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CURRENT DISTRIBUTION ON A ROTATING SPHERE BELOW THE LIMITING CURRENT

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Current Distribution on a Rotating Sphere below the Limiting Current

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Abstract

The current distribution on a rotating spherical electrode is calculated at appreciable fractions of the limiting current. Numerical results are given for Tafel kinetics and for high rotation speeds. The current distribution depends only on the specified current level and becomes uniform when this level is set below 68 percent of the limiting current at high rotation speeds. In general, the results disclose a number of complementary aspects of the spherical electrode alongside the disk electrode in electroanalytical applications.

Key Words: current distribution, mass transfer, electrode kinetics.

Introduction

The sphere has been employed in the past as an important electrode geometry in electrochemical research such as the investigation of the double-layer structure on mercury drops[1] and the study of the overpotential and reaction kinetics on copper electrodes by transient methods.[2] The effects of diffusion were either eliminated or ignored in that work. The rotating sphere has been proposed anew as a potential tool in studies of mass transfer and reaction kinetics in electrochemical systems.[3,4] The convective diffusion equation for a thin diffusion layer at limiting current conditions has been solved recently[3,5,6] and compared successfully with experimental data.[7]

The present interest in the rotating sphere arises from the fact that the mass transfer and current distribution characteristics of the disk and the sphere turn out to be rather complementary in some respects. For instance, the rotating disk exhibits a uniform limiting current distribution,[8] which makes it attractive for mass transfer work. On the other hand, it has a highly nonuniform primary distribution,[9] and consequently serious errors may result in the assessment of exchange current densities in investigations of reaction kinetics.[10] The spherical electrode does not have the same drawback, owing to its uniform primary distribution. The disk electrode can be polished very easily, but the surface preparation for the sphere electrode does not seem to be just as straightforward if a reasonably spherical shape is to be maintained. However, in high-rate metal deposition or dissolution studies the disk electrode tends to rise above or recede below the insulating surface rapidly, thereby altering seriously the hydrodynamic conditions prevailing at the surface.[3] This effect is within a much lesser degree for the

sphere, which maintains its geometry to the extent permitted by the degree of uniformity of the current distribution existing at its surface. Below the limiting current, the current distribution on a rotating disk is nonuniform.[11,12] It is possible in principle to attain a uniform distribution of current on a rotating sphere below the limiting current even in the presence of concentration variations at the surface as will be shown in this paper.

The mathematical treatment of thin diffusion layers with the complicating effect of nonuniform current distribution has become possible in the last decade. The underlying theory has been discussed in detail[13-16] and applied to a number of electrode geometries.[11,12,17-20] The same theory and numerical techniques are employed here to investigate mass transfer and current distribution on a rotating spherical electrode at appreciable fractions of the limiting current. The following assumptions are made:

1. The rotating sphere is suspended and allowed to rotate with respect to a fixed axis in an otherwise stagnant electrolyte. The analysis also applies to a hemispherical cap on an insulating plane.[3]

2. Dilute solution theory is applicable with constant transport and thermodynamic properties.

3. For simplicity, the analysis is restricted to metal deposition from a single salt solution and electrode reactions with an excess of supporting electrolyte. Migration is not accounted for explicitly. Results can be obtained for more complex systems, and corrections can be made for migration effects, if necessary, with added numerical effort.[15]

4. The fluid flow around the sphere is laminar, and the hydrodynamic

boundary layer is thin (high Reynolds numbers), so that the boundary-layer solution of the Navier-Stokes equations[21] is an adequate description of the hydrodynamic conditions near the surface. The dimensionless shear-stress distribution is given by[5]

$$B(\theta) = \beta\nu^{1/2}/r_o\Omega^{3/2} \tag{1}$$

$$= 0.51023\ \theta - 0.1808819\ \theta^3 - 0.040408\ \sin^3\theta \quad ,$$

where β is the velocity derivative $\partial v_x/\partial y$ at the surface. The boundary-layer approximation is known to break down at a region near the equator[22] with the magnitude O(1/Re), but the size of this region can be rendered small by increasing the Reynolds number.

5. Diffusion in the direction parallel to the electrode surface can be neglected whenever the diffusion layer is thin compared to the size of the sphere. It is further assumed that the diffusion layer is thin compared to the hydrodynamic boundary layer (high Schmidt numbers), so that the fluid velocity inside the diffusion layer can be approximated by

$$v_x = \beta y, \quad v_y = -\frac{1}{2}\, y^2\, \frac{1}{\mathcal{R}}\, \frac{d\mathcal{R}\beta}{dx} \quad , \tag{2}$$

where x is the distance along the electrode from its upstream end, y is the perpendicular distance from the electrode surface, and $\mathcal{R}$ is the distance of the axisymmetric surface from the axis of symmetry (see Fig. 1).

