UCRL-18160
cy. 2

University of California

Ernest O. Lawrence Radiation Laboratory

TWO-WEEK LOAN COPY

This is a Library Circulating Copy which may be borrowed for two weeks. For a personal retention copy, call Tech. Info. Division, Ext. 5545

CURRENT DISTRIBUTION ON A PLANE ELECTRODE BELOW THE LIMITING CURRENT

W. R. Parrish and John Newman

April 1968

RECEIVED
LAWRENCE
RADIATION LABORATORY
MAY 6 1968
LIBRARY AND
DOCUMENTS SECTION

Berkeley, California

UCRL-18160
cy. 2

DISCLAIMER

This document was prepared as an account of work sponsored by the United States Government. While this document is believed to contain correct information, neither the United States Government nor any agency thereof, nor the Regents of the University of California, nor any of their employees, makes any warranty, express or implied, or assumes any legal responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by its trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or the Regents of the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof or the Regents of the University of California.

Submitted to J. Electrochem. Soc.

UCRL-18160

UNIVERSITY OF CALIFORNIA

Lawrence Radiation Laboratory
Berkeley, California

AEC Contract W-7405-eng-48

CURRENT DISTRIBUTION ON A PLANE ELECTRODE BELOW THE LIMITING CURRENT

W. R. Parrish and John Newman

April, 1968

Current Distribution on a Plane Electrode below the Limiting Current

W. R. Parrish and John Newman

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

April, 1968

Abstract

The current distribution on a short, plane electrode in the wall of a flow channel is calculated at various fractions of the limiting current. Near the limiting current, the current density exceeds the local limiting value near the downstream end of the electrode.

Introduction

An important geometry in electrochemical industries involves channel flow between two plane, parallel electrodes as shown in figure 1. A complicated procedure for treating this problem is outlined in reference 1. This is based on the concept[2] that concentration variations are restricted to thin diffusion layers near the electrodes, which allows separate treatment of the diffusion layer and the potential distribution outside the diffusion layer. This concept has been applied to the rotating disk electrode.[3,4] However, it is difficult to treat the channel problem, and the present paper is restricted to the consideration of one electrode. If the distance between the electrodes is much greater than the length of the electrodes, each electrode behaves independently. This assumption greatly simplifies the determination of the current and concentration distributions on the electrodes.

The following assumptions will also be made:

1. The electrode is embedded in an infinite, plane, insulating wall.
2. Fully developed, laminar flow prevails, and the velocity can be approximated by a linear profile near the wall, within the diffusion layer.
3. Dilute-solution theory with constant physical properties is applicable.
4. The transport equations used here apply to either the deposition of an ion of a single salt or the reaction of an ion in an excess of supporting electrolyte. The effect of ionic migration for intermediate cases is not considered.

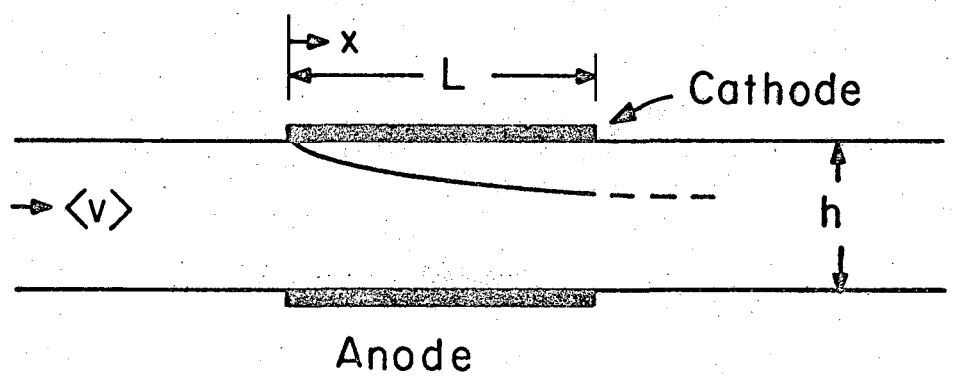


Figure 1.

Plane electrodes in the walls of a flow channel

XBL673-2382A

Mathematical Formulation of the Problem

The mode of approach is described in references 1, 2, and 3. The potential in the electrolytic solution outside the diffusion layer satisfies Laplace's equation in two-dimensional form:

$$\frac{\partial^2\Phi}{\partial x^2} + \frac{\partial^2\Phi}{\partial y^2} = 0 \ , \tag{1}$$

where Φ is the potential measured by a reference electrode of the same type as the working electrode. The appropriate boundary conditions are

$$\partial\Phi/\partial y = 0 \quad \text{at } y = 0 \text{ for } x < 0 \text{ and } x > L \ , \tag{2}$$

$$\partial\Phi/\partial y = -i/\kappa_\infty \quad \text{at } y = 0 \text{ for } 0 < x < L \ . \tag{3}$$

Equation 2 applies to the insulating surface bounding the electrode, and equation 3 relates the normal potential gradient to the electrode current density, where κ_∞ is the conductivity of the solution outside the diffusion layer.

