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Mass Transfer in AC Electrolysis

Part I: Theoretical Analysis Using a Film Model for Sinusoidal Current on a Rotating Hemispherical Electrode

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A film model is presented for the analysis of mass transfer to a rotating hemispherical electrode when sinusoidal alternating current (AC) together with direct current (DC) are flowing across the electrode surface. The concentration of a diffusing ion is separated into two independent components: a constant DC component and a periodic AC component. The DC concentration is obtained by solving the steady-state convective mass transport equation with the perturbation method. The periodic AC concentration distribution is analyzed by the solution to the one-dimensional transient diffusion equation based on the concept of Nernst diffusion layer. The limiting AC current densities corresponding to a zero surface concentration of a reactive ion are investigated for various DC current densities and AC frequencies. The resulting periodic concentration overpotential wave and its phase shift with respect to the applied AC are examined. A comparison with a previous rigorous model indicates that the film model is a good approximation to the mass transfer calculation in the regimes of a dimensionless AC frequency $K = (\omega/\Omega)Sc^{1/3}$ greater than 2 and less than 0.01.

SCOPE

Electrolysis with a direct current superimposed with a periodically alternating current component has been long used in pulse plating, in electrodissolution to increase anode corrosion, in AC anodizing to improve color and dye penetration, and in the AC corrosion processes (Venkatesh, 1979). AC can enhance the kinetics of electrochemical reactions, change the morphology of electrodeposits, and cause the pitting corrosion of passive metals. AC also improves the mass transfer rate by producing a pulsating concentration boundary layer of reactive ions near the electrode surface, and a very large AC of an order of 10–100 times greater than the DC-limitng current density can be used for electrolysis without affecting the coulombic efficiency of the electrode reaction.

This work examines the mass transfer to a rotating hemi-

spherical electrode (RHE) when a sinusoidal AC and a DC current are flowing across the electrode/electrolyte interface. The system is galvanostatically controlled, and a periodical flux of reactive ion of a constant amplitude would prevail at the electrode surface. The present analysis assumes that the concentration of reactive ion consists of a steady-state DC concentration component corresonding to the DC current density, and a periodic AC concentration component corresponding to the superimposed AC current density. The convective diffusion equation for the DC concentration component in laminar flow is solved with a perturbation technique. The thickness of the steady-state Nernst diffusion layer is then determined from the profile of the DC concentration component.

For the periodic AC concentration component, a stationary film model is used for the solution of the nonsteady-state diffusion equation. The film model assumes that the periodic concentration fluctuations occur essentially within the steady-state Nernst diffusion layer, where the magnitude of convective mass flux terms is negligibly small compared to the diffusional flux. The fluid flow of the electrolyte simply plays the role of determining the diffusion layer thickness and thus affects the overall rate of mass transfer to the electrode surface. This assumption greatly simplifies the mathematical complication of the nonsteady-state convective diffusion equation. The assumption has been shown to be reasonably good for AC electrolysis at large AC frequencies and high Schmidt numbers (Silver, 1960; Hale, 1963; Chin, 1980, 1981). In this way, the limiting AC current density corresponding to an instantaneous zero surface concentration of reactive ion has been numerically evaluated for various DC levels and AC frequencies. The waveform of the periodic surface AC concentration component and the resulting periodic concentration overpotentials are analyzed and compared to a rigorous mathematical model (Chin, 1980) to determine the applicable frequency ranges of the film model.

CONCLUSIONS AND SIGNIFICANCE

A film model is presented for the concentration distribution of a diffusing ion near a rotating hemispherical electrode when both sinusoidal AC and DC are flowing to the electrode surface. The limiting AC current density corresponding to a zero concentration at the electrode surface is found to increase with AC frequency and to decrease with DC current. A comparison with the results of a rigorous model indicates that the film model is a good approximation to the mass transfer calculation in the regimes of a dimensionless frequency $K = (\omega/\Omega)Sc^{1/3}$ greater than 2 and less than 0.01. Within the intermediate frequency regime of $0.01 < K < 2$, the maximum deviation between the two models is approximately 10% at $K = 0.4$. The periodic AC surface concentration diminishes with increasing AC frequencies. The phase shift between the concentration wave and the applied sinusoidal AC current increases with AC frequency and asymptotically approaches to −45° at large AC frequencies. The effect of ohmic potential drop on the measurement of the concentration overpotential in AC mass transfer experiments has been examined. The results indicate that the experimental error due to the ohmic potential drop will be rather significant at high AC frequencies, and provisions should be made to locate the reference probe as close to the working electrode as possible in the experimental measurements.

INTRODUCTION

Alternating current electrolysis has been used extensively in electroplating, electrodissolution and AC anodizing (Venkatesh, 1979). AC shifts the corrosion potential and accelerates the corrosion rate of metals (Chin, 1979a, 1979b, 1981). Extremely high AC current densities can be applied for electrolysis because of an improvement in mass transfer rate by AC(Ibl, 1978; Chin, 1982b, 1983). Also, AC improves the properties of electrodeposits by retarding dendrite formation, increasing ductility, and reducing the need for levelling agents (Ibl, 1978, 1980; Pavlovic, 1978; Chin, 1982a; McBreen, 1983).

This work is concerned with the mass transfer process with a sinusoidal AC modulation onto a rotating hemispherical electrode (RHE). The RHE has been used as a supplementary tool to the rotating disk electrode (RDE) because of its advantage of having a more uniform current distribution below the limiting current density, and its versatility for the study of high-rate corrosion and dissolution reactions (Chin, 1971a, 1971b, 1973, 1979b). Chin has made an analysis of the sinusoidal AC modulation onto the RHE in laminar flow (Chin, 1980). The present work attempts to examine the concentration changes of a reacting species when a sinusoidal AC together with a DC component are flowing across the electrode/electrolyte interface. The concentration profile is split into a steady-state DC component and a periodic AC component. The DC concentration component is obtained by solving the convective diffusion equation with constant flux. A film model is used to determine the AC concentration component. Numerical results are presented for the limiting AC current densities corresponding to a zero concentration on the electrode surface. The resulting concentration overpotential fluctuations, and the phase shift between the AC current and the AC potential are examined and compared to the predictions of a rigorous model (Chin, 1980).

