

A Steady-State One-Dimensional Analysis of an Oxygen Electrode in Stationary and Flowing Liquid

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정체 및 유동액체에서 산소전극의 안정상태 일차원적 해석

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ABSTRACT

The characteristics of a commercial membrane-covered electrode in air-saturated saline solution were investigated in terms of a steady-state one-dimensional model. The electrode system immersed in an aqueous medium consists of three layers: an external concentration boundary layer (medium), a membrane, and an inner electrolyte layer. The membrane can be permeable to the water and impermeable to the ionic species. In stationary medium, the water migrates from the external medium to the inner electrolyte layer until a thermodynamic equilibrium is reached. In a flowing medium, however, there is a reverse direction of water movement due to the hydrodynamic pressure differential until both thicknesses of the electrolyte layer and the membrane are equal.

INTRODUCTION

During the study of the Clark-type polarographic electrode, many researchers assumed that the effect of the trapped electrolyte layer in flowing medium was negligible. A few investigators, however, have considered its effect. Mancy et al. (9), assumed one-dimensional diffusion through the membrane and electrolyte layer covering a planar cathode. They presented an unsteady-state one-dimensional model derived from Fick's second law. The general model solved by the Laplace transform method was divided into three special cases, depending upon the geometry of the electrode. Gutherman and Goldstick (5) described a numerical solution of Laplace's equation in cylindrical coordinates in a semi-infinite, three-layered system. Using this model, they compared the simulated dimensionless PO_2 profiles along the

axis of a membrane-covered electrode in water, with the analytical solution for the bare electrode. It has been pointed out that liquid velocity and oxygen tension can be simultaneously measured by using a catheter electrode system consisting of a large and a small cathode that are operated in parallel (6). The purpose of the present paper is to propose a simple mathematical description of the flow sensitivity of inner electrolyte layer due to chemical potential and/or hydrodynamic pressure differences.

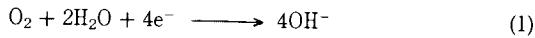
THEORY

Bare Electrode

In order to understand the relationship between current and diffusional resistances of each layer in membrane-covered electrodes, it is necessary first to consider the bare electrode system. It can be described by a model for planar shape electrode immersed in a liquid medium whose

undisturbed oxygen electrode immersed in a liquid medium whose undisturbed oxygen concentration is C_∞ . In that case, a finite value of concentration boundary layer thickness β develops adjacent to the electrode surface.

Note that at the plateau region of oxygen polarogram the following overall electrochemical reaction occurs(4):



Thus, the total flux N can be expressed as :

$$N = N_{O_2} + N_{H_2O} + N_{OH^-} \quad (2)$$

Suppose now the reduction of oxygen at the electrode surface is irreversible (7) and a buffer solution is used to maintain constant pH at the electrode surface, then the diffusional flux of hydroxyl ion is also negligible. The behavior of the bare electrode can be thus visualized by steady-state, isothermal, one-dimensional binary system :

$$N_A = N \left(\frac{C_A}{C} \right) - D \frac{dC_A}{dz} \quad (3)$$

Since water is stagnant with respect to the oxygen transport toward the electrode surface, the total flux is nothing but the oxygen flux. Hence, equation 3 reduces to :

$$N_A = N_A \frac{C_A}{C} - D \frac{dC_A}{dz} \quad (4)$$

If one is concerned with a dilute solution, D can be replaced by D_o which is independent of concentration (13). Integration of equation 4 with appropriate boundary conditions gives as :

$$N_A = \frac{CD_o}{\beta} \left[\ln \left(1 - \frac{C_o}{C} \right) - \ln \left(1 - \frac{C_\infty}{C} \right) \right] \quad (5)$$

Assume the oxygen concentration at electrode surface is zero(1). Also, note that (C_∞/C) is the mole fraction of oxygen in bulk medium, which is far less than unity in a dilute solution. Thus, the rearrangement of equation 5 with the Henry's law and Taylor series expansion yields as :

$$N_A = \frac{C_\infty D_o}{\beta} = \frac{K_1 P_b P O_2}{\beta} \quad (6)$$

Since the electrochemical reaction is limited by the oxygen flux, the current density can be expressed as [2]:

$$i/A = n F N_A \quad (7)$$

Equation 6 is based on the assumption that diffusion occurs only in a direction perpendicular to the electrode. The area, A , through which oxygen diffuses is then equal to the area of the electrode. This assumption is easily justified in the case where the thickness of the boundary layer is so thin compared to the characteristic length of the electrode that the lines of oxygen tension are parallel to the surface of the electrode.