Wagner[5] gives the solution of equation 1 subject to conditions 2 and 3:

$$\Phi = \Phi^* - \frac{1}{2\pi\kappa_\infty}\int_0^L i(x')\, ln\, [(x-x')^2 + y^2]\, dx' \ , \tag{4}$$

where Φ^* is an integration constant reflecting the arbitrary zero of potential. The potential Φ_o near the electrode surface is then

$$\Phi_o = \Phi^* - \frac{1}{2\pi\kappa_\infty}\int_0^L i(x')\, ln\, (x-x')^2 dx' \ . \tag{5}$$

This should be regarded as the potential of the solution outside the diffusion layer extrapolated to the electrode surface as if the actual current distribution prevails but there is no concentration variation near the electrode.

Another integral equation can be developed for the diffusion layer.[1] The limiting current distribution for such a plane electrode is

$$i(x) = -\frac{nFDc_\infty}{(1-t)\Gamma(4/3)}\left(\frac{b}{9Dx}\right)^{1/3}, \qquad (6)$$

where b, a constant, is the slope of the velocity profile at the wall ($b=\partial v_x/\partial y$ at $y=0$). We assume here that the concentration variation is confined to a thin region near the electrode surface. Thus the velocity profile within this diffusion layer is linear in y. This approximation is valid when $L < 0.02 \langle v \rangle h^2/D$. Equation 6 applies when the concentration of the reactant is zero at the electrode surface. Application of Duhamel's theorem to equation 6 gives a relationship between the current density distribution and the surface concentration, for currents below the limiting current.

$$i(x) = -\frac{nFD}{(1-t)\Gamma(4/3)}\left(\frac{b}{9D}\right)^{1/3}\int_0^x \frac{dc_o(x')}{dx'}\frac{dx'}{(x-x')^{1/3}}. \qquad (7)$$

In many cases the electrode kinetics allow the current density and the surface overpotential η_s to be related by an exponential expression:

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

where α and β are characteristic parameters of the electrode and i_o is the exchange current density at the bulk concentration. The exchange current density at the electrode is taken to be proportional to the surface concentration c_o raised to the power γ. The surface overpotential is related to the electrode potential V by

$$\eta_s = V - \Phi_o - \eta_c, \qquad (9)$$

where η_c is the concentration overpotential and is taken to be[2]

