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**Singular Perturbation Analysis of the Faradaic Impedance of Copper Dissolution
Accounting for the Effects of Finite Rates of a Homogeneous Reaction**

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Abstract

The frequency response of the dissolution of a copper rotating disk in 0.1 N HCl is investigated. Specifically, the effect of accounting for finite rates of the homogeneous complexing reaction is explored by utilizing a perturbation analysis to split the diffusion boundary layer into inner and outer regions so that the salient features of the problem can be examined separately. Formulating the singular perturbation problem leads to a better understanding of the physical nature of the faradaic impedance of the system and enables one to characterize quantitatively the numerical errors resulting from the Stefan-Maxwell impedance algorithm that arise for certain values of the rate constants and frequency range. Complex-plane plots, calculated from the SM model and the perturbation analysis, illustrate the frequency dependence of the faradaic impedance for different values of the homogeneous rate constant $\hat{k}_b$ and allow comparisons to be made. Introduction of the dimensionless impedance is useful for eliminating the strong and overriding dependence of the steady-state current on $\hat{k}_b$. Additionally, both low-to-moderate and high-frequency approximations for the impedance are given, and the regions of validity of the different analytic solutions are illustrated with a reaction zone diagram. Finally, the perturbation analysis provides a basis for enabling the homogeneous-reaction rate constant to be determined from frequency-response data.

key words: rotating disk, complex-plane and Bode plots, *EC* reaction zone diagram

1. Introduction

The Stefan-Maxwell model^[1] is capable of predicting the faradaic impedance as a function of frequency for many electrochemical systems. However, interpreting the numerical impedance results is not always easy, for just as in an ac experiment, several processes occur simultaneously with overlapping time constants, making it difficult to understand what physical phenomena determine the specific frequency dependence of the impedance. For this reason, a mathematical treatment of the frequency-response characteristics of a rotating disk electrode is to be presented. The perturbation analysis enables one to see separately the effect of individual reactions and other transport effects on the faradaic impedance.

A steady-state perturbation analysis^[2] has been carried out to characterize the effects of finite rates of a homogeneous reaction that follows an electrode reaction. In that problem, the diffusion-boundary layer was split into two regions: an inner region where convection to the disk is neglected and an outer region where the homogeneous reaction is assumed to be equilibrated. A similar approach is used here to solve the frequency-dependent problem for a wide range of rate constants of the homogeneous reaction. As in the steady-state perturbation analysis, the largely mass-transfer controlled anodic dissolution of copper in chloride solutions^[3] is investigated, where the following $E_r C_i$ mechanism[†] is applicable:

[†] E_r refers to a nearly reversible electrochemical reaction; and C_i refers to a following, somewhat irreversible homogeneous chemical reaction.

Here, the product of the nearly reversible electrode reaction, the cuprous ion, reacts homogeneously with the added ion of the supporting electrolyte to produce the copper complexed species CuCl_2^- . Many electrochemical techniques have been applied to study this type of reaction mechanism, and their theoretical treatments have been summarized in reference [4].

In this paper, we are interested in characterizing theoretically the effects of fast, but finite rates of the homogeneous reaction on the faradaic impedance at a rotating disk. Applications of the perturbation analysis include not only interpretation of the experimental frequency response but also data reduction that will enable the determination of the desired homogeneous reaction rate constant. Additionally, the perturbation analysis will aid in determining sources of numerical errors in the Stefan-Maxwell program that can arise for certain values of the input parameters, and the perturbation solution then will be used to estimate the order of magnitude of these errors.

