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A.C. West and J. Newman

December 1987

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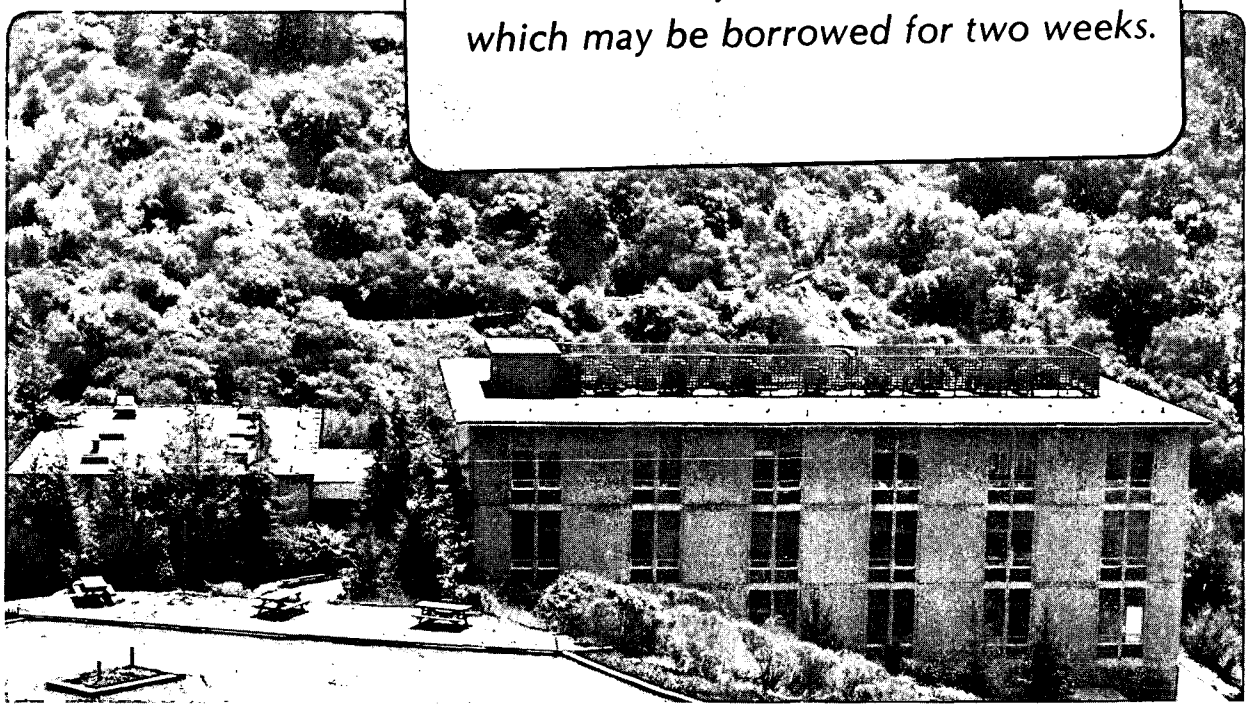

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Corrections to Kinetic Measurements Taken on a Disk Electrode

Alan C. West and John Newman

Materials and Chemical Sciences Division, Lawrence Berkeley Laboratory,
and Department of Chemical Engineering, University of California,
Berkeley, California 94720

December 10, 1987

Abstract

Below the limiting current, the rotating disk electrode has a nonuniform current distribution. When the nonuniformities are not explicitly accounted for, errors in values of kinetic parameters determined through measurements on a disk can result. In this analysis, valid for Tafel kinetics, correction factors are obtained as a function of the dimensionless average current density. It is assumed that ohmic corrections are made by the interruption of current. The results indicate that, under certain conditions, the errors are negligible and that the disk geometry, despite its nonuniformities, is adequate for the investigation of systems characterized by Tafel kinetics.

Key words: Tafel kinetics, current distribution

Introduction

Newman [1], [2] has suggested that a nonuniform ohmic-potential drop to an electrode can lead to errors in the determination of kinetic parameters. A subsequent paper [3] showed that for linear kinetics the error in the measured exchange current density, i_o, can be as great as 300 percent, depending on the reference electrode placement and the dimensionless exchange current density, J, defined by Newman [4]. This analysis considers the errors in kinetic parameters determined on the disk for the Tafel region. The apparent surface overpotential is taken to be that measured by a reference electrode of the same kind, with the ohmic-potential drop being determined by the interruption of the current. In the Tafel region, J is no longer an important parameter in determining the distribution of current density and potential in the solution. Instead, the relevant parameter is a dimensionless average current density, δ, defined by

$$\delta = \frac{\alpha_a F r_o i_{avg}}{RT\kappa}. \tag{1}$$

This analysis presents the error in the measured exchange current density as a function of δ and three reference electrode placements.

Analysis

The potential in solution, outside the double layer, in the absence of concentration variations, is given by Laplace's equation,

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

with boundary conditions,

$$\frac{\partial \Phi}{\partial z} = 0 \text{ for } r > r_o \text{ and } z = 0 \tag{3}$$

$$\Phi = 0 \text{ as } r^2 + z^2 \longrightarrow \infty$$

and

$$i(r) = f(\eta_s) \text{ for } r < r_o \text{ and } z = 0.$$

η_s is the local surface overpotential given by

$$\eta_s = V - \Phi(r,0), \tag{4}$$

where V is the potential of the electrode and $\Phi(r,0)$ is the potential of the solution just outside the diffuse double layer measured with a reference electrode of the same kind as the working electrode. In the Tafel region, the boundary condition describing the electrode kinetics for anodic currents is

$$i(r) = i_o \exp\left(\frac{\alpha_a F \eta_s}{RT}\right). \tag{5}$$

Without the sectioning of an electrode, local current densities and overpotentials cannot be measured. Common practice, then, is to relate the average current density to the apparent surface overpotential, given by [5]

$$\eta_{s,app} = V - \Phi(r,z) - \bar{\Phi}(r,0) + \bar{\Phi}(r,z). \tag{6}$$

$\Phi(r,z)$ is the potential of the reference electrode, and $\bar{\Phi}(r,z) - \bar{\Phi}(r,0)$ represents the potential change observed upon interruption of the current and corresponds to the ohmic drop associated with the primary distribution of the same average current density [5].

