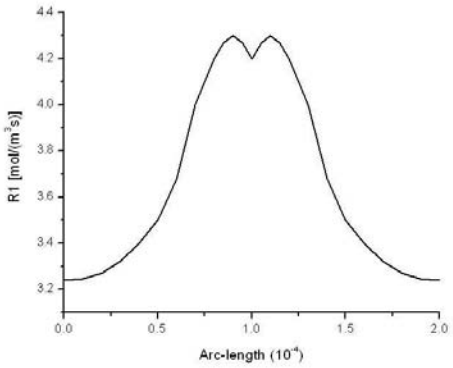
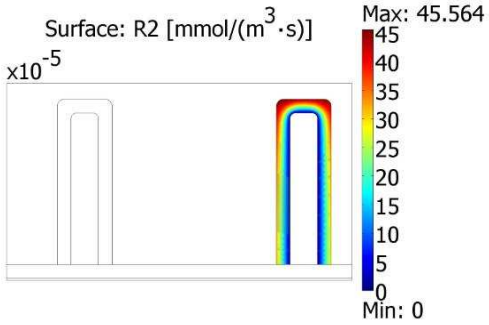


Figure 2 (a) Subdomain plot of anode reaction rate (R1)**; (b)** reaction rates from the whole surface of anode.

Cathode: (a)



(b)

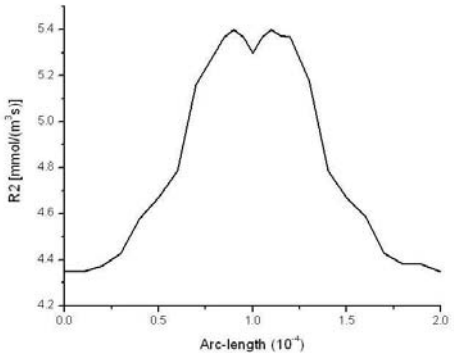


Figure 3 (a) Subdomain plot of cathode reaction rate (R2); (b) reaction rates from the whole surface of cathode.

From the Fig 2 and Fig 3, the reaction rate decreased from the top to the bottom along the surface of both electrodes due to the diffusion of the substrate; also the outer surfaces of the electrodes have the larger reaction rate in the enzyme layer.

Furthermore, we simulated a series of electrodes with different height and well width to find out the maximum enzyme reaction rate. Proper arrangement of geometry may increase the diffusion of glucose in between electrodes which can maximize the biofuel performance. In order to find out suitable configuration to consider these issues, we have simulated different design for cylindrical electrodes. All electrodes have the same thickness of enzyme and are of the same diameter 30 µm so the heights are 60 µm, 120 µm and 240 µm respectively according to the ratio. There are three different ratio of height and width which are 1:2, 1:4 and 1:8 at a range of well widths from 10 µm to 180 µm. The enzyme reaction rates for various models are shown in Fig 4 and Fig 5.

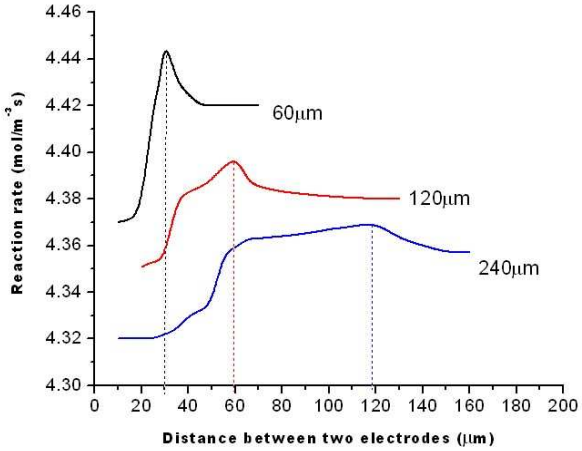


Figure 4 Anode reaction rate curves vs. well width at different ratio of electrode dimensions.

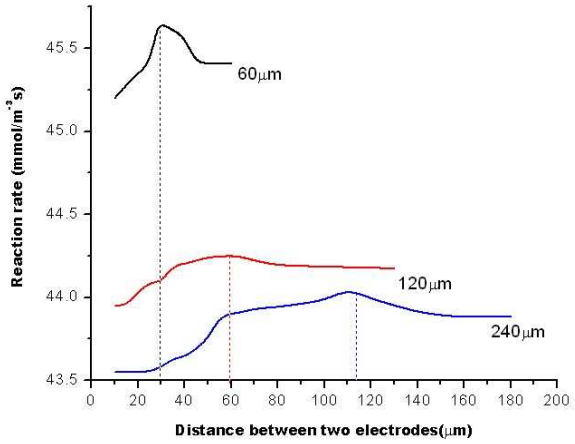


Figure 5 Cathode reaction rate curves vs. well width at different ratio of electrode dimensions.