MATHEMATICAL MODELING

Convective Mass Transfer Equations

Consider a redox reaction of the type

$$Ox + ne^- = Red \tag{1}$$

taking place at the surface of a rotating hemispherical electrode. The objective of this analysis is to determine the concentration distribution of the *Ox* species when the electrode is galvanostatically polarized with a DC superimposed with a sinusoidal AC. To simplify the analysis, we small make the following assumptions:

(1) The bulk concentration of *Red* (reduced) species is much larger than that of *Ox* species, such that the concentration overpotential is only related to convective diffusion of *Ox* species.

(2) There is an excess of a supporting electrolyte so that the electric migrational effect is negligible.

(3) The Schmidt number of the electrolytic system is so large that the Nernst diffusion layer lies within a thin region inside the momentum boundary layer.

(4) The concentration fluctuations occur essentially within the Nernst diffusion layer such that a stationary film model can be used for the analysis of the AC concentration component (Chin, 1981, 1983; Venkatesh, 1982; Sethi, 1984).

(5) The current distribution on the RHE is uniform.

(6) The flow is laminar and the system has constant physical properties.

(7) The double layer effect is neglected in the system.

Assuming axial symmetry, the governing equation for the analysis of mass transfer to a RHE in laminar flow can be summarized in spherical polar coordinates as:

$$\frac{\partial C}{\partial t} + V_r \frac{\partial C}{\partial r} + \frac{V_\theta}{a}\frac{\partial C}{\partial \theta} = D\frac{\partial^2 C}{\partial r^2} \tag{2}$$

with the boundary conditions:

at

$$\begin{array}{lll} t = 0 \text{ (beginning of current pulse)} & & C = C_\infty \\ \theta = 0 \text{ (axis of rotation)} & \dfrac{\partial C}{\partial \theta} = 0 & \\ r = a \text{ (electrode surface)} & -D\dfrac{\partial C}{\partial r} = \dfrac{i(t)}{nF} & \\ r \rightarrow \infty \text{ (bulk of the electrolyte)} & & C = C_\infty \end{array} \qquad (3)$$

When an AC component, $\tilde{i}$, is superimposed onto a DC component, $\bar{i}$, the controlled input current density is equal to

$$i(t) = \bar{i} + \tilde{i}(t) \qquad (4)$$

For a sinusoidal AC, $\tilde{i}$ is related to the amplitude of the AC current density i_p by

$$\tilde{i} = i_p e^{j\omega t} \qquad (5)$$

where $j = \sqrt{-1}$ and ω is the AC frequency in rad/s. Accordingly, the concentration C can be assumed to be:

$$C(r,\theta,t) = \bar{C}(r,\theta) + \tilde{C}(r,\theta,t) \qquad (6)$$

where $\bar{C}$ is the steady-state DC concentration component, and $\tilde{C}$ is the periodic AC concentration component. Substituting Eqs. 4–6 into Eqs. 2–3, one obtains two sets of differential equations, one for the DC concentration component $\bar{C}$, and the other for AC concentration $\tilde{C}$.

The differential equations for the DC concentration, $\bar{C}$, is:

$$V_r\frac{\partial \bar{C}}{\partial r} + \frac{V_\theta}{a}\frac{\partial \bar{C}}{\partial \theta} = D\frac{\partial^2 \bar{C}}{\partial r^2} \qquad (7)$$

with the boundary conditions:

at

$$\left.\begin{array}{ll} \theta = 0 & \dfrac{\partial \bar{C}}{\partial \theta} = 0 \\ r = a & -D\dfrac{\partial \bar{C}}{\partial r} = \dfrac{\bar{i}}{nF} \\ r \rightarrow \infty & \bar{C} = C_\infty \end{array}\right\} \qquad (8)$$

The equations for the AC concentration $\tilde{C}$ can be expressed as:

$$\frac{\partial \tilde{C}}{\partial t} + V_r\frac{\partial \tilde{C}}{\partial r} + \frac{V_\theta \partial \tilde{C}}{a\ \partial \theta} = D\frac{\partial^2 \tilde{C}}{\partial r^2} \qquad (9)$$

with the boundary conditions:

at

$$\left.\begin{array}{ll} \theta = 0 & \dfrac{\partial \tilde{C}}{\partial \theta} = 0 \\ t = 0 & \tilde{C} = 0 \\ r = a & -D\dfrac{\partial \tilde{C}}{\partial r} = \dfrac{i_p e^{j\omega t}}{nF} \\ r \rightarrow \infty & \tilde{C} = 0 \end{array}\right\} \qquad (10)$$

Using assumption 4, one can simplify Eqs. 9–10 with a film model (Chin, 1981, 1982b, 1983; Nernst, 1904; Silver, 1960; Venkatesh, 1982; Sethi, 1984) by droping the convective flux terms $V_r \partial C/\partial r$ and $V_\theta/a \partial C/\partial \theta$, and Eqs. 9–10 may be reduced to

$$\frac{\partial \tilde{C}}{\partial t} = D\frac{\partial^2 \tilde{C}}{\partial r^2} \qquad (11)$$

at

$$\left.\begin{array}{ll} t = 0 & \tilde{C} = 0 \\ \theta = 0 & \dfrac{\partial \tilde{C}}{\partial \theta} = 0 \\ \quad) & \\ r = a + \delta(\theta) & \tilde{C} = 0 \\ r = a & -D\dfrac{\partial \tilde{C}}{\partial r} = \dfrac{i_p e^{j\omega t}}{nF} \end{array}\right\} \qquad (12)$$

This assumption implies that the rate of concentration changes occurs essentially within the Nernst diffusion layer where the magnitude of the convective fluxes may be assumed to be negligibly small. This has been proven by Siver (1960), Hale (1963) and Chin et al. (Chin, 1980, 1981; Venkatesh, 1982, Sethi, 1984) to be a reasonable assumption for AC modulation at reasonably high frequencies.