To interpret a polarization curve obtained with a disk electrode, equation (5) may be more appropriately written as

$$i_{avg} = i_{o,app} \exp\left(\frac{\alpha_{a,app} F \eta_{s,app}}{RT}\right). \tag{7}$$

Two defined parameters, $i_{o,app}$ and $\alpha_{a,app}$, are involved in this equation, and there are at least two possibilities for determining them from the experimental data. One is to take $\alpha_{a,app}F/RT$ to be the slope of the line tangent to the Tafel plot of the data and $i_{o,app}$ to be an intercept obtained when this tangent line is extrapolated to $\eta_{s,app} = 0$. Then $i_{o,app}$ and $\alpha_{a,app}$ would be, in general, functions of δ, since the data will not yield exactly a straight line on a semi-logarithmic plot. Another approach is to assume that α_a is known and that its value is used for $\alpha_{a,app}$. A line of slope $\alpha_a F/RT$ is extrapolated through the data to obtain $i_{o,app}$. Again, the value obtained depends on the position along the Tafel plot through which the line is extrapolated.

Figure (1) shows a simulated plot of i_{avg} *vs.* $\eta_{s,app}$ for three reference electrode placements. For values of $\ln(\delta) < -1$, $\alpha_a \approx \alpha_{a,app}$. Additionally, for $\ln(\delta) > 3$ and for a reference electrode placed at the center of the disk or at infinity, $\alpha_a \approx \alpha_{a,app}$. For a reference electrode placed adjacent to the edge of the disk, $\alpha_{a,app} = \alpha_a/2$ as $\delta \rightarrow \infty$. For values of $\ln(\delta) > 4$, $\eta_{s,app}$ should be determined by the asymptotic solution shown with the dashed line. The deviation of the solid and dashed lines shows the difficulty in calculating potentials at the edge of the disk for high values of δ. Only for intermediate values of δ will $\alpha_a \neq \alpha_{a,app}$; therefore, it is reasonable to assume that one typically has a good estimate of α_a. The following analysis will develop the equations for the more general case but will emphasize the results for the case of $\alpha_a = \alpha_{a,app}$.

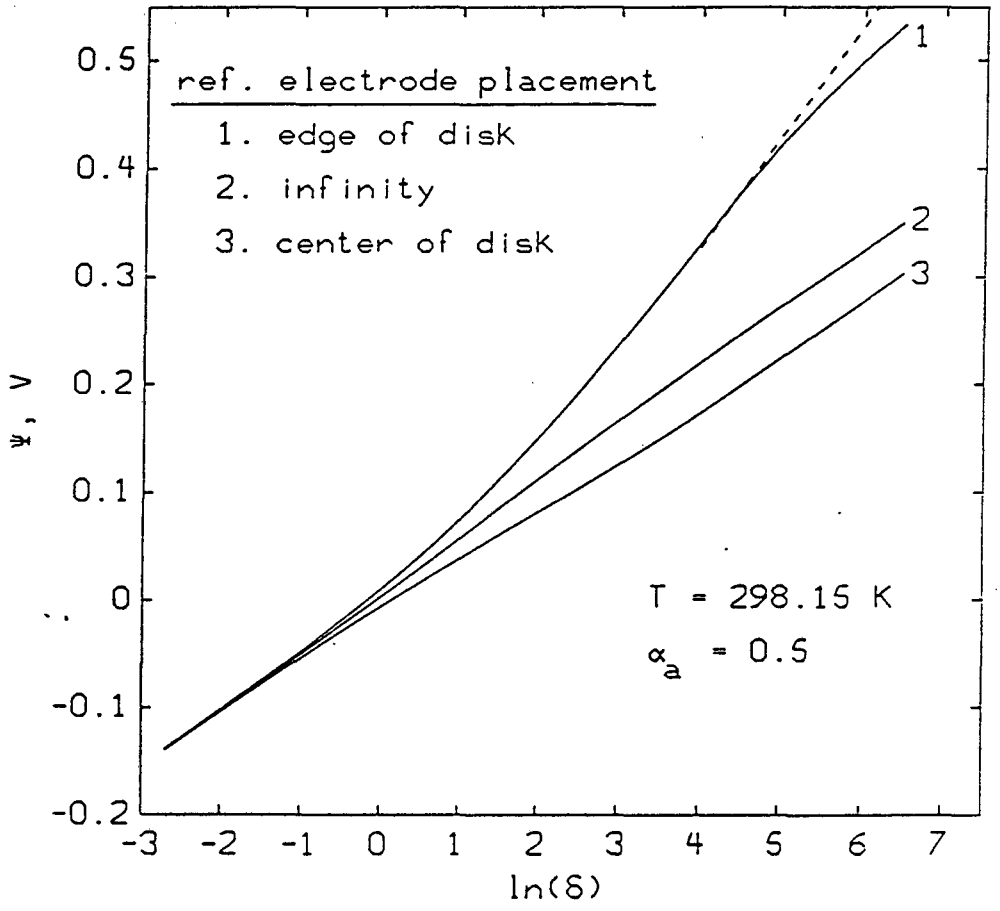

Figure 1. Average current density vs. Ψ, where

$$\Psi = \eta_{s,app} + \frac{RT}{\alpha_a F} \ln\left(\frac{i_o \alpha_a F r_o}{RT\kappa}\right)$$

To develop the relationships between the apparent parameters and the true parameters, it is covenient to introduce a new variable,

$$A = \frac{\alpha_a F r_o i_o}{RT\kappa} \exp\left(\frac{\alpha_a FV}{RT}\right). \tag{8}$$

As is suggested in the appendix, A is a function only of δ. The relationship defined by equation (8) can be used to determine the disk potential necessary for a given average current. Originally, A was calculated by a boundary integral method developed in this laboratory for axisymmetric problems. The method, as written, can not be used for high values of δ, since, as δ becomes large, the problem of the secondary current distribution becomes singular. Smyrl and Newman [6] give a parameter, E, valid for all δ, which can be related to A through

$$A = \frac{E}{2}\,\delta\,\exp\left(\frac{\pi\delta}{4}\right). \tag{9}$$

E is shown in figure (2) and can be used to obtain A for any δ.