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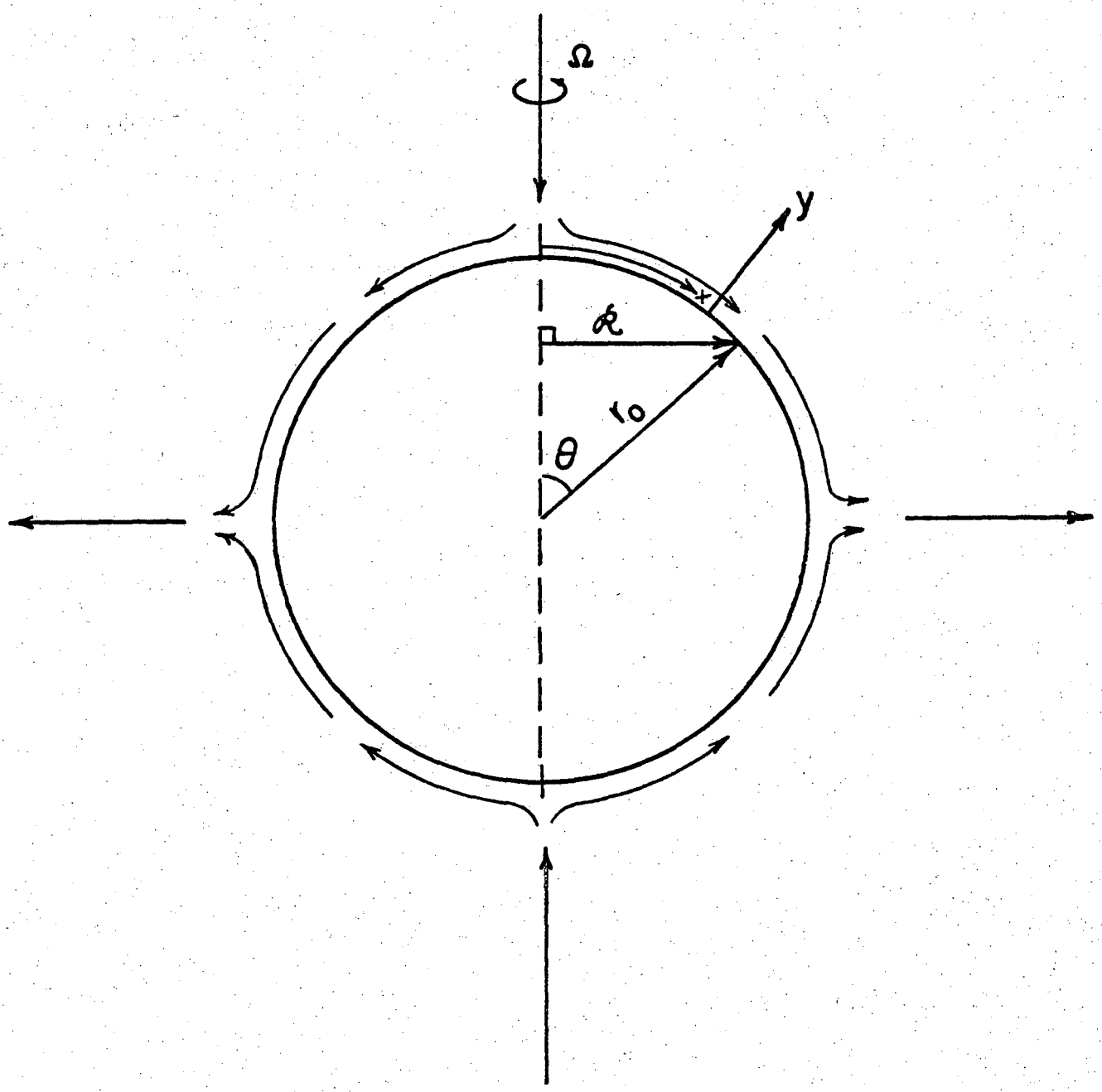

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Figure 1. The rotating sphere

Mathematical Formulation

In light of the above assumptions, the convective diffusion equation can be written in the form

$$y\beta \frac{\partial c}{\partial x} - \frac{1}{2} y^2 \frac{1}{\mathcal{R}} \frac{d\mathcal{R}\beta}{dx} \frac{\partial c}{\partial y} = D \frac{\partial^2 c}{\partial y^2} \quad , \tag{3}$$

where c is the concentration of the reactant. The boundary conditions are

$$\left.\begin{array}{l} c = c_\infty \text{ as } y \to \infty \\ \partial c/\partial x = 0 \text{ at } x = 0 \end{array}\right\} \quad , \tag{4}$$

$$i = \frac{nFD}{1-t} \frac{\partial c}{\partial y} \text{ at } y = 0 \quad , \tag{5}$$

where i is the normal current density at the electrode surface, n is the number of electrons produced when a reactant ion or molecule reacts, and t is the transference number. The solution satisfying the first set of boundary conditions 4 can be expressed as an integral equation for the concentration at the surface[15,16,19]

$$\left.\frac{\partial c}{\partial y}\right|_{y=0} = - \frac{\sqrt{\mathcal{R}\beta}}{\Gamma(\frac{4}{3})} \int_0^x \left.\frac{dc_o}{dx}\right|_{x=x'} \frac{dx'}{\left[9D\int_{x'}^{x} \mathcal{R}\sqrt{\mathcal{R}\beta}\, dx\right]^{1/3}} \quad , \tag{6}$$

or equivalently,

$$c_o(x) - c_\infty = - \frac{(D/3)^{1/3}}{\Gamma(\frac{2}{3})} \int_0^x \left.\frac{\partial c}{\partial y}\right|_{\substack{y=0 \\ x=x'}} \frac{\mathcal{R}dx'}{\left[\int_{x'}^{x} \mathcal{R}\sqrt{\mathcal{R}\beta}\, dx\right]^{2/3}} \quad . \tag{7}$$

The current density is assumed to be related to the surface overpotential by the Butler-Volmer expression

$$i = i_o \left(\frac{c_o}{c_\infty}\right)^\gamma \left[\exp\left\{\frac{\alpha ZF}{RT} \eta_s\right\} - \exp\left\{-\frac{\beta ZF}{RT} \eta_s\right\}\right] \quad , \tag{8}$$

where i_o is the exchange current density at the bulk concentration, and α, β, and γ are kinetic parameters. The surface overpotential is in turn related to the electrode potential by

$$\eta_s = V - \Phi_o - \eta_c \quad , \tag{9}$$

where Φ_o is the potential in the solution just outside the diffusion layer, and η_c is the concentration overpotential given by

$$\eta_c = \frac{RT}{ZF}\left[\ln\left(\frac{c_o}{c_\infty}\right) + t\left(1 - \frac{c_o}{c_\infty}\right)\right] \quad . \tag{10}$$

The parameter Z is equal to $-z_+z_-/(z_+ - z_-)$ for a single salt and $-n$ with supporting electrolyte. The transference number t is zero if excess supporting electrolyte is present.