Substitution equation 6 into 7, we can express the current of the bare electrode as :

$$i_B = K_T A P O_2 \frac{P_b}{\beta} \quad (8)$$

In order to specify β in terms of a dimensionless correlation, we can use the following equation [12] to the bare electrode case :

$$Sh = Sh_o + k R_e^a S_c^b \quad (9)$$

Equation 9 can be alternatively written as :

$$\ell / \beta = \ell / \beta_o + k (\ell U / \nu)^a (\nu / D_o)^b \quad (10)$$

Substituting this result into equation 8, we obtain the current of bare electrode due to the natural convection ($U = 0$), i_{B_o} , as :

$$i_{B_o} = K_T A P O_2 \frac{P_b}{\beta_o} \quad (11)$$

If i_{B_o} is known from an experiment, then the corresponding boundary layer thickness β_o can be computed. In the case that the medium achieves a finite velocity, equation 11 can be subtracted from equation 8 in order to reduce the experimental data to a natural convection free basis:

$$i_B - i_{B_o} = K_T A P O_2 P_b \left(\frac{1}{\beta} - \frac{1}{\beta_o} \right) \quad (12)$$

From equations 10 and 12 we can obtain a relationship between the bare electrode current and the medium flow velocity :

$$i_B - i_{B0} = [K_T A P O_2 P_b (k/\ell) (\ell/\nu)^a (\nu/D_0)^b] U^a \quad (13)$$

Membrane-Covered Electrode

Some of the practical problems associated with bare electrodes can be solved by using a gas-permeable membrane over the surface of the electrode, as initiated by Clark (3). The behavior of the membrane-covered electrode can be visualized by dividing it into two cases, depending upon the condition of the external medium.

Stationary Medium

The tip of a bare electrode, previously covered with a KCl electrolyte, is dipped into a solution of rubber modified polystyrene in toluene (11). The membrane-covered electrode can be then activated by placing it in a saline solution. This activation results in significant swelling and therefore thickening of the electrolyte layer. Consider that one observes an infinitely dilute water vapor in KCl electrolyte layer side (phase II), retained inherently by membrane, and a pure water solution, for the sake of argument, in stationary medium side (phase I). The free energy change is then the sum of the changes occurring in each phase.

$$dG = dG^I + dG^{II} \quad (14)$$

Suppose a binary system of KCl and water at constant temperature and pressure:

$$dG = \sum_{i=1}^2 \mu_i^I dn_i^I + \sum_{i=1}^2 \mu_i^{II} dn_i^{II} \quad (15)$$

From the conservation of mass:

$$dn_1^I = -dn_1^{II} \quad (16)$$

Thus, the free energy change for the system is:

$$\begin{aligned} dG &= \sum_{i=1}^2 (\mu_i^{II} - \mu_i^I) dn_i^{II} \\ &= (\mu_{H_2O}^{II} - \mu_{H_2O}^I) dn_{H_2O}^{II} + (\mu_{KCl}^{II} - \mu_{KCl}^I) dn_{KCl}^{II} \end{aligned} \quad (17)$$

Postulate that membrane is permeable to the water and impermeable to the KCl.

Equation 17 is then reduced to :

$$dG = RT (\ln \gamma_{H_2O}^{II} X_{H_2O}^{II}) dn_{H_2O}^{II} \quad (18)$$

Note that dG is negative for the spontaneous process and $\ln (\gamma_{H_2O}^{II} X_{H_2O}^{II})$ is also negative. Therefore, $dn_{H_2O}^{II}$ is always positive, which implies that: During the immersion of the membrane-covered electrode into a stationary medium, the liquid water and/or its vapor diffuses from the medium side to the KCl electrolyte layer side until chemical potentials of water on the two sides are in equilibrium at room temperature and pressure. Thus, we can observe a resultant current when a finite thickness of electrolyte layer is established. The relationship between current and membrane-covered electrode in a stationary medium will be described in a manner that external medium and electrolyte layer have maximal thicknesses of β_0 and γ_0 , respectively.