$$\eta_c = -(RT/ZF)[\ln (c_\infty/c_o) - t\ (1-c_o/c_\infty)]\ , \tag{10}$$

where

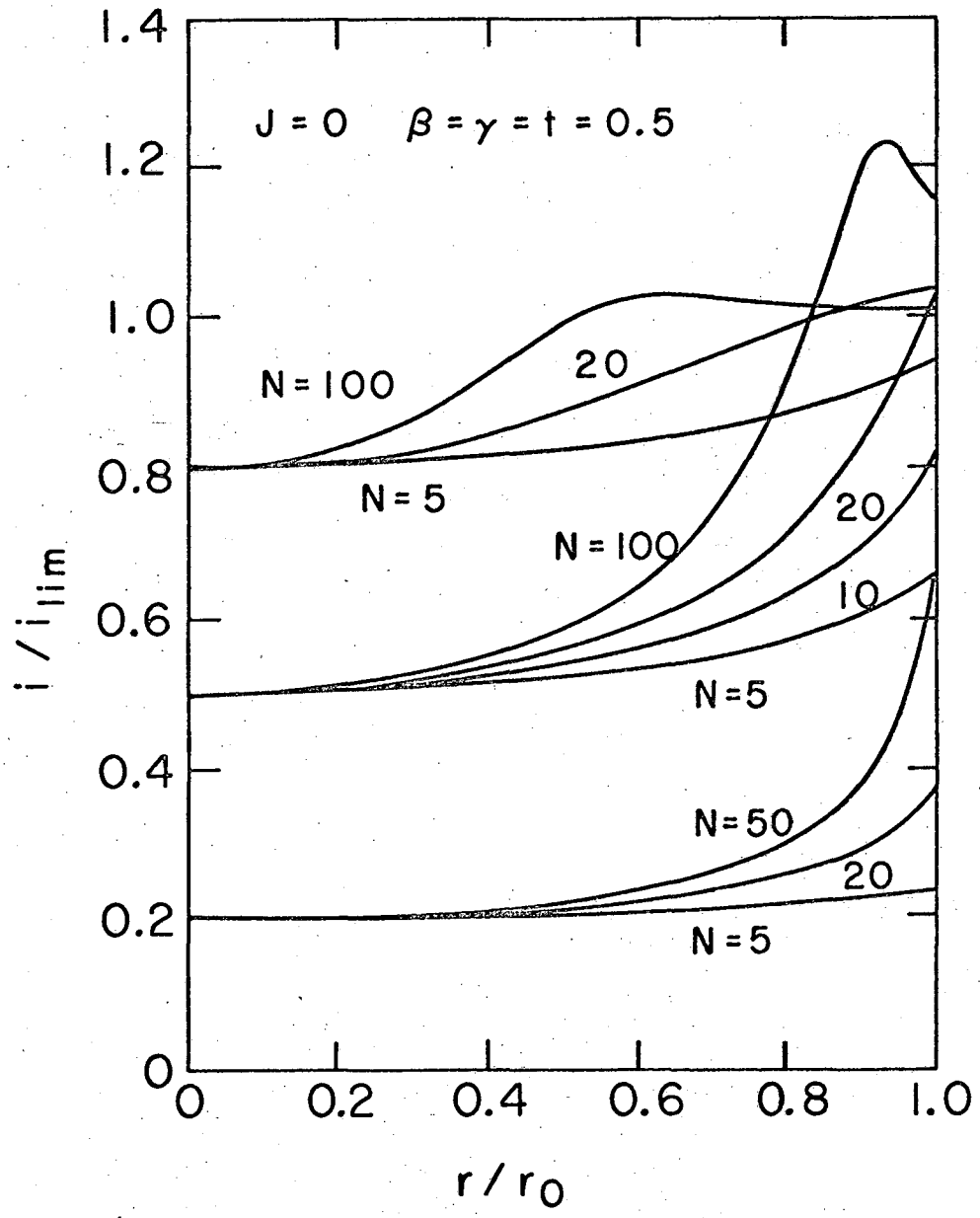
$$\begin{aligned} Z &= -z_+z_-/(z_+-z_-) \text{ for a single salt,} \\ Z &= -n \text{ with supporting electrolyte.} \end{aligned} \tag{11}$$

If there is an excess of supporting electrolyte, the transference number t will be zero.

Instead of the integral equation 7, it might have been possible to treat the diffusion layer with some sort of power series in x, similar to the method used for the rotating disk.[3] However, even with the disk, a power series introduces numerical difficulties which can be avoided with an integral equation.[4] This is demonstrated in figure 2, recalculated for the rotating disk with an integral equation similar to equation 7. Comparison with figure 7 of reference 3 shows that the curves are nearly the same with one important exception. The current density can rise above the limiting current near the edge of the disk and then go through a maximum as the limited supply of reactant becomes decisive. However, it cannot rise again near the edge of the disk as shown in the earlier work. Thus, from a practical point of view, the integral equation is superior to a power series and will be used in the present work.

Numerical Calculations

To determine the current and concentration distributions along the electrode, equations 5 and 7 must be solved along with equations 8, 9, and 10. The integral in equation 5 was evaluated by Simpson's method. The singularity at $x'=x$ was removed by adding and subtracting $i(x)$ as



XBL682-2028

Figure 2. Current distribution on a rotating disk for Tafel kinetics. For the definition of the parameters, see reference 3.

suggested by Kantorovich and Krylov.[6] For a given distribution of total overpotential $\eta_c+\eta_s$, the integral equation 7 was solved in conjunction with equations 8 and 10 by the method of Acrivos and Chambré. It might be noted that equation 7 is a special form of a more general equation which can be applied to other flow geometries, for example, the rotating disk electrode.

The number of intervals required to obtain accurate results varied between 50 and 140, depending upon the uniformity of the current distribution. The answers were checked by increasing the number of intervals and were considered to be satisfactory if they did not vary by more than 1 percent with an increase of 20 intervals.

The following iteration procedure was used:

1. The current density was specified at x=0. Since $c_o=c_\infty$ at x=0, this also specifies the total overpotential at x=0. As a first guess, this total overpotential was assumed to apply over the entire electrode.
2. For a given distribution of total overpotential, the current density and surface concentration were determined from equations 7, 8, and 10.
3. From the current distribution, new values of the total overpotential were calculated from equations 5 and 9. If the new and old values of the total overpotential differed by more than 0.01 percent, these values were averaged (usually with unequal weights on the two values) and put back into step 2.

This procedure appears to work well over almost the entire range between the secondary and limiting current distributions. Convergence was always achieved in less than 35 iterations for the cases considered.

