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CURRENT DISTRIBUTION NEAR AN ELECTRODE EDGE AS a PRIMARY DISTRIBUTION IS APPROACHED

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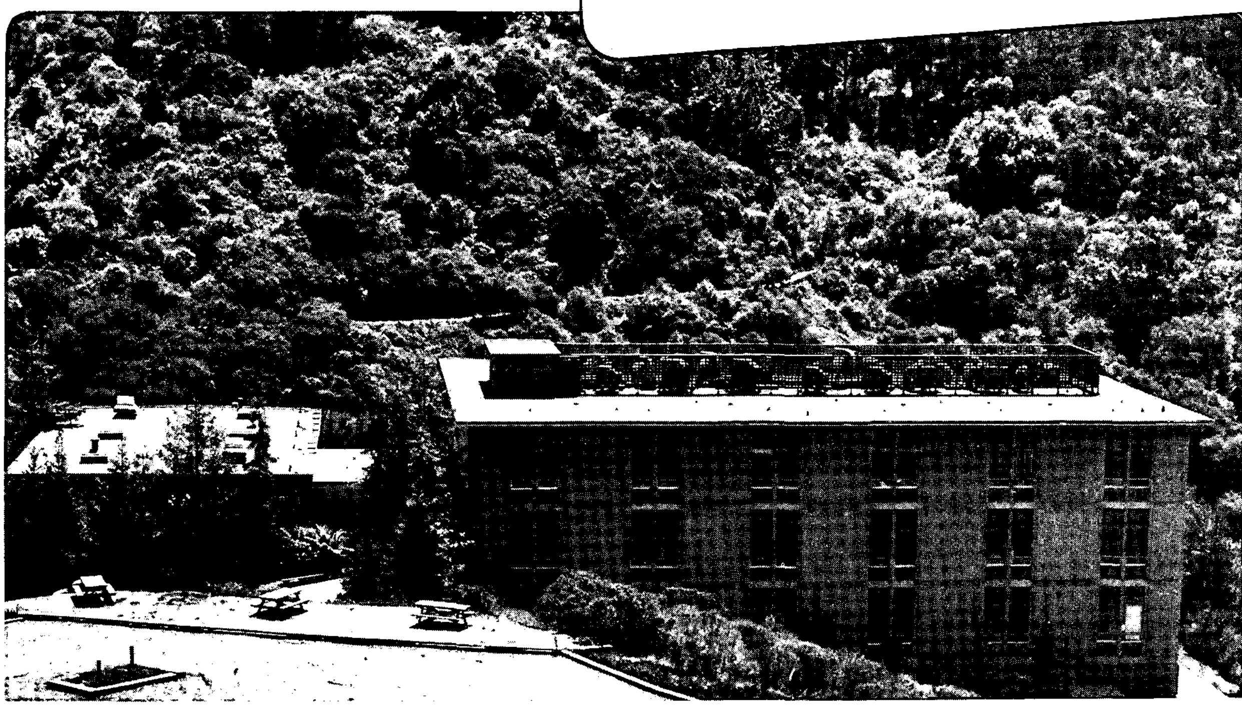

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Abstract

When ohmic resistances dominate over electrode kinetic resistances, the distribution of current density on an electrode can be highly nonuniform. In the limit of zero kinetic resistance (*i.e.*, a primary current distribution) the current density at the edge of an electrode will be infinite if the interior angle of intersection between the electrode and insulator is obtuse. In practical cases, nonzero kinetic resistances exist, and the current density remains finite.

Previous results demonstrate that, when the ohmic resistance is large compared to the kinetic resistance, the current distribution can be described by the primary distribution everywhere except the edge region. The purpose of this paper is to describe the deviations from the primary distribution and to show explicitly the manner in which the current density at the edge of the electrode approaches extreme values as the ohmic resistance becomes large.

Key words: current distribution, linear kinetics, Tafel kinetics, singular-perturbation analysis, boundary integral methods

The analysis is valid for any angle of intersection and can be applied in the edge region (for a large ohmic resistance) regardless of the geometric details of the rest of the electrochemical cell. Results are given for linear and Tafel kinetics.

Introduction

It is well known [1] that the primary current density is infinite at an edge of an electrode if the angle of intersection between the electrode and insulator is obtuse. Also, the primary current density at the edge is zero for an acute angle. In all practical cases, the kinetics of the interfacial reaction enter, and these extreme values do not occur.

The purpose of this paper is to demonstrate how the potential and current approach a primary distribution as the kinetic resistance becomes negligible (compared to the ohmic resistance). The analysis is valid in the edge region of an electrode and insulator, is a function of the angle, β, shown in figure 1, and is independent of the geometric details of the rest of the electrochemical cell. Results from this abstract geometry can be use to verify numerical investigations of actual geometries. Additionally, an *a priori* estimate of the behavior in an edge region can aid in the development of more efficient and more accurate numerical procedures.

Nişancioğlu and Newman [2] solved this problem for linear kinetics in the edge region of a disk electrode. Smyrl and Newman [3] extended the results for the linear kinetics case and gave results for Tafel kinetics. Their results are valid for an angle of $\beta = \pi$.