From all these three sets of models both in anode and cathode, we can conclude that the reaction rates of one pair of electrodes reach the maximum when the well width is half as the height of electrodes.

In order to investigate the maximum potential generation throughout the electrodes combined with enzymes kinetics based on the geometry of electrodes, we have simulated the same model we used for enzyme kinetics by further incorporating Nernst potential theory which was introduced in our previous research[4]. The Nernst Planck's equations for output potential are shown below.

$E_{anode} = E^0_{anode} - 0.05916/2 * \lg (C_1/Co_2)$

$E_{cathode} = E^0_{cathode} - 0.05916 * \lg (1/C_2)$

C_1 and C_2 are the variables in the two models, representing the concentration of glucose and O_2. Because the O_2 is not effective substrate for anode, so we consider Co_2 is constant around the anode [2, 4].

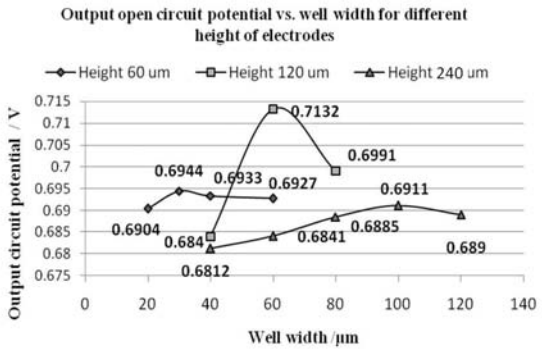


Figure 6 Output potential vs. well width for different ratio of electrode dimesions.

The output potential for the different ratio of electrode dimension is showed in Fig 6. From the results of simulation, we could find out an empirical relationship between electrodes height and well width to achieve optimized output potential is when height of electrodes is twice than that of well width.

It is found out that both simulation results indicated that the design rule is the height of electrodes is twice than that of well width.

3. 3-D model

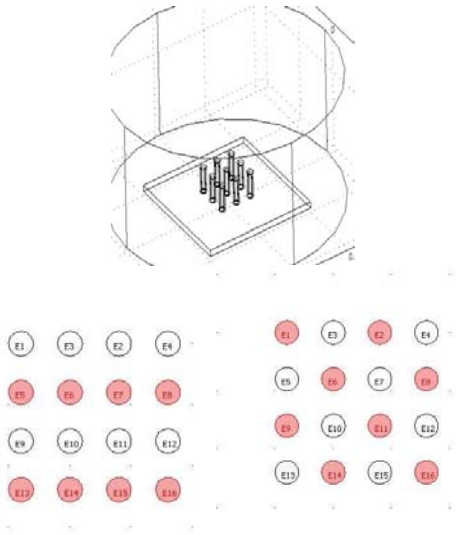


Figure 7 A schematic diagram of 3D cylindrical battery arrays in parallel row (left) and alternating anode/cathode (right) configurations.

In 3 D model, we simulated cylindrical electrode arrays (Fig 7) in parallel row (left) and alternating anode/cathode (right) configuration based on our 2 D design to compare which configuration can optimize the output potential.

The result of this simulation:

configuration	E_{Anode}(V)	$E_{cathode}$(V)	$E=E_{cathode}-E_{anode}$(V)
Parallel	-0.452	0.550	8.016
alternating	-0.465	0.567	8.256

Table 1 output potential of each configuration.

From our results, in the power generation area, the output potential of alternating configuration is higer than parallel.

4. Conclusions

From 2-D model, we have derived the relationship between 1) reaction activity of immobilized enzyme on the surface of and 2) output potential of biofuel cell and the dimensions, relative placement of electrodes.

From the simulation results of both critical parameters: enzyme kinetics and output potential, it is concluded that optimum design rule of electrodes is the well width is half as the height of electrodes.

In the 3-D model based on the 2-D results, we obtained the better configuration of anode and cathode to reach the maximum output potential is alternating anode/cathode configuration.

5. References

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6. Acknowledgements

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7. Appendix

Constants name	Values (unit)	Description
R	8.314[J/(mol*K)]	Gas constant
T	300[K]	Body temperature_37C
F	96485[C/mol]	Faraday's constant
Vm_1	22.5806[mol/m^3·s]	Maximum reaction rate of GOx
k_1	1400[1/s]	Reaction constant of GOx
cGOx	0.016129[mol/m^3]	Concentration of active GOx
Km_1	33[mol/m^3]	Michaelis–Mente constant of GOx
Vm_2	4.185[mol/m^3·s]	Maimum reaction rate of laccase
k_2	310[1/s]	Reaction constant of laccase
cLaccase	0.0135[mol/m^3]	Concentration of active laccase
Km_2	6.8[mol/m^3]	Michaelis–Menten constant of laccase
cO_2	0.1[mol/m^3]	Concentration of oxygen in blood