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Authors

Homsy, Robert V.
Newman, John.

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Current Distribution on a Plane Below a Rotating Disk

Robert V. Homsy and John Newman

Inorganic Materials Research Division,
Lawrence Berkeley Laboratory, and
Department of Chemical Engineering;
University of California, Berkeley 94720

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ABSTRACT

The current distribution on a stationary disk electrode below a rotating disk at high Schmidt numbers is calculated at various fractions of the limiting current. Numerical results for the case of Tafel polarization show that the current density on the plane becomes more nonuniform as the limiting current is approached.

Key Words: current distribution, mass transfer, electrode kinetics

Introduction

The rotating disk system has been used extensively in electrochemical investigations primarily because the disk is a surface of uniform accessibility and it is easy to use. A slightly more complicated system consisting of a fluid driven by a rotating disk above a stationary plane has been studied recently.^{1,2,3} The electrode surface is a coaxial disk imbedded in the stationary plane. Figure 1 shows the system. A diffusion-layer solution to the equation of convective diffusion was found for high Schmidt numbers at conditions of limiting current.¹ The current distribution was found to be nonuniform, increasing from zero at the center of the electrode to infinity at the leading edge. We shall apply here the same procedure which has been used previously⁴⁻¹⁰ for various geometries to study the behavior of this system at current densities below the limiting current.

In the treatment of the problem the following assumptions are made:

1. The working electrode is a coaxial disk imbedded in an infinite, insulating plane.
2. The rotating disk acts as a counter electrode at infinity.
(For the case in which the separation distance between the rotating disk and the plane is finite, Laplace's equation should be solved in a different way for the potential in the solution outside the diffusion layer, in order to account for the fact that the rotating disk is an insulator, or another electrode, as the case might be.)

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Figure 1. Disk electrode imbedded in a stationary plane below a rotating disk.

3. The flow is fully developed and laminar.
4. Dilute solution theory applies with constant diffusion coefficients, mobilities, and activity coefficients.
5. Radial diffusion is negligible (valid at high Péclet numbers).
6. The treatment presented here applies to either metal deposition from a single salt solution or electrode reactions with an excess of supporting electrolyte.

Mathematical Formulation

At high Schmidt numbers the concentration varies from its bulk value only in a thin diffusion layer near the electrode surface, well within the hydrodynamic boundary layer. It is then valid to approximate the radial velocity by the first term in an expansion in distance from the electrode

$$v_r = -y \beta(r) \quad (1)$$

where $\beta = -\partial v_r / \partial y$ at $y=0$. A full discussion of the hydrodynamics of this system may be found elsewhere.¹ For this system

$\beta = -r\Omega\sqrt{\Omega/\nu} F'(0)$, where $F'(0)$ is a constant determined by the dimensionless separation distance, $\delta = L\sqrt{\Omega/\nu}$.

The axisymmetric diffusion-layer solution may be superposed⁸ to yield the concentration derivative evaluated at the electrode surface in terms of the derivative of the surface concentration

$$\left. \frac{\partial c}{\partial y} \right|_{y=0} = -\frac{\sqrt{r\beta}}{\Gamma(4/3)} \int_0^x \frac{dc_0}{dx} \bigg|_{x=x_0} \frac{dx_0}{[9\delta \int_{x_0}^x r\sqrt{r\beta} dx]^{1/3}} \quad (2)$$

where $x = r_0 - r$ is the distance from the edge of the electrode.

Substitution for x and β yields

$$\left. \frac{\partial c}{\partial y} \right|_{y=0} = - \frac{(1-\zeta)^{1/3}}{r_0 \Gamma(4/3)} \left(\frac{2Pe}{3} \right)^{1/3} \int_0^\zeta \frac{dC_0}{d\zeta} \bigg|_{\zeta=\zeta_0} \frac{d\zeta_0}{(\zeta-\zeta_0)^{1/3}} \quad (3)$$

where $Pe = \beta r_0^3 / 2rD = - \frac{1}{2} F'(0) Sc Re^{3/2}$ is a Péclet number,

$Re = r_0^2 \Omega / \nu$ is the Reynolds number based on the radius of the electrode,

$\zeta = 1-\xi^3$ and $\xi = r/r_0$ is the dimensionless radius.