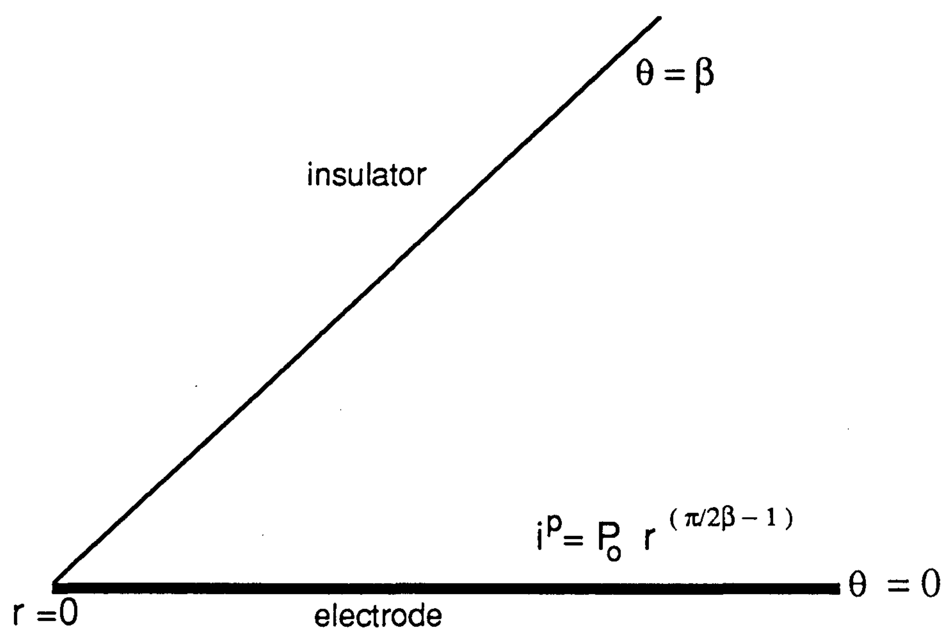

Figure 1. Primary current distribution in the *edge region* of an electrode and insulator.

In both of these papers, it was recognized that, for high ohmic resistances, the current distribution could be described adequately by the primary distribution away from the edge region but showed large deviations from this distribution near the edge. Stated another way, the resistance of the Faradaic reaction is important only in the edge region. They realized that this suggests that the problem is treated properly by a singular-perturbation analysis.

Primary Current Distribution

The primary current distribution in the edge region shown in figure 1 can be determined by Laplace's equation in cylindrical coordinates, which reduces to

$$\frac{1}{r}\frac{\partial}{\partial r}\left(r\frac{\partial \Phi}{\partial r}\right) + \frac{1}{r^2}\left(\frac{\partial^2 \Phi}{\partial \theta^2}\right) = 0. \tag{1}$$

The boundary conditions are

$$\frac{\partial \Phi}{\partial \theta} = 0 \quad \text{at} \quad \theta = \beta \tag{2}$$

and

$$\Phi = 0 \quad \text{at} \quad \theta = 0. \tag{3}$$

The solution (for small r) to equations (1) through (3) is

$$\Phi^P = -\frac{2\beta}{\pi\kappa} P_o \, r^{\pi/2\beta} \sin\left(\frac{\pi\theta}{2\beta}\right) , \tag{4}$$

where P_o relates to the magnitude of the primary current distribution:

$$i^P(r) = -\frac{\kappa}{r}\frac{\partial \Phi^P}{\partial \theta} = P_o \, r^{(\pi/2\beta - 1)} . \tag{5}$$

It is necessary to introduce P_o because equations (1) through (3) do not completely specify the solution, and the magnitude of the current can be changed by changing the cell potential. The placement of the counterelectrode and the geometric details of the working electrode in the region *away* from the corner region are not given. To do so would eliminate the possibility of a general analysis. In a region sufficiently close to the corner, the distribution of current density behaves in a manner independent of these details. In general, the details of the geometry away from the edge region are incorporated into P_o, which is determined through comparisons of equation (4) with the primary current distribution valid for the entire geometry. Smyrl and Newman [3] show that $P_o = i_{avg}\sqrt{r_o/8}$ for the rotating disk electrode. They also give P_o for the flow-channel geometry.

Linear Kinetics

For linear kinetics, the boundary condition along the working electrode becomes

$$-\frac{\kappa}{r}\frac{\partial\Phi}{\partial\theta} = \frac{(\alpha_a+\alpha_c)Fi_o}{RT}(V-\Phi_o) \ , \tag{6}$$

where V is the potential of the electrode and Φ_o is the potential of the solution adjacent to the electrode. For large values of the exchange current density, the current is given adequately by equation (5) for large (but not too large) values of r. Near the corner, though, kinetics is important, and the current deviates from the primary distribution. To emphasize this corner region, a stretched radial distance should be defined by

$$\bar{r} = rS_L = r\,\frac{(\alpha_a+\alpha_c)Fi_o}{RT\kappa} \ , \tag{7}$$

and a stretched potential by

$$\bar{\phi} = (\Phi - V)\,\frac{\kappa S_L^{\pi/2\beta}}{P_o} \quad . \tag{8}$$

The problem, in terms of these variables, is given by

$$\frac{1}{\bar{r}}\frac{\partial}{\partial \bar{r}}\left(\bar{r}\,\frac{\partial \bar{\phi}}{\partial \bar{r}}\right) + \frac{1}{\bar{r}^2}\left(\frac{\partial^2 \bar{\phi}}{\partial \theta^2}\right) = 0 \ , \tag{9}$$

with the boundary conditions,

$$\frac{\partial \bar{\phi}}{\partial \theta} = 0 \quad \text{at} \quad \theta = \beta \tag{10}$$

and

$$\frac{1}{\bar{r}}\frac{\partial \bar{\phi}}{\partial \theta} = \bar{\phi}_o \quad \text{at} \quad \theta = 0. \tag{11}$$