As discussed previously, the oxygen flux for the medium is:

$$N_A = \frac{CD_0}{\beta_0} \ln \left[\frac{1 - \frac{C_m}{C}}{1 - \frac{C_\infty}{C}} \right] \quad (19)$$

which can be simplified by Taylor series expansion as:

$$N_A = \frac{D_0}{\beta_0} (C_\infty - C_m) \quad (20)$$

As for the membrane, the water is no longer stagnant with respect to the oxygen transport, but a finite amount of water vapor passes continuously through the membrane to reach the electrolyte layer and keep a constant current output. Considering the overall electro-chemical reaction (equation 1), we can see the molar flux of water is two times of the oxygen flux with the same direction. Thus,

$$\begin{aligned} N_A &= \frac{D_m C}{3\omega} \ln \left[\frac{1 - \frac{3C_e}{C}}{1 - \frac{3C_m}{C}} \right] \\ &\cong \frac{D_m}{\omega} (C_m - C_e) \end{aligned} \quad (21)$$

As for the electrolyte layer, the water is still stagnant with respect to the oxygen transport:

$$N_A = \frac{CD_0}{\gamma_0} \ln \left[\frac{1 - \frac{C_0}{C}}{1 - \frac{C_e}{C}} \right] \quad (22)$$

Since the oxygen concentration at the electrode surface, C_0 , is negligible [1], equation 22 reduces to:

$$N_A = -\frac{CD_0}{\gamma_0} \ln \left(1 - \frac{C_e}{C} \right) \cong \frac{C_e D_0}{\gamma_0} \quad (23)$$

At steady state N_A must be the same throughout the planar layers. Thus, equations 20, 21, and 23 can be combined in order to eliminate the unknown interfacial oxygen concentrations:

$$N_A = \frac{K_1 PO_2}{\frac{\omega}{P_m} + \frac{(B_0 + \gamma_0)}{P_b}} \quad (24)$$

Substituting equation 24 into equation 7, we can express the current of the membrane-covered electrode in a stationary medium as:

$$i_{MO} = \frac{K_T APO_2}{\frac{\omega}{P_m} + \frac{(B_0 + \gamma_0)}{P_b}} \quad (25)$$

Finitely Flowing Medium

If there is a difference in absolute pressure across the membrane, a hydrodynamic flow of liquid through the membrane can occur (14). The schematic representation of this behavior for the present case is expressed in Figure 1.

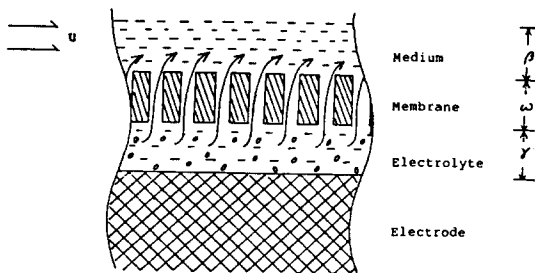


Fig. 1. Schematic Representation of the Electrolyte Movement in Flowing Medium.

Assume that the thickness of electrolyte layer has its maximum value, γ_0 , in a stationary medium and is inversely proportional to the velocity of medium. Then, a reasonable empirical representation for the flow sensitivity of the electrolyte layer thickness is:

$$\gamma = \frac{\ell}{\ell/\gamma_0 + K_2 U^r}, \quad (26)$$

where K_2 is an unknown constant, presumably a function of factors such as properties of both membrane and medium (8). The flow sensitivity of the electrolyte layer can be analyzed by means of a cylindrical model. Postulate that U_r is only a function of radius, r , and other components of the electrolyte velocity are negligible. Then, the equation of continuity gives:

$$rU_r = \psi, \quad (27)$$

and the equation of motion gives:

$$\rho U_r \frac{dU_r}{dr} = -\frac{dP}{dr} \quad (28)$$

Combine equation 28 with 27, and integrate it with proper boundary conditions:

$$P_{R+\omega} - P_{R+\gamma} = \frac{1}{2} \rho U_r \left|_{r=R+\gamma}^{r=R+\omega} \left[1 - \left(\frac{R+\gamma}{R+\omega} \right)^2 \right] \right. \quad (29)$$

