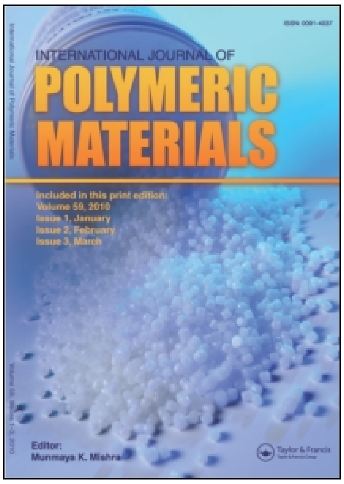

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EFFECT OF MASS TRANSFER RESISTANCE ON ELECTROCHEMICAL BIOSENSORS WITH ASYMMETRICAL SANDWICH MEMBRANES

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A mathematical model of a sandwich membrane biosensor with an enzyme layer between two membranes is considered. The electrochemically active product of the enzymatic reaction is detected by a catalytic electrode on one side of the sandwich membrane. A finite but different mass transfer resistance across the solution–membrane interface was assumed for the substrate and product. The steady state solution depended on the Biot numbers and the diffusivities of the substrate and electrochemically active product. At low Biot numbers the signal depended on the mass transfer coefficient and was independent of the membrane thickness. At high Biot numbers the signal depended on the position of the enzyme layer and the relative diffusivity of the electrochemically active product in the two membranes.

Keywords: amperometric biosensors, enzyme electrodes, membranes, mass transfer, diffusion

INTRODUCTION

Many amperometric membrane biosensors are based on the enzymatic reaction of a substrate with an oxidase immobilized in a porous membrane, and electrochemical detection of the generated H_2O_2 on a catalytic electrode [1–3]. Using glucose as the example, the reactions are:

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$$\text{Glucose} + O_2 \xrightarrow{\text{Glucose Oxidase}} \text{gluconolactone} + H_2O_2 \tag{1}$$

$$H_2O_2 \xrightarrow{\text{Platinum Electrode}} O_2 + 2H^+ + 2e^- \tag{2}$$

Electrons in Eq. (2) provide the electric current, which is used for the determination of the substrate concentration. The oxygen generated by Eq. (2) is recycled back to provide oxygen needed in Eq. (1) and there is no net use of oxygen in the enzyme electrode. Biosensor with sandwich membranes is made by incorporating a layer of immobilized enzyme between two outside membranes. The enzyme layer can be made separately depending on the nature of the enzyme, whereas the outside layers can be universal materials. The main function of the membrane is to provide a consistent environment and to prevent other proteins such as catalase from reacting with H_2O_2, or other reducing chemicals such as ascorbic acid to react on the platinum electrode. A charged dialysis membrane [4] can be used as the outer membrane to prevent the deposition of protein molecules. The inner membrane can be made of a hydrophobic perforated Teflon® membrane or a polyurethane membrane [3].

The transient solution of asymmetrical sandwich membranes has been studied by Iliev et al. [5] with the assumption of no mass transfer resistance at the membrane–solution interface. Under this assumption the concentration of H_2O_2 is zero at the membrane–solution interface. It is also assumed that the thickness of the enzyme layer is negligible compared to both outside membranes and the reaction rates of the enzyme and electrode are very high so that the respective concentrations of the substrate and H_2O_2 are zero at the interface. The diffusivity of H_2O_2 is assumed to be the same in both membranes, but it is different from the diffusivity of the substrate. Using these assumptions the transient solution for concentrations was solved and it was concluded that the signal is independent of the location of the enzyme layer and is inverse to the total thickness of the membranes. Also, an increase of the ratio of the outer membrane to inner membrane thickness lengthens the response time, especially when the diffusivity of the substrate is lower than the diffusivity of H_2O_2.

DIFFUSIONAL RESISTANCE IN MEMBRANES

Two assumptions in the aforementioned model can be relaxed. The first is that the diffusivity of H_2O_2 can be different for outer and inner membranes because they are frequently made of different materials. The second is that the convection mass transfer rate between the outer membrane and solution is finite and its effect should be included in the model.