Finally, for large $\bar{r}$ (but small r) $\bar{\phi}$ must satisfy the condition that

$$\bar{\phi} \longrightarrow -\frac{2\beta}{\pi}\,\bar{r}^{\pi/2\beta}\,\sin\left(\frac{\pi\theta}{2\beta}\right) \quad \text{as} \quad \bar{r} \longrightarrow \infty \ . \tag{12}$$

($\bar{r} \longrightarrow \infty$ because S_L becomes large.)

It should be noted that V has effectively been set equal to zero in the matching condition given by equation (12). This is justified for obtuse angles because the primary current density (see equation (5)) decreases for large $\bar{r}$. Acute angles require the treatment outlined in the appendix.

Details of the numerical solution for $\bar{\phi}$ are given below. It should be recognized that the equations are free of parameters and that $\bar{\phi}$ is therefore independent of the stretching parameter S_L.

An important result of this section is that, for high exchange current densities, the current density in the corner region is given by

$$\frac{i(r)}{P_o} = - \left[\frac{(\alpha_a+\alpha_c)Fi_o}{RT\kappa}\right]^{(1-\pi/2\beta)} \bar{\phi}_o \ . \tag{13}$$

That the current density at the edge of the electrode approaches infinity as a power of a parameter involving the exchange current density should not be too surprising since previous experience [4] suggests that such a parameter dictates the distribution of current for linear kinetics.

Tafel Kinetics

For anodic Tafel kinetics, the boundary condition along the electrode is

$$- \frac{\kappa}{r} \frac{\partial \Phi}{\partial \theta} = i_o \exp\left[\frac{\alpha_a F}{RT} (V - \Phi_o)\right] \ . \tag{14}$$

The exchange current density is no longer a key variable in determining the distribution of current. Previous experience suggests that a dimensionless average current density is the important parameter. Since a characteristic length is missing from this problem, no such parameter can be defined. P_o, though, is analogous in that it specifies the magnitude of the current, and it may be expected to be important for the case of Tafel kinetics.

If P_o is large—so that the ohmic resistance is large and the analysis is valid—the current distribution far from the edge is given adequately by the primary distribution. To investigate the region where the primary distribution does not apply, the potential should be stretched as

$$\bar{\phi} = \frac{\alpha_a F}{RT} (\Phi - V) - \ln(S_T) + \ln\left[\frac{\alpha_a F i_o}{RT\kappa}\right], \tag{15}$$

and the radial distance by

$$\bar{r} = rS_T = r \left[\frac{\alpha_a F P_o}{RT\kappa}\right]^{2\beta/\pi} . \tag{16}$$

In terms of these variables, equations (9) and (10) apply, and the boundary condition along the electrode becomes

$$\frac{1}{\bar{r}} \frac{\partial\bar{\phi}}{\partial\theta} = - \exp(-\bar{\phi}_o) \quad \text{at} \quad \theta = 0. \tag{17}$$

For large $\bar{r}$, $\bar{\phi}$ must approach the asymptotic solution suggested by Smyrl and Newman [3]:†

$$\bar{\phi} \longrightarrow - \frac{2\beta}{\pi} \bar{r}^{\pi/2\beta} \sin\left(\frac{\pi\theta}{2\beta}\right) + \left(\frac{\pi}{2\beta} - 1\right) \ln(\bar{r}) \quad \text{as} \quad \bar{r} \longrightarrow \infty. \tag{18}$$

The numerical procedure used to solve for $\bar{\phi}$ is discussed in the next section. For large values of P_o, the current in the edge region is given by

$$\frac{i(r)}{P_o} = \left[\frac{\alpha_a F P_o}{RT\kappa}\right]^{(2\beta/\pi-1)} \exp(-\bar{\phi}_o) . \tag{19}$$

Just as for equation (13), it should be comforting that the parameter which is important for specifying the current density in the edge region is consistent with previous experience.

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† A complication which could arise in the analysis is that Tafel kinetics may no longer apply at distances at which the primary distribution is approached. The possibility of entering a linear kinetics regime before the primary distribution is approached was not investigated.

