

COMPUTATIONAL ANALYSIS OF MICROFLUIDIC BIOFUEL CELLS

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ABSTRACT

Biofuel cells are devices that convert biochemical energy directly into electrical energy. They are distinguished from conventional fuel cells by the use of biocatalysts (enzymes/microbes) to generate electricity from organic substrates such as carbohydrates. Microfluidic biofuel cells exploit the difficulty of mixing at low Reynolds number to eliminate the use of membranes, which are commonly used in conventional fuel cell systems. Simulation of the microfluidic fuel cell by solution of the governing 3-D conservation equations (flow, species transport) reveals that the oxygen transport limits the performance of the cathode compartment. An exponential decay in the availability of oxygen at the cathode is also observed, indicating that increasing the number of electrode pairs reduces the overall current density. This conclusion is consistent with experimental observations. Increasing electrolyte flow rates can reduce the mass transport limitations by decreasing the diffusion thickness, but disparity between the anolyte and catholyte flow rates can induce wastage of dissolved oxygen.

Keywords: Biofuel cell, microfluidics, laccase, glucose, virtual prototyping, biocatalysis

1. INTRODUCTION

Biological fuel cells (biofuel cells) are distinguished from conventional fuel cells by their use of biomass (such as carbohydrates, sugars, etc) as a fuel. Fuel is oxidized by biochemical reaction at the anode of the cell, while oxygen is reduced at the cathode to generate electricity at near neutral pH and ambient temperature. A biofuel cell may use either microbes or biocomponents such as an enzyme or ATP for energy creation/extraction. Some advances have been recently reported in the development of miniaturized "biofuel cells" that utilize enzymes and/or whole microbial cells to generate energy from fuels such as glucose. Much of this research is focused on the generation of protons at the anode. Heller et al. have demonstrated a miniaturized biofuel cell [1,2,3] that utilizes the enzyme glucose oxidase (GOx) to convert glucose into gluconolactone at the anode. Electron transport from the enzymatic reaction system and the electrode is achieved through the use of a redox polymer mediator containing osmium. This biofuel cell is able to operate at a potential of 0.4V, while generating a power density of 64 μ W/cm². Katz et al. [4] have used a GOx monolayer-functionalized anode with a pyrroquinoline quinone (PQQ) mediator and a cytochrome c-cytochrome oxidase (COx) cathode to reduce dioxygen to water. This system produces an open circuit voltage of only 0.16V. Lin et al. [5,6] have used whole microbial cells (bacteria, yeast) in a microfabricated biofuel cell using methylene blue as a mediator to transfer electrons from the metabolic pathway to the electrode. This cell produced an open circuit voltage of 0.3V, and a current density of 0.286 μ A/cm². Very little has been reported about the use of enzymatic (or microbial) systems as catalysts at the cathode to convert oxygen to water. As far as cathodic compartment is concerned very little research has been done. Palmore et al. [7] have demonstrated the use of ABTS (2'-azinobis[3-ethylbenzothiazoline-6-sulfonate) as an electron

donor for use in the cathodic compartment and hence selected it as electron mediator. It allows a cathodic reduction of oxygen at 0.5V versus a Standard Calomel Electrode (SCE) at a current density of $50\mu\text{A cm}^{-2}$ and at pH 4.0. This is an efficient bioelectrocatalytic system from the point of view of the overvoltage; the reduction of dioxygen starts at the potential of 0.5 V, which is only 0.25 V more negative than the redox potential of $\text{O}_2/\text{H}_2\text{O}$ (0.751 V versus SCE at this pH) [8]. The same enzyme has also been used by Heller et al. [1,2,3]. The present effort focuses on the analysis of a microfluidic fuel cell that uses enzymatic catalysts at both the anode and the cathode to generate electrical energy by oxidation of glucose at the anode. A microfluidics based (i.e. miniaturized) system allows several advantages: large surface-to-volume ratios, leading to greater power density; sub-microliter reagent volumes, easy large-scale manufacture and ease of scale-up for greater power output.