2. Model Development

The governing equations, using dilute-solution theory with no migration, are presented here for the transient copper electrodisolution process. The minor species, Cu^+ and CuCl_2^- , are treated in an excess of supporting electrolyte, *i.e.*, HCl, such that the chloride concentration can be taken to be constant. Each minor species concentration takes the form $c_i = \bar{c}_i + \tilde{c}_i \exp(j\omega t)$, where the transient solution is

obtained for a sinusoidal perturbation around the steady state $\bar{c}_i$. The ac equations are changed from the time domain to the frequency domain ($j\omega\tilde{c}_i$ replaces $\partial c_i/\partial t$, where ω is the perturbation frequency) yielding the following material balances for the alternating concentrations $\tilde{c}_3$ and $\tilde{c}_4$ of Cu^+ and CuCl_2^- , respectively:

$$j\omega\tilde{c}_3 + v_z \frac{\partial \tilde{c}_3}{\partial z} = D_3 \frac{\partial^2 \tilde{c}_3}{\partial z^2} + \hat{k}_b(\tilde{c}_4 - \hat{K}^* \tilde{c}_3) \quad (3)$$

$$j\omega\tilde{c}_4 + v_z \frac{\partial \tilde{c}_4}{\partial z} = D_4 \frac{\partial^2 \tilde{c}_4}{\partial z^2} - \hat{k}_b(\tilde{c}_4 - \hat{K}^* \tilde{c}_3) \quad (4)$$

$\hat{k}_b$ is the homogeneous-reaction backward rate constant, and $\hat{K}^* = \hat{k}_f/\hat{k}_b$ is the equilibrium ratio of c_4 to c_3 at the bulk concentration of chloride ion. For large Schmidt numbers, the axial velocity is given by^[5]

$$v_z = -a\Omega \left(\frac{\Omega}{\nu} \right)^{1/2} z^2, \quad (5)$$

and the parameters have the same meaning as in the previous paper.^[2] Introduction of the dimensionless distance and frequency,

$$\xi = z \left(\frac{\Omega}{\nu} \right)^{1/2} \left(\frac{a\nu}{3D} \right)^{1/3} = \frac{z}{\delta}, \quad K = \frac{\omega}{\Omega} \left(\frac{9\nu}{a^2 D} \right)^{1/3}, \quad (6)$$

respectively, where the effective diffusion coefficient is given by

$$D = \frac{D_3 + \hat{K}^* D_4}{1 + \hat{K}^*}, \quad (7)$$

enables the material balances to be rewritten in terms of these dimensionless parameters accordingly

$$jK\tilde{c}_3 = 3\xi^2 \frac{\partial \tilde{c}_3}{\partial \xi} + \frac{D_3}{D} \frac{\partial^2 \tilde{c}_3}{\partial \xi^2} + \frac{1}{\Delta^2 D^2} \frac{D_3 D_4}{1 + \hat{K}^*} (\tilde{c}_4 - \hat{K}^* \tilde{c}_3) \quad (8)$$

$$jK\tilde{c}_4 = 3\xi^2 \frac{\partial \tilde{c}_4}{\partial \xi} + \frac{D_4}{D} \frac{\partial^2 \tilde{c}_4}{\partial \xi^2} - \frac{1}{\Delta^2 D^2} \frac{D_3 D_4}{1 + \hat{K}^*} (\tilde{c}_4 - \hat{K}^* \tilde{c}_3) \quad (9)$$

The perturbation parameter

$$\Delta = \left[\frac{1}{\hat{k}_b \delta^2} \frac{D_3 D_4}{D_3 + \hat{K}^* D_4} \right]^{1/2} \quad (10)$$

is a dimensionless penetration depth and characterizes the homogeneous reaction zone next to the electrode surface. Δ is a dimensionless form of the homogeneous reaction thickness given by Levich^[5] as $\hat{\delta} = \sqrt{D/\hat{k}_f^*}$, where $\hat{k}_f^*$ is the forward rate constant of the homogeneous complexing reaction (equation 2). $\hat{\delta}$ is the distance over which the cuprous ion, once formed via the electrode dissolution reaction (equation 1), has to diffuse before it is complexed with chloride to form CuCl_2^- . The lifetime $\hat{\tau}$ of Cu^+ is $\hat{k}_f^{*-1}$, and in a time interval $\hat{\tau}$, the cuprous ion will diffuse for a distance $\sqrt{D\hat{\tau}}$.^[6] In this paper, Δ will be used to characterize the effect of finite rates of the homogeneous reaction ($\Delta \rightarrow 0$ as $\hat{k}_b \rightarrow \infty$ and $\Delta \rightarrow \infty$ as $\hat{k}_b \rightarrow 0$).