The potential in the solution satisfies Laplace's equation,

$$\nabla^2\Phi = 0, \tag{11}$$

and the boundary conditions are

$$\left.\begin{aligned} &\Phi = 0 \text{ as } y \to \infty \\ &\partial\Phi/\partial\theta = 0 \text{ at } \theta = 0 \\ &-\kappa\,\partial\Phi/\partial y = i \text{ at } y = 0 \end{aligned}\right\} \quad , \tag{12}$$

where κ is the conductivity of the bulk solution. At $y = 0$, the solution can be expressed as

$$\Phi_o = \frac{RT}{ZF}\sum_{m=0} B_m P_{2m}(\cos\theta) \quad , \tag{13}$$

where $P_{2m}(\cos\theta)$ is the Legendre polynomial of order 2m. The coefficients B_m are given by

$$B_m = \frac{ZFr_o}{\kappa RT}\,\frac{4m+1}{2m+1}\int_0^1 i\,P_{2m}(\cos\theta)\,d(\cos\theta) \quad . \tag{14}$$

Equations (5), (6), (8), (9), (10), (13), and (14) are solved numerically for the unknowns c_o, $(\partial c/\partial y)_{y=0}$, i, η_s, η_c, Φ_o, and B_m. One has the freedom to specify the electrode potential V or the current level $i/(i_{lim})_{ave}$. Equivalently, one can instead fix the concentration or the current density at a given point on the sphere, such as the pole. This last choice avoids an additional iteration loop in the numerical procedure.

Results for Tafel Kinetics

A scaling of all parameters which appear in the problem suggest that the results can be best presented in terms of the dimensionless quantities

$$J = \frac{i_o r_o ZF}{RT\kappa} , \tag{15}$$

$$N = -\frac{nZF^2 Dc_\infty}{RT\kappa(1-t)} \sqrt{\frac{r_o^2 \Omega}{\nu}} \left(\frac{\nu}{9D}\right)^{1/3} , \tag{16}$$

in addition to the kinetic parameters α, β, and γ, and the transference number t. Since the primary distribution is uniform, the secondary current distribution, which is obtained by ignoring the concentration polarization, is also uniform regardless of the reaction kinetics. As a consequence, the results do not depend strongly upon the dimensionless exchange current density J even when concentration polarization is present. Our numerical calculations for different J values, although not shown here, confirm this conclusion. Current and concentration distributions thus largely depend on N, which can be regarded as a dimensionless limiting current, and the specified current level with respect to the average limiting current. In view of these observations, and because mass transfer effects are important at high current densities, we have chosen to report results for Tafel kinetics, thus, for the parameter J tending toward zero.

Figures 2 and 3 show the current and concentration distributions respectively for various current levels at N = 10. All other parameters are arbitrarily set at 0.5. The current becomes more nonuniform as the limiting current is approached whereas the concentration shows