Therefore, there will be a pressure differential and/or water movement until γ is equal to ω , which can be possible when the medium flows significantly fast (see equation 26). At a low flow rate of external medium, γ will always be greater than ω for the thin membrane-covered electrode, as is the present case ($\omega = 11.5 \mu m$). Since the second term in the right-hand side of equation 29 is then negative water diffuses from electrolyte side to external medium side.

The molar flux of water passing through the membrane is two times of the oxygen flux with the reverse direction. Thus, for membrane,

$$N_A = -N_A \left(\frac{C_A}{C} \right) - D_m \frac{dC_A}{dZ} \quad (30)$$

$$N_A = -\frac{CD_m}{\omega} \ln \left[\frac{1 + \frac{C_e}{C}}{1 + \frac{C_m}{C}} \right] \cong \frac{D_m}{\omega} (C_m - C_e) \quad (31)$$

which is equal to equation 21 of stationary medium, Note that the molar fluxes of oxygen for the medium and the electrolyte layer are not different from the case of a stationary medium because the water is still stagnant with respect to the oxygen transport. Therefore, we can express the current of the membrane-covered electrode in a finitely flowing medium as :

$$i_M = \frac{K_T A P O_2}{\frac{\omega}{P_m} + \frac{(\beta + \gamma)}{P_b}} \quad (32)$$

MATERIALS AND METHOD

The catheter tip electrode used for the present study is produced by G. D. Serle & Co. in England. The electrode is commercially designed to operate as a flow-insensitive PO_2 monitor with the axial silver tip acting as the cathode and the outer silver cap as the anode [11]. In this study, the outer silver cap was operated as cathode and referenced to an external silver-silver chloride anode. To produce an upward-flowing stream impinging on the catheter tip, a flow cell was fabricated from a block of solid Plexiglas. The flow cell with 250 ml. peripheral volume had an inlet diameter of a quarter inch and was covered with a Plexiglas covering plate. The silver-silver chloride reference anode was attached to the inside of this plate. A supporting tube (12 gauge, stainless steel) was placed in the covering plate and allowed the flexible catheter-tip electrode to be kept in the vertical position. With this arrangement, the cathode is situated parallel to the velocity. The inlet tube to the flow cell was 16 inches long; this was long enough to establish a fully developed flow. The flow velocity of medium was controlled by a needle valve and a rotameter (Emerson 1355). The flowing medium used for the present work was a physiological saline solution consisting of 19.9 mM HEPES buffer mixed with 120 mM NaCl and 4.62 mM KCl. The pH of the solution was adjusted to be 7.40 ± 0.04 at $25^\circ C$ by titration with about 10 ml of 1 N NaOH. The liquid was maintained at room temperature ($25.8 \pm 2.4^\circ C$). In order to prevent the temperature rise due to the action of the gear pump (Micropump, 12A-00-303/316), continuous air cooling was provided.

RESULTS AND DISCUSSION

Figure 2 presents the currents of bare and membrane-covered electrodes, following the cessation of velocity at time zero in an air-equilibrated solution. These behaviors cannot be explained on the basis of pure molecular diffusion, but with instead be interpreted by the empirical correlation for natural convection (15). Initially, i_{B0} decays due to the depletion of oxygen on the electrode surface. However, within a period of about 1000 sec, there is a sharp rise of the current, which reflects the onset of natural convection. Eventually, natural convection reaches a steady level as indicated by the constant output current. The general behavior of membrane-covered electrode in stationary medium was different from that of the bare electrode. In particular, although i_{M0} reaches a plateau after about 600 sec, this was followed by a significant decline which leads to a final lower steady level; such an intermediate decline in the output current was never observed for the bare electrode experiment (see Figure 2). This difference can be explained by the behavior of the electrolyte layer in membrane-covered electrode: the medium was made stationary by turning off the pumps; thereafter, the thickness of the diffusion resistance of the electrolyte layer can increase because of the influx of water from the external