Numerical Analysis

Since, in two dimensions, currents can not flow to infinity without an infinite potential drop, it is necessary to calculate deviations from the primary potential distribution. A new potential, ψ, is defined as

$$\psi = \overline{\phi} - \overline{\phi}^{P} \quad , \tag{20}$$

where $\overline{\phi}^{P}$ is given by equation (12). To facilitate the solution for ψ, the geometry of figure 1 can be mapped conformally so that the insulator and electrode are coplanar. The coordinates of this new geometry are related to the original coordinates through

$$x = \overline{r}^{\pi/\beta} \quad \text{and} \quad \Theta = \frac{\theta\pi}{\beta} \ . \tag{21}$$

In terms of these new variables, the problem can be stated as

$$\frac{1}{x}\frac{\partial}{\partial x}\left(x\frac{\partial\psi}{\partial x}\right) + \frac{1}{x^2}\left(\frac{\partial^2\psi}{\partial\Theta^2}\right) = 0 \ , \tag{22}$$

with the boundary conditions:

$$\frac{\partial\psi}{\partial\Theta} = 0 \quad \text{at} \quad \Theta = \pi \tag{23}$$

and

$$\frac{1}{x}\frac{\partial\psi}{\partial\Theta} = \frac{\beta}{\pi}\left(f(\psi_o)\ x^{(\beta/\pi - 1)} + x^{-1/2}\right) \quad \text{at} \quad \Theta = 0 \ . \tag{24}$$

For linear kinetics, $f(\psi_o) = \psi_o$, and for Tafel kinetics, $f(\psi_o) = -\exp(-\psi_o)$.

Boundary integral methods are often used for solving Laplace's equation [5]. For this problem, the equation describing the potential of the solution adjacent to the electrode is

$$\psi_o(x_q) = \frac{\beta}{2\pi^2} \int_0^\infty \ln(x-x_q)^2 \left[f(\psi_o)\ x^{(\beta/\pi-1)} + x^{-1/2}\right] dx. \tag{25}$$

For linear kinetics and $\beta \le \pi/2$, the integrand does not approach zero quickly enough for the integral to converge. The appendix demonstrates the modification to the solution procedure necessary to obtain convergence.

A finite-difference approximation to this equation was solved with an iterative procedure. An upper limit of integration, x_{max}, was chosen to set a finite domain of integration. The contribution of the integral for $x > x_{max}$ was assumed to be negligible, which is consistent with requiring that the primary current distribution be approached at x_{max}.

The accuracy of this procedure was verified by increasing x_{max} until the value of the current at the corner changed by some small amount. A procedure of node-point doubling was also used. The results for the case of $\beta = \pi$ were compared with the results from references (2) and (3). Finally, an integral constraint can be used to check the accuracy of the answer. This arises from the asymptotic behavior expressed in equations (12) and (18) and takes the form, for linear kinetics (obtuse angles),

$$0 = \int_0^\infty \left[\psi_o x^{(\beta/\pi-1)} + x^{-1/2}\right] dx\ , \tag{26}$$

and, for Tafel kinetics,

$$\pi \left[1 - \frac{\pi}{2\beta}\right] = \int_0^\infty \left[x^{-1/2} - \exp(-\psi_o) x^{(\beta/\pi-1)}\right] dx. \tag{27}$$

The reported values are estimated to be accurate within 0.5 percent.

Results and Discussion

Results for linear kinetics are shown in figures 2 and 3. It is important to recall that these figures with equation (13) should give a good estimate of the current density in the corner region only for large values of $(\alpha_a+\alpha_c)Fi_o/RT\kappa$. Figure 4 shows results for Tafel kinetics. It can be used with equation (19) to predict current distributions near corner regions for high values of $\alpha_a FP_o/RT\kappa$.

Our experience has shown (and this analysis suggests) that numerical difficulties can arise when ohmic resistances begin to dominate. In other words, the results of this paper begin to become applicable when other numerical analyses begin to become suspect. A practical use, then, of these results could be as a tool for the verification of other results. One test which could be made for linear kinetics is to determine whether

$$\frac{i_{edge}}{P_o} = A_L(\beta) \left[\frac{(\alpha_a+\alpha_c)Fi_o}{RT\kappa}\right]^{(1-\pi/2\beta)} \tag{28}$$

as the right side of the equation goes to infinity. The test for Tafel kinetics is whether

$$\frac{i_{edge}}{P_o} = A_T(\beta) \left[\frac{\alpha_a FP_o}{RT\kappa}\right]^{(2\beta/\pi-1)} \tag{29}$$

as the right side of the equation goes to infinity. Smyrl and Newman [3] have demonstrated such tests for the case of $\beta = \pi$. The coefficients, $A_L(\beta)$ and $A_T(\beta)$, are shown in figure 5. As is indicated in the appendix, the value of A_L is 6.0 for an angle of $\beta = \pi/8$.