For small values of Δ (or $\hat{\delta}/\delta$), the homogeneous reaction thickness is small relative to the diffusion boundary layer, and a perturbation problem results as described for the steady-state case in reference [2]. The distance variable ξ needs to be stretched according to the different ranges of frequency. It will be shown later that stretching makes the diffusion term appear to be the same order as the homogeneous reaction terms, and that the convective terms are negligible in the inner region close to the electrode surface. Before presenting the appropriate equations for the inner and outer regions of the perturbation problem, let us discuss the boundary conditions.

The ac boundary conditions in the bulk are

$$\tilde{c}_i = 0 \quad \text{and} \quad \tilde{\Phi} = 0 \quad \text{at} \quad z = z_{\max} \quad (11)$$

The arbitrary zero of potential is specified at the frequency dependent $z_{\max} = \delta \xi_{\max}$, where the rotating-disk problem is scaled using the largest diffusion coefficient $D_{\max}$. The frequency dependence of $\xi_{\max}$ was cited by Vetter,^[7] yielding^[1]

$$\frac{1}{\xi_{\max}} = \frac{(D/D_{\max})^{1/3}}{2.0} + \left(\frac{p Sc^{1/3}}{5.4} \right)^{1/2}, \quad (12)$$

where $p = \omega/\Omega$ is the dimensionless frequency and $Sc = \nu/D$ is the effective Schmidt number. The boundary condition at the electrode relates the flux of species i to the electrochemical reaction occurring at the surface

$$\tilde{N}_i = -D_i \frac{d\tilde{c}_i}{dz} = -\frac{s_i}{nF} \tilde{i}_n, \quad (13)$$

where $\tilde{i}_n$ is the normal component of the alternating faradaic current density. Next, we are interested in obtaining approximate analytic solutions to the transient material-balance equations 8 and 9 for small Δ , since an exact solution is not possible.

In the outer region, setting Δ equal to zero in equations 8 and 9 yields two identical equations signifying homogeneous-reaction equilibrium: $\tilde{c}_4 = \hat{K}^* \tilde{c}_3$. To get a second, independent equation, equations 8 and 9 are added to eliminate the homogeneous reaction terms. Either $\tilde{c}_3$ or $\tilde{c}_4$ is eliminated by means of the equilibrium relation, and a simple transient convective diffusion equation is obtained for the remaining variable. Thus, the alternating concentrations are given by

$$\tilde{c}_4 = \hat{K}^* \tilde{c}_3 = P \theta(\xi, K), \quad (14)$$

where θ is the solution to the equation

$$jK\theta = 3\xi^2 \frac{\partial \theta}{\partial \xi} + \frac{\partial^2 \theta}{\partial \xi^2} \quad (15)$$

By introducing the coefficient P , so that $\theta = 1$ at $\xi = 0$, one recognizes that the ac-

concentration function θ is the well-known^{[8], [9]} basis for the convective Warburg impedance. Although numerical solutions have been given,^{[10], [11]} it is pertinent to recall that the derivative $-1/\theta'(0)$ can be approximated^{[12], [11]} by the relation for a stagnant Nernst layer:

$$\frac{-1}{\theta'_N(0)} = \frac{\tanh\left(\Gamma(4/3) \sqrt{jK}\right)}{\sqrt{jK}} \quad (16)$$

In the inner limit ($\xi \rightarrow 0$), the outer solution (equation 14) becomes

$$\tilde{c}_4 = \hat{K}^* \tilde{c}_3 = P \left[1 + \xi \theta'(0) \right] \quad (17)$$

These concentration profiles do not reflect the differences between species 3 and 4 as required by stoichiometry of the reaction; that is, equations 14 and 17 do not satisfy the boundary condition at the surface as given by equation 13.