Normalization

Equations 7–8 and 11–12 can be normalized by using the following dimensionless parameters and variables:

Reynolds Number	$Re = \dfrac{a\Omega^2}{\nu}$	(13a)
Schmidt Number	$Sc = \dfrac{\nu}{D}$	(13b)
Dimensionless distance from the electrode	$Z = (r - a)\left(\dfrac{\Omega}{\nu}\right)^{1/2} Sc^{1/3}$	(13c)
Dimensionless DC concentration component	$\bar{\Phi} = \dfrac{(\bar{C} - C_\infty)nFD}{\bar{i}}\left(\dfrac{\Omega}{\nu}\right)^{1/2} Sc^{1/3}$	(13d)
Dimensionless AC concentration component	$\tilde{\Phi} = \dfrac{\tilde{C}nFD}{i_p}\left(\dfrac{\Omega}{\nu}\right)^{1/2} Sc^{1/3}$	(13e)
Dimensionless AC frequency	$K = \dfrac{\omega}{\Omega} Sc^{1/3}$	(13f)
Dimensionless DC current density	$\bar{i}^* = \dfrac{\bar{i}}{nFDC_\infty}\left(\dfrac{\Omega}{\nu}\right)^{-1/2} Sc^{-1/3}$	(13g)
Dimensionless amplitude of AC current density	$\hat{i}_p^* = \dfrac{i_p}{nFDC_\infty}\left(\dfrac{\Omega}{\nu}\right)^{-1/2} Sc^{-1/3}$	(13h)
Dimensionless radial velocity	$H = \dfrac{V_r}{(\nu\Omega)^{1/2}}$	(13i)
Dimensionless meridional velocity	$F = \dfrac{V_\theta}{a\Omega}$	(13j)
Dimensionless time	$\tau = \omega t$	(13k)
Dimensionless boundary layer thickness	$\delta^* = \delta\left(\dfrac{\Omega}{\nu}\right)^{1/2} Sc^{1/3}$	(13l)

The normalized equations can be rearranged as

$$H\,Sc^{1/3}\frac{\partial \bar{\Phi}}{\partial Z} + F\frac{\partial \bar{\Phi}}{\partial \theta} = Sc^{-1/3}\frac{\partial^2 \bar{\Phi}}{\partial Z^2} \qquad (14)$$

with the boundary conditions as:

$$\left.\begin{array}{ll} \theta = 0 & \dfrac{\partial \bar{\Phi}}{\partial \theta} = 0 \\ Z = 0 & \dfrac{\partial \Omega}{\partial Z} = -1 \\ Z \rightarrow \infty & \bar{\Phi} = 0 \end{array}\right\} \qquad (14a)$$

and

$$\frac{\partial \tilde{\Phi}}{\partial \tau} = \frac{1}{K}\frac{\partial^2 \tilde{\Phi}}{\partial Z^2} \qquad (15)$$

with the boundary conditions:

$$\left.\begin{array}{ll} \tau = 0 & \tilde{\Phi} = 0 \\ Z = \delta^* & \tilde{\Phi} = 0 \\ Z = 0 & \dfrac{\partial \tilde{\Phi}}{\partial Z} = -e^{j\tau} \end{array}\right\} \qquad (15a)$$

Solution for the DC Concentration Component, $\overline{\Phi}$

The present electrolytic system is galvanostatically controlled, and there is a constant mass flux of the *Ox* species on the electrode surface. Previous works on the analysis of convective mass transfer to the RHE (Chin, 1971, 1972) have all been concerned with the condition of a constant surface concentration. No work has been reported in the literature for a constant mass flux to the RHE.

Following the perturbation procedures illustrated in Chin's work (1972), the DC concentration component, $\overline{\Phi}$, with a constant mass flux can be expressed in a power series of θ and an asymptotic series expansion of $Sc^{-1/3}$ as:

$$\overline{\Phi} = \Phi_{11}(Z) + Sc^{-1/3}\Phi_{12}(Z) + Sc^{-2/3}\Phi_{13}(Z) + \cdots + \theta^2(\Phi_{31}(Z) + Sc^{-1/3}\Phi_{32}(Z) + Sc^{-2/3}\Phi_{33}(Z) + \cdots) + \cdots \tag{16}$$

The velocity profile required for the solution of $\overline{\Phi}$ in Eq. 14 can be found from the works by Cochran (1934), Rogers (1960), and Banks (1965) as:

$$H = H_1(Z) + \theta^2 H_3(Z) + \cdots \tag{17a}$$

$$F = \theta F_1(z) + \theta^3 F_3(Z) + \cdots \tag{17b}$$

with

$$F_1 = a_1 Sc^{-1/3}Z - (1/2)Sc^{-2/3}Z^2 + (-b/3)Sc^{-1}Z^3 + (-b^2/12)Sc^{-4/3}Z^4 + \cdots \tag{17c}$$

$$H_1 = -a_1 Sc^{-2/3}Z^2 + (1/3)Sc^{-1}Z^3 + (b/6)Sc^{-4/3}Z^4 + \cdots \tag{17d}$$

$$F_3 = f Sc^{-1/3}Z + (1/3)Sc^{-2/3}Z^2 + (b - 2g)Sc^{-1}Z^3/6 + \cdots \tag{17e}$$

$$H_3 = (a_1/6 - 2f)Sc^{-2/3}Z^2 - (1/2)Sc^{-1}Z^3 + \cdots \tag{17f}$$

where

$$a_1 = 0.51023$$
$$b = -0.61592$$
$$f = -0.22129$$
$$g = 0.24765$$

Substituting Eqs. 17a–17f to Eqs. 14–14a and rearranging the differential equations for the same order of θ and $Sc^{-1/3}$ one has

