ABSTRACT

A numerical simulation of an enzyme-catalyzed oxygen cathode is presented and applied to the analysis of transport limitations in such electrodes, with the goal of optimization for maximum electrode current density. Based on macrohomogeneous and thin-film theories, and accounting for Michaelis-Menten enzyme kinetics, the one-dimensional model predicts a maximum current density of 7.8 mA/cm² for a 300 μm thick electrode relying on diffusion of dissolved oxygen. However, by introducing gas-phase diffusive transport, or alternatively a convective, flow-through design, current densities near 100 mA/cm² may be achieved. Such current densities would move biocatalytic oxygen electrodes closer to practical implementation in low-temperature fuel cells such as direct methanol fuel cells.

INTRODUCTION

The field of biocatalytic fuel cells is currently emerging in response to growing demand for electrical power devices that can operate under conditions where conventional fuel cell and battery technologies fail. Key characteristics of redox enzymes such as selectivity and room temperature activity may be exploited in, for example, physiologically implantable fuel cells and direct methanol fuel cells. The limitations of current biofuel cells for conventional applications are low achievable current density and low stability. Substantial efforts are required to study and develop materials, electrode structures, and devices that fully harness enzyme activity within a stable environment. The focus of this work is the issue of achievable current density. Recent efforts have led to improvements in the operating current density and potential of an oxygen cathode using a novel electrocatalyst made of 10 μm diameter hydrophilic carbon fibers coated with a crosslinked electrostatic adduct of laccase from Coriolus hirsutus (a polyanion above pH 4) and an electron-conducting redox polymer (a polycation) (1,2). The redox polymer electrically connects the laccase reaction centers to the carbon fibers, and when chemically crosslinked forms a hydrogel. With this approach, mass-transfer...
limited oxygen reduction current densities near 6 mA/cm² at 0.6 V (SHE) were obtained in pH 5 citrate buffer at room temperature up to 37°C.

The reaction scheme for catalytic electroreduction of O₂ to water is shown in Figure 1: The copper-containing reaction centers of laccase are oxidized by O₂. These centers, having a redox potential of +0.82 V based on open-circuit potential measurements, oxidize Os²⁺ centers of the electron and ion-conducting redox polymer to Os³⁺, and the redox polymer is reduced at a potential negative of its +0.78 V redox potential. Although the performance of these enzyme electrodes is at least an order of magnitude higher than values reported for other biofuel cells, and is sufficient for microwatt-scale implantable applications, it falls orders of magnitude short of power densities required by conventional fuel cell electrodes, typically 0.25 to 1 W/cm² (3-6).

For biocatalysts to replace precious metals in low power fuel cell applications, current densities an order of magnitude higher than the ~ 5 mA/cm² achievable today are required. In this work, we have used a one-dimensional, porous electrode model to estimate the performance improvements obtainable by the following modifications to the biocathode described above:

1. Optimizing the morphology of porous conducting structures in which biocatalysts are immobilized. Key parameters are porosity, thickness, and fiber diameter.
2. Improving transport of oxygen via gas diffusion or convective, flow through designs. The additional key parameter here is gas-phase porosity, or fraction of the electrode structure open to convective flow.

MODEL

Several assumptions have been made here to simplify the analysis. Migration effects due to the presence of electrical potential gradients are neglected. Additionally, mass transfer resistance external to the electrode is ignored, and the enzyme kinetics are treated with a “ping-pong” type Michaelis-Menton model (7,8). Geometric parameters such as the active area of the carbon structure and the effective thickness of the hydrogel film deposited on that structure are obtained from simple geometric arguments. The model is developed from a macrohomogeneous viewpoint and treats the gas diffusion and flow-through systems using the well-known film diffusion approach (9,10).