The mass transfer resistance at the membrane–solution surface is characterized by a convection mass transfer coefficient, k [6]. The relative importance between the mass transfer resistance of the solute–membrane interface and diffusion through the membrane is calculated by the dimensionless Biot number, which is defined as:

$$\mathrm{Bi} = \frac{\mathrm{kL}}{\mathrm{Ds}} \tag{3}$$

where Ds is the diffusivity of the substrate in the membrane and L is the thickness of the membrane. When Bi is much larger than unity the diffusional resistance at the solution–membrane interface is relatively small and the concentration at the membrane surface is the same as the bulk solution. When Bi is smaller than 0.2 the concentration gradient across the solid membrane is small but a large decrease of concentration is observed between bulk solution and the interface.

The value of Bi is critical in a membrane process and should be maintained at a high value. Correlation between Bi and other dimensionless parameters is available for several common geometries [6]. For a sensor located in a flowing system the correlation expression is $\mathrm{Sh} = 1.834$ for a laminar flow in a tube. The Sherwood number is defined as $\mathrm{Sh} = \mathrm{kd/D}$. Using a typical value of tube diameter, $\mathrm{d} = 1$ mm, and diffusivity of the substrate in solution, $\mathrm{D} = 10^{-9}\ \mathrm{m^2/s}$, the value of k is about $2 \times 10^{-6}\ \mathrm{m^2/s}$. For a film with thickness 10^{-5} m and $\mathrm{Ds} = 10^{-9}\ \mathrm{m^2/s}$ the Bi number is estimated to be 0.2. A higher flow rate can generally be achieved on a rotating disk. When the electrode is mounted on a rotating disk, the convection mass transfer coefficient has an analytical expression: $\mathrm{k} = 0.62\ \mathrm{D}^{2/3}\, \nu^{-1/6}\, \omega^{1/2}$ where D, ν, and ω represent diffusivity of the substrate in solution, kinematic viscosity of the solvent, and the rotating speed of the disk, respectively [6–9]. Using a typical value of $\mathrm{D} = 10^{-9}\ \mathrm{m^2/s}$, $\nu = 10^{-6}\ \mathrm{m^2/s}$, $\mathrm{L} = 10^{-5}$ m, and $\omega = 50$ rad/s, the value of k is estimated to be 4×10^{-4} m/s. With $\mathrm{L} = 10^{-5}$ m and $\mathrm{Ds} = 10^{-9}\ \mathrm{m^2/s}$ the value of Bi is 4, which is higher than unity. The value of Bi numbers is likely to be in the range of unity, which makes it an important factor to be considered in the model.

MODEL AND RESULTS

Figure 1 shows the structure of the sandwich membrane. It includes two layers of membranes with a layer of enzyme between them. The total thickness is L, and the enzyme layer with a negligible thickness is located at distance pL from the solution−membrane interface. The dimensionless number p has a value between zero and unity. The outer membrane contacts the solution and the inner membrane contacts the catalytic electrode. It is assumed that both enzyme and catalytic electrode reactions are rapid and the concentrations of reactants are zero at the respective interfaces. In the steady state the concentration of the substrate and H_2O_2 is described by:

$$D\frac{\partial^2 C(x,t)}{\partial x^2} = 0 \tag{4}$$

The solution of Eq. (4) is a linear equation. Note that the diffusivity is different between the substrate and H_2O_2, and the diffusivity is also different in each membrane. However, the substrate will not diffuse beyond the enzyme layer because it reacts completely in the enzyme layer. Therefore, three diffusivisties are necessary. They are diffusivity of the substrate in the outer membrane, Ds, diffusivity of H_2O_2 in the outer membrane, $D_{r,I}$, and diffusivity of H_2O_2 in the inner membrane, $D_{r,II}$. Different boundary conditions are needed for the substrate and H_2O_2. For the substrate the concentration, $C_s(x)$, depends on its convection mass transfer coefficient, k_s, and its diffusivity, Ds:

$$k_s(C_o - C_s) = -D_s\frac{\partial Cs}{\partial x} \qquad \text{at } x = 0 \tag{5}$$

$$C_s = 0 \qquad \text{at } x = 0 \tag{6}$$

For H_2O_2 the concentration, Cr(x), depends on its convection mass transfer coefficient, k_r, and its diffusivity, D_r:

$$k_r Cr = D_{r,I}\frac{\partial Cr}{\partial x} \qquad \text{at } x = 0 \tag{7}$$

$$Cr = Cm \qquad \text{at } x = pL \tag{8}$$

$$Cr = 0 \qquad \text{at } x = L \tag{9}$$

The concentration Cm is the concentration of H_2O_2 at $x = pL$. The concentration profile of the substrate is solved as:

$$\frac{Cs(x)}{Co} = \frac{p + \frac{x}{L}}{p + 1/Bi,s} \tag{10}$$

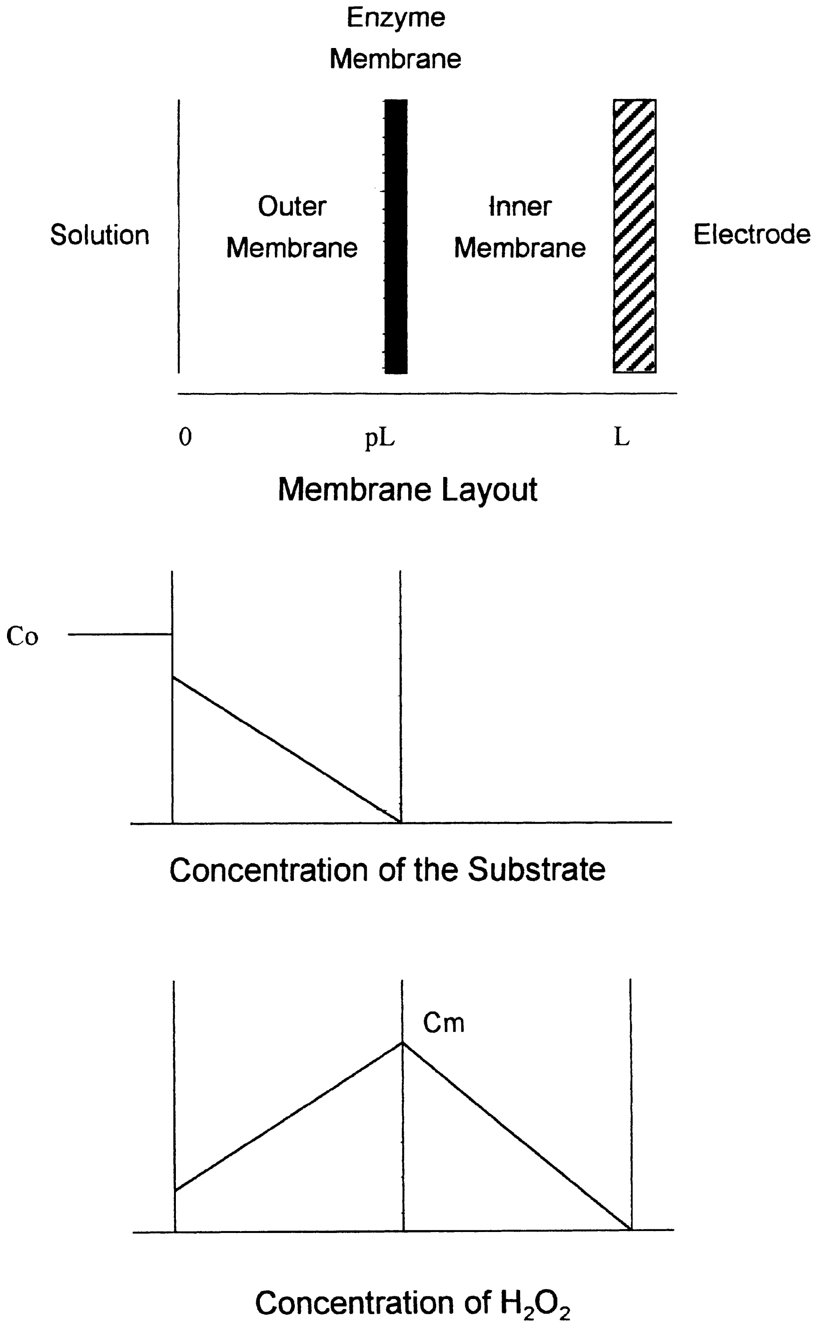

FIGURE 1 Schematic view of asymmetrical sandwich membrane biosensor.

where Bi,s is the Biot number, calculated based on the properties of the substrate. The reaction rate of the substrate is:

$$\mathrm{Rate} = \frac{\mathrm{CoDs}}{\mathrm{L(p + 1/Bi, s)}} \tag{11}$$

The concentration of H_2O_2in the outer membrane is:

$$\frac{\mathrm{Cr(x)}}{\mathrm{Cm}} = \frac{\frac{\mathrm{x}}{\mathrm{L}} + 1/\mathrm{Bi, r}}{\mathrm{p} + 1/\mathrm{Bi, r}} \tag{12}$$

where Bi,r is calculated based on the properties of H_2O_2. The concentration of the H_2O_2in the inner membrane is:

$$\frac{\mathrm{Cr(x)}}{\mathrm{Cm}} = \frac{1 - \frac{\mathrm{x}}{\mathrm{L}}}{1 - \mathrm{p}} \tag{13}$$

The reaction product can diffuse through the outer membrane into the solution or to the inner membrane where it reacts on the electrode to produce the signal. The value of Cm is determined by the rate of production in Eq. (11) and the rate of diffusion through Eqs. (12) and (13). The value of Cm is solved to be:

$$\mathrm{Cm} = \mathrm{Co}\frac{\frac{\mathrm{Ds}}{\mathrm{p+1/Bi,s}}}{\frac{\mathrm{D_{r,I}}}{\mathrm{p+1/Bi,r}} + \frac{\mathrm{D_{r,II}}}{1-\mathrm{p}}} \tag{14}$$

The rate of electrode signal per unit area is calculated by the flux in the inner membrane as:

$$\mathrm{Signal} = \frac{\mathrm{CoDs}}{\mathrm{L}}\mathrm{F} \tag{15}$$

where

$$\mathrm{F} = \frac{\mathrm{D_{r,II}(p + 1/Bi, r)}}{\mathrm{[D_{r,I}(1 - p) + D_{r,II}(p + 1/Bi, r)](p + 1/Bi, s)}} \tag{16}$$

In the event that Bi $\rightarrow \infty$ and $\mathrm{D_{r,I}} = \mathrm{D_{r,II}}$ the value of F is unity and the signal is a simple expression as if all the substrate reacted at the electrode surface through a homogeneous membrane with thickness L. This is the same result as in Iliev et al. [5]. In a more general situation F depends on Bi,s, Bi,r, and the ratio $D_{r,II}/D_{r,I}$. An inner membrane with a higher diffusivity for H_2O_2 is a preferred situation because more flux of H_2O_2 can reach the platinum electrode. Therefore, the case $D_{r,II}/D_{r,I} > 1$ is more likely to occur. Bi,s and Bi,r are not separate variables. When flow rate increases, the convection of both substrate and H_2O_2 increases, but their ratio likely remains relatively constant. Therefore, Bi,s and Bi,s/Bi,r are chosen as the parameters. The value of Bi,s/Bi,r is near unity because the molecular size dependency of k and diffusivity cancel each other, making Bi insensitive to the molecular size. Under these assumptions:

$$F = \frac{r(p + s/Bi,s)}{[1 - p + r(p + s/Bi,s)](p + 1/Bi,s)} \tag{17}$$

where $r = D_{r,II}/D_{r,I}$ and $s = Bi,s/Bi,r$. At a high value of Bi,s the value of F gradually reaches a constant value that depends on r but not on s. The following expression for F was obtained at high value of Bi,s:

$$F = \frac{r}{1 - p + rp} \tag{18}$$

This expression is independent of Bi. Figure 2 shows the value of F as function of p using r as the parameter. The result is larger than unity when $p < 1$ and $r > 1$. At the limit $p = 0$ the value of F is equal to r. At the limit of $p = 1$ the value of F is unity. When p increases from zero to unity the value of F decreases rapidly. A most likely value for p is 0.5. At this value F is not significantly greater than unity. At sufficiently large r the value of F is inverse to p. Therefore, the limit of F is about two when a very permeable inner film is used. This is the result as if the diffusional resistance of the inner membrane were zero.

Figure 3 shows the value of F versus, Bi,s at $p = 0.5$ and $s = 1$ for three values of r. It can be seen that at very high value of Bi,s the value of F reaches a constant that is dependent on the value of r. At very low value of Bi the value of Bi terms in Eq. (17) dominates and the value of F reaches an inverse relationship with Bi,s independent of the parameter r:

$$F = Bi,s \tag{19}$$

F is proportional to Bi,s and independent of other parameters. This is because at low Bi the mass transfer through the solution–membrane interface is the rate determining process. The expression for the signal is Cok_s. The expression is independent of the thickness

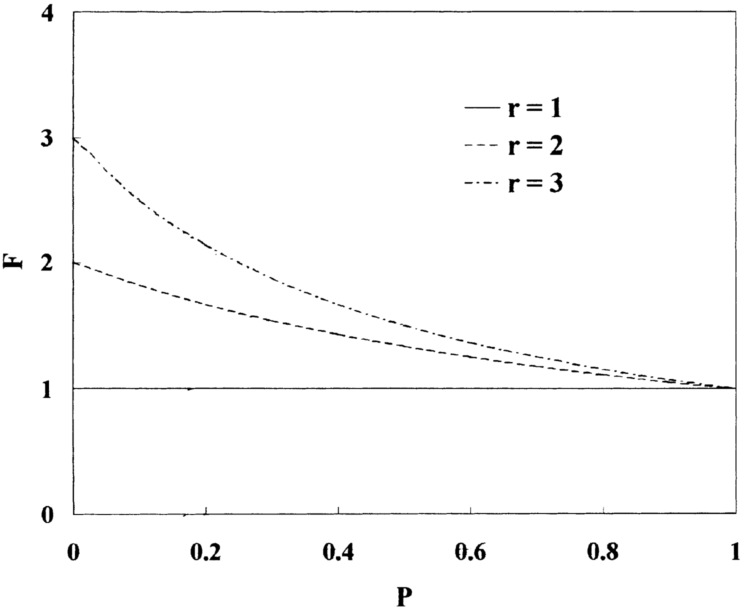

FIGURE 2 Asymptotic value of F at high Bi,s for several values of r.

of each membrane, but increases when flow rate increases, which increases the value of k. An increase of electrode signal, when the speed of a rotating electrode [8] increases, has been observed, and indicated the dependence of signal on mass transfer resistance. A higher order approximation in the case of small Bi is:

$$\frac{1}{F}=\frac{(1-p)(p+s/\mathrm{Bi,s})}{r(p+s/\mathrm{Bi,s})}+p+\frac{1}{\mathrm{Bi,s}} \tag{20}$$

The first term on the right-hand side is relatively constant; therefore, a plot of 1/F vs. 1/Bi,s or 1/Bi,r yields a curve close to a straight line. In the rotating disk study Bi is proportional to $\sqrt{\omega}$. It is known as the Koutecky–Levich plot [9].