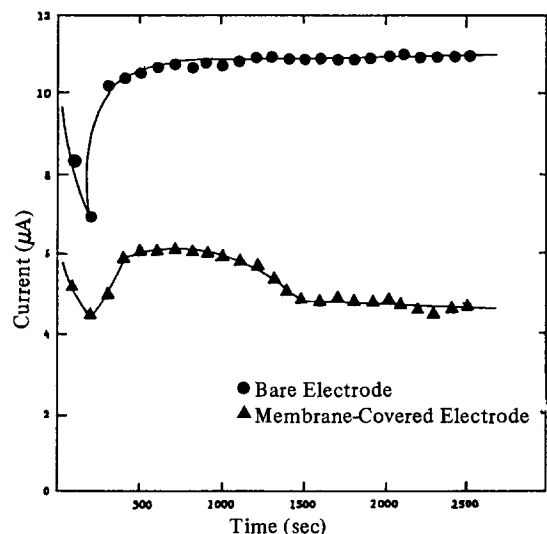


Fig. 2. Stationary Current of Bare and Membrane-Covered Electrodes.

medium. This process occurs until a thermodynamic equilibrium is established between the external medium and the inner electrolyte layer, as described previously.

From equations 8, 12, and 32, it can be seen that the current of the bare electrode is greater than that of the membrane-covered electrode. Also, i_M can be less dependent upon the boundary layer resistance and thus less flow sensitive than i_B at the higher flow velocities. This is well illustrated in Figure 3.

Figure 4 summarizes the general behavior of the resistance layers of a membrane-covered electrode in flowing medium saturated with room air. Its ordinate indicates the normalized thickness with respect to the membrane. Note that the thickness of the electrolyte layer approaches asymptote equivalent to the thickness of membrane, as theoretically predicted (see equation 29).

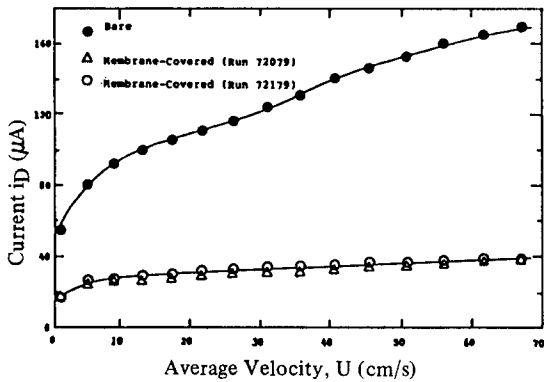


Fig. 3. Flow Response of Bare and Membrane-Covered Electrodes.

요 약

안정상태 일차원적 모델을 이용하여 막으로 덮힌 상업적인 산소 전극의 특성을 공기포화된 식염수에서 연구하였다. 전극은 세개의 층으로 이루어져 있는데, 이는 외부 농도 경계층(용액), 반투성 막, 내부 전해질용액 층으로 구분된다.

정체 용액에서, 물은 외부 용액층으로부터 내부 전해질 용액 쪽으로 열역학적 평형을 이룰 때까지 이동한다.

한편 유동 용액에서, 물은 수력학적 압력차때문에 전해질 층의 두께가 막의 두께와 같아질 때까지 반대 방향

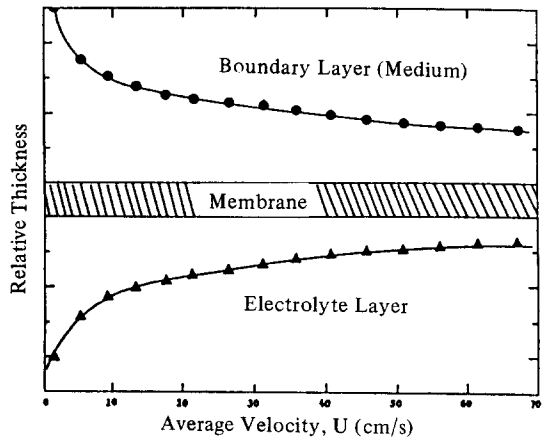


Fig. 4. Flow Response of Layers in Membrane-Covered Electrode.