The ratio of the actual exchange current density to the apparent exchange current density as a function of δ can be found by combining equations (5), (7), and (8):

$$i_o/i_{o,app} = \frac{A}{\delta}\exp\left(\frac{-\alpha_a FV}{RT}\right)\exp\left(\frac{\alpha_{a,app} F\eta_{s,app}}{RT}\right). \tag{10}$$

The ohmic drop between a disk with a primary current distribution and a reference electrode at infinity is given by

$$\bar{\Phi}(r,z) - \bar{\Phi}(r,0) = -\frac{\pi\delta RT}{4\alpha_a F}. \tag{11}$$

Therefore, for a reference electrode at infinity, equation (10) becomes

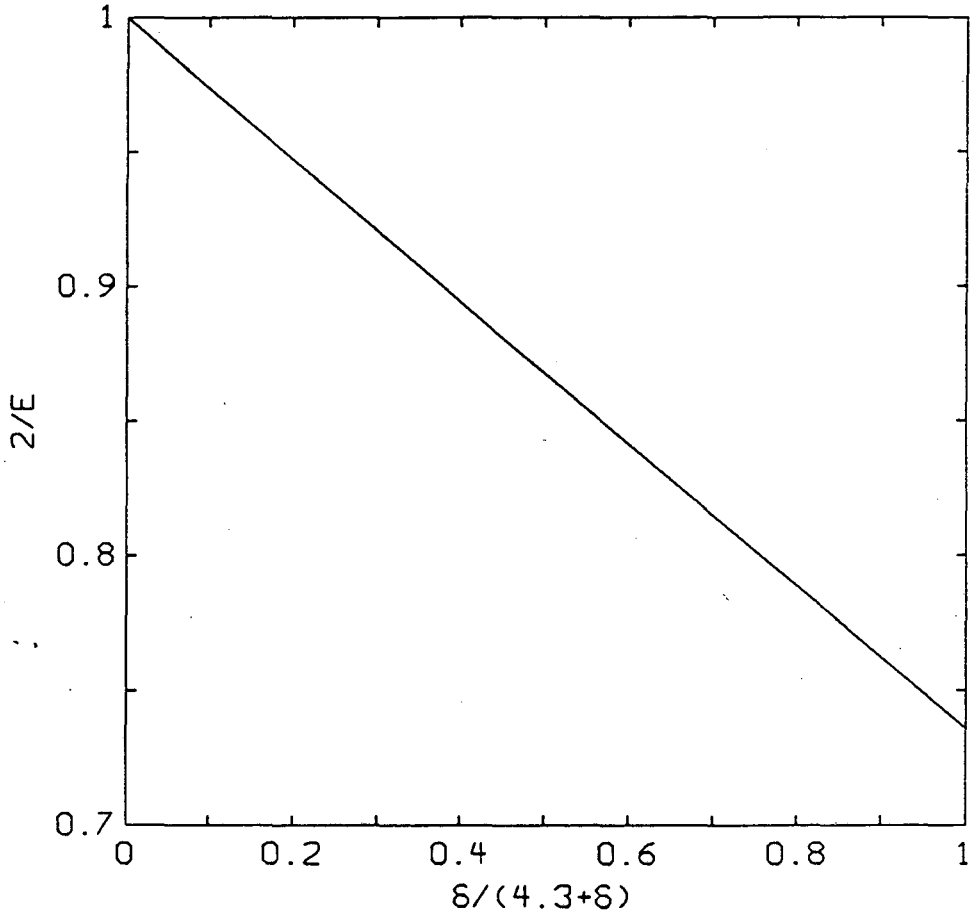

Figure 2. E vs. δ (Adopted from Smyrl and Newman [6]). As $\delta \longrightarrow \infty$, E $\longrightarrow$ e, the base of the natural logarithm.

$$i_o/i_{o,app} = \frac{A}{\delta} \exp\left[\frac{\alpha_a FV}{RT}\left[\frac{\alpha_{a,app}}{\alpha_a} - 1\right]\right] \exp\left[\frac{-\pi\delta\alpha_{a,app}}{4\alpha_a}\right]. \tag{12}$$

With the reference electrode placed adjacent to the surface,

$$i_o/i_{o,app} = \frac{A}{\delta} \exp\left[\frac{\alpha_a FV}{RT}\left[\frac{\alpha_{a,app}}{\alpha_a} - 1\right]\right] \exp\left[\frac{-\alpha_{a,app}F}{RT}\,\Phi(r,0)\right]. \tag{13}$$

The potential of the solution at the interface, $\Phi(r,0)$, is given by Smyrl and Newman[6] and is shown in figure (3) as a function of δ for $r = 0$ and $r = r_o$.

When $\alpha_a = \alpha_{a,app}$, equation (12) reduces to

$$i_o/i_{o,app} = \frac{E}{2}, \tag{14}$$

and equation (13) reduces to

$$i_o/i_{o,app} = \frac{E}{2} \exp\left[\frac{\pi\delta}{4} - \frac{\alpha_a F}{RT}\,\Phi(r,0)\right]. \tag{15}$$

Equations (14) and (15), the latter for $r = 0$ and $r = r_o$, are shown in figure (4). Smyrl and Newman [6] imply that, as $\delta \longrightarrow \infty$, $i_o/i_{o,app}$ goes to 0.5 for a reference electrode at the center of the disk, infinity for a reference electrode at the edge of the disk, and e/2 for a reference electrode at infinity, where e is the base of the natural logarithm.

Figure (1) shows that, for intermediate values of δ, α_a may not equal $\alpha_{a,app}$. In the rare case that experimental data exist only in this intermediate range, α_a, if determined by differentiation of exact data, would be given by

$$\alpha_a/\alpha_{a,app} = 1 + \frac{d\ln E}{d\ln\delta} + \frac{d\ln g(\delta)}{d\ln\delta}, \tag{16}$$

where $g(\delta)$ is one for a reference electrode at infinity and $\exp(\pi\delta/4 - \alpha_a F\Phi(r,0)/RT)$ for a reference electrode adjacent to the surface. The second term on the right side of equation (16) is shown in