Enzyme Kinetics

The overall reaction described in Fig. 1 can be expressed in three steps: Reduction of oxygen by the enzyme; regeneration of the enzyme by the mediator; and electron transfer between the mediator and an electrode:

\[ \text{O}_2 + 4\text{H}^+ + \text{E}_{\text{red}} \rightarrow 2\text{H}_2\text{O} + \text{E}^{\text{ox}} \]  \[\text{(1)}\]

\[ 4\text{M}_{\text{red}} + 4\text{E}_{\text{ox}} \rightarrow 4\text{M}_{\text{ox}} + 4\text{E}_{\text{red}} \]  \[\text{(2)}\]

\[ \text{M}_{\text{ox}} \rightarrow \text{M}_{\text{red}} + ne^- \]  \[\text{(3)}\]
where $E_{\text{red}}$ and $E_{\text{ox}}$ are the reduced and oxidized form of the enzyme, and $M_{\text{red}}$ and $M_{\text{ox}}$ are the reduced and oxidized form of the electron mediator; $k'_S$, $k'_M$ and $k$ are rate constants. The effect of pH on enzyme kinetics is complex and dependent on the mediator involved. Reaction rate dependence on the proton ($H^+$) will therefore not be considered here. Reactions 1 and 2 can be described by Michaelis-Menten kinetics by expanding the rate coefficients $k'_S$ and $k'_M$ to:

$$k'_S = \frac{k_S}{K_S + [S]}; \quad k'_M = \frac{k_M}{K_M + [M_{\text{red}}]}$$

where $[S]$ is the concentration of the substrate oxygen, and $K_S$ and $K_M$ are Michaelis constants for the substrate and reduced form of the mediator, $M_{\text{red}}$, respectively. With this substitution, the steady-state rate expression is

$$R = -\frac{\partial [S]}{\partial t} = \frac{k_{\text{cat}} [E]}{1 + \frac{K'_M}{[M_{\text{red}}]} + \frac{K'_S}{[S]}}$$

where $k_{\text{cat}}$ is the effective rate constant and $K'_M$ and $K'_S$ are effective Michaelis constants for the “ping-pong” kinetics and are defined as

$$k_{\text{cat}} = \frac{k_M k'_S}{k_M + k'_S}; \quad K'_S = K_S \frac{k_{\text{cat}}}{k_S}; \quad K'_M = K_M \frac{k_{\text{cat}}}{k_M}$$

Unsupported electrode

The core of the model considers a one-dimensional, unsupported hydrogel film immobilized on a conducting surface, as shown in Fig. 2 except without carbon fibers. Conservation of mass, accounting for diffusion and reaction within polymer film, again assuming steady state, gives two differential equations:

$$D_m \frac{\partial^2 [M_{\text{red}}]}{\partial x^2} = s_M R; \quad D_S \frac{\partial^2 [S]}{\partial x^2} = s_SR$$

where $D_m$ and $D_S$ are diffusion coefficients and $s_M$ and $s_S$ are stoichiometric coefficients for the mediator and substrate, respectively, $x$ defines the local position within the film, and $R$ is defined by the rate expression, Eq. 5.

Boundary conditions at the solution side of the film are bulk concentration of substrate and zero mediator flux, or

$$At x = L: [S] = [S]_w, \frac{d[M]}{dx} = 0$$

On the electrode side of the film, the substrate concentration gradient is zero, corresponding to zero diffusive flux. The mediator concentration is controlled by the applied potential, and for fast electron transfer kinetics can be treated with a Nernstian expression:

$$At x = 0: \frac{d[S]}{dx} = 0, [M_{\text{red}}] = [M]\left[1 + \exp\left(-\frac{nF(E - E^\circ)}{RT}\right)\right]$$

where $E$ is the electrode potential and $E^\circ$ is the redox potential of the mediator couple.
Upon solution for the substrate concentration \([S]\) as a function of position within the electrode film, electrode current density can be calculated from the substrate concentration gradient on the solution side of the film, by the expression:

\[
\iota = \frac{n F D_s [S]_i}{s_s} \frac{d[S]}{dx} \bigg|_{x=L} \tag{10}
\]