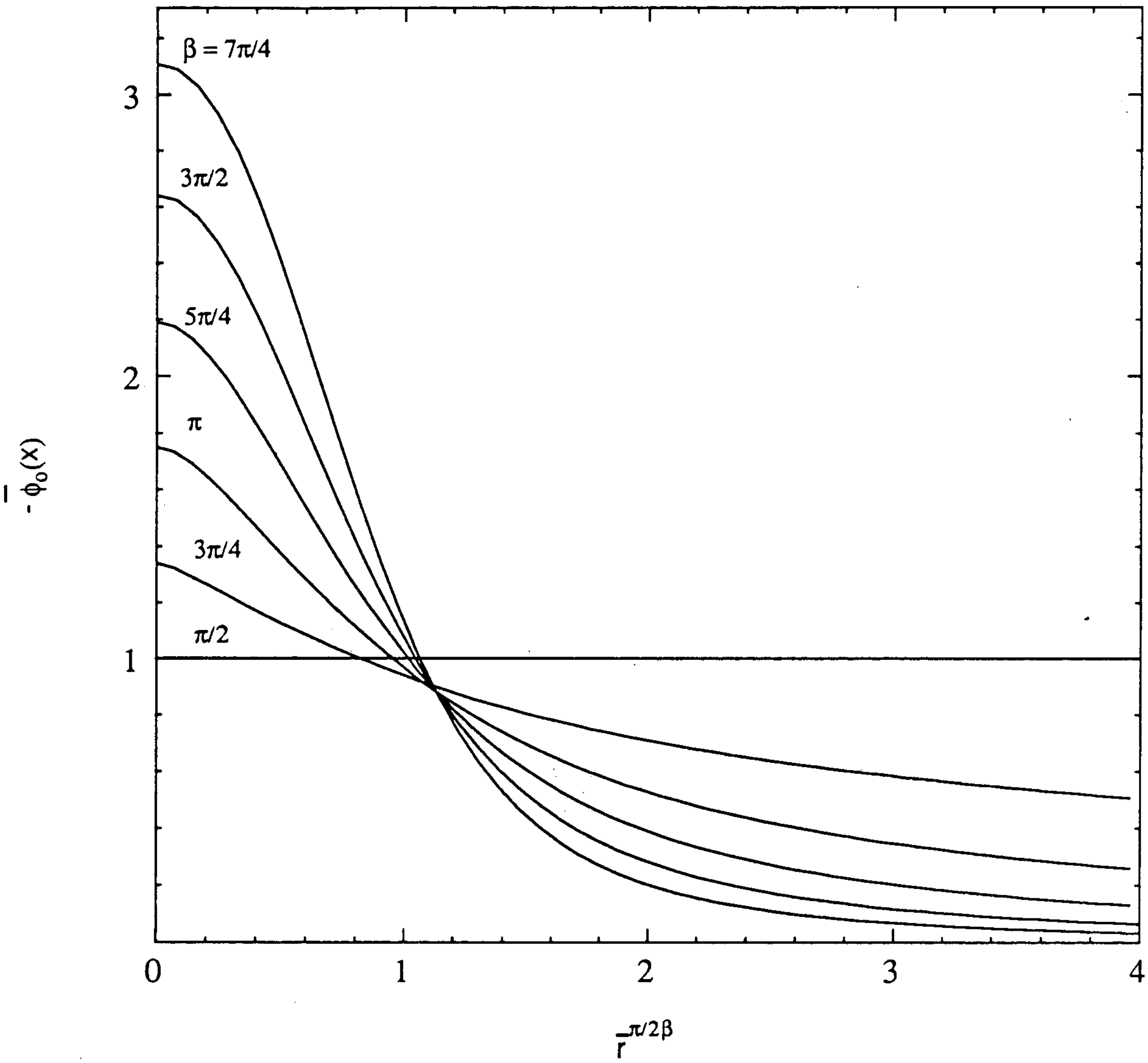

Figure 2. Current distribution for linear kinetics (obtuse angles).