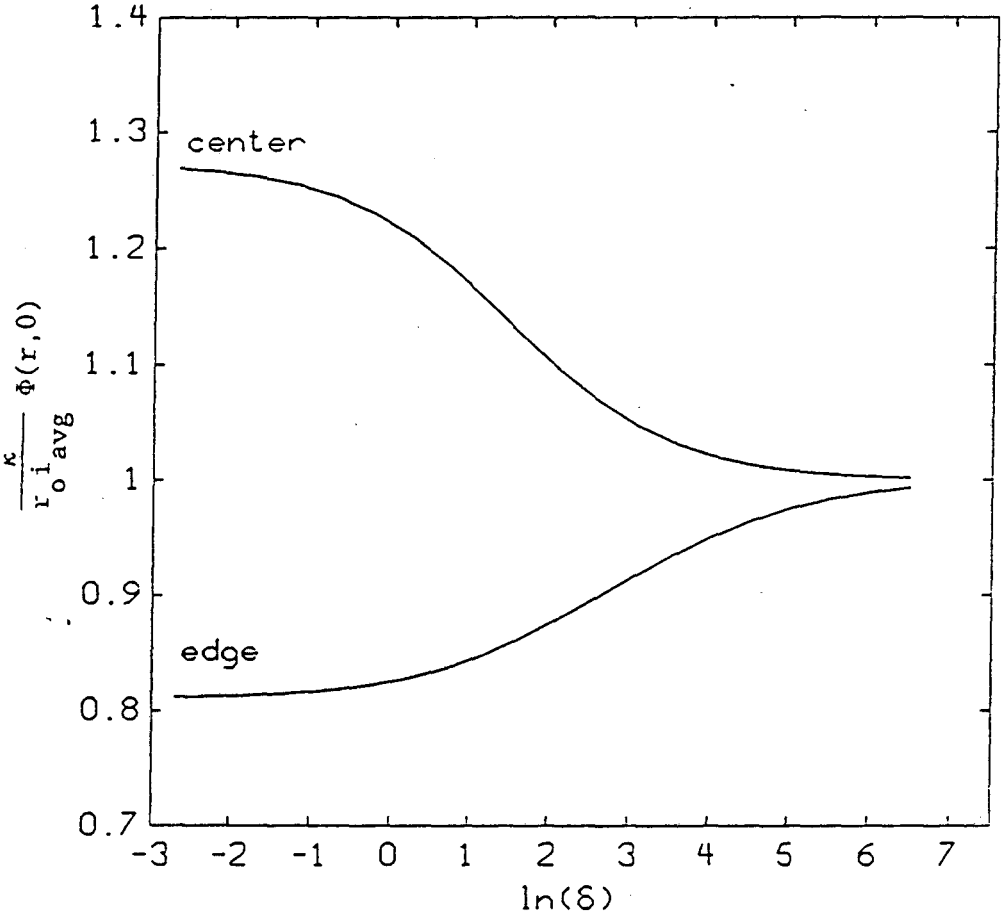

Figure 3. Dimensionless potential at the center and edge of the disk.

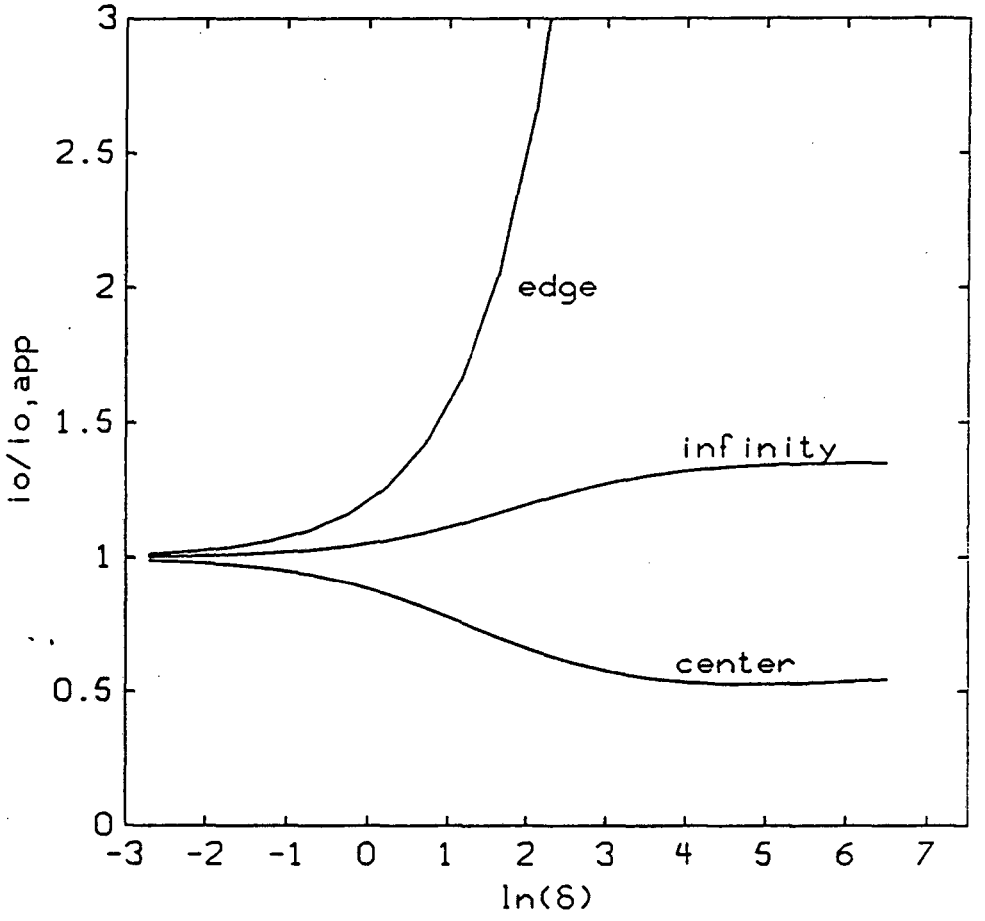

Figure 4. Correction to the exchange current density for three reference electrode placements, assuming $\alpha_a = \alpha_{a,app}$.

figure (5). The last term is shown in figure (6) for a reference electrode at the center of a disk and at the edge of a disk. The true value of α_a can be determined from figure (7), where

$$\delta_{app} = \frac{\alpha_{a,app} F r_o i_{avg}}{RT\kappa}. \tag{17}$$

For a reference electrode placed at infinity, the apparent transfer coefficient differs from the true value of the transfer coefficient by less than four percent for any value of δ. For a reference electrode placed adjacent to the disk electrode, the maximum errors can be rather large. For any reference electrode placement other than at the edge of the disk, the errors become negligible at low and high values of δ.