$$\frac{d^2\Phi_{11}}{dZ^2} + 0.51023\,Z^2\frac{d\Phi_{11}}{dZ} = 0 \tag{18a}$$

$$\frac{d^2\Phi_{12}}{dZ^2} + 0.51023\,Z^2\frac{d\Phi_{12}}{dZ} = 1/3\,Z^3\frac{d\Phi_{11}}{dZ} \tag{18b}$$

and

$$\frac{d^2\Phi_{13}}{dZ^2} + 0.51023\,Z^2\frac{d\Phi_{13}}{dZ} = 1/3\,Z^3\frac{d\Phi_{12}}{dZ} - 0.10265\,Z^4\frac{d\Phi_{11}}{dZ} \tag{18c}$$

$$\frac{d^2\Phi_{31}}{dZ^2} + 0.51023\,Z^2\frac{d\Phi_{31}}{dZ} - 1.02046\,Z\Phi_{31} = 0.52762\,Z^2\frac{d\Phi_{11}}{dZ} \tag{18d}$$

$$\frac{d^2\Phi_{32}}{dZ^2} + 0.51023\,Z^2\frac{d\Phi_{32}}{dZ} - 1.02046\,Z\Phi_{32} = 0.52762\,Z^2\frac{d\Phi_{12}}{dZ} - 0.5\,Z^3\frac{d\Phi_{11}}{dZ} + 1/3\,Z^3\frac{d\Phi_{31}}{dZ} - Z^2\Phi_{31} \tag{18e}$$

$$\frac{d^2\Phi_{33}}{dZ^2} + 0.51023\,Z^2\frac{d\Phi_{33}}{dZ} - 1.02046\,Z\Phi_{33} = 0.52762\,Z^2\frac{d\Phi_{13}}{dZ} - 0.5\,Z^3\frac{d\Phi_{12}}{dZ} + 0.20231\,Z^4\frac{d\Phi_{11}}{dZ} + 1/3\,Z^3\frac{d\Phi_{32}}{dZ} - 0.10265\,Z^4\frac{d\Phi_{31}}{dZ} - Z^2\Phi_{32} + 0.41062\,Z^3\Phi_{31} \tag{18f}$$

with boundary conditions:
at

$$\left.\begin{aligned} Z = 0 \qquad & \frac{d\Phi_{11}}{dZ} = -1 \\ & \frac{d\Phi_{12}}{dZ} = \frac{d\Phi_{13}}{dZ} = \frac{d\Phi_{31}}{dZ} = \frac{d\Phi_{32}}{dZ} = \frac{d\Phi_{33}}{dZ} = 0 \\ Z \to \infty \qquad & \Phi_{1i} = \Phi_{3i} = 0 \text{ where } i = 1,2,3 \end{aligned}\right\} \tag{18g}$$

The solutions to Eqs. 18a–18c are summarized as:

$$\Phi_{11} = 1.6117 - \int_0^Z \exp(-0.51023\,Z^3/3)dZ \tag{19a}$$

$$\Phi_{12} = 0.48031 + \int_0^Z (-1/12\,Z^4)\exp(-0.51023\,Z^3/3)\,dZ \tag{19b}$$

$$\Phi_{13} = 0.23393 + \int_0^Z (0.020531\,Z^5 - 1/288\,Z^8)\exp(-0.51023\,Z^3/3)\,dZ \tag{19c}$$

These equations are the same as those on a rotating disk electrode, and the properties of Φ_{11}, Φ_{12}, Φ_{13} have been discussed by Chin (1972). On the other hand, the quantities Φ_{31}, Φ_{32}, Φ_{33}, for the constant flux have not been previously reported and Eqs. 18d–18e have been integrated numerically in the present work. The results are shown in Figure 1. It has been found that when Z is greater than 4, the values of Φ_{31}, Φ_{32} and Φ_{33} become negligibly small.

The surface concentration for DC component can be obtained by setting Z = 0

$$\overline{\Phi_s} = 1.6117 + 0.48031\,Sc^{-1/3} + 0.023393\,Sc^{-2/3} + (0.2435 + 0.0455\,Sc^{-1/3} - 0.00454\,Sc^{-2/3})\theta^2 \tag{20}$$

The Nernst boundary layer thickness, $\delta(\theta)$, may be expressed as:

$$\delta = \left.\frac{C_\infty - C_s}{\dfrac{\partial C}{\partial r}}\right|_{r=a} = \overline{\Phi_s}\left(\frac{\Omega}{\nu}\right)^{-1/2} Sc^{-1/3} \tag{21}$$

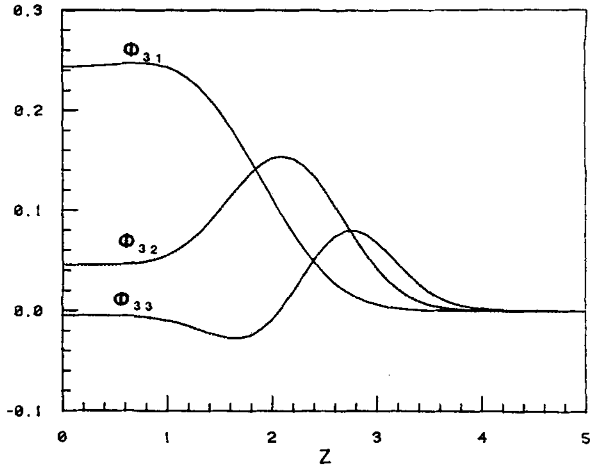

Figure 1. Dimensionless DC concentration components, Φ_{31}, Φ_{32} and Φ_{33} on the rotating hemispherical electrode at constant flux.