**Supported electrode**

In the case of the composite electrode, where the hydrogel is assumed to be supported by carbon fibers, the hydrogel is treated as a film on the fibers, the thickness of which, \(l_f\), is related to the average fiber spacing. The total fiber area per unit electrode volume, \(a\), is estimated from the fiber diameter and the void fraction. The expressions used to calculate the effective hydrogel film thickness and fiber area per unit volume were:

\[
a = 4 \left(1 - \varepsilon \right) / \left(\varepsilon f - \varepsilon_f\right) \tag{11}
\]

A modified version of the unsupported model given above can then be used to calculate an effective reaction rate, \(j_{in}\) (consumption of substrate per unit area) for a given effective film thickness \(l_f\) as a function of substrate concentration. In this approach, the local substrate concentration is treated as the bulk concentration \([S]^\infty\) in the context of the unsupported model. The reaction rate \(j_{in}\) is related to the current obtained by Eq. 10 by

\[
\dot{j}_{in} = \frac{s_s}{nF} i \tag{12}
\]

Using a macrohomogeneous model of the composite electrode, a single mass balance for the substrate concentration is therefore required (9):

\[
\varepsilon D_s \frac{d^2[S]}{dx^2} = a j_{in}(S) \tag{13}
\]

with boundary conditions

At \(x = 0\): \(d[S]/dx = 0\). At \(x = L\), \([S] = [S]^\infty\) \tag{14}

Electrode current density can be calculated using Eq. 10, substituting \(\varepsilon D_s\) for the diffusion coefficient \(D_s\).

**Gas diffusion electrode**

The gas diffusion electrode case is treated by dedicating an a volume fraction in the electrode, \(\varepsilon_g\), to which gas-phase diffusion of substrate. The presence of the gas phase reduces the volume fraction occupied by the film, used in Eq. 11, to \(\varepsilon - \varepsilon_g\). Additionally, the gas-phase diffusion coefficient, \(D_{sg}\), must be introduced to Eq. 13, as well as a partition coefficient, \(k_{p,s}\), to account for the concentration drop across the gas-liquid interface. Eq. 13 then becomes

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Flow-through electrode

The flow-through electrode is treated by replacing gas diffusion with liquid convection in Eq. 15. The gas-phase porosity now becomes the open, non-hydrogel, liquid-filled volume fraction. Eq. 15 then becomes

\[ \varepsilon D \frac{d^2[S]}{dx^2} - \varepsilon D \frac{d[S]}{dx} = a j_{in}(k_{x,S}[S]) \]  

[15]

Here, the current-collecting electrode is itself assumed to be porous, such that the flow velocity is parallel to the electrode thickness. Pressure drop can be calculated for a given flow velocity, \( v \), using Darcy’s law (11)

\[ \Delta P = \frac{\mu v}{l} \]  

[17]

where the permeability term \( K \) is a function of fiber diameter and volume fraction, and can be estimated according to a pseudo-Carman-Kozeny relation:

\[ K = \frac{d^2 \varepsilon^3}{K' (1 - \varepsilon)^2} \]  

[18]

The coefficient \( K' \) was estimated from data supplied for Toray carbon papers.

Parameter values and numerical solution.

Values and sources of fixed parameters are given in Table 1. Numerical solution of equations 7 (unsupported electrode), 13 (supported electrode), 15 (gas diffusion electrode) and 16 (flow-through electrode), cast in nondimensional form with appropriate boundary conditions, were obtained using the finite difference method and a linear, coupled differential equation solver (9). In all supported-electrode cases, the unsupported case was solved for the given film thickness \( \ell_f \), Eq. 11) as a function of substrate concentration. These results were expressed as \( j_{in}(S) \) to be used as input to Eqs. 13, 15 and 16.

RESULTS

Unsupported electrode

Calculated results for the unsupported case are shown in Fig. 3 in comparison to experimental data, acquired using a rotating disk electrode (2). These results were fit to experiment in order to extract the kinetic parameters \( k_{cat} \) and \( K_i \); resulting values are given in Table 1. Concentration profiles through the electrode are shown in Fig. 4a. Due to the extremely low value of the mediated electron diffusion coefficient \( D_m \), nonzero concentrations of the oxidized mediator exist only in a very small portion of the electrode.
near the carbon surface \((x/L = 0)\). Therefore, utilization and current density are limited by electron diffusion.