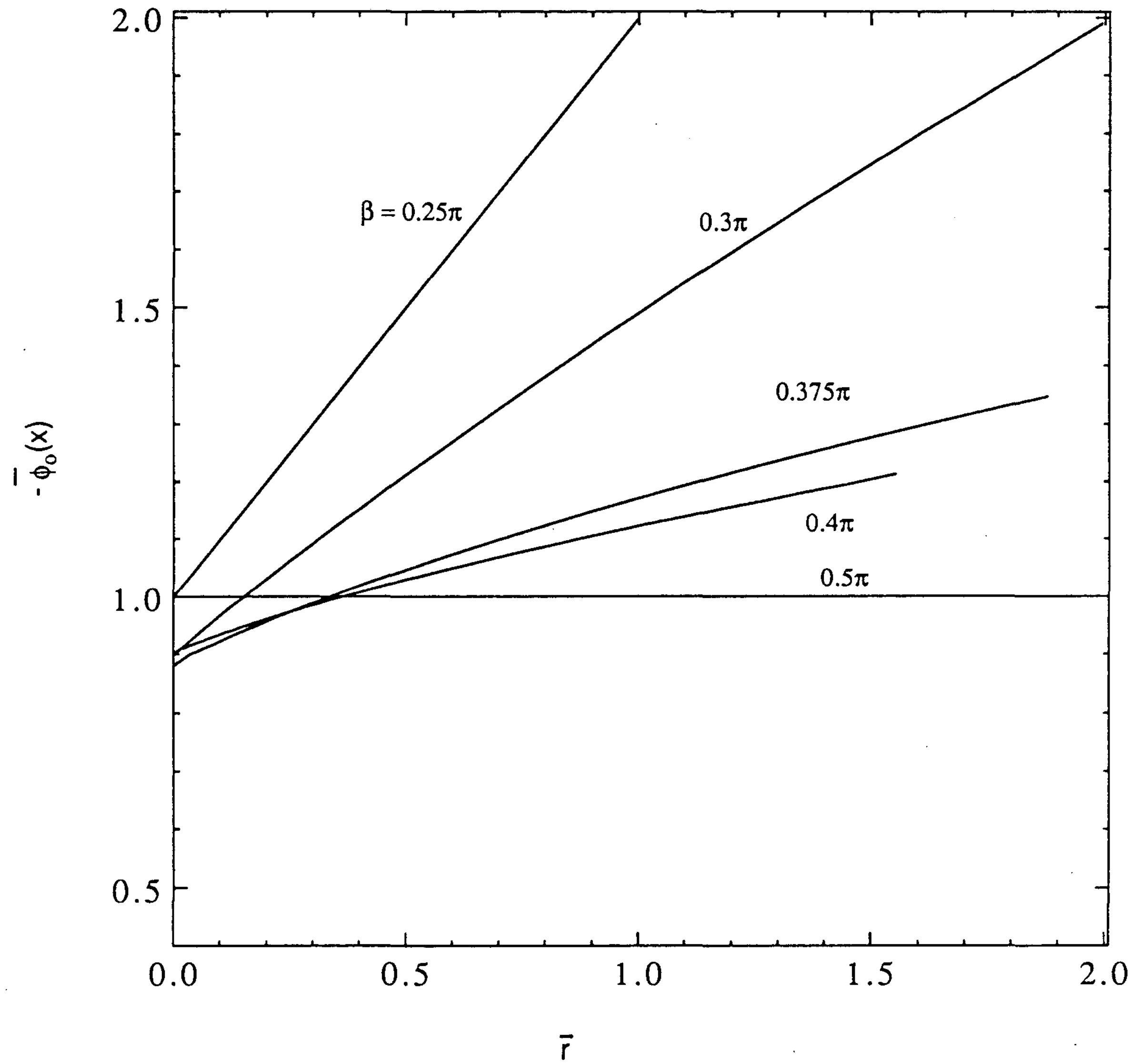

Figure 3. Current distribution for linear kinetics (acute angles).

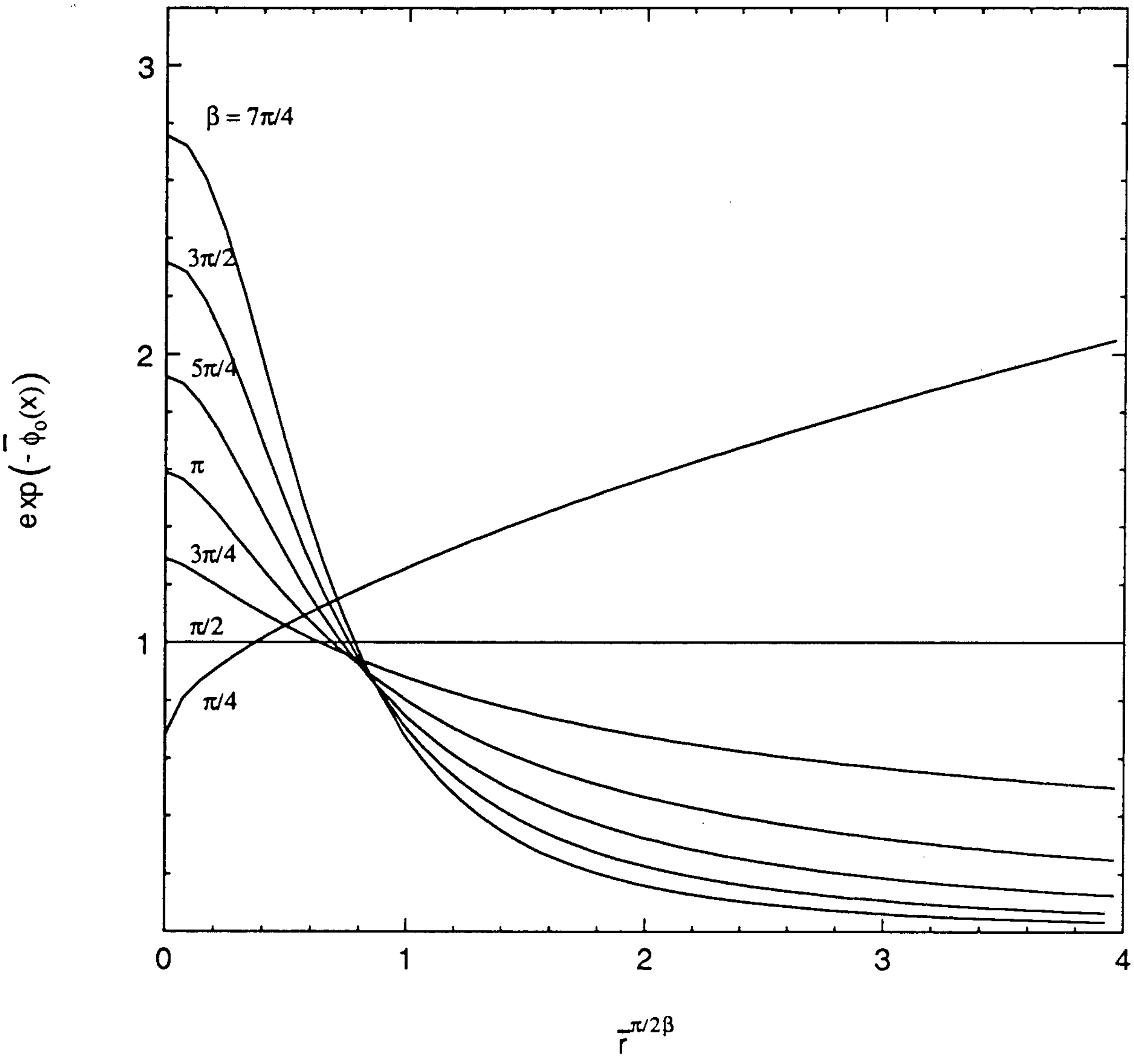

Figure 4. Current distribution for Tafel kinetics.