Once α_a is known, two approaches are posible to determine the true value of the exchange current density. In the first approach, equations (12) or (13) could be used to obtain i_o. These equations can be rewritten as

$$\frac{i_o}{i_{o,app}} = \frac{E}{2}\, g(\delta)\, \chi^{(\alpha_{a,app}/\alpha_a - 1)}. \tag{18}$$

The last term in equation (17) can be thought of as a correction to figure (4), where

$$\chi = \exp\left(\frac{\alpha_a FV}{RT} - \frac{\pi\delta}{4}\right) g(\delta) = \frac{E}{2}\,\frac{i_{avg}}{i_o}\, g(\delta). \tag{19}$$

Unfortunately, as is suggested by the last term in equation (19), χ can vary over many orders of magnitude.

Since χ can be very different from one, the value of i_o obtained from equation (18) is very sensitive to the value of $\alpha_{a,app}$ determined from experimental data. Any uncertainty in this value can cause even

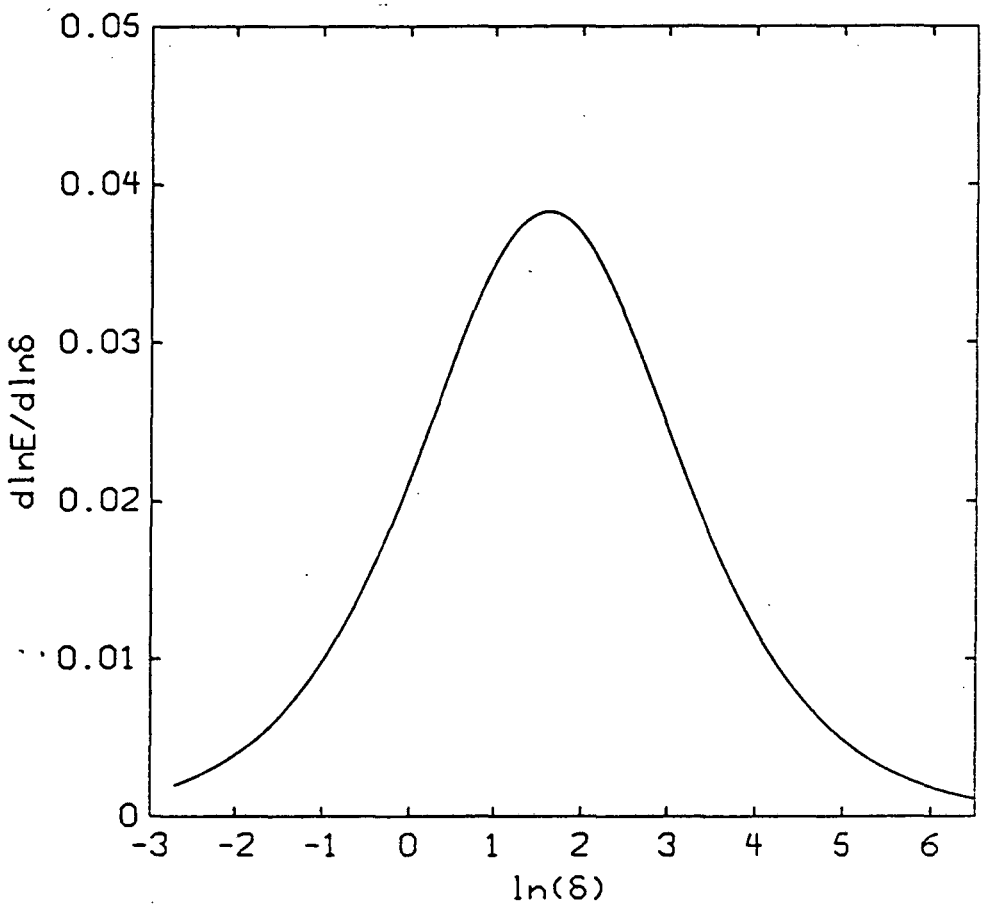

Figure 5. Correction term for the transfer coefficient, used in equation (16).

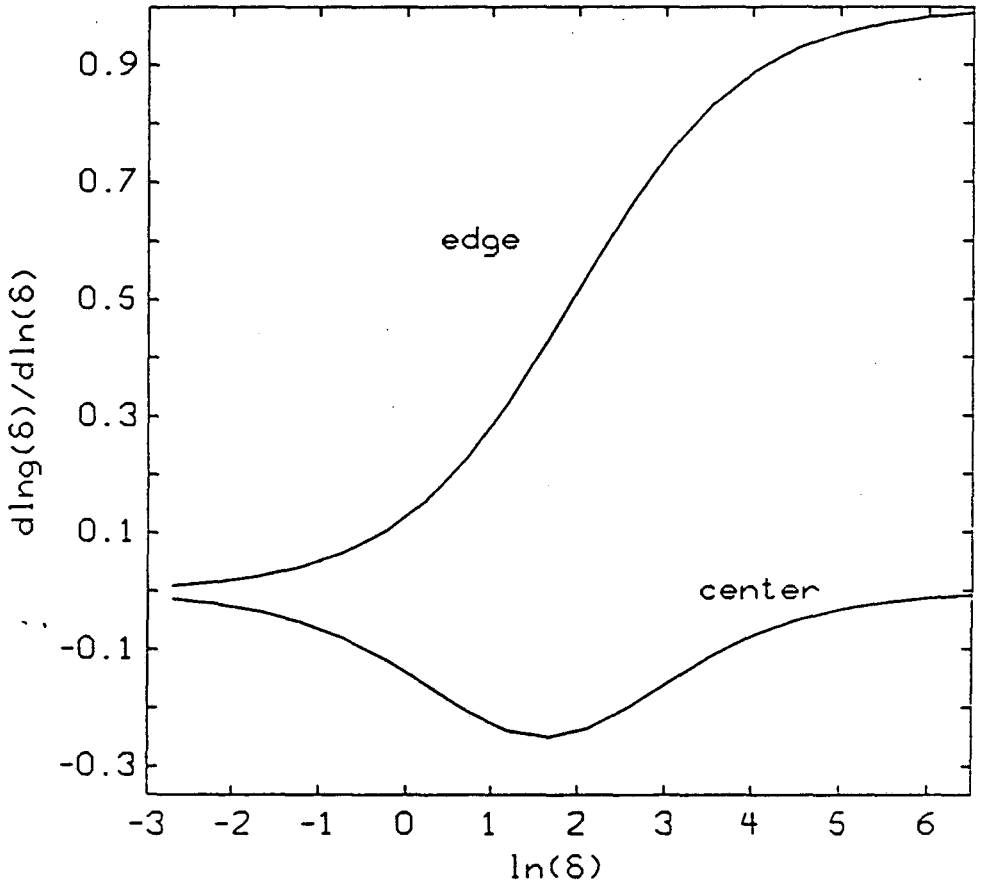

Figure 6. Correction term in equation (16) for a reference electrode at the edge and center of the disk.