**Carbon supported electrode**

Calculated results for the supported electrode using diffusion of dissolved oxygen are also shown in Fig. 3 compared to experimental results (2). A poor match with experiment is obtained in two respects. First, the maximum current density, \(i_{\text{max}}\), is of by 40\% (3.6 compared to 6.1 mA/cm\(^2\)). This discrepancy is most likely due to the presence of convection in the experimental electrode. The electrode structure is thick \((L = 300 \mu\text{m})\) compared to the Levich mass transfer boundary layer \((\sim 4 \mu\text{m} \text{ at } 4000 \text{ rpm})\). This fact, combined with large void fraction of the supporting carbon paper, point to the possibility of significant convective transport within the electrode structure. Current density enhancement due to convective transport of substrate can be harnessed in a flow-through electrode, as discussed below. Second, the activation potential is too high by more than 100 mV. This error could be due to the assumption of fast kinetics at the carbon surface (Eq. 9), migration effects, or errors in estimates of the Michaelis constant for the mediator. These possibilities are currently under investigation. In any case, the key polarization value in this study is maximum current density, \(i_{\text{max}}\), therefore errors in potential were ignored.

Calculated polarization of the optimized supported electrode is also shown in Fig. 3. Optimization was achieved by decreased electrode thickness, \(L\), and fiber diameter, \(d_f\), and by increasing porosity, \(e\) (refer to Table 2). Maximum current density, \(i_{\text{max}}\), increases only by a factor of two, but utilization is increased substantially using the thinner electrode, as shown in Fig. 5, where substrate concentration and reaction rates of the baseline and optimized cases are profiled. Even in the optimized case, however, low substrate concentrations lead to near-zero local reaction rates far from the electrolyte interface, and therefore control overall current density.

**Gas diffusion electrode**

Calculated results for the gas diffusion electrode predict that devotion of just 20\% of the available void volume to gas transport leads to dramatically increased current density. Electrode utilization is increased to near unity in an electrode of identical thickness to the baseline supported electrode, as shown in Fig. 5. In Fig. 6, \(i_{\text{max}}\) is shown to become independent of electrode thickness above \(L = 30 \mu\text{m}\) for the dissolved \(O_2\) case, but the gas diffusion electrode favors thicknesses approaching 500 \(\mu\text{m}\). In saturated oxygen gas, the model predicts current densities exceeding 100 mA/cm\(^2\) for thick electrodes. In air, current densities above 30 mA/cm\(^2\) are expected with slightly different geometry (Table 2).

**Flow-through electrode**

Convective flow-through electrodes provide the opportunity to achieve, in the dissolved-substrate electrode, current densities approaching those predicted for the gas diffusion electrode. In Fig. 7a are presented predictions of maximum current density for
O₂-saturated and air-saturated liquid substrate, as functions of bulk flow velocity, v. Velocity approaching 1 cm/s is required to achieve current density comparable to the gas diffusion electrode, but velocities near 0.1 cm/s lead to five-fold improvement in current density. Fig 7b gives estimated pressure drops associated with convection through the porous electrode, along with relative parasitic losses for both air-saturated and O₂-saturated liquids. According to this estimate, parasitic losses do not exceed 5% in the velocity range shown, even for the saturated air case.

CONCLUSIONS

A simple numerical simulation has enabled visualization and analysis of mass transfer limitations in composite oxygen biocathodes. The simulation predicts current densities approaching 100 mA/cm² for pure O₂-breathing enzyme electrodes, and 30 mA/cm² for air-breathing electrodes. Additionally, flow-through electrodes are predicted to provide similarly favorable performance in systems where oxygen is available in dissolve form.