For large Schmidt numbers, Eq. 20 can be simplified to

$$\overline{\Phi_s} = 1.6117 + 0.2435\,\theta^2 \tag{22}$$

AC Concentration Component, $\tilde{\Phi}$

Using the method of separation of variables, the steady-state periodical AC concentration, $\tilde{\Phi}$, may be expressed as

$$\tilde{\Phi} = \Phi_p{}^{j(\theta+\Delta)} \tag{23}$$

where

$$\Phi_p = \sqrt{(\alpha_1^2 + \alpha_2^2)(\alpha_3^2 + \alpha_4^2)/K} \tag{23a}$$

$$\Delta = \tan^{-1}\left(\frac{\alpha_1\alpha_4 + \alpha_2\alpha_3}{\alpha_1\alpha_3 - \alpha_2\alpha_4}\right) - \pi/4 \tag{23b}$$

$$\alpha_1 = \frac{\cos h(\beta_1)\cos(\beta_1)}{\cos^2(\beta_1) + \sin h^2(\beta_1)} \tag{23c}$$

$$\alpha_2 = \frac{-\sin h(\beta_1)\sin(\beta_1)}{\cos^2(\beta_1) + \sin h^2(\beta_1)} \tag{23d}$$

$$\alpha_3 = \sin h(\beta_2)\cos(\beta_2) \tag{23e}$$

$$\alpha_4 = \cos h(\beta_2)\sin(\beta_2) \tag{23f}$$

and

$$\beta_1 = \overline{\Phi_s}\,(K/2)^{1/2} = \delta\left(\frac{\omega}{2D}\right)^{1/2} \tag{23g}$$

$$\beta_2 = (\overline{\Phi}_s - Z)(K/2)^{1/2} = (\delta - r + a)\left(\frac{\omega}{2D}\right)^{1/2} \tag{23h}$$

The periodic AC concentration component at the surface may be obtained from Eqs. 23–23h by letting Z = 0

$$\tilde{\Phi}_s = (1/2K^{1/2})\left(\frac{\sin h^2(2\beta_1) + \sin^2(2\beta_1)}{\cos^2(\beta_1) + \sin h^2(\beta_1)}\right)e^{j(\tau+\Delta_s)} \tag{24a}$$

where

$$\Delta_s = \tan^{-1}\left(\frac{\sin(2\beta_1)}{\sin h(2\beta_1)}\right) - \pi/4 \tag{24b}$$

Thus, the AC concentration component is a function of distance from the surface Z, AC frequency, K, and meridional angle θ. As K approaches infinity, $\tilde{\Phi}_s$ becomes zero, and the phase shift between the applied AC, $\tilde{i}$, and the periodic surface concentration, $\tilde{\Phi}_s$, asymptotically approaches to $-\pi/4$. The root mean square of the periodic surface concentration is

$$\bar{\tilde{\Phi}}_{s,rms} = \sqrt{\frac{\int_0^{2\pi} \tilde{\Phi}_s^2\,d\tau}{2\pi}} \tag{25}$$

For a sinusoidal wave, the root mean square value is equal to 0.707 of the amplitude of the surface AC concentration component.

Concentration Overpotential and Limiting AC Current Density

The resulting concentration overpotential can be expressed by the Nernst equation as:

$$\eta^*_{\text{conc}} = \frac{nF}{RT}\,\eta_{\text{conc}} = ln\,\frac{C_s + \tilde{C}_s(t)}{C_\infty} = ln\,(1 + \bar{i}^*\overline{\Phi}_s + \tilde{i}_p^*\tilde{\Phi}_s(\tau)) \tag{26}$$

The DC component of the concentration overpotential can be obtained by taking the time-average of Eq. 26 over one period of time

$$\overline{\eta^*_{\text{conc}}} = \frac{1}{2\pi}\int_0^{2\pi} \eta^*_{\text{conc}}\,dt \tag{27}$$

and the root mean square of η^*_{conc} is evaluated by

$$\tilde{\eta}^*_{\text{conc},rms} = \sqrt{\frac{\int_0^{2\pi} (\eta^*_{\text{conc}} - \overline{\eta^*_{\text{conc}}})^2}{2\pi}\,d\tau} \tag{28}$$

Equation 26 indicates that the applied AC has a maximum limit upon which the instantaneous surface concentration becomes zero:

$$\frac{\overline{C}_s + \tilde{C}_s(t_0)}{C_\infty} = 1 + \bar{i}^*\overline{\Phi}_s + \tilde{i}_p^*\tilde{\Phi}_s(\tau_0) = 0 \tag{29}$$

and η^*_{conc} becomes infinitely large. The quantities t_0 and τ_0 in Eq. 29 refer to the time at which the surface concentration becomes zero. This maximum amplitude of AC is called limiting AC current density, i_{plim}. For the rotating hemispherical electrode, it has been found that the zero surface concentration occurs first at a location corresponding to θ = 90° (i.e. at the equator). Thus one may evaluate i_{plim} for RHE from the following equation:

$$\tilde{i}^*_{\text{plim}} = \frac{i_{\text{plim}}}{nFDC_\infty}\left(\frac{\Omega}{\nu}\right)^{-1/2} Sc^{-1/3} = \frac{-1 - \bar{i}^*\overline{\Phi}_s}{\tilde{\Phi}_s(\tau_0)}\bigg|_{\theta=\pi/2} \tag{30}$$

RESULTS AND DISCUSSION

Film Model vs. Rigorous Model

Chin (1980) has developed a rigorous mathematical model for sinusoidal AC modulation onto the RHE by solving a set of complete convective transport equations. He calculated the periodic concentration changes for the case of a zero DC current. In the present work, a film model is used for the superimposition of AC onto a DC component on the RHE. A comparison between the two models would give an insight into the accuracy of the film model for the prediction of the concentration changes and the limiting AC current densities in AC electrolysis.