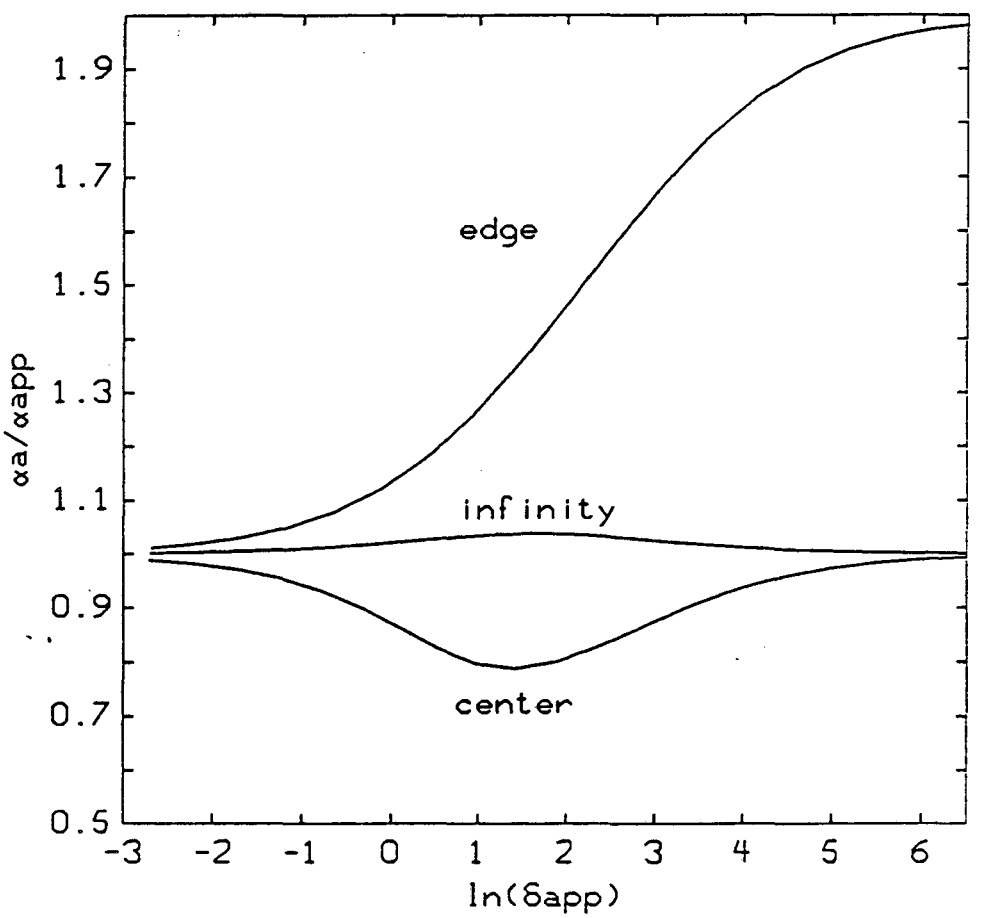

Figure 7. Correction to the transfer coefficent for three reference electrode placements as a function of δ_{app}.

greater uncertainties in i_o. The more accurate approach would be to fit a line of slope $\alpha_a F/RT$ through the data to obtain a new $i_{o,app}$, where α_a was determined through figure (7). Then, equation (14) or (15) would be valid and figure (4) could be used to obtain i_o.

It has been suggested in the literature that one can, through the linearization of Tafel kinetics, use solutions obtained for linear kinetics, and, therefore, compare the results of this analysis directly with the results for the linear kinetics analysis. This is valid only for modest average current densities. A linearization of equation (A4) around an average dimensionless potential suggests that linearization is only valid for $\delta \leq 1.2$, if the criterion is a two percent error in the value of the calculated current density at the edge of the disk.

The above analysis can also be applied to cathodic Tafel kinetics. The appropriate kinetic boundary condition becomes

$$i(r) = - i_o \exp\left(\frac{-\alpha_c F \eta_s}{RT}\right). \tag{20}$$

If one now takes

$$A = \frac{\alpha_c F r_o i_o}{RT\kappa} \exp\left(\frac{-\alpha_c FV}{RT}\right), \tag{21}$$

the results, equations (10), (12), and (13), will be identical if absolute values of δ and $\Phi(r,0)$ are used in the analysis. Additionally, one would want to substitute cathodic transfer coefficients and apparent cathodic transfer coefficients everywhere in the analysis.

Discussion

Since $i_o/i_{o,app}$ and $\alpha_a/\alpha_{a,app}$ are functions of the average current density, this analysis suggests better ways of plotting experimental data. Specifically, it suggests plotting $\eta_{s,app}$ *vs.* $\ln(i_{avg}g(\delta)E/2)$, where $g(\delta)$ has the same meaning as in equation (16). Figure (8) shows $\ln(i_{avg})$ and $\ln(i_{avg}E/2)$ *vs.* $\eta_{s,app}$ for a reference electrode placed at infinity. Experimental values of δ are often sufficiently small that $\alpha_a = \alpha_{a,app}$. Additionally, the effect of $i_o/i_{o,app}$ varying with δ is minimal on a semi-logarithmic plot. Therefore, the traditional plot is adequate for many purposes.

In practice, a Tafel plot of experimental data will not extend as a straight line through the abscissa since, as $\delta \longrightarrow 0$, the cathodic term of the Butler-Volmer equation becomes important. As is shown in figure (9), the common practice is to extend the straight part of the curve through $\eta_{s,app} = 0$, which gives $i_{o,app}$. By determining the value of δ at some point near which the slope of the curve deviates from the Tafel slope, one can use figure (4) to calculate the true exchange current density. It is important to realize that, for a given average current density, the error becomes larger for low solution conductivities and large disk radii.