Technical hurdles remain to be overcome in order to realize practical enzymatic gas diffusion electrodes, such as chemical-mechanical stability and the need to provide ionic conductivity in the gas diffusion electrode. It is envisioned, however, that such electrodes as described here would provide an attractive replacement for noble metal-catalyzed cathodes in low-temperature, low power density fuel cells such as direct methanol fuel cells.

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### Table 1. Fixed Parameter Values

| Parameter | Value | Source |
|-----------|-------|--------|
| [S]₀ (mM) | 1 (aq) 8 (air) 40 (O₂) | (12) |
| kₚ,O₂ | 0.025 | From (12) |
| [M] | 131 mM | Measured |
| [E] | 1.9 mM | Measured |
| D₂O (cm²/s) | 3×10⁻⁶ (aq) 1×10⁻³ (gas) | (13,14) |
| Dₘ | 1×10⁻⁸ cm²/s | (15) |
| kₙ | 50 /s | Fit to experiment |
| Kₛ | 500 µM | Fit to experiment |
| Kₘ | 500 µM | (16) (typ.) |
| E₀ | 0.77 V re: SHE | (1) |
| K'ₜₙ | 1.2×10⁻⁴ cm² | From Toray data |

### Table 2. Experimental and Optimized Parameter Values

| Parameter | Unsupported (experiment) | Supported (experiment) | Supported (Optimum) | Gas Diffusion (Optimum, O₂) | Gas Diffusion (Optimum, air) |
|-----------|-------------------------|------------------------|---------------------|-----------------------------|------------------------------|
| L (µm)    | 50                      | 300                    | 30ᵇ                 | 450ᵇ                        | 470ᵇ                        |
| dₖ (µm)   | —                       | 10                     | 1.0ᵃ                | 1.0ᵃ                        | 1.0ᵃ                        |
| e          | —                       | 0.78                   | 0.9                 | 0.92                        | 0.95                        |
| e₂         | —                       | —                      | —                   | 0.18                        | 0.29                        |
| iₙ (mA/cm²) | 1.1                    | 6.1                    | 7.8                 | 116                         | 34                          |

ᵃChosen as realistic minimum;ᵇBeyond this value, i ≈ 0.95 iₙmax.
Figure 1. Reaction schematic for oxygen-reducing laccase cathode.

Figure 2. One-dimensional model diagram for supported laccase cathode.
Figure 3. Potential-dependence of the O\textsubscript{2} electroreduction current density, comparing simulation results with experiment. Conditions: 1 mV/s sweep rate at 1 atm O\textsubscript{2} pressure, 0.2 M citrate buffer, pH 5, 37°C. Current densities were based on the projected area of a 4-mm carbon cloth disk (0.13 cm\textsuperscript{2}) Electrode geometry as in Table 2.

![Graph showing potential-dependence of O2 electroreduction current density.](image)

Figure 4. Calculated concentration and rate profiles in baseline (a) unsupported electrode and (b) carbon-fiber supported electrode. Conditions as in Fig. 2, at 0.6 V re: SHE. In the unsupported electrode, utilization is strongly limited by electron transport via the redox mediator, in the supported electrode oxygen transport limits utilization.

![Graph showing concentration and rate profiles in unsupported and supported electrodes.](image)
Figure 5. Calculated concentration and rate profiles in optimized, carbon-fiber supported electrode. Conditions as in Fig. 2, \( L = 300 \, \mu m \) for gas diffusion case) at 0.6 V re: SHE. Changes to electrode morphology and enhanced oxygen transport via gas phase improves utilization, and therefore current density (see Fig. 6.)

Figure 6. Effect of electrode thickness. Conditions as in Fig. 2, at 0.6 V re: SHE. Limited dissolved oxygen diffusion favors thin electrodes. Gas diffusion favors thick electrodes.
Figure 7. Effect of flow-through convection. (a) Maximum current density; (b) Predicted pressure drop and parasitic loss. Parameters as in O₂ gas diffusion electrode case (Table 2), 300 μm electrode thickness. Velocities near 0.4 cm/s are required to approach GDE current densities.