Results

The number of parameters required to describe a given situation can be minimized by defining three dimensionless quantities:

$$J = \frac{ZFL}{RT\ \kappa_\infty}\, i_o\ , \tag{12}$$

$$N = -\frac{nZF^2 Dc_\infty}{(1-t)RT\ \kappa_\infty}\left(\frac{L^2 b}{D}\right)^{1/3}\ , \tag{13}$$

$$\delta = \frac{ZFL}{RT\ \kappa_\infty}\left|i_{avg}\right|\ . \tag{14}$$

These are analogous to those defined for the rotating disk problem.[3] J, N, and δ can be regarded as dimensionless exchange, average limiting, and average current densities. The limiting current corresponds to $\delta = 0.807$ N. The total number of parameters required to define the problem will now be seven--J, N, and δ, the transference number t, and α, β, and γ characteristic of the electrode.

The two extreme cases are the primary and limiting current distributions, shown in figure 3. The primary current occurs when the electrode is reversible and there are no concentration effects ($N=\infty$ and $J=\infty$). Wagner[5] gives the primary current distribution as

$$i/i_{avg} = (1/\pi)\ [x/L - (x/L)^2]^{-1/2}\ . \tag{15}$$

When the current is limited solely by the rate of mass transfer through the diffusion layer, the limiting current distribution, obtained from equation 6 is