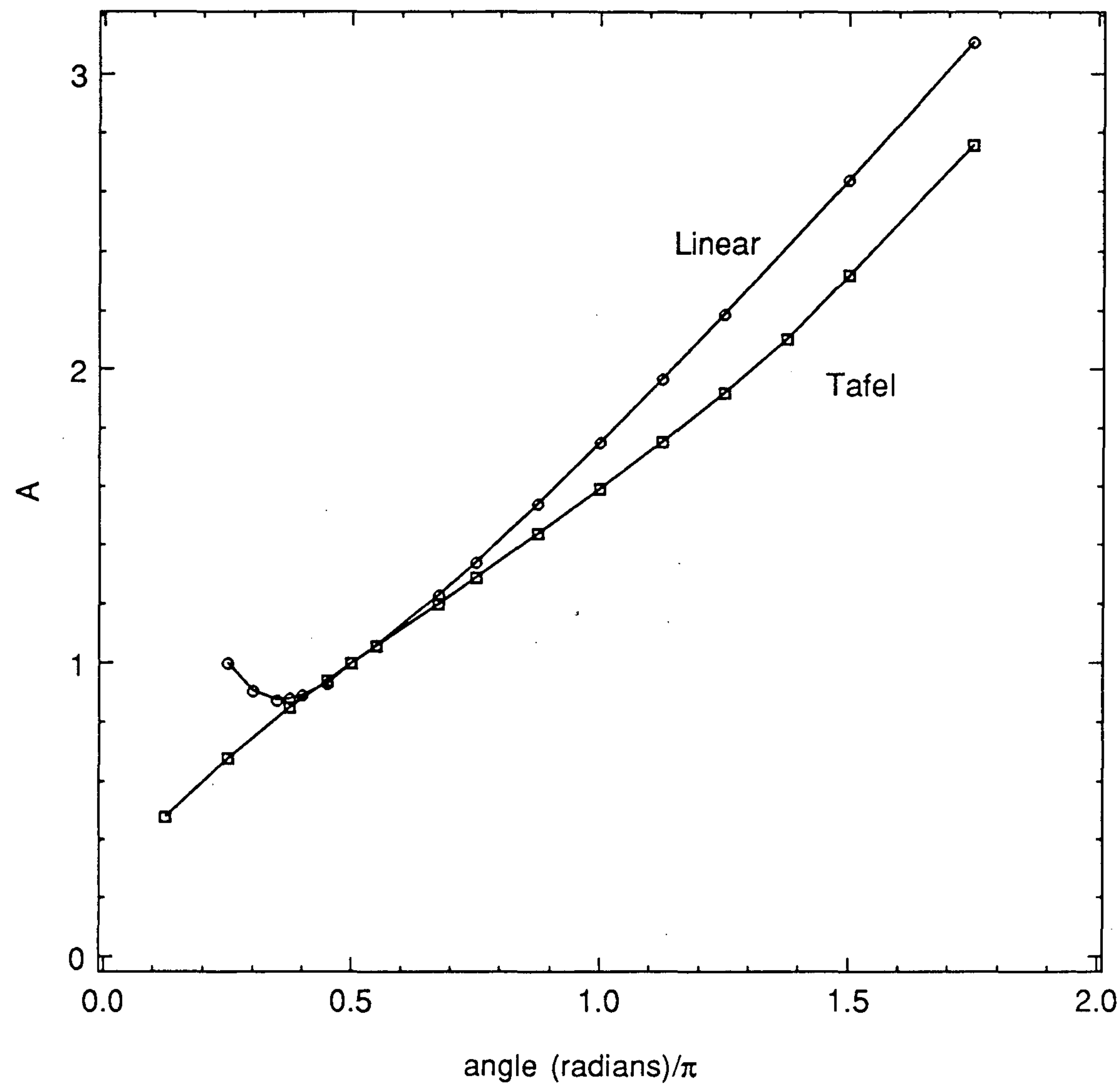

Figure 5. Dimensionless coefficient which specifies the value of the stretched current density at the edge. See equations (28) and (29).

By solving the *primary* current distribution for an actual cell, it is possible to relate P_o to measureable electrochemical and geometric variables. It might, though, not be desired to take the time to determine the exact relation between P_o and these other variables. As a quick check, one might recall that P_o is proportional to i_{avg} and determine whether the proper relationship, suggested by equations (28) and (29), is followed.

The analysis can also be used to establish the proper mesh-spacing for an accurate and efficient finite-difference procedure. For linear kinetics, the region where the primary distribution does *not* apply is of the order $\left(\frac{(\alpha_a+\alpha_c)Fi_o}{RT\kappa}\right)^{-1}$. For Tafel kinetics, the region where the kinetic resistance is important is of the order $\left(\frac{\alpha_a FP_o}{RT\kappa}\right)^{-2\beta/\pi}$.

Conclusions

A singular-perturbation analysis has shown explicitly the manner in which the current density near an electrode edge approaches extreme values as the primary current distribution is approached. The results are consistent with previous analyses of a coplanar electrode and insulator and also with the special case of $\beta = \pi/2$.