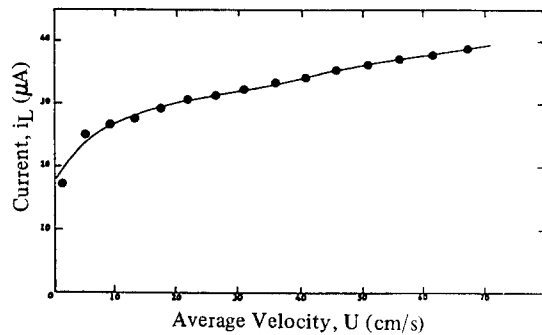


Fig. 5. Comparison of Experimental Data with Predicted Curve for Membrane-Covered Electrode.

으로 이동한다.

NOMENCLATURE

- A = Surface area of cathode (cm²)
- a = Power dependence of Reynolds number
- b = Power dependence of Schmidt number
- C = Concentration(mole/cm³)
- C_A = Concentration of oxygen in medium(mole/cm³)
- C_∞ = Concentration of oxygen in bulk medium (mole/cm³)
- C_e = Concentration of oxygen at the interface between membrane and electrolyte layer (mole/cm³)
- C_m = Concentration of oxygen at the interface be-

tween membrane and electrolyte layer (mole/cm³)

C_o = Concentration of oxygen at electrode surface (mole/cm³)

D = Diffusion coefficient of oxygen in medium (cm²/s)

D_m = Diffusion coefficient of oxygen in medium (cm²/s)

D_0 = Diffusion coefficient of oxygen in infinitely dilute medium (cm²/s)

F = Faraday constant (96500 Coulombs)

f = Power dependence of electrolyte layer thickness

G = Free energy (Btu)

i = Current (amp)

i_B = Diffusion current of bare electrode (amp)

i_{B0} = Value of i_B at $Re = 0$ (amp)

i_M = Diffusion current of membrane-covered electrode (amp)

i_{M0} = Value of i_M at $Re = 0$ (amp)

k' = Empirical constant

k_1 = Dimensional constant ($=1/22400$)

K_T = Overall dimensional constant ($=nFK_1$)

ℓ = Characteristic length of cathode (cm)

N = Net flux relative to a fixed surface (mole/cm²-s)

N_A = Molar flux of oxygen relative to a fixed surface (mole/cm²-s)

n = Number of electrons per mole of oxygen reduced

n_i = Number of moles of component i

P = Pressure (mm Hg)

P_b = Permeability of medium/electrolyte layer for oxygen (cm³02(STP)-cm²/cm²-s-atm)

P_m = Permeability of membrane for oxygen (cm³02(STP)-cm²/cm²-s-atm)

PO_2 = Oxygen tension (partial pressure of oxygen (mm Hg))

R = Radius of bare electrode (cm)

r = Local radius of bare electrode (cm)

Re = Reynolds number, $\ell U/\nu$

Sc = Schmidt number, ν/D

Sh = Sherwood number, ℓ/β

Sh_0 = Value of Sh at $Re = 0$ (ℓ/β_0)

T = Absolute temperature (°K)

U = Average flow velocity of medium (cm/s)

V = Volume (ft³)

X_i = Mole fraction of component i

Greek Letters

β = Thickness of concentration boundary layer of medium (cm)

β_0 = Value of β at $Re = 0$ (cm)

γ = Thickness of electrolyte layer (cm)

γ_i = Activity coefficient of component i

γ_0 = Value of γ at $Re = 0$ (cm)

μ = Viscosity of medium (g/cm-s²)

μ_i = Chemical potential of component i

ρ = Average density of medium (g/cm³)

ν = Kinematic viscosity of medium (cm²/s)

ψ = Constant

ω = Thickness of membrane (cm)

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