Let us next treat the region next to the electrode surface where the complexing reaction is not equilibrated and finite rates of the homogeneous reaction must be accounted for. Corrections Θ_3 and Θ_4 to the approximate solutions given in equation 14 are defined as follows:

$$\tilde{c}_4 = P\theta + \Delta\Theta_4 \quad \text{and} \quad \tilde{c}_3 = \frac{P}{K^*}\theta + \Delta\Theta_3 \quad (18)$$

Again, the first terms on the right of these equations account for convective diffusion and an equilibrated homogeneous reaction. The second terms on the right are corrections for finite rates of the homogeneous reaction, and, in the outer region, these corrections arise from terms neglected in equations 8 and 9 and thus are of order Δ^2 . The failure of the first terms to satisfy the boundary condition 13 at the electrode gives rise to correction terms of order Δ , but these are important only in the inner region

where ξ is of order Δ . Let us now describe how to obtain the Θ_3 and Θ_4 functions.

Addition of equations 8 and 9, with substitution of equations 18 and rearrangement, yields

$$jK(\Theta_3 + \Theta_4) = 3\xi^2 \frac{\partial(\Theta_3 + \Theta_4)}{\partial \xi} + \frac{D_3}{D} \frac{\partial^2 \Theta_3}{\partial \xi^2} + \frac{D_4}{D} \frac{\partial^2 \Theta_4}{\partial \xi^2} \quad (19)$$

The θ terms cancel since θ is an exact solution to equation 15. For small values of the perturbation parameter Δ (a fast homogeneous reaction), the inner region is small relative to the outer region, and a new "stretched" inner-region distance variable is introduced $\bar{\xi} = \xi/\Delta$. Equation 9, upon substitution of equation 18, takes the form

$$jK\Delta^2\Theta_4 = 3\Delta^3\bar{\xi}^2 \frac{\partial\Theta_4}{\partial\bar{\xi}} + \frac{D_4}{D} \frac{\partial^2\Theta_4}{\partial\bar{\xi}^2} - \frac{D_3D_4/D^2}{1+\hat{K}^*} (\Theta_4 - \hat{K}^*\Theta_3) + \frac{P}{\Delta} \left(\frac{D_4}{D} - 1 \right) \left[jK\Delta^2\theta - 3\Delta^3\bar{\xi}^2 \frac{\partial\theta}{\partial\bar{\xi}} \right] \quad (20)$$

The stretching makes the diffusion term appear to be the same order as the homogeneous reaction terms, thereby ensuring that the boundary condition at the electrode can be satisfied. The stretching also shows that the convective terms (those multiplied by $\bar{\xi}^2$) are negligible in the inner region. With neglect of the remaining term in θ , equation 20, rewritten in terms of ξ , becomes

$$jK\Theta_4 = \frac{D_4}{D} \frac{\partial^2\Theta_4}{\partial\xi^2} - \frac{1}{\Delta^2D^2} \frac{D_3D_4}{1+\hat{K}^*} (\Theta_4 - \hat{K}^*\Theta_3) \quad (21)$$

Equation 19, with neglect of convection and subtraction of equation 21, yields

$$jK\Theta_3 = \frac{D_3}{D} \frac{\partial^2\Theta_3}{\partial\xi^2} + \frac{1}{\Delta^2D^2} \frac{D_3D_4}{1+\hat{K}^*} (\Theta_4 - \hat{K}^*\Theta_3) \quad (22)$$

In the inner region, the alternating-concentration approximations take the form $\Theta_3 = A_3 \exp(-B\xi)$ and $\Theta_4 = A_4 \exp(-B\xi)$ for the cuprous and copper chloride complex

species, respectively. Substitution into equations 21 and 22 yields a set of linear algebraic equations for the constants A_3 and A_4 , such that the array of coefficients is a second-order determinant equal to zero. After rearrangement, the complex coefficients B can be written as follows

$$B^2 = \frac{jK \frac{D_3 + D_4}{D} + \frac{D_3 D_4}{D^2 \Delta^2}}{2 \frac{D_3 D_4}{D^2}} \quad (23)$$

$$\pm \frac{D^2}{2 D_3 D_4} \left\{ \left(jK \frac{D_3 + D_4}{D} + \frac{D_3 D_4}{D^2 \Delta^2} \right)^2 - 4 \frac{D_3 D_4}{D^2} \left(j^2 K^2 + jK \frac{D_3 D_4}{D^2 \Delta^2} \right) \right\}^{1/2}$$