2. SYSTEM DESCRIPTION

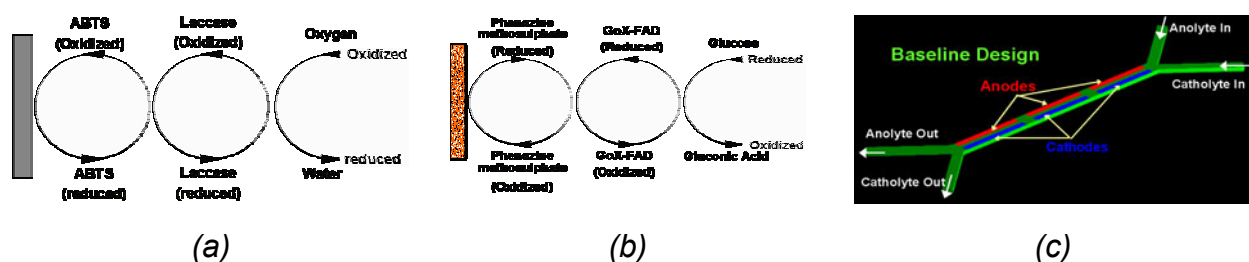


Figure 1. Mechanisms Showing (a) Reduction of Oxygen to Water at Cathode; (b) Oxidation of Fuel (Glucose) at Anode; and (c) Schematic of the Microfluidic biofuel cell Used in the Present Study

The biofuel cell studied in the present effort (Figure 1) consists of an anode where the fuel (glucose) is oxidized to gluconolactone by using the enzyme Glucose Oxidase (GOx) and a cathode where oxygen is reduced to water using the enzyme Laccase [9]. The reactions taking place at each electrode consist primarily of three steps and are summarized in Figure 1. The mediators chosen at the anode and cathode are Phenazine Methosulphate (PMS) and 2'-azinobis{3-ethylbenzothiazoline-6-sulfonate (ABTS), respectively. The formal potentials of the anode (PMS) and cathode (ABTS) electrode reactions are -0.06V (v/s SCE, pH 5.8) and 0.45V (v/s SCE, pH 4.0) respectively. As a result, under standard conditions, the cell potential is expected to be at 0.51V . The anolyte and catholyte streams come into direct contact with each other near the inlet and remain so throughout the length of the channel and separating only near the exit. In other words, there is a single channel for flow of both electrolytes. The electrodes are laid at the base of this channel. The performance of each design depends upon a number of geometric as well as process parameters. These include geometric (channel and electrode dimensions) and process (flow rates, concentration, pH, temperature) parameters. The baseline model has a channel of $800\ \mu\text{m}$ wide, $50\ \mu\text{m}$ height and $5\ \text{cm}$ long. The electrodes are $300\ \mu\text{m}$ wide and $4\ \text{mm}$ long, with $200\ \mu\text{m}$ gap between electrode pairs as well as anode and cathode. Na-phosphate; pH 7.0 buffer consisting of 0.5mM Glucose, $5\ \text{mg/mL}$ Glucose Oxidase (Enzyme), FAD, 25mM PMS (mediator) is used as anolyte while, Na-acetate; pH 4.0 buffer consisting of Saturated with dioxygen ($\sim 0.2\text{mM}$), $5\ \text{mg/mL}$ Laccase (Enzyme), 25mM ABTS (mediator) is used as the catholyte. Typical flow rates are varied between 20 to $90\ \mu\text{L}/\text{min}$ with an electrical load of $75\text{K}\Omega$.

3. GOVERNING EQUATIONS & METHODOLOGY

The mechanism of power generation in a biofuel cell is comprises a combination of complex, interacting physicochemical and electrical phenomena. Analysis of device functioning requires an understanding of (a) diffusion, (b) electrostatic fields, and (c) mechanical or convective forces [10]. For fundamental understanding physical processes and optimization of the design, we will use physics-based modeling and simulation of the system. A computational model of the biofuel cell system to simulate fluid flow, analyte transport, chemistry and electric current in the device were developed in the commercial CFD software CFD-ACE+ [11]. Following governing equations are solved:

Fluid Flow:

$$\nabla \cdot \bar{u} = 0 \quad (1)$$

$$\nabla \cdot \bar{u} + \bar{u} \cdot \nabla \bar{u} = \mu \nabla^2 \bar{u} \quad (2)$$

where \bar{u} is the velocity vector, ∇ is the gradient operator, μ is the dynamic viscosity of the electrolyte solution.