Appendix

For linear kinetics, the solution to equations (9) through (12) might be approximated by

$$\bar{\phi} = \sum_{i=0} A_i \bar{r}^{n_i} \cos\left[n_i(\beta - \theta)\right], \qquad (30)$$

where n_i and A_i are determined through the boundary conditions and the matching condition. This series diverges except for certain angles, β, where it terminates. Three angles which terminate are $\beta = \pi/2$, $\beta = \pi/4$, and $\beta = \pi/8$. For these angles, the potential of the solution adjacent to the electrode edge is given by

$$\bar{\phi}_o = -1 \quad (\beta = \pi/2), \tag{31}$$

$$\bar{\phi}_o = -1 - \bar{r} \quad (\beta = \pi/4), \tag{32}$$

and

$$\bar{\phi}_o = -6 - 14.4852\bar{r} - 7.2464\bar{r}^{\,2} - \bar{r}^{\,3} \quad (\beta = \pi/8). \tag{33}$$

As $\bar{r} \longrightarrow \infty$, the difference between the actual stretched current and the stretched primary current (in terms of x) is of the order given by

$$\psi_o x^{(\beta/\pi-1)} + x^{-1/2} \propto x^{-(1/2+\beta/\pi)}. \tag{34}$$

For angles, β, less than $\pi/2$, the integral equation (25) is unbounded since the first neglected term is of order greater than x^{-1}.

Stated another way, for linear kinetics and acute angles, the first neglected term in the matching condition is sufficiently large along the electrode surface that the integral does not converge. For $\pi/4 < \beta \leq \pi/2$, equations (30) and (34) suggest that an equation which calculates the deviations of the current density from the first *two* terms of the series will converge. A potential defined in this manner is

$$\psi' = \bar{\phi} + \frac{2\beta}{\pi}\,\bar{r}^{\pi/2\beta}\cos\left[\frac{\pi}{2\beta}(\beta - \theta)\right] - A_1\bar{r}^{(\pi/2\beta-1)}\cos\left[\left(\frac{\pi}{2\beta} - 1\right)(\beta - \theta)\right]. \tag{35}$$

A_1 is determined by applying the matching and boundary conditions:

$$A_1 = \frac{-1}{\sin(\beta)}. \tag{36}$$

The integral equation which gives ψ' is

$$\psi_o' = \frac{\beta}{2\pi^2} \int_0^\infty \ln(x-x_q)^2 \left\{\psi_o' x^{(\beta/\pi-1)} - A' x^{(-1/2-\beta/\pi)}\right\} dx, \tag{37}$$

where

$$A' = \left(\frac{\pi}{2\beta} - 1\right) \frac{-1}{\tan(\beta)} . \tag{38}$$

The matching condition used numerically for ψ_o' is given by the next term of the series:

$$\psi_o' \longrightarrow A_2 \bar{r}^{(\pi/2\beta-2)} \cos\left(\frac{\pi}{2} - 2\beta\right) \text{ as } \bar{r} \longrightarrow \infty. \tag{39}$$

For example, for $\beta = 3\pi/8$, the potential at the electrode surface is

$$\bar{\phi}_o = -\bar{r}^{\,1/3} - 0.13807\bar{r}^{\,-2/3} + \ldots \tag{40}$$

For $\beta \le \pi/4$, additional terms need to be subtracted from ψ'. The number of additional terms is given by equation (30), the solution for $\bar{\phi}$ as $\bar{r} \longrightarrow \infty$.

To obtain results for $\beta \le \pi/2$, this appendix is necessary. It can also be used with obtuse angles because it shows how asymptotic corrections can be used to relax the assumption that the integrand in equation (25) is zero for $x > x_{max}$. This reduces the value of x_{max} needed to obtain accurate results.

Appendix B of Smyrl and Newman [3] can be used to show that, for Tafel kinetics, the difference between the current density and the primary current density is sufficiently small that the integral equation (25) converges for acute, as well as obtuse, angles.

Acknowledgements

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List of Symbols

A_L, A_T	dimensionless coefficients given in figure 5
F	Faraday's constant, 96487 C/equiv
i	current density, A/cm^2
i_{avg}	average current density, A/cm^2
i_{edge}	current density at the electrode/insulator edge, A/cm^2
i_o	exchange current density, A/cm^2
P_o	parameter defined in equation (5), A/cm$^{(1+\pi/2\beta)}$
R	universal gas constant, 8.3143 J/mol-K
r	radial distance variable, cm
$\bar{r}$	stretched, dimensionless radial distance variable, defined by equation (7) or (16)
S_L	stretching variable for linear kinetics, cm^{-1}
S_T	stretching variable for Tafel kinetics, cm^{-1}
T	absolute temperature, K
x, x_q	dimensionless position in transformed coordinate system
V	electrode potential, V
α_a, α_c	transfer coefficients
β	angle defined in figure 1, radians

θ	angular coordinate in cylindrical coordinates
Θ	angular coordinate of transformed geometry
π	3.141592654
κ	specific conductivity, $ohm^{-1}cm^{-1}$
Φ	potential, V
Φ^p	primary potential, V
$\bar{\phi}$	stretched, dimensionless potential
ψ	dimensionless potential defined by equation (20)
ψ'	dimensionless potential defined by equation (35)

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