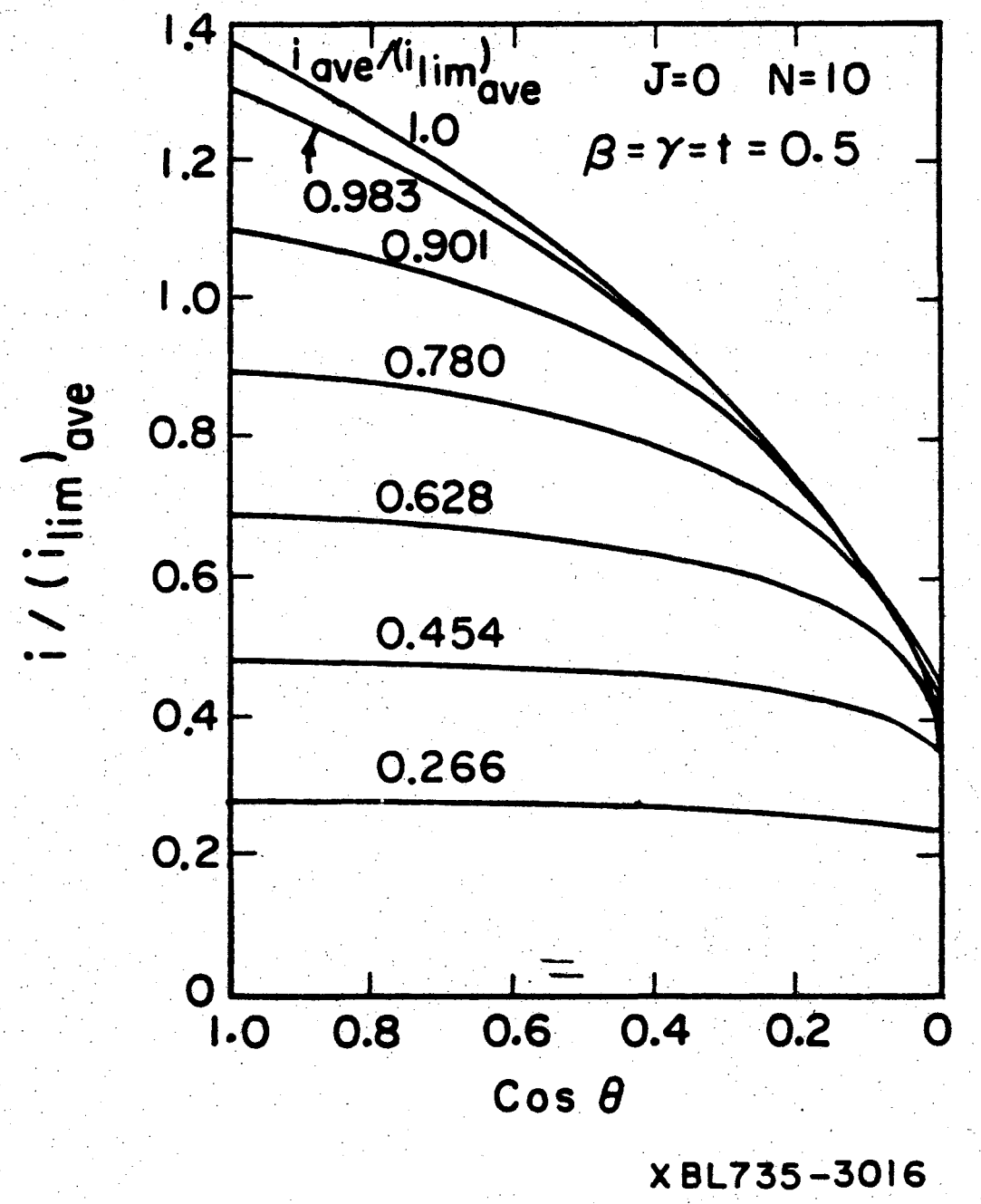

Figure 2. Current distribution for Tafel kinetics

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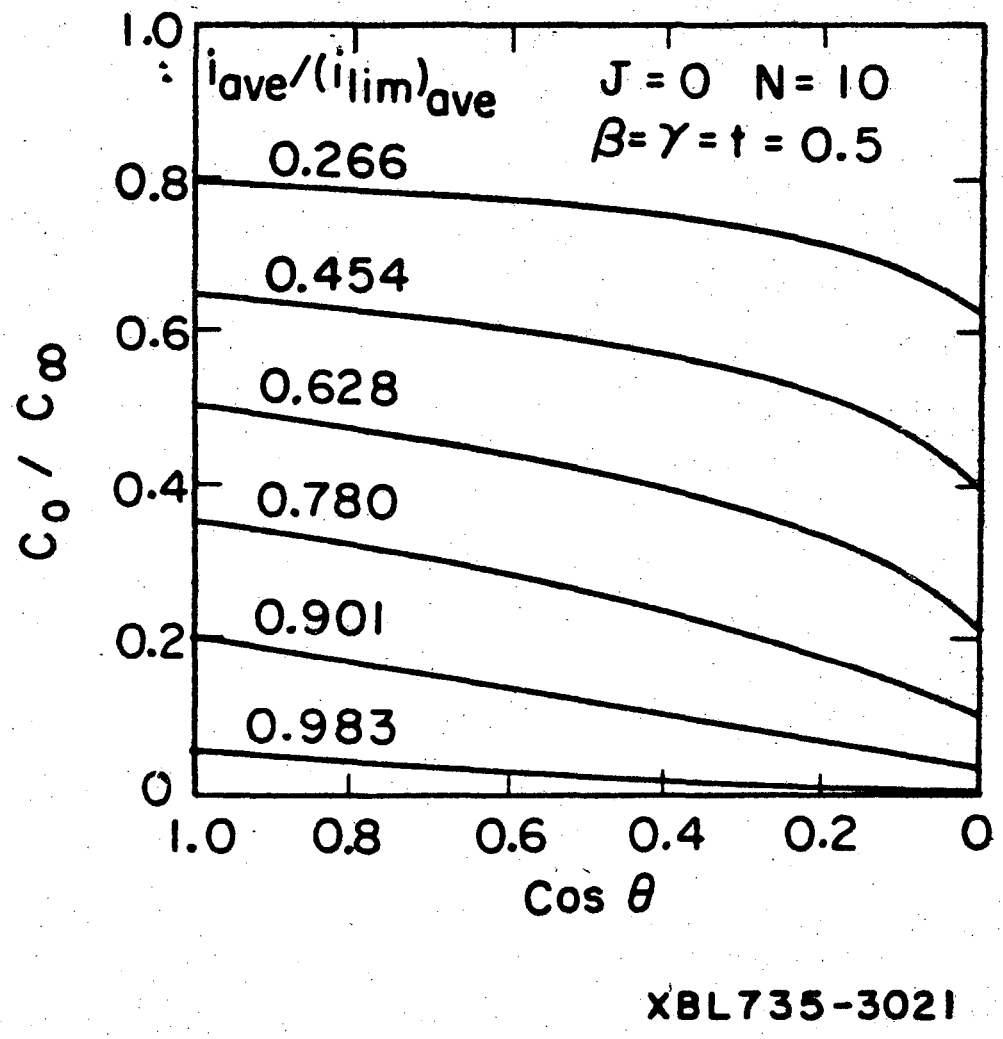

Figure 3. Concentration distribution for Tafel kinetics

marked deviations from its average value at intermediate current levels. Figures 4 and 5 show the effect of increasing N (or increasing rotation speed) on the current and concentration distributions for a fixed concentration ($c_o = 0.5\ c_\infty$) at the pole. The current density exceeds the limiting current locally close to the equator. This can also be observed in Fig. 2 for large enough current levels. The same phenomenon has been reported for other geometries under similar conditions.[11,17,18] With increasing N, the concentration distribution becomes slightly more nonuniform and appears to be approaching an asymptotic profile. Meanwhile, the current distribution becomes more uniform, and the current level tends toward a limiting value different from the limiting current distribution. This represents a contrast to what has been observed for the disk[11] and plane electrodes,[17,18] where the diffusion layer is completely depleted of the reactant near the trailing edges for large enough flow rates, thereby limiting the local current density. The present results suggest the possibility of attaining a uniform current distribution for large N on a rotating sphere in the presence of appreciable concentration polarization. Further investigation is in order below.