Species Transport:

$$\frac{\partial c_i}{\partial t} = -(\nabla \cdot \mathbf{J}_i) \quad (3)$$

where the flux vector \mathbf{J}_i is given by Nernst-Planck equation [12] as

$$\mathbf{J}_i = -\omega_i z_i \nabla \phi + \mathbf{D}_i \nabla^2 c_i - \bar{u} c_i \quad (4)$$

Here z_i , ω_i , D_i and c_i are valence, mobility, diffusivity and molar concentration of the i^{th} specie, respectively, and ϕ is the electric potential.

Electric Current:

To compute the electric field $\mathbf{E} = \nabla \phi$, we need to solve the continuity equation for current

$$\nabla \cdot \mathbf{j} = 0 \quad (5)$$

where \mathbf{j} is the flux that can be described by generalized Ohm's law:

$$\mathbf{j} = \sigma \nabla \phi + F z_i \mathbf{D}_i \nabla c_i \quad (6)$$

Here σ is the electrical conductivity of the buffer and F is Faraday constant. In the above equation, electroneutrality condition is assumed.

Electrode Reactions:

The overall of redox reaction at the electrode surface is assumed to be reversible and can be described as



where the subscripts "ox" and "red" represent oxidized and reduced species, respectively, and n is the number of electrons transferred during the reaction. The normal current at the electrode surface can be estimated using the Butler-Volmer condition. However, if the oxidized specie is depleted rapidly at the electrode, then the total current is limited by the rate of diffusion of oxidized (or reduced) species from the bulk solution. In that scenario, the transport

equations can be solved in a decoupled manner and the value of the diffusion-limited current is obtained from the Fick's first law of diffusion. On the other hand, when the exchange current density is large or the system exhibits very facile kinetics, it can be shown [13] that electrode potential-concentration relationship can be reduced to a Nernst form as:

$$\phi = \phi_0 + \frac{RT}{nF} \ln \frac{c_{ox}}{c_{red}} \quad (9)$$

and is used to as a boundary condition to couple potential and electrolyte transport equations. In addition, several assumptions have been made to simplify the computational model:

- Electrode reactions are assumed to be instantaneous.
- The complete enzyme-fuel-mediator system has been simplified by assuming it be a two-species system where only the oxidized and reduced forms of the two mediators (ABTS and PMS) determine total current/potential developed in the system.
- The fluxes of the oxidized and reduced mediator species at the electrode are assumed equal
- The overpotential drop was assumed symmetric
- Species transport equations are solved for both oxidized and reduced species and the current is estimated from the total flux of oxidized and reduced species at the cathode and anode respectively.

4. RESULTS AND DISCUSSIONS

Model Validation: The biofuel cell was fabricated using PDMS by conventional soft lithography techniques. The electrolytes were flowed and the electrical resistances connected in series with the biofuel cell were varied (1Ω-1MΩ) to generate the current-voltage curve. A series of parametric simulations was performed for different values of the electrode potential. Simulated Power Density v/s Voltage curve is shown in Figure 2, along with experimentally measured data.

The models matched very well with the experiment in the following aspects:

- The power density increased with increasing voltage, and reached a maximum. Increasing the voltage further resulted in a decrease in the power density.
- At low cell voltages, the current density was nearly constant and rapidly decreased when the voltage was decreased.
- When the number of cathodes in the system was increased, the power density and current density were both reduced.

The quantitative disagreement between simulated and observed data may be due to:

- Simplification of the reaction system (kinetic descriptions of individual reactions were not accounted for)
- The boundary condition at the electrode surface should ideally be calculated using detailed Butler-Volmer condition, which would account for exchange current density.

- The internal (Ohmic) resistance of the fuel cell was not taken into account.
- The enzyme has not been completely characterized (in terms of activity).