Figure 2 shows the root mean square of the dimensionless AC frequency K at three different θ locations. The dashed lines in the figure are the numerical results from Chin's rigorous model. The results for the film model are given as the solid lines. The root mean square of the surface Ac concentration, $\tilde{\Phi}_{s,rms}$ decreases with increasing K. At θ = 0°, the two models are in good agreement; the maximum deviation which occurs at K = 0.8 is less than 5%. The agreement becomes worse as θ increases. At θ = 90°, the maximum deviation between the two models is 9% at K = 0.4. According to Eq. 2 the contribution of the convective mass flux consists of two terms: one is related to the radial velocity component and the other is due to the meridional velocity component. Using the velocity profile shown in Eqs. 17a–17f and the dimensionless parameters shown in Eqs. 13a–13k, this convective mass flux near the electrode surface can be arranged as:

$$N_{\text{conv}} = 0.51023\,\frac{i}{nF}\left(\frac{\Omega}{\nu}\right)^{1/2} Sc^{1/3}\,Z\left(-Z\frac{\partial\Omega}{\partial Z} + \theta\,\frac{\partial\Omega}{\partial\theta}\right) \tag{31}$$

This equation indicates that for small Z and small θ, the value of N_{conv} approaches zero. The contribution of N_{conv} increases with

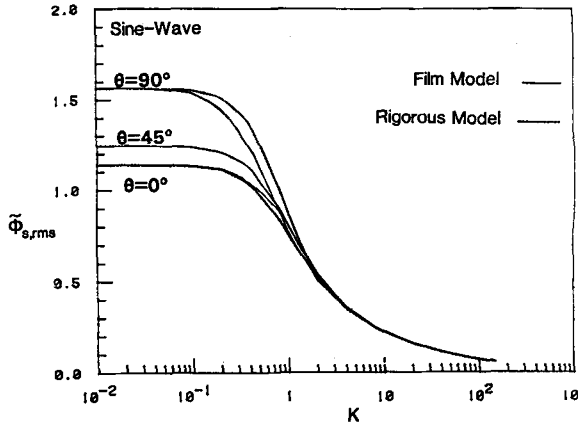

Figure 2. Root mean square of the AC surface concentration component as a function of AC frequency at θ = 0°, 45°, 90°.

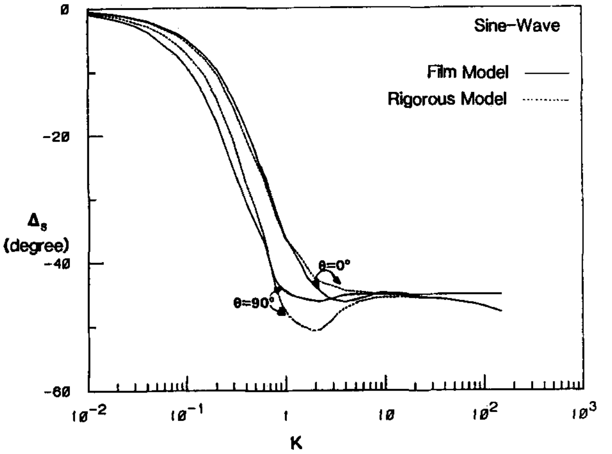

Figure 3. Phase shift between the applied AC and periodic concentration overpotential at $\theta = 0°, 90°$.

increasing θ and consequently the discrepancy between the present results and Chin's work is larger at $\theta = 90°$. The figure also indicates that the film model is a good approximation to the mass transfer calculation in the regimes of a dimensionless AC frequency K greater than 2 and less than 0.01. For K larger than 2, the surface concentration is independent of θ.

Figure 3 shows the phase shift Δ_s between the applied AC and the surface AC concentration as a function of K at $\theta = 0°, 90°$. The results indicate that as K becomes larger than 10, the phase shift asymptotically approaches to $-45°$ independent of θ and K. The trend for the discrepancy between the film and the rigorous models is the same as that of $\tilde{\Phi}_{s,rms}$. The maximum difference is found to be 5.9% at $K = 2$ for $\theta = 0°$ and 10.6% at $K = 2$ for $\theta = 90°$.

Concentration Overpotential and Limiting AC Current Density

Figure 4 shows the shape of the concentration overpotential wave for $K = 10$ at various superimposed AC levels (at $\bar{i} = 0$). The concentration overpotential is dependent on the magnitude of the AC levels. At very small $\tilde{i}$, η^*_{conc} shows a sinusoidal form. At large $\tilde{i}_p$, the waveform is distorted from the sinusoidal form. However, judging from the shape of the curves in the figure, the phase shift of the concentration overpotential is independent of $\tilde{i}_p$.

Figure 5 shows the root mean square of η^*_{conc} for the superimposition of sinusoidal AC onto various DC current densities for $K = 10$. The results indicate that with increasing DC current density, $\bar{i}$, the value of $\tilde{\eta}^*_{\text{conc},rms}$ increases. The figure also shows that there is a maximum limit for $\tilde{i}_p$ for which the value of $\tilde{\eta}^*_{\text{conc},rms}$ becomes infinitely large. The maximum $\tilde{i}_p$ is called the limiting AC current density, $\tilde{i}_{p\text{lim}}$.

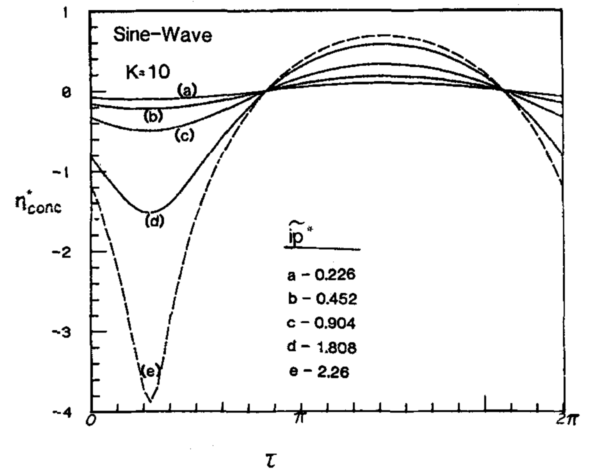

Figure 4. Concentration overpotential wave for $\tilde{i}^*_p$ = 0.226, 0.452, 0.904, 1.808, 2.26, at K = 10 and $\bar{i}^*$ = 0.