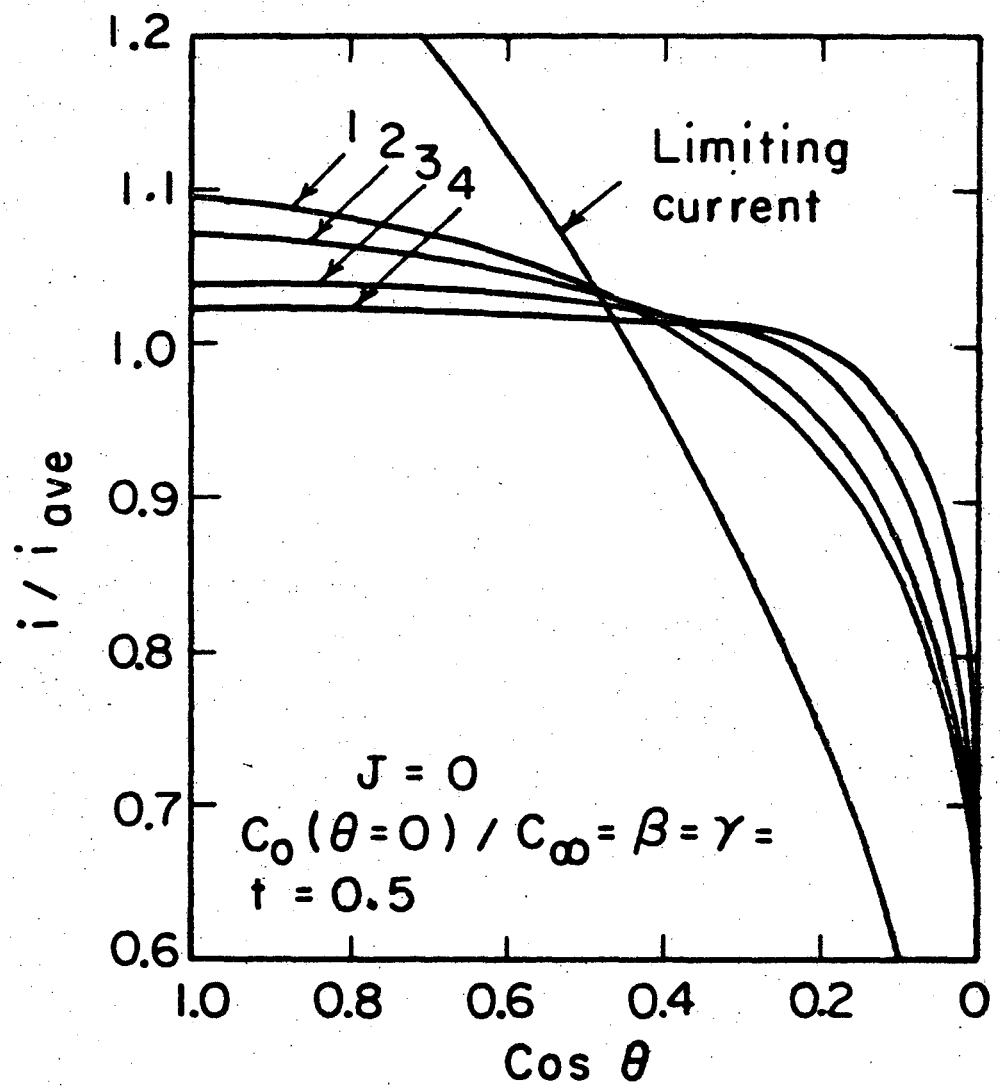

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Figure 4. The effect of rotation speed on the current distribution for Tafel kinetics: (1) N=10, $i_{ave}/(i_{lim})_{ave}$ = 0.6277; (2) N=20, $i_{ave}/(i_{lim})_{ave}$ = 0.6432; (3) N=50, $i_{ave}/(i_{lim})_{ave}$ = 0.6623; (4) N=100, $i_{ave}/(i_{lim})_{ave}$ = 0.6722