These models will be implemented in the follow-up studies.

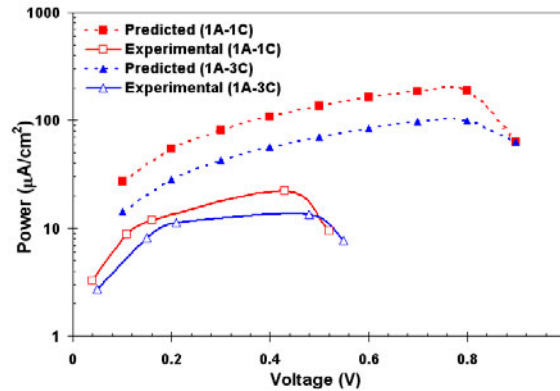


Figure 2. Comparison of simulated and experimental data for power density as a function of the cell voltage. In the Plots, “C” Represents the Cathode and “A” Represents the Anode. For Example, 1A-3C Represents the Data When One Anode and Three Cathodes Were Activated (Electrically Connected) During Experiments.

Characterization of the Biofuel Cell: The primary objective of this study was to characterize the biofuel cell and identify the key influencing factors on the performance. The salient results of this study are as follows:

- **Limiting electrolyte - Oxygen:** Glucose and oxygen contours are plotted on a cutting plane moving along the length of the geometry, with initial and final positions shown in Figure 3(a) and (b) respectively. A comparison of oxygen and glucose depletion along the length of the linear channel is shown in Figure 3(c). The figures are shown for a flow rate of 50 $\mu\text{L}/\text{min}$. It is seen that along the length of the channel, oxygen is almost completely depleted near the exit. This result is a consequence of the limited solubility of oxygen in the electrolyte (saturation concentration $\sim 0.2\text{mM}$) and hence a limited supply. As a result the oxygen flux is very low, limiting the current that can be generated.

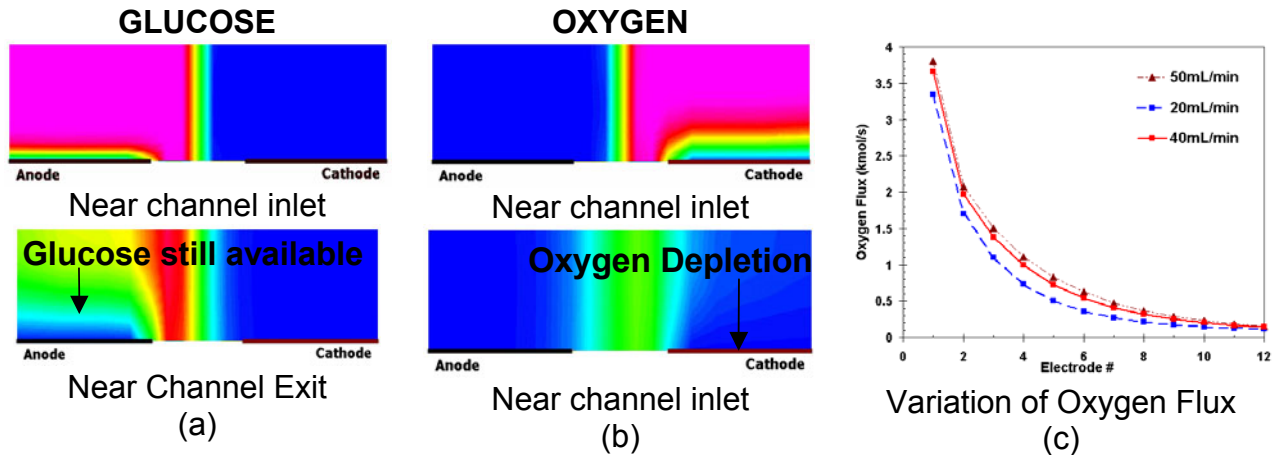


Figure 3. (a) Contours of Glucose Concentration across the channel cross-section near the channel inlet and exit; (b) Corresponding contours for oxygen concentration; (c) Exponential Variation of oxygen flux with electrode position along the length of the linear channel system.