With the use of only one root of B , $\tilde{c}_4$ and $\tilde{c}_3$ become

$$\tilde{c}_4 = P\theta + \Delta A_{4,1} e^{-B_1 \xi} \quad \text{and} \quad \tilde{c}_3 = \frac{P}{K^*} \theta + \Delta A_{3,1} e^{-B_1 \xi}, \quad (24)$$

where B_1 is the root with a large positive real part of B , chosen so that the corrections fall off rapidly with distance from the electrode. The algebraic equation relating the coefficients is

$$A_{3,1} = \frac{A_{4,1}}{K^*} \left[1 + \frac{(1 + \hat{K}^*) D^2 \Delta^2}{D_3 D_4} \left(jK - \frac{D_4}{D} B_1^2 \right) \right] \quad (25)$$

The Faraday's law boundary condition (equation 13) allows the determination of the unknown constants from

$$\frac{\partial \tilde{c}_4}{\partial \xi} = 0 = P\theta'(0) - \Delta B_1 A_{4,1} \quad \text{and} \quad \frac{\partial \tilde{c}_3}{\partial \xi} = \frac{-i_n \delta}{D_3 F} = \frac{P\theta'(0)}{K^*} - \Delta B_1 A_{3,1} \quad (26)$$

Equations 24, 25, and 26, valid for small values of the perturbation parameter Δ , yield the alternating concentration of species 3 at the surface over the entire frequency range:

$$\frac{\tilde{c}_{3,0}}{\tilde{i}_n} = \frac{\delta}{D_3 F} \left[\frac{1}{B_1} + \frac{D_3 D_4}{\Delta^2 D^2} \frac{1}{1 + \hat{K}^*} \frac{\frac{1}{B_1} - \left\{ \frac{-1}{\theta'(0)} \right\}}{jK - \frac{D_4}{D} B_1^2} \right] \quad (27)$$

The result in equation 24 is not quite straightforward since there are four separate values of B , and three of these have been ignored. Appendix A gives separate, straightforward treatments for high frequencies and for low to moderate frequencies. Appendix B develops a solution where all four B values are used and convection is effectively ignored in a stagnant Nernst diffusion layer. This last approach gives a solution which is approximately valid, even for larger values of Δ . Equation 24 accounts for convection by using the θ solution in both the inner and outer regions, effectively replacing a solution with a second value of B , and thereby encompasses a range of conditions in a fairly simple form.

3. Faradaic Impedance

The ac faradaic current density is a function of the kinetic potential difference $\tilde{V}$ and the concentration $\tilde{c}_{i,0}$ at the electrode surface. Linearization of the modified Butler-Volmer rate equation 27 in reference [2], using the following Taylor expansion around the steady-state values of $\bar{c}_{i,0}$ and $\bar{V}$,

$$\tilde{i}_n = \left(\frac{\partial i_n}{\partial V} \right)_{c_i} \bigg|_{\bar{c}_{i,0}, \bar{V}} \tilde{V} + \sum_i \left(\frac{\partial i_n}{\partial c_i} \right)_V \bigg|_{\bar{c}_{i,0}, \bar{V}} \tilde{c}_{i,0} \quad (28)$$

enables the faradaic impedance $Z_F = \tilde{V} / \tilde{i}_n$ to be determined. A new dimensionless faradaic impedance is defined as

$$Z_F = \frac{F \bar{i}_n}{RT} \frac{\bar{V}}{\bar{i}_n} = \frac{F \bar{i}_n}{RT} Z_F \quad (29)$$

and can be rewritten as

$$Z_F = \frac{\frac{\tilde{c}_{3,0}}{\tilde{i}_n} + \frac{\exp(\beta F \bar{V}/RT)}{F k_c}}{\bar{c}_{3,0}/\bar{i}_n} \quad (30)$$

where the steady-state function is given by^[2]

$$\frac{\bar{c}_{3,0}}{\bar{i}_n} \frac{FD}{\delta} = \frac{\Gamma(4/3)}{1 + \hat{K}^*} + \Delta \frac{D_4}{D_3} \frac{\hat{K}^*}{1 + \hat{K}^*} \quad (31)$$

For fast electrode kinetics of the copper system, with the expected values of k_a , k_c , and $\bar{V}$, the last term in the numerator on the right of equation 30 is negligible, as one would have obtained by using a Nernst equation. With this simplification, the dimensionless impedance can be written

$$Z_F = \frac{\tilde{c}_{3,0}/\tilde{i}_n}{\bar{c}_{3,0}/\bar{i}_n} \quad (32)$$

where $\tilde{c}_{3,0}/\tilde{i}_n$ is given by equation 27 in this perturbation analysis for small Δ .