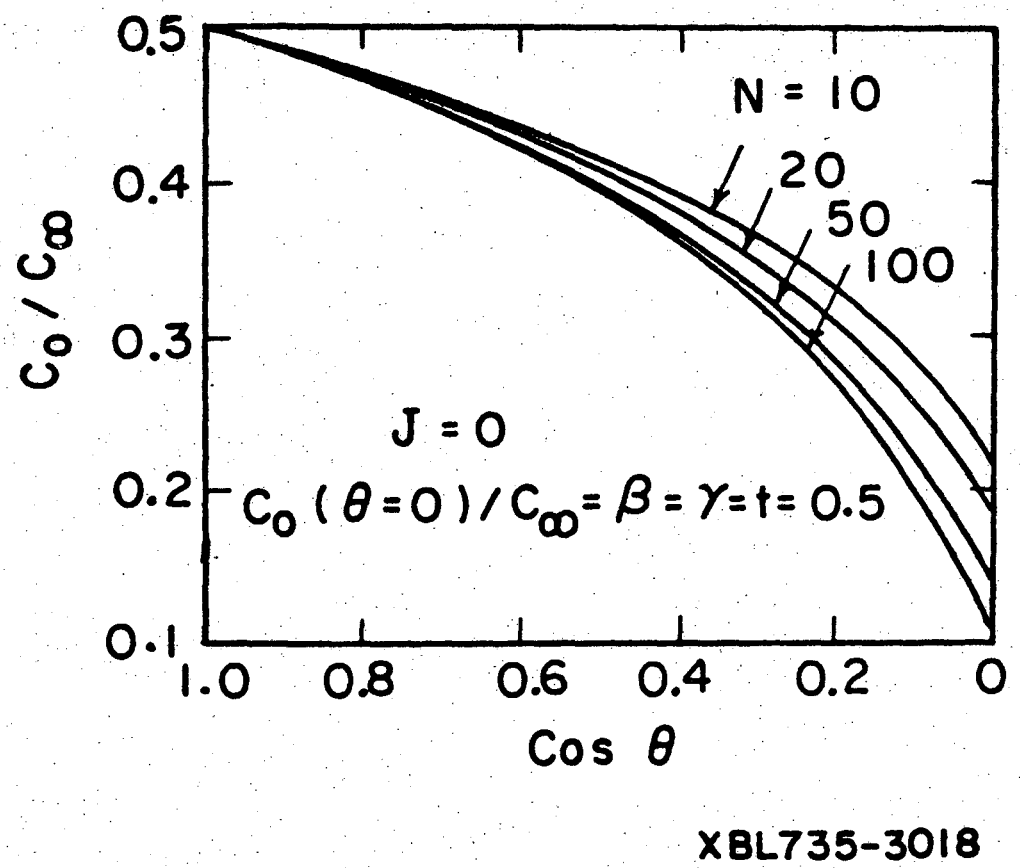

Figure 5. The effect of rotation speed on the concentration distribution for Tafel kinetics

Conditions at High Rotation Speeds

If a constant flux situation prevails on the surface of the sphere, the concentration derivative inside the integral in Eq. (7) is constant and related to the uniform current density by Eq. (5). After scaling the current with respect to the average limiting current density,[5] Eq. (7) reduces to

$$1 - c_o/c_\infty = 0.230825\ F(\theta)\ i/(i_{lim})_{ave} \quad , \tag{17}$$

where

$$F(\theta) = \int_0^\theta \frac{\sin\theta' d\theta'}{\left[\int_{\theta'}^{\theta} \sin\theta\sqrt{B\sin\theta}\ d\theta\right]^{2/3}} \quad . \tag{18}$$

This function $F(\theta)$ increases from the value 3.14768 at $\theta = 0$ (the pole) to the value 6.36850 at $\theta = \pi/2$ (the equator). Since the surface concentration is always positive or zero, Eq. (17) can be satisfied over the entire surface if and only if

$$i/(i_{lim})_{ave} < 0.680267 \tag{19}$$

It also follows from Eq. (17) that for currents restricted by condition 19 the concentration at the pole will be given by

$$c_o(0)/c_\infty > 0.505742 \tag{20}$$

Equation (19) or (20) is the condition, therefore, for which a uniform distribution of current is possible on the sphere. The corresponding concentration distribution is given by Eq. (17).

If condition 19 or 20 is not met, the concentration becomes zero at a certain angle θ^*, which can be determined from Eq. (17) by setting $c_o = 0$. The current becomes limited for $\theta > \theta^*$ due to this zero concentration distribution and is expected to be nonuniform. Hence Eq. (17)

is no more applicable in this region. Under these circumstances, the current density can be calculated from Eq. (6). After combining with Eqs. (5) and (17) and some rearrangement, this becomes

$$\frac{i(\theta)}{(i_{lim})_{ave}} = 0.379408\,[1 - c_o(0)/c_\infty]\sqrt{B\sin\theta} \times \int_0^{\theta^*} \left.\frac{dF}{d\theta}\right|_{\theta=\theta'} \frac{d\theta'}{\left[\int_{\theta'}^{\theta} \sin\theta\sqrt{B\sin\theta}\, d\theta\right]^{1/3}} \qquad (\theta>\theta^*) \quad . \tag{21}$$

Numerical calculations for various current levels yield the interesting results depicted in Figs. 6 and 7. Note that Eqs. (17) and (21) do not depend on any of the kinetic parameters or the exchange current density; the current and concentration distributions are determined only by the specified current level for a galvanostatic process. The reaction parameters are necessary, however, to calculate the overpotential, or conversely, to calculate the current level if the electrode potential is fixed (potentiostatic process). These remarks are also true for the secondary distribution. In fact, the results of this section map out the transition from the secondary current distribution, which is uniform, to the limiting current distribution, which is nonuniform.