$$i/i_{avg} = (2/3)\ (x/L)^{-1/3}\ . \tag{16}$$

The secondary current will result when there is a surface over-

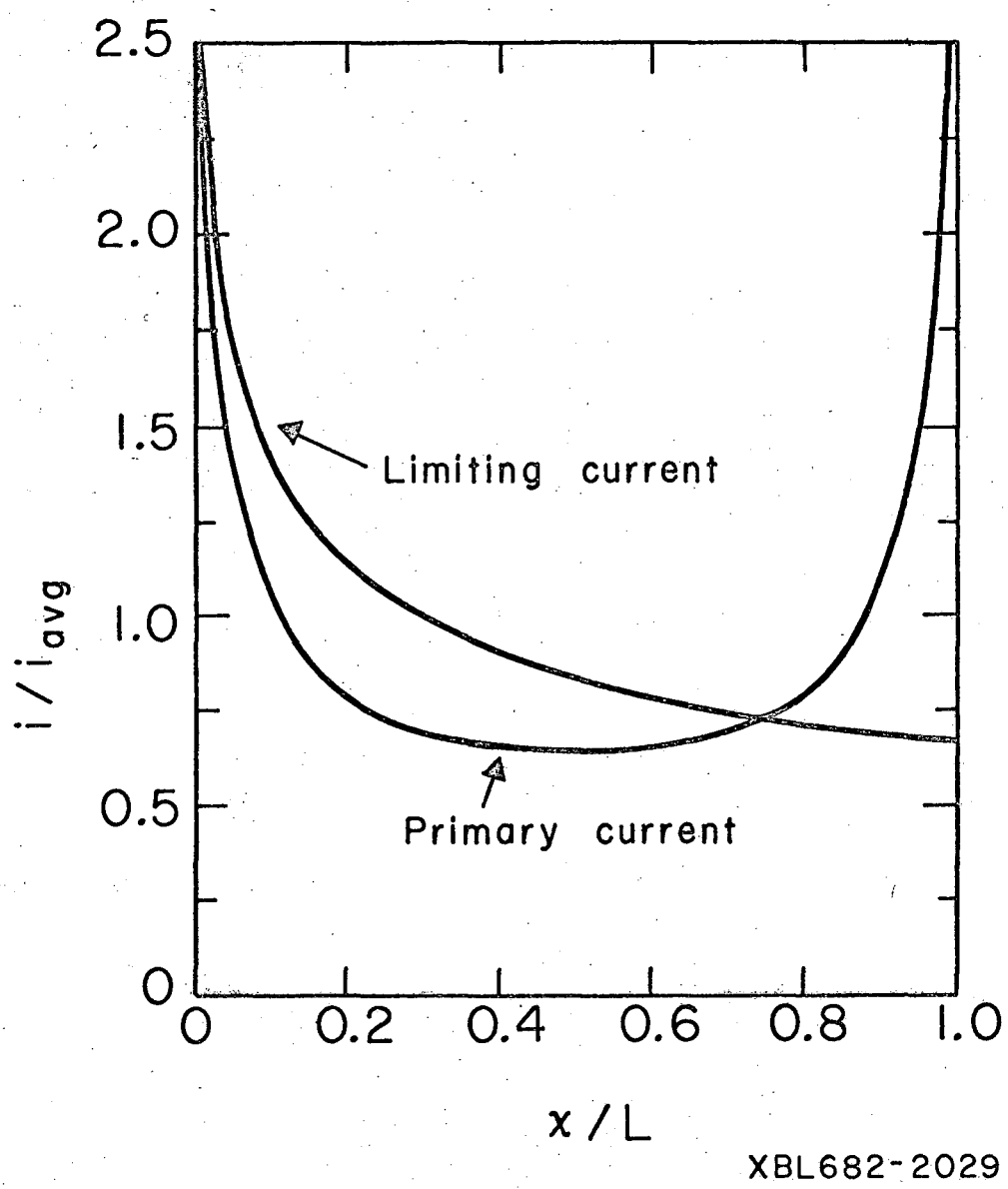


Figure 3. Primary and limiting current distributions on a plane electrode.

potential but no mass transfer effects. For sufficiently small currents ($\delta \ll J$), the polarization law 8 can be linearized to

$$i = (\alpha+\beta)(ZF/RT)\, i_o \eta_s \,. \tag{17}$$

Wagner[5] calculated secondary current distributions as a function of the coefficient in equation 17. A linear approximation can also be made if the current distribution is fairly uniform, say $\delta < 0.5$, even if J is small.

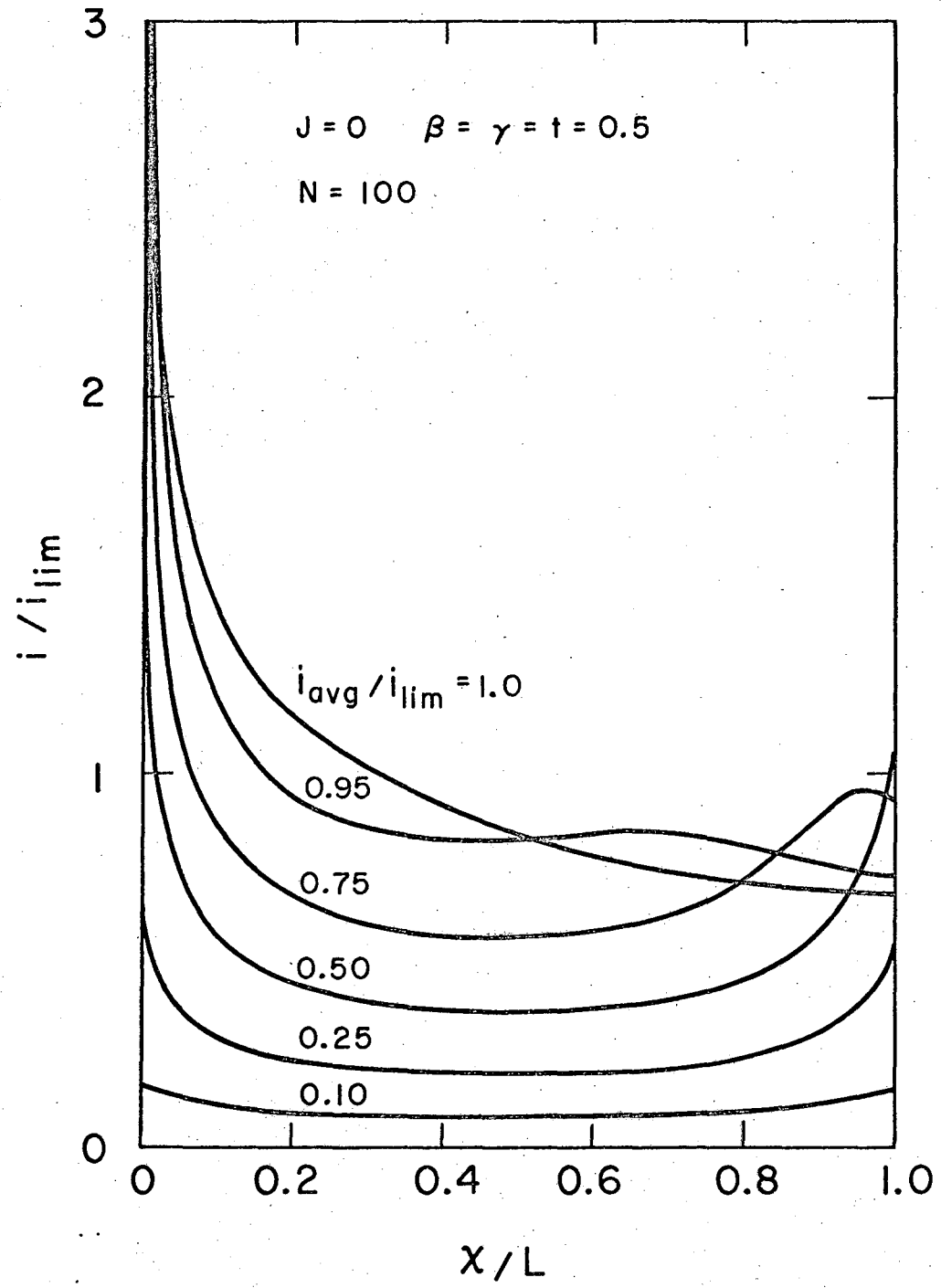
If, on the other hand, the average current is much greater than the exchange current ($\delta \gg J$), Tafel polarization will apply