Whenever possible, exchange current densities should be determined from data taken in the linear kinetics region. Errors could then be determined from reference [3]. For high exchange current densities, sufficient data should be available in this linear region. For more practical reasons, it is also desirable to use linear data, since, for Tafel data, ohmic potential drops may dominate the measurements.

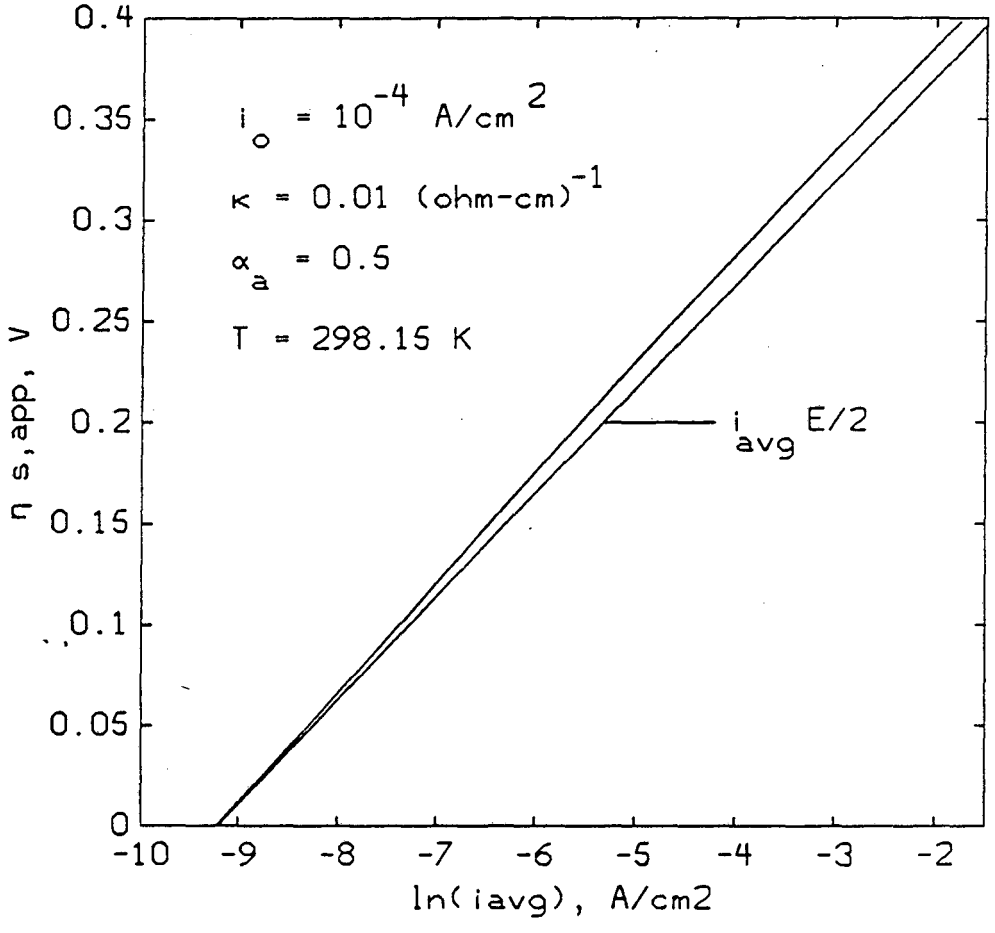

Figure 8. Simulated Tafel data plotted in the traditional manner and with corrections for the effects of nonuniform current distributions.

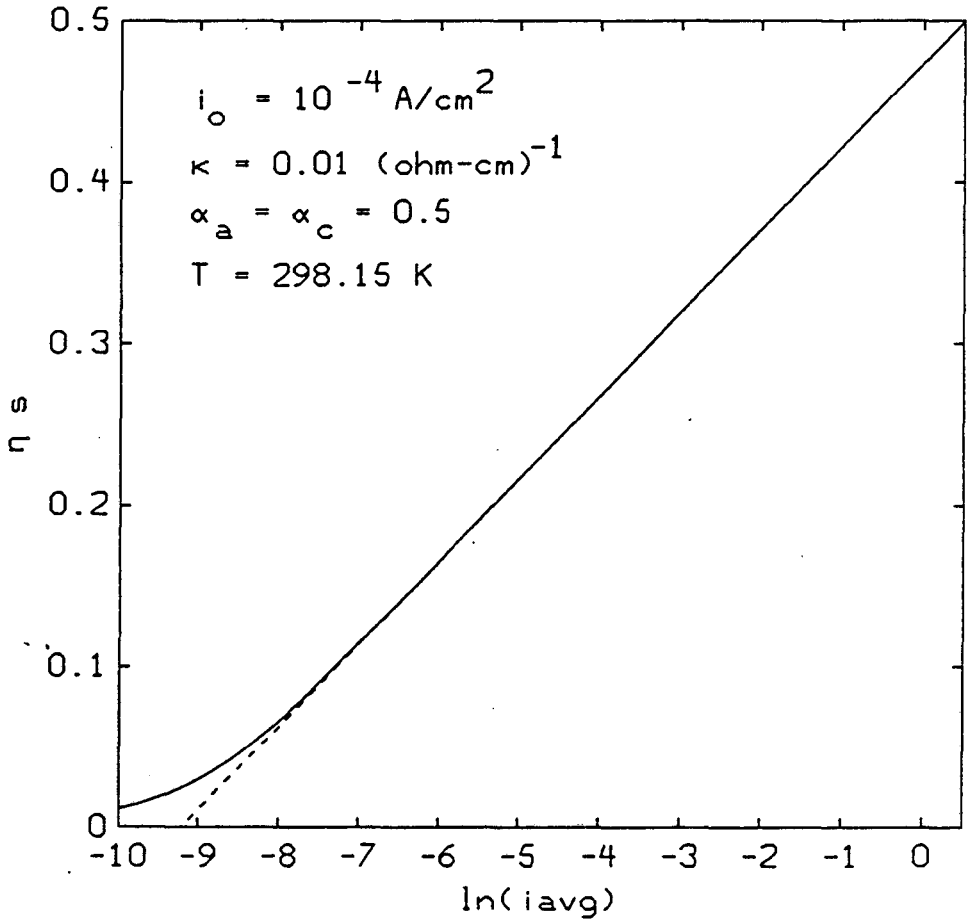

Figure 9. Simulated Butler-Volmer data, showing how experimental data may be expected to deviate from its Tafel slope.