At low current levels ($|i| \ll i_{lim}$), the secondary distribution prevails, and the surface concentration is equal to the bulk concentration. As a result, the concentration overpotential is negligible, and the electrode potential is due to the surface overpotential and the ohmic drop in the solution, the latter being given by

$$\Phi = \frac{I}{4\pi\kappa r} \quad , \tag{22}$$

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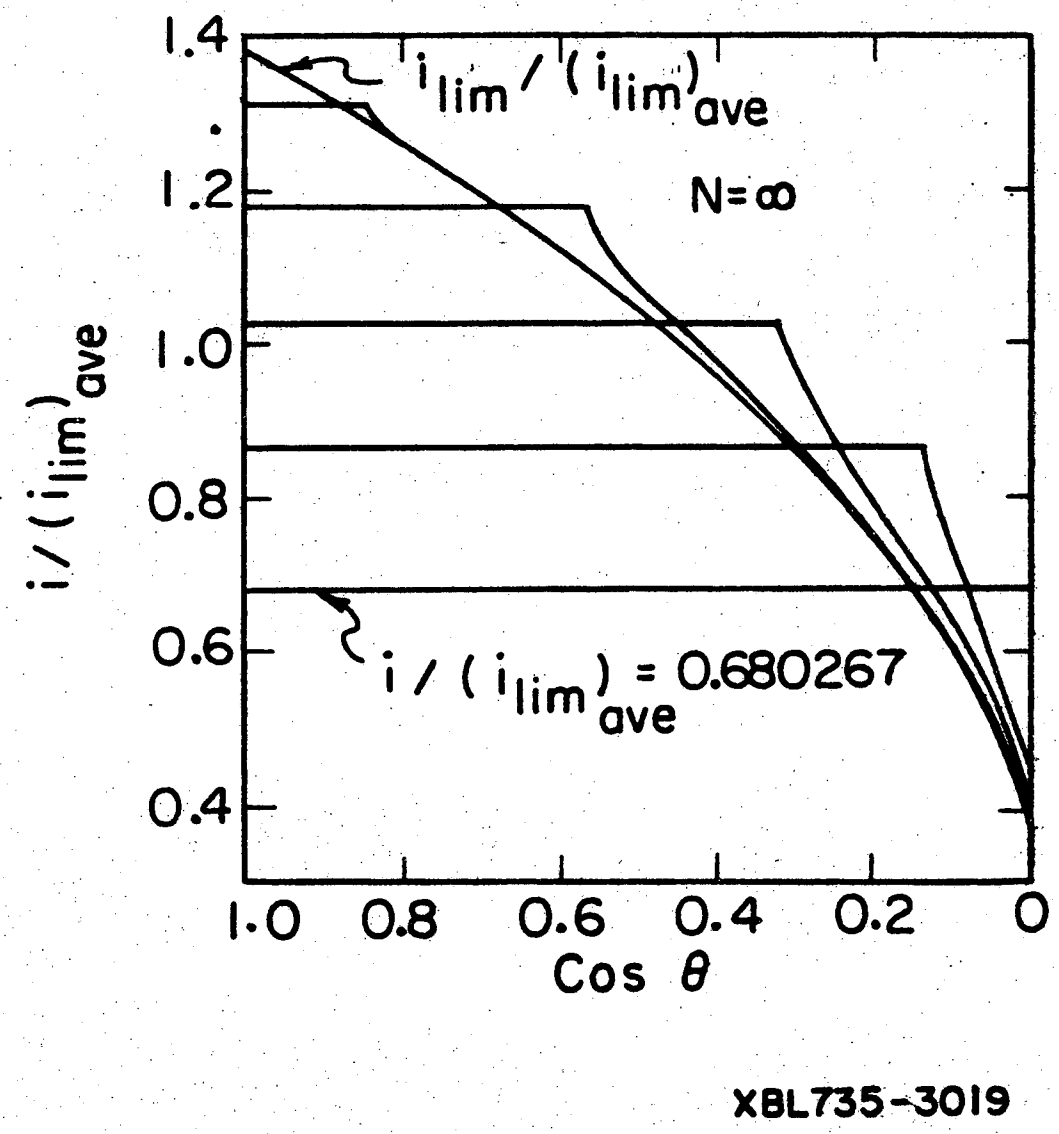