Figure 4 shows the plot of F versus Bi,s at p = 0.5 and r = 1 for three values of s. It can be seen that at very high value of Bi,s the curves of different s converge to a constant value. At very low value of Bi the curves reach an inverse relationship to Bi,s and are also independent of s. Only in the intermediate range of Bi,s the value of F is higher when s is large. The parameter s is a function of the relative diffusivity of the substrate and reactant of the electrochemical reaction, and is less dependent on the design and operating parameters. Therefore, it is not subject to control by experimental conditions.

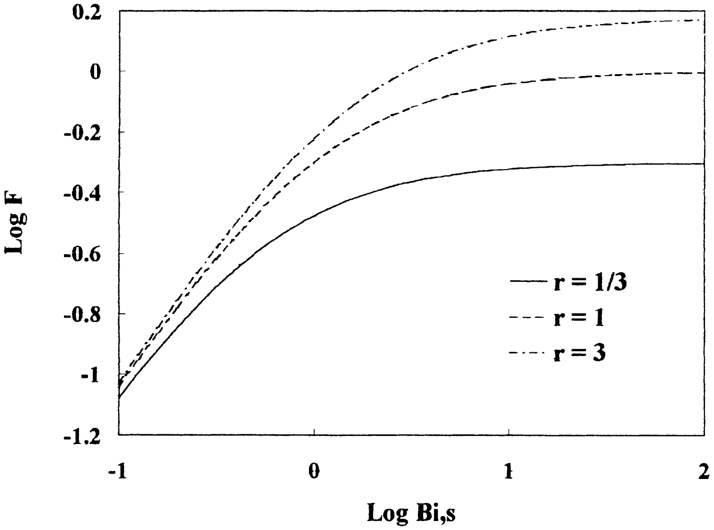

FIGURE 3 Value of F for several values of r at $p = 0.5$ and $s = 1$.

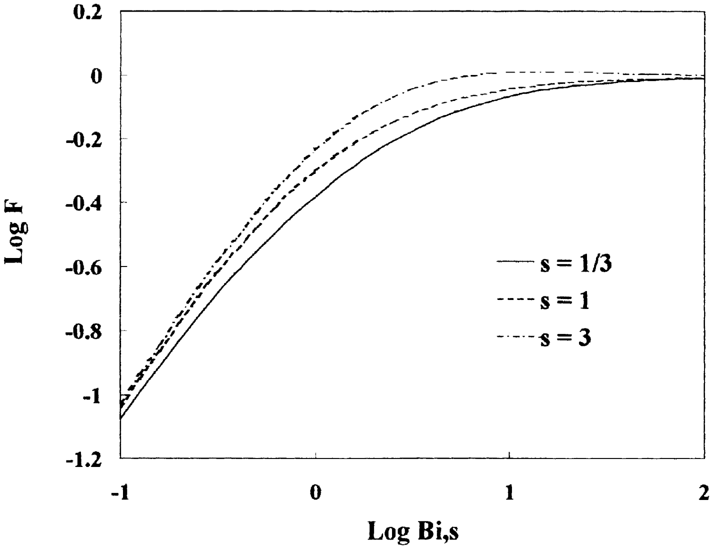

FIGURE 4 Value of F for several values of s at $p = 0.5$ and $r = 1$.

The value of Bi,s increases when D_s decreases or L increases. But these conditions are unfavorable for obtaining a signal, as shown in Eq. (15). To obtain a high electrode signal, it is important to use high flow velocity to ensure a high Bi value, and to use thin polymer films with highly porous structure to facilitate diffusion of the substrate and H_2O_2. In summary, the mass transfer resistance is important, and the assumption of a constant substrate concentration at the surface must be used with caution.

CONCLUSIONS

The effect of finite mass transfer resistance is considered together with the possibility that the electrochemical reaction product has different diffusivity in two membranes. At low Bi numbers the signal depends on the convection mass transfer coefficient but is independent of the membrane thickness. At high Bi numbers a constant value of signal is obtained. When a highly permeable inner membrane is used, a higher signal could be obtained.

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