It should be emphasized that the perturbation analysis of the diffusion layer has applicability independent of the applicability of the Nernst equation to the electrode reaction. We have generally retained the extra term in the numerator of equation 30, for it causes no additional numerical complication. We point out the simplification due to reversible electrode kinetics because it is characteristic of the reaction sequence under study.

4. Results

Calculated impedance results are presented here for the electrodisolution of copper in chloride solutions. Unless specified otherwise, all cases are for a copper disk rotating at 2000 rpm in 0.1 N HCl with a kinetic viscosity of $\nu = 8.9 \times 10^{-3} \text{ cm}^2/\text{s}$ at $T = 298.15 \text{ K}$. The kinetic and thermodynamic input parameters are the same as in reference 2 for the two-step copper dissolution mechanism given by equations 1 and 2. The potential between the working and saturated calomel reference electrode is $\bar{V} = -0.205 \text{ V}$ because experimental results^[3] are available.

The faradaic impedance as a function of frequency, as calculated by the Stefan-Maxwell macroscopic model,^[1] is given in figure 1, where the impedance is normalized with respect to the resulting steady-state current density. Figure 1 illustrates results for four values of the homogeneous complexing reaction rate constant $\hat{k}_b = 0 \text{ s}^{-1}$, 10^{-2} s^{-1} , 10^0 s^{-1} , and ∞ . The $\hat{k}_b = 0 \text{ s}^{-1}$ and ∞ cases are indistinguishable in this figure. However, one must keep in mind that the magnitudes of the complex impedance spectrum for the two cases is the same only when normalized with the current density. The polarization resistance, $R_p = \lim_{\omega \rightarrow 0} \{Z_F\}$ is a good indication of the magnitude of the nonnormalized impedance. R_p is given in table 1 as a function of the homogeneous-reaction rate constant (or Δ), clearly indicating the difference between the $\hat{k}_b = 0 \text{ s}^{-1}$ and ∞ cases.[†] The other curves in figure 1 also appear to be similar to each

[†] The steady-state potential profiles^[2] also display significantly different behavior for these two cases. Specifically, the slope of the potential profile at the surface reverses itself. Although this phenomenon does not affect the faradaic impedance, it will have an effect on the solution impedance and will be discussed in another paper.

Figure 1. Complex-plane plot of the dimensionless faradaic impedance calculated by the Stefan-Maxwell model as a function of frequency and the homogeneous rate constant $\hat{k}_b$ (s^{-1}).

Table 1. Comparison of the numerical Stefan-Maxwell results for 321 mesh points (in parentheses) with those from the analytic solutions as functions of the homogeneous backward rate constant.

Δ	Homogeneous rate constant, $\hat{k}_b$ (s^{-1})					
	0	10^{-2}	10^0	10^2	10^4	∞
	∞	1.0	0.1	0.01	0.001	0
$\bar{i}_n$ ($\mu A/cm^2$)	0.03476 (0.03385)	0.03347 (0.04525)	0.3299 (0.3278)	2.8842 (2.0242)	12.776 (2.7418)	20.642 (20.223)
R_p ($\Omega \cdot cm^2$)	739,115 (758,914)	767,547 (567,688)	77,875 (78,373)	8,908 (12,693)	2,012 (9,371)	1,245 (1,272)

other. For example, the magnitude of the imaginary part of the impedance is smaller for $\hat{k}_b = 10^0 s^{-1}$ and $10^{-2} s^{-1}$, but the shape is generally the same (except for the low-frequency impedance tail for $\hat{k}_b = 10^0 s^{-1}$).