Figure 6. Current distribution at high rotation speeds

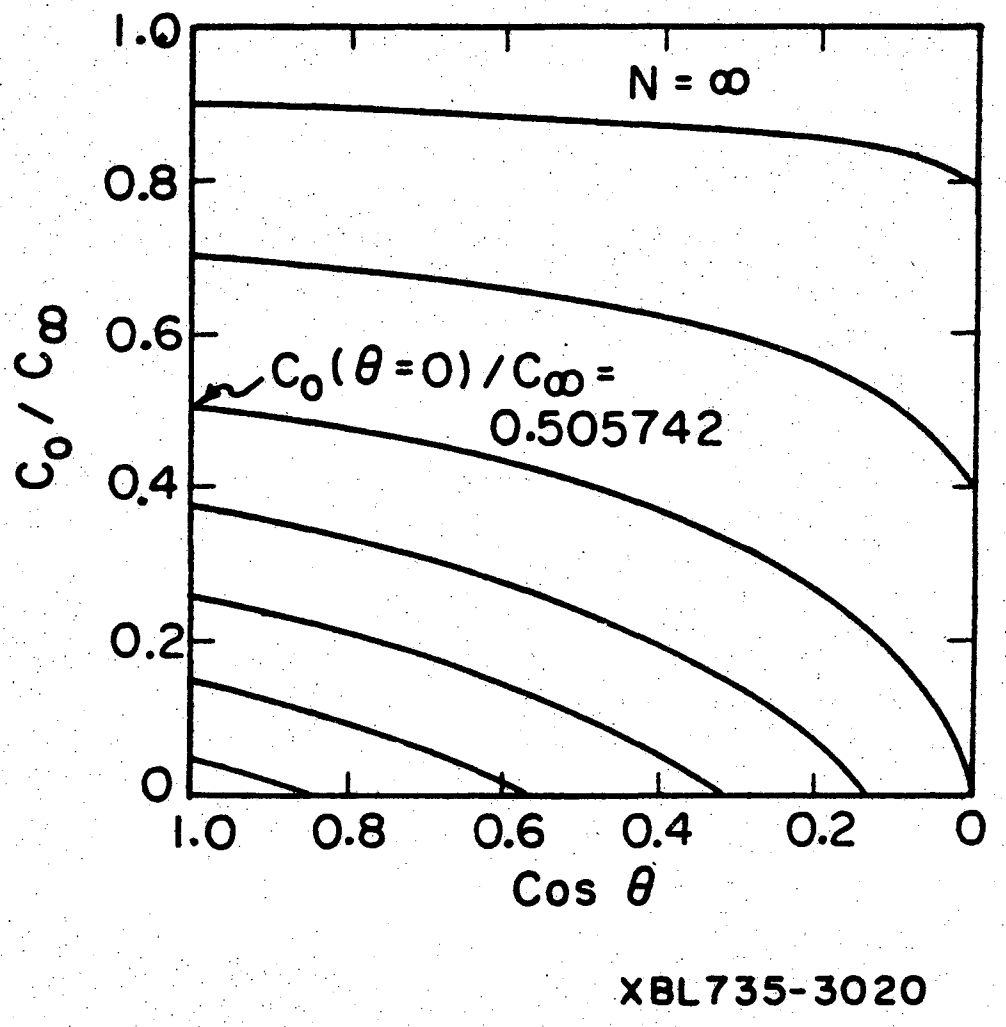

Figure 7. Concentration distribution at high rotation speeds

where I is the total applied current. As the current level increases, the ohmic drop rises linearly with I according to Eq. (22), and the surface overpotential increases as lnI according to the Tafel expression. If there are no mass transfer limitations, the concentration overpotential does not vary significantly. Therefore, the current distribution is controlled by the large ohmic drop, which remains uniform at the surface in the absence of mass transfer limitations, and the current distribution is also uniform. The concentration becomes zero at the equator once a critical current level is reached as specified by Eq. (19). With increasing current, the depleted portion of the diffusion layer grows from near the equator toward the poles, and correspondingly the region of uniform current density shrinks in the same direction. Finally, the limiting current distribution is attained.

The present results are significant, first of all, in high rate dissolution or deposition studies because the spherical electrode maintains its geometry, especially when the current level is kept below $0.68\ (i_{lim})_{ave}$, and high rotation speeds are applied. Secondly, the placement of the reference electrode is not as crucial as for the disk[9,10] because the potential distribution is uniform if constant flux prevails at the surface. If the reference electrode is close to the surface, a correction for radial position is required. This consists of a simple extrapolation to infinity since the primary distribution (Eq. (22)) is a function of radial displacement only. Under these conditions, the assessment of the ohmic drop by the interrupter technique, which measures the value corresponding to the primary distribution,[23] is also much more straightforward[2] in comparison to the disk electrode.[10,24]

Conclusions

The current and concentration distributions below the limiting current have been calculated for a rotating spherical electrode employing a general theoretical and numerical approach applied earlier to the disk and plane electrodes. Mass transfer is assumed to be restricted to a thin diffusion layer near the electrode surface so that the potential distribution can be obtained by solution of Laplace's equation in the bulk and convective diffusion equation in the diffusion layer. The two solutions are matched according to the conditions at the electrode surface including complex electrode kinetics.

Numerical results indicate that the current distribution becomes more nonuniform with increasing mass transfer limitations, and that the exchange current density is not an important parameter, in contrast to the previous results obtained for the disk and planar geometries. Furthermore, the current density is shown to reach a uniform distribution below a certain current level, suggesting the possibility of operating at uniform flux below the limiting current even if the concentration distribution may be nonuniform.

Acknowledgement

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Nomenclature

B	dimensionless velocity derivative at the surface
B_m	coefficients in series for the potential
c	concentration of reactant, mole/cm^3
c_o	concentration of reactant at the electrode surface, mole/cm^3
c_∞	concentration of reactant in the bulk, mole/cm^3
D	diffusion coefficient of the reactant, cm^2/sec
F	Faraday's constant, 96,487 coulomb/equiv.
$F(\theta)$	see Eq. (18)
i	current density, A/cm^2
i_o	exchange current density, A/cm^2
I	total applied current, A
J	dimensionless exchange current density
n	number of electrons transferred in the electrode reaction
N	dimensionless limiting current density
P_{2m}	Legendre polynomial of order 2m
r	radial coordinate, cm
r_o	radius of sphere, cm
R	universal gas constant, 8.3143 joule/mole-deg.
$\mathcal{R}$	normal distance of surface from axis of symmetry, cm
Re	$r_o^2\Omega/\nu$, rotational Reynolds number
t	transference number of reactant
T	absolute temperature, °K
v_x, v_y	velocity components, cm/sec
V	electrode potential, V
x	distance along electrode from its upstream end, cm

y	normal distance from the electrode surface, cm
z	see Eq. (10)
α,β,γ	parameters in kinetic expression (see Eq. (8))
β	velocity derivative at the surface, sec^{-1}
$\Gamma(\frac{4}{3})$	0.89298, the gamma function of 4/3
η_c	concentration overpotential, V
η_s	surface overpotential, V
κ	conductivity of the bulk solution, ohm^{-1} - sec^{-1}
ν	kinematic viscosity, cm^2/sec
Φ	potential in the bulk solution, V
Φ_o	potential in the bulk extrapolated to the electrode surface, V
Ω	angular rotation speed, radians/sec
θ	angle from the pole of the sphere

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