The current density normal to the surface of the electrode is related to the concentration derivative by the relation

$$i = \frac{nFD}{1-t} \left. \frac{\partial c}{\partial y} \right|_{y=0} \quad (4)$$

where n is the number of electrons produced when one reactant ion or molecule reacts and t is the transference number.

The potential in the solution outside the diffusion layer is the same as that for the rotating disk. At the surface of the electrode the potential is given by⁴

$$\phi_0 = \frac{RT}{ZF} \sum_{m=0}^{\infty} B_m P_{2m}(\eta) \quad (5)$$

where $Z = -z_+ z_- / (z_+ - z_-)$ for a single salt and $-n$ with supporting electrolyte, $P_{2m}(\eta)$ is the Legendre polynomial of order $2m$ and $\eta = \sqrt{1-\xi^2}$ is the rotational elliptic coordinate at $y=0$. The

expansion coefficients B_m are given by

$$B_m = - \frac{ZF r_o}{\kappa RT} \pi \frac{(4m+1) [(2m)!]^2}{2(2^m m!)^4} \int_0^1 \ln P_{2m}(\eta) d\eta \quad (6)$$

where κ is the conductivity of the bulk solution.

The electrode potential is the sum of the potential drop in the solution Φ_o , the concentration overpotential η_c , and the surface overpotential η_s

$$V = \Phi_o + \eta_c + \eta_s \quad (7)$$

The concentration overpotential is taken to be¹¹

$$\eta_c = \frac{RT}{ZF} \left[\ln \left(\frac{c_o}{c_\infty} \right) + t \left(1 - \frac{c_o}{c_\infty} \right) \right] \quad (8)$$

while the surface overpotential may be related to the current density by the Butler-Volmer expression

$$i = i_o \left(\frac{c_o}{c_\infty} \right)^\gamma \left[\exp \left(\frac{\alpha ZF}{RT} \eta_s \right) - \exp \left(- \frac{\beta ZF}{RT} \eta_s \right) \right] \quad (9)$$

where i_o is the exchange current density at the bulk concentration, and α , β , and γ are kinetic parameters. It is convenient to refer the current density to the average limiting current density¹

$$\langle i_{lim} \rangle = - \frac{i_o}{\Gamma(4/3)} \frac{N}{J} \quad (10)$$

where

$$N = - \frac{nZF^2 DC_{\infty}}{RT\kappa(1-t)} \left(\frac{2Pe}{3}\right)^{1/3} \quad (11)$$

and

$$J = \frac{i_o r_o ZF}{RT\kappa} \quad (12)$$

are dimensionless parameters.

Equations (3-9) constitute a set of seven equations containing the seven unknowns, c_o , $\partial c/\partial y$ at $y=0$, i , ϕ_o , B_m , η_c and η_s . The numerical method of calculation is the same as has been used previously.⁷ There are six parameters which must be specified in the dimensionless problem: N , J , t , α , β , and γ , along with the fraction of limiting current we wish to study. The latter may be set by specifying the current density at the leading edge of the electrode, $i(1)$. Such a choice eliminates an iteration loop in the numerical procedure.

Results and Discussion

Because mass transfer effects are important at higher current densities, we have used Tafel polarization ($J=0$) throughout in calculating the current distributions. Figures 2 and 3 show respectively the dimensionless current density and concentration distributions on the surface of the electrode for $N=10$ at various fractions of the limiting current. All other parameters were arbitrarily set at 0.5. The limiting current curve was obtained from previous work.¹ Figures 4 and 5 show the effect of increasing N on the current density and surface concentration for a fixed current density at the leading edge ($i/i_{lim} = 1.429$).