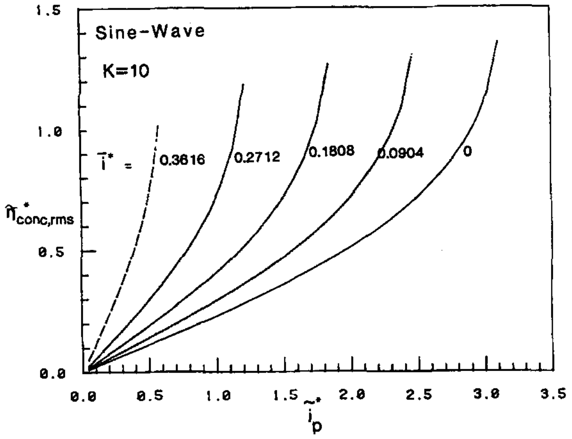

Figure 5. Root mean square of the periodic concentration overpotential as a function of peak AC current density (K = 10) for $\bar{i}^*$ = 0, 0.0904, 0.1808, 0.2712, 0.3616.

Figure 6 shows that $\tilde{i}^*_{p\text{lim}}$ is a function of AC frequency, K, and DC current density, $\bar{i}$. The limiting AC current density increases with increasing K; however, it decreases with increasing DC current density.

Effect of Ohmic Potential Drop on Overpotential Response

According to electrokinetics, there are three components responsible for the potential change during an electrochemical reaction. They are the concentration overpotential, η_{conc}, the surface overpotential, η_s, and the ohmic potential drop, η_{ohm}. For a mass transfer controlled electrochemical system, one may assume a linear polarization for the surface overpotential, and the total overpotential can be estimated by:

$$\eta_{\text{total}} = \eta_{\text{conc}} + \eta_{\text{s}} + \eta_{\text{ohm}}$$

$$= \frac{RT}{nF} ln(1 + \bar{i}^* \bar{\Phi}_s + \tilde{i}^*_p \tilde{\Phi}_s) + \frac{iRT}{i_0 nF} + i\rho l \tag{32a}$$

and

$$\eta^*_{\text{total}} = \eta^*_{\text{total}} \frac{nF}{RT} \tag{32b}$$

Equations 32a–32b indicate that in AC electrolysis, the resulting overpotential and its waveform depend on both the total current density, i, and the position of the reference electrode, l.

A sample calculation has been made for the reduction of ferricyanide ion to ferrocyanide ion in the presence of a NaOH supporting electrolyte. This system has been extensively used in electrochemical mass transfer measurements. The concentrations of the electrolyte chosen for the calculation are: 0.01 M $Fe(CN)_6^{-3}$,

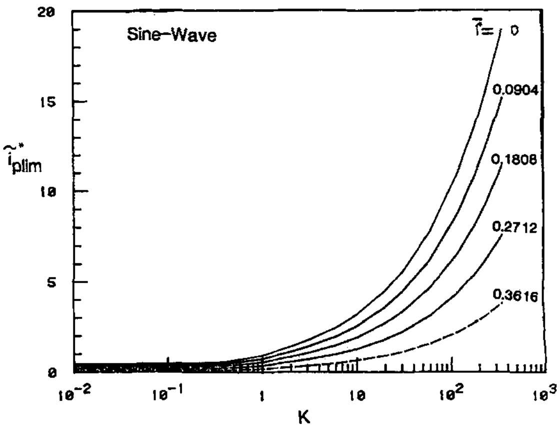

Figure 6. Dimensionless limiting AC current density as a function of AC frequency for $\bar{i}^*$ = 0, 0.0904, 0.1808, 0.2712, 0.3616.