- Electrode-to-Electrode Variation (Exponential Decay): The oxygen and glucose fluxes at the electrode (which will determine the current generated) decrease exponentially at each electrode along the length of the channel. This is primarily due to a depletion of oxygen along the length of the channel. This has been shown in the oxygen contours in Figure 3(c), where it is observed that the oxygen availability decreases, as more and more cathodes are available. Subsequently, the overall diffusion distance to the electrode also increases along the length of the channel. The cumulative effect is the exponential decrease in oxygen flux as leading to a decrease in overall current density with the inclusion of additional electrodes to the system [Figure 3(c)].
- Effect of Anolyte Flow Rate (Incomplete Utilization of Oxygen): In the system studied, electrodes do not occupy the complete width of the catholyte flow area. As a result, there is a zone of oxygen that remains unutilized [Figure 4(a)]. This is an undesirable situation in a system that is already affected by the limited availability of oxygen. This was even more pronounced at lower anolyte (glucose) flow rates, where the catholyte occupied a higher volume fraction in the channel resulting in a zone of oxygen that did not contact the cathode. This led to an even more inefficient utilization of oxygen [Figure 4(b)]. It is therefore essential for the electrolyte to have complete access to the entire electrode area. An increase in the anolyte flow rate (up to the point where it was equal to the catholyte flow rate) resulted in an increase in current density due to increased contact of the catholyte (oxygen) with the cathode (as a result of “squeezing” of the catholyte flow towards the cathode half of the biofuel cell). The variation of current is shown in Figure 4(c).

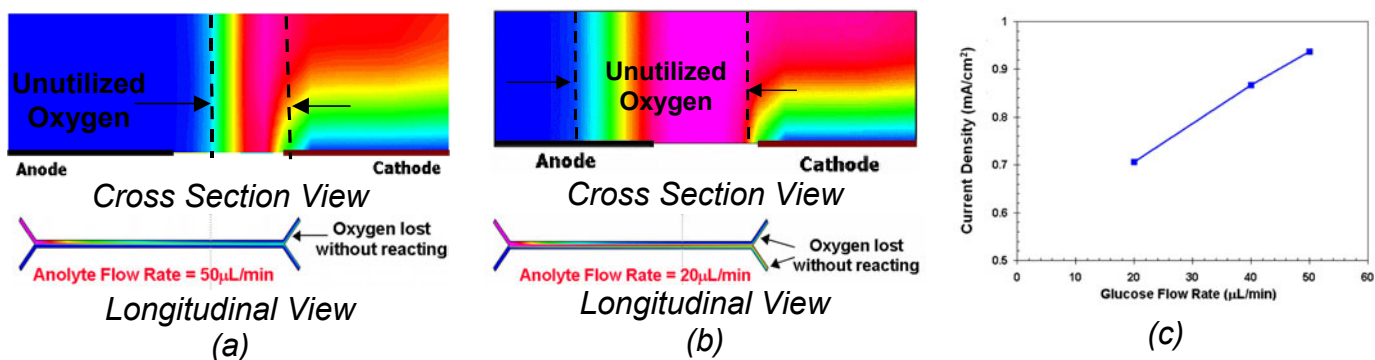


Figure 4. (a) Oxygen concentration profile at an anolyte flow rate of 50 $\mu\text{L}/\text{min}$; (b) Oxygen concentration profile at an anolyte flow rate of 20 $\mu\text{L}/\text{min}$; (c) Effect of Anolyte (Glucose) Flow Rate on the Current Density

5. CONCLUSIONS

A detailed experimental and simulation based characterization of a microfluidic biofuel cell reveals that overall current density of the cell is limited by the oxygen transport in the cathode half-cell. Detailed simulations revealed an exponential decay in the availability of oxygen at the cathode, indicating that increasing the number of electrode pairs will reduce the overall current density. This conclusion is consistent with experimental observation. Increasing the flow rates can reduce the mass transport limitations by decreasing the diffusion thickness, but disparity between the anolyte and catholyte flow rates can induce wastage of dissolved oxygen.

6. REFERENCE

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