The numerically calculated results for steady-state current densities and polarization resistances, tabulated in parentheses in table 1, become progressively less reliable as $\hat{k}_b$ increases — except for the values for $\hat{k}_b = \infty$, which are calculated by incorporating the homogeneous reaction into the boundary condition. For example, the values are off by a factor of 4.7 at $\hat{k}_b = 10^4 s^{-1}$. The values calculated analytically by the perturbation analysis for small Δ become progressively less reliable as $\hat{k}_b$ decreases, and the numerical value would be preferred at $\hat{k}_b = 10^{-2} s^{-1}$. (The analytic value at $\hat{k}_b = 0$ is calculated differently, by ignoring the presence of the chloride complex

altogether.) These, essentially dc, results are also discussed in reference 2.

The impedance spectra calculated from both the Stefan-Maxwell model and the perturbation analysis are given in figure 2 for a $\hat{k}_b$ of 10^0 s^{-1} . Numerical results for 321 mesh points in the Stefan-Maxwell calculation are much closer to those from the perturbation analysis than those with 161 mesh points, demonstrating that at least 321 mesh points should be used.

Figure 3 shows an enlargement of the low-frequency results. Plots from the perturbation analysis (equations 27 and 32) (closed circles) and the Stefan-Maxwell solution (open circles) both appear to be a superpositions of loops giving rise to the tail in the impedance. Results from appendix A for high and moderate frequency solutions are also shown in figure 3, denoted by $\square$ and ∇ , respectively.

For high frequencies, convection can be ignored altogether, and $\tilde{c}_{3,0}/\tilde{i}_n$ can be approximated by equation A9 in the appendix yielding the corresponding impedance equation A10. Therefore, for frequencies greater than $K = 10$, this curve (denoted by squares), yields the proper high-frequency dependence by accounting for the finite rate of the homogeneous reaction. This solution fails at low frequencies because convection becomes important but is not accounted for, and the curve goes off toward infinite impedance at a 45° angle typical of the Warburg impedance at zero frequency.

For moderate-to-low frequencies, transient behavior is less important in the inner, reaction zone, and any impedance loop arises from transient effects in the region where the homogeneous reaction is essentially equilibrated. The impedance equation 32 reduces to equation A7 (see derivation of equation A6 for $\tilde{c}_{3,0}/\tilde{i}_n$). Thus, for frequencies below $K = 4$, the moderate-frequency solution (given by ∇) as determined

Figure 2. Complex-plane plots of the dimensionless faradaic impedance as calculated from the Stefan-Maxwell (SM) model ($n_j = 161$ and 321) and the perturbation analysis (PA) for $\hat{k}_b = 10^0 \text{s}^{-1}$.

Figure 3. Enlargement of the low-frequency dimensionless impedance ($\hat{k}_b = 10^0 \text{ s}^{-1}$) results: $\bullet$ perturbation analysis from text; $\circ$ Stefan-Maxwell numerical results (321 mesh points); $\square$ high frequency analysis and ∇ low-to-moderate frequency analysis, both from appendix A.

from equation A7, yields the proper zero-frequency limit by accounting for convection.

Finally, one can see how the analysis leading to equations 27 and 32 gives the overall composite "best" solution and has the proper limiting behavior for both high and low frequencies. By showing these limiting-case impedances as calculated using approximate solutions (found in appendix A), the importance of the different physical phenomena as a function of frequency can be elucidated. Most importantly, the effect of finite rates of the homogeneous complexing reaction corresponds to a high-frequency impedance loop relative to the low-frequency convective-diffusion loop. At higher values of $\hat{k}_b$, the two loops will be shown to overlap more.

Examination of the frequency dependence of the boundary-layer thickness is useful for illustrating and quantifying what phenomena determine the faradaic impedance in the high and low-frequency approximations just discussed. The maximum dimensionless distance, $\xi_{\max}$, was given by equation 12 and is plotted in figure 4 as a function of the dimensionless frequency. Also plotted on the figure is a dimensionless form of the diffusion-layer thickness given by $\xi_{\bar{t}} = \Gamma(4/3)(D/D_{\max})^{1/3} \xi_{\max}/2$ (accounting for the fact that $\xi_{\max}$ was chosen to include any variations in concentration). Different values of the dimensionless perturbation parameter Δ are included on the figure; departures from homogeneous reaction equilibrium are important for values of ξ less than Δ . The intersection of a horizontal Δ line with the $\xi_{\bar{t}}$ line delimits high frequencies from low.