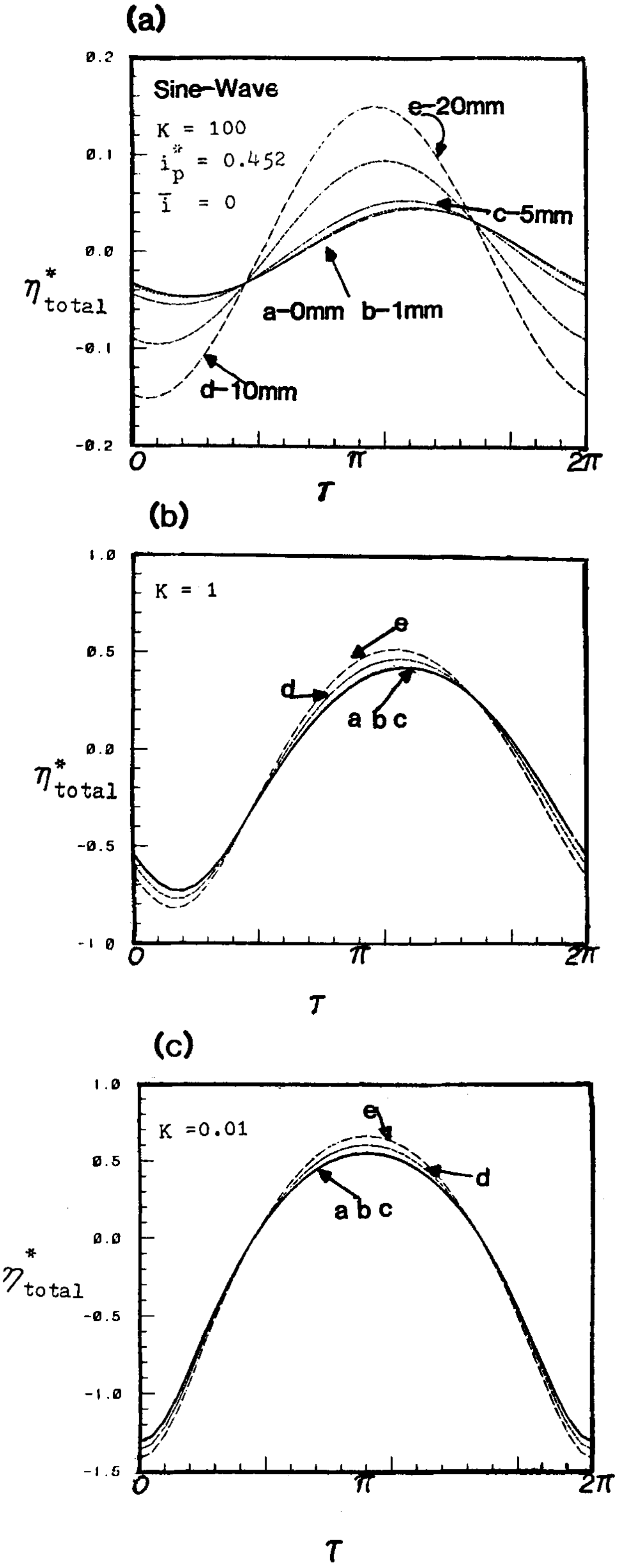

Figure 7. Effect of ohmic overpotential drop on the total overpotential profile at $\theta = 0$; $\bar{i} = 0$; and $\tilde{i}_p^* = 0.452$. The distance of the reference probe from the electrode surface are: 0 mm for curve a; 1 mm for curve b; 5 mm for curve c; 10 mm for curve d; and 20 mm for curve e. The superimposed AC frequencies are: K = 100 for Figure a; K = 1 for Figure b; and K = 0.01 for Figure c.

0.1 M $Fe(CN)_6^{-4}$ and 1 M NaOH, for which the exchange current density i_0 and the specific resistance have been found to be 30.5 mA/cm^2 and 3.7 Ω cm, respectively (Tanaka, 1964). The results are shown in Figure 7. The curves indicate that with increasing distance of the reference probe, l, the waveform of the total overpotential η^*_{total} is distorted, and there is a change of the local maximum and minimum on the waveform. The distortion increases with increasing dimensionless frequency K. The results indicate that if one attempts to make experimental measurements of the concentration overpotential for the AC mass transfer processes, the effect of the ohmic potential drop on the phase shift and the magnitude will be rather significant at high frequencies. Provisions should be made to locate the reference probe as close to the working electrode as possible to reduce experimental errors.

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NOTATION

a = radius of rotating hemispherical electrode, m
a_1 = 0.51023
b = −0.61592
C = concentration of reacting species, kmol/m^3
C_s = surface concentration, kmol/m^3
C_∞ = bulk concentration, kmol/m^3
$\bar{C}$ = DC concentration component, kmol/m^3
$\tilde{C}$ = AC concentration component, kmol/m^3
D = diffusivity, m^2/s
e = electron
f = −0.22129
F = Faraday constant, 9.65 × 10^7 C/kg equiv.
F = dimensionless radial velocity, defined in Eq. 13i
F_i = dimensionless radial velocity, defined in Eq. 17a
g = 0.24765
H = dimensionless meridional velocity in Eq. 13j
H_i = dimensionless meridional velocity in Eq. 17b
i = applied current density, A/m^2
$\bar{i}$ = applied DC current density, A/m^2
$\tilde{i}$ = applied AC current density, A/m^2
$\bar{i}^*$ = dimensionless DC current density
i_p = amplitude of AC current density, A/m^2
i_p^* = dimensionless amplitude of AC current density
$i_{p\lim}$ = limiting AC current density, A/m^2
$i^*_{p\lim}$ = dimensionless limiting AC current density
j = imaginary number, $\sqrt{-1}$
K = dimensionless AC frequency in Eq. 13f
l = distance between the working and reference electrode, m
n = number of electrons, kg equiv./kmol
N_{conv} = convective mass flux, kmol/m·s in Eq. 30
r = radial component, m
R = gas constant, J/kmol·K
Re = Reynolds number in Eq. 13a
Sc = Schmidt number in Eq. 13b
t = time, s
t_0 = time at which the surface concentration becomes zero, s
V_r = radial velocity, m/s
V_θ = meridional velocity, m·rad/s
Z = dimensionless distance from the electrode surface in Eq. 13c

Greek Letters

α_i = dimensionless parameters in Eqs. 23c–23f, i = 1,2,3,4
β_i = dimensionless parameters in Eqs. 23g–23h, i = 1,2
δ = Nernst boundary layer thickness, m
δ^* = dimensionless boundary layer thickness
Δ = phase shift between AC and $\tilde{\Phi}$, rad
Δ_s = phase shift between AC and $\tilde{\Phi}_s$, rad
η_{conc} = concentration overpotential, V

η^*_{conc} = dimensionless concentration overpotential
$\bar{\eta}^*_{\mathrm{conc}}$ = dimensionless DC component of the concentration overpotential
$\tilde{\eta}^*_{\mathrm{conc},rms}$ = root mean square of η^*_{conc}
η_{ohm} = ohmic potential drop, V
η_s = surface overpotential, V
η_{total} = total overpotential, V
η^*_{total} = dimensionless total overpotential
ν = kinematic viscosity, m^2/s
ρ = resistivity of electrolyte, Ω·cm
τ = dimensionless time in Eq. 13k
τ_0 = dimensionless time at zero surface concentration
$\bar{\Phi}$ = dimensionless DC concentration component in Eq. 13d
$\tilde{\Phi}$ = dimensionless AC concentration component in Eq. 13e
Φ_p = dimensionless amplitude of AC concentration
$\bar{\Phi}_s$ = dimensionless surface DC concentration component
$\tilde{\Phi}_s$ = dimensionless surface AC concentration component
$\tilde{\Phi}_{s,rms}$ = root mean square of $\tilde{\Phi}_s$
Φ_{tf} = dimensionless DC concentration component in Eq. 16
ω = AC frequency, rad/s
Ω = rotating speed, rad/s

Subscripts

rms = root mean square
s = surface value
p = amplitude
∞ = bulk value

Superscript

$*$ = dimensionless value

Other Symbols

$-$ = DC component
$\sim$ = AC component

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