$$\eta_s = -(RT/ZF\beta)[\ln |i| - \ln i_o] \,. \tag{18}$$

(For anodic currents, the term in α would be retained.) Gnusin, Poddubnyi, Rudenko, and Fomin[8] determined the secondary current distribution as a function of the average current.

Before considering the case where mass transfer effects are important, we compared our calculated secondary distributions with those in these two papers. Comparison for the rotating disk[3] served as a check on the mass transfer calculations.

Because mass transfer effects occur at higher current densities, we used a Tafel polarization law in subsequent work considering concentration variations. Figure 4 shows the current distribution for N=100 and average current densities at various fractions of the average limiting current. At low currents, the distribution is close to the secondary distribution, and mass transfer becomes important only at higher currents. At greater than about 75 percent of the limiting current, the current cannot continue to increase near the end of the electrode because of mass transfer limitations.



XBL682-2030

Figure 4. Current distribution for Tafel polarization at various fractions of the average limiting current.

Concentration profiles are shown in figure 5 for various values of N. For the case of N=100 at 75 and 95 percent of the limiting current, there is a slight increase of reactant concentration near the front of the electrode ($x/L \approx 0.1$), resulting from the rapid drop in current density near the front of the electrode. The concentration then has a chance to increase a little before the current density begins to increase.

In figure 6 the ratio of the maximum to minimum current density has been plotted against the fraction of the limiting current, giving an indication of the uniformity of the current distribution. At a given fraction of the limiting current, the current distribution becomes less uniform with increasing N. In all cases the effect of mass transfer is to make the current distribution more uniform near the back end of the electrode.

Conclusions

Current distributions on a plane electrode in the wall of a flow channel are calculated while taking into account concentration variations near the electrode, electrode kinetics, and the ohmic potential drop in the bulk of the solution. The procedure is similar to that for a rotating disk, leading to the conclusion that the diffusion layer can be treated by a general method for hydrodynamic situations where the velocity derivative at the electrode surface is known. Such calculations can thus be carried out for geometric arrangements where it is also possible to treat the potential distribution outside the diffusion layer.