Figure 2 shows that the current density rises monotonically from zero at the center of the electrode to a finite value at the leading edge for current densities below limiting. This behavior would be expected since both the limiting¹ and primary⁴ current distributions are infinite at the leading edge of the electrode. The current density becomes more nonuniform as the limiting current is approached and may be seen to exceed the limiting current locally near the center of the electrode. This latter behavior has been observed for other geometries.^{4,6,7,10} The surface concentration increases monotonically from zero at the center of the electrode to its bulk value at the leading edge (see Figure 3). As the current density approaches its limiting value, the surface concentration tends towards zero. Figures 4 and 5 show that as N is increased, both the current density and concentration distributions tend to be more uniform, as might be expected since the rate of stirring (Péclet number) is increased.

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Figure 2. Current distribution for Tafel polarization.

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Figure 3. Surface concentration distribution for Tafel polarization.

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Figure 4. Effect of variation of N on the current distribution for Tafel polarization.

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Figure 5. Effect of variation of N on the surface concentration distribution for Tafel polarization.

Summary

The current density and concentration distributions on the surface of an electrode imbedded in a stationary plane below a rotating disk have been calculated at various fractions of the limiting current. At high Schmidt numbers the concentration varies from its bulk value only in a thin diffusion layer near the electrode surface. The potential distribution in the diffusion layer is determined from a superposition of the diffusion-layer solution to the equation of convective diffusion and electrode kinetic expressions, while the potential in the bulk of the solution is obtained from Laplace's equation. The calculation method used here is the same as was applied previously to the rotating disk and sphere and plane electrodes. Results for the case of Tafel polarization show that the current density becomes more nonuniform as the limiting current is approached.

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Nomenclature

B_m	expansion coefficients in the series for the potential
c	concentration of the reactant, mole/cm ³
c_o	concentration of the reactant at the electrode surface, mole/cm ³
c_∞	concentration of the reactant in the bulk, mole/cm ³
D	diffusion coefficient of the reactant, cm ² /sec
F	Faraday's constant, 96,487 coulomb/equiv.
$F'(0)$	dimensionless radial velocity derivative evaluated at the plane
i	normal current density at the electrode surface, amp/cm ²
i_o	exchange current density, amp/cm ²
$\langle i \rangle$	average current density, amp/cm ²
$\langle i_{lim} \rangle$	average limiting current density, amp/cm ²
J	dimensionless exchange current density
L	separation distance between stationary plane and rotating disk, cm
m	index of summation in the series for the potential
n	number of electrons produced when one reactant ion or molecule reacts
N	dimensionless parameter related to the significance of mass transfer (see Equation 11)
P_{2m}	Legendre polynomial of order 2m
Pe	Péclet number, $-F'(0) Sc Re^{3/2}/2$
r	radial coordinate, cm
r_o	radius of electrode, cm
R	universal gas constant, 8.3143 joule/mole-deg
Re	Reynolds number, $r_o^2 \Omega / \nu$

Sc	Schmidt number, ν/D
t	transference number of reactant
T	absolute temperature, °K
v_r	radial velocity component, cm/sec
V	potential of the electrode, volt
x	distance from the edge of the electrode, cm
x_0	integration variable in Equation 2
y	normal distance from the electrode surface, cm
z_i	charge number of species i
Z	$-z_+ z_- / (z_+ - z_-)$ for a single salt -n for reactions with excess supporting electrolyte
δ	dimensionless separation distance between stationary plane and rotating disk, $L\sqrt{\Omega/\nu}$
α, β, γ	parameters in the kinetic expression (see Equation 9)
$\beta(r)$	radial velocity derivative at the plane, $-\partial v_r / \partial y$ at $y=0$, sec^{-1}
$\Gamma(4/3)$	the gamma function of 4/3, 0.89298
ζ	$1-\xi^3$
ζ_0	integration variable in Equation 3
η	rotational elliptic coordinate at $y=0$, $\sqrt{1-\xi^2}$
η_c	concentration overpotential, volt
η_s	surface overpotential, volt
θ_0	dimensionless concentration of the reactant at the electrode surface, c_0/c_∞
κ	conductivity of the bulk solution, $\text{ohm}^{-1} \text{cm}^{-1}$
ν	kinematic viscosity, cm^2/sec

- ξ dimensionless radial coordinate, r/r_0
 π 3.14159
 Φ_0 potential in the bulk extrapolated to the electrode surface, volt
 Ω angular velocity of rotating disk, rad/sec

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