Conclusions

This analysis again confirms suggestions that the reference electrode should be placed far from the disk when possible. In addition to the reduction in measurement errors, errors due to the distortion of current lines near the working electrode can be avoided. Contamination of the working electrode due to the reference electrode can also be minimized.

In the literature, reported exchange current densities for a given system can vary by well over one hundred percent. Therefore, depending on the application, the magnitude of the errors shown in the analysis may be considered minor. For more complicated kinetics, though, the errors may become much more significant. For example, in a study of passivation phenomena, the use of a disk electrode could easily lead to much larger errors than those calculated unless the nonuniform current distribution is explicitly taken into account[7].

In the study of such complex kinetics or when high precision is desired, a geometry with a uniform current distribution should be chosen. Better geometries include rotating cylinder and rotating hemisphere electrodes. The disk electrode, though, is easier to manufacture and polish. Therefore, for many applications, the disk will very likely remain a popular choice.

The rotating disk electrode can be a valuable tool when mass-transfer and concentration effects can not be eliminated completely. Newman [1] outlined a method of studying electrode kinetics under such conditions. His analysis is valid for Butler-Volmer kinetics with a concentration dependent exchange current density. In the most general

case, both δ and J are important parameters. Additionally, a dimensionless mass-transfer rate, the order of the reaction, α_a/α_c, and the transference number of the reactant are important.

More specifically, the approach involves determining the current density at the center of the disk for the appropriate set of parameters. Additionally, the potential at the center of the disk can be determined through knowledge of $i(r = 0)/i_{avg}$, the disk radius, and the conductivity of the bulk electrolyte. True kinetic constants can then be determined. This approach may involve an iterative procedure.

The qualitative conclusions of this analysis are valid for any geometry with a nonuniform current distribution. In designing kinetic experiments, one should try to use a cell geometry that will avoid these nonuniformities. Additionally, mass-transfer effects should be minimized by having uniformly accessible surfaces and operating under the proper hydrodynamic conditions.

Appendix

Axisymmetric boundary integral equations are given by Ligget and Liu[8]. For a disk geometry, these become (see also Newman[9])

$$\Phi(r_q) = \frac{2}{\pi\kappa} \int_0^{r_o} \frac{i(r)K(m)r}{r + r_q}\, dr \ , \tag{A1}$$

where K(m) is the complete elliptic integral of the first kind, defined by

$$K(m) = \int_0^{\pi/2} \frac{d\alpha}{(1 - m \sin^2\alpha)^{\frac{1}{2}}}. \tag{A2}$$

For the problem of interest, m is given by

$$m = 1 - \frac{|r - r_q|}{r + r_q}. \tag{A3}$$

Tabulated values of $K(m)$ and various approximate forms are given by Abramowitz and Stegun[10]. For anodic Tafel kinetics, the expression relating the potential and current, in dimensionless form, is

$$\frac{\partial\Phi^*}{\partial z^*} = -A \exp\left[- \Phi^* \right] \tag{A4}$$

where $z^* = z/r_o$,

$$\Phi^* = \frac{\alpha_a F\Phi}{RT},$$

and A is given by equation (8). Equations (A1) and (A4) were solved through an iterative procedure. Details of the application of this method to more general axisymmetric geometries will be published later.

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List of Symbols

A	dimensionless parameter, defined by equation (9)
E	dimensionless parameter, shown in figure (2)
$g(\delta)$	function defined below equation (16)
i	current density, A/cm^2
i_o	exchange current density, A/cm^2
J	dimensionless exchange current density
$K(m)$	complete elliptic integral of the first kind
r	radial position coördinate, cm
r_o	radius of the disk, cm
r_q	radial position at which the potential is being solved, cm
R	universal gas constant, 8.3143 J/mol-K
T	absolute temperature, K
V	electrode potential, V
z	distance from electrode surface, cm
α_a, α_c	transfer coefficients
δ	dimensionless average current
η_s	surface overpotential, defined by equation (3), V
κ	solution conductivity, mho/cm
π	3.141592654
Φ	potential of the solution, V

Subscripts

a	anodic
app	apparent
c	cathodic

References

[1] John Newman, "Current Distribution on a Rotating Disk below the Limiting Current," *J. Electrochem. Soc.*, 113, 1235 (1966).

[2] John Newman, "Engineering Design of Electrochemical Systems," *Ind. Eng. Chem.*, 60, no. 4, 12 (1968).

[3] W. H. Tiedemann, J. Newman, and D. N. Bennion, "The Error in Measurements of Electrode Kinetics Caused by Nonuniform Ohmic-Potential Drop to a Disk Electrode," *J. Electrochem. Soc.*, 120, 256 (1973).

[4] John S. Newman, *Electrochemical Systems*, p. 346, Prentice-Hall, Englewood Cliffs, N. J. (1973).

[5] John Newman, "Ohmic Potential Measured by Interrupter Techniques," *J. Electrochem. Soc.*, 117, 507 (1970).

[6] William H. Smyrl and John Newman, "Current Distributions at Electrode Edges at High Current Densities," *J. Electrochem. Soc.*, to be submitted.

[7] Phillip Paul Russell, *Corrosion of Iron: The Active-Passive Transition and Sustained Electrochemical Oscillations*, Ph. D. Thesis, University of California, Berkeley (February, 1984).

[8] J.A. Ligget and P. L-F. Liu, *The Boundary Integral Equation Method for Porous Media Flow*, Allen and Unwin, Boston (1983).

[9] J. Newman, "The Fundamental Principles of Current Distribution and Mass Transport in Electrochemical Systems," in *Electroanalytical*

Chemistry, A. J. Bard, Editor, pp. 187-351, Marcel Dekker, Inc., New York (1973).

[10] M. Abramowitz and I. A. Stegun, eds., *Handbook of Mathematical Functions*, National Bureau of Standards, Washington (1964).

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