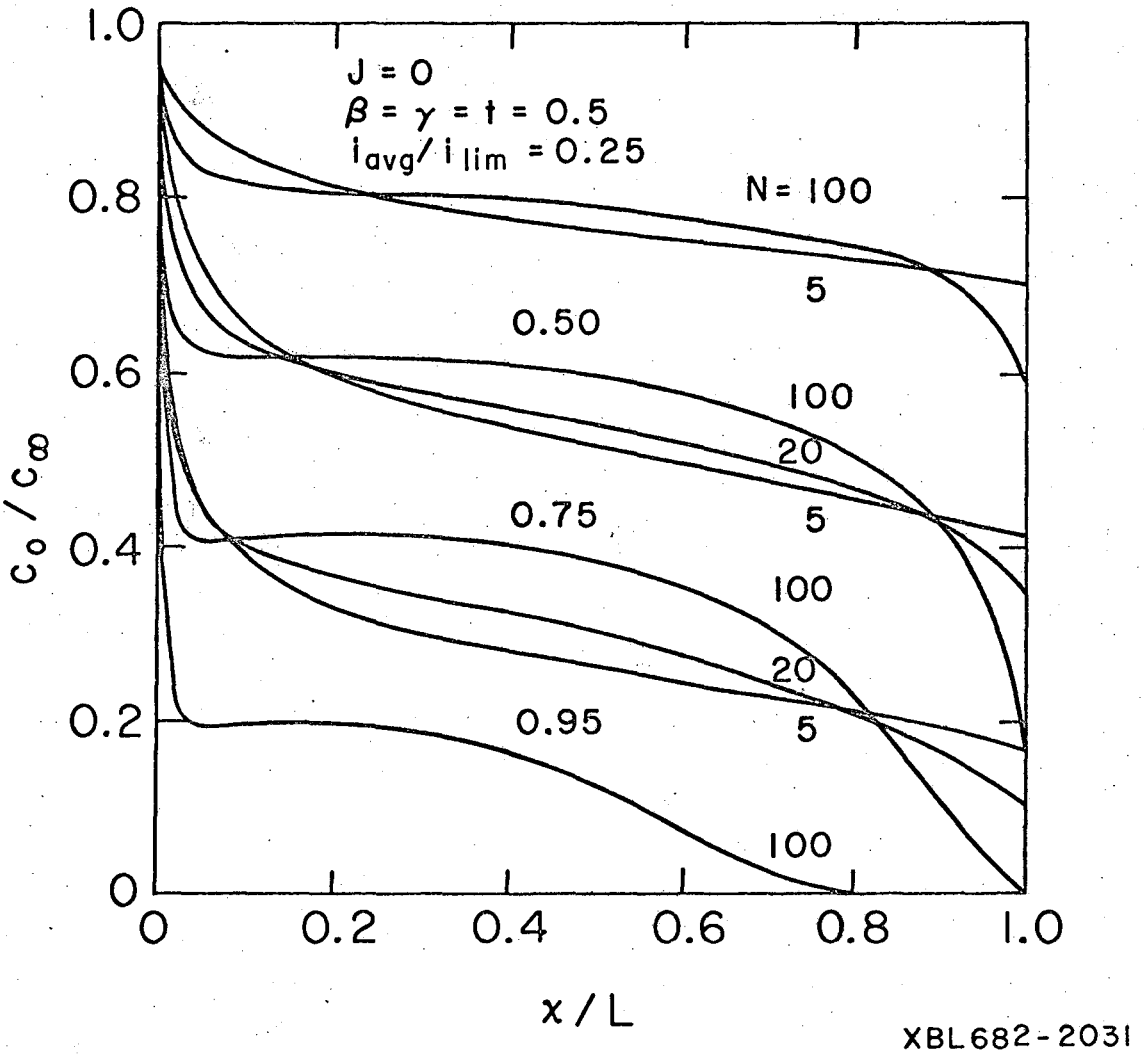
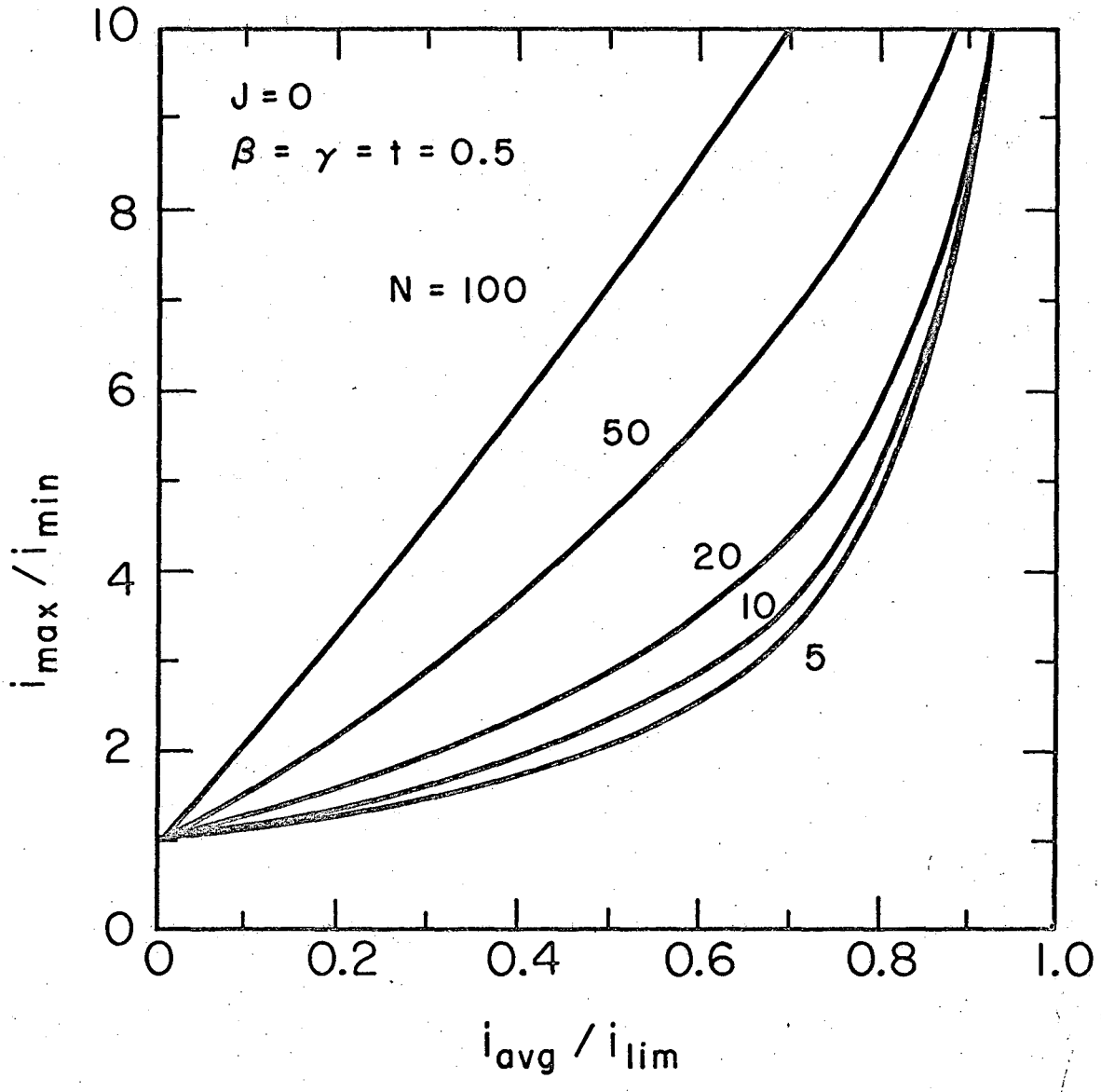


Figure 5. Surface concentration distribution for Tafel polarization near the limiting current.



XBL682-2032

Figure 6. Ratio of maximum to minimum current for Tafel polarization versus the fraction of the average limiting current.

Acknowledgment

This work was supported by the United States Atomic Energy Commission.

Nomenclature

b = $6\langle v\rangle/h$, velocity derivative at the wall of the channel, sec^{-1}

c_o - concentration at electrode surface, $mole/cm^3$

c_∞ - bulk concentration of reactant, $mole/cm^3$

D - diffusion coefficient of reactant or of binary electrolyte, cm^2/sec

F - Faraday's constant, 96,487 coul/equiv

h - height of channel, cm

i - normal current density at electrode surface, amp/cm^2

i_o - exchange current density, amp/cm^2

i_{avg} - average current density, amp/cm^2

i_{lim} - average limiting current density, amp/cm^2

J - dimensionless exchange current density [see equation 12]

L - length of electrode, cm

n - number of electrons produced when one reactant ion or molecule reacts

N - dimensionless limiting current [see equation 13]

R - universal gas constant, joule/mole-deg

t - transference number of reactant

T - absolute temperature, deg K

$\langle v\rangle$ - average velocity, cm/sec

V - potential of electrode, volt

x - distance along electrode, cm

y - normal distance from electrode, cm

z_i - charge number of species i

Z - see equation 11.

α, β, γ - parameters in kinetic expression [see equation 8]

$\Gamma(4/3) = 0.89298$, the gamma function of 4/3

δ - dimensionless average current density [see equation 14]

η_c - concentration overpotential, volt

η_s - surface overpotential, volt

κ_∞ - conductivity of bulk solution, $ohm^{-1}\text{-}cm^{-1}$

Φ - potential in bulk solution, volt

Φ_o - potential in bulk solution extrapolated to electrode surface, volt

References

1. John Newman. "Engineering Design of Electrochemical Systems." Ind. Eng. Chem., 60 (no.4), 12-27 (April, 1968).

2. John Newman. "The Effect of Migration in Laminar Diffusion Layers." Intern. J. Heat Mass Transfer, 10, 983-997 (1967).

3. John Newman. "Current Distribution on a Rotating Disk below the Limiting Current." J. Electrochem. Soc., 113, 1235-1241 (1966).

4. John Newman. "The Diffusion Layer on a Rotating Disk Electrode." J. Electrochem. Soc., 114, 239 (1967).

5. Carl Wagner. "Theoretical Analysis of the Current Density Distribution in Electrolytic Cells." J. Electrochem. Soc., 98, 116-128 (1951).

6. L. V. Kantorovich and V. I. Krylov. Approximate Methods of Higher Analysis. Translated by Curtis D. Benster. New York: Interscience Publishers, Inc., 1959.

7. Andreas Acrivos and Paul L. Chambré. "Laminar Boundary Layer Flows with Surface Reactions." Ind. Eng. Chem., 49, 1025-1029 (1957).

8. N. P. Gnusin, N. P. Poddubnyĭ, E. N. Rudenko, and A. G. Fomin. "Raspredelenie toka na katode v yide polosy v poluprostranstve elektrolita s polyarizatsionnoĭ krivoĭ vyrazhaemoĭ formuloĭ Tafelya." Elektrokhimiya, 1, 452-459 (1965).