Let us first discuss a specific case of a small Δ (e.g., $\hat{k}_b = 10^4 \text{ s}^{-1}$). At low frequencies ($K \ll 10^6$), there are two distinct regions. The small inner zone next to the electrode (shaded area), where convection is not important, is characterized by diffusion and finite rates of the homogeneous reaction. Convection is important in the larger

Figure 4. Frequency dependence of the diffusion boundary-layer thicknesses showing different regions of importance adjacent to the electrode. The inner, homogeneous reaction zone is illustrated for different values of Δ .

outer region, where the complexing reaction can be assumed to be equilibrated. As the frequency increases, the diffusion boundary-layer thickness (Warburg line) decreases until the outer region, where equilibration occurs, disappears. However, an alternative simplification occurs: convection is unimportant throughout the diffusion layer. For larger values of Δ (e.g., $\hat{k}_b = 10^0 \text{ s}^{-1}$), the thickness of the inner region is of the same order as the convection layer (enclosed by $\xi_{\max}$ and the Nernst line), and the perturbation analysis begins to break down.

In figure 5, dimensional impedance results from the perturbation analysis for $\hat{k}_b = 10^2 \text{ s}^{-1}$ and 10^4 s^{-1} are presented. Two distinct loops with impedance maxima at different characteristic frequencies result because significant overlapping of the high and moderate-frequency approximate solutions occurs. Although clear separation of loops did not occur for the $\hat{k}_b = 10^0 \text{ s}^{-1}$ case, the reasoning given there for the frequency dependence of the impedance loops applies here as well. Again, convective-diffusion is important at low frequencies, whereas effects of finite rates of the homogeneous reaction appear at high frequencies.

The low-frequency limit of each curve corresponds to the polarization resistance R_p , given in table 1. On the scale of this graph, the magnitude of the convective-diffusion (moderate-frequency) loop is independent of Δ (or $\hat{k}_b$), while the high-frequency loop decreases in magnitude as the rate constant $\hat{k}_b$ of the homogeneous reaction increases. The homogeneous reaction time constant $\hat{\tau}$ and the resistance R' characterize the magnitude of the inner loop. $R' = \lim_{K \rightarrow \infty} Z_F^{(MF)}$ is given by the high-frequency limit of the low-to-moderate frequency impedance function (A7), and values of R' are summarized in table 2 as a function of Δ . The characteristic frequency, $K'_{\max}$, at the

Figure 5. Complex-plane plot of the dimensional faradaic impedance as calculated from the perturbation analysis for $\hat{k}_b = 10^2$ and 10^4 s^{-1} .

impedance maximum of the inner loop is proportional to $\hat{k}_b$ or Δ^{-2} ; whereas, the maximum in the convective-diffusion loop occurs at $K_{\max} = 3$. The magnitude and the characteristic frequency $K_{\max}$ of the convective-diffusion (outer) loop remain constant because the mass-transfer resistance, $R_0 = R_p - R'$, and the convective-diffusion time constant, $\tau_{MT} \propto Sc^{1/3}/\Omega$, are independent of the homogeneous rate constant.

The dimensionless faradaic impedance as calculated by the perturbation analysis for different values of $\hat{k}_b = 10^x$, where x ranges from 0 to 10, is given in figure 6. The figure is somewhat busy, but it clearly summarizes the point that significant differences in the frequency response occur for different values of $\hat{k}_b$. As $\hat{k}_b$ increases, the homogeneous reaction resistance decreases, and the relative sizes of the two loops are

Table 2. The frequency dependence of the impedance maxima and minima.

$\hat{k}_b \text{ (s}^{-1}\text{)}$	Δ	$K_{\max}$	$K_{\min}$	$K'_{\max}$	$R' \text{ (}\Omega \cdot \text{cm}^2\text{)}$
10^0	10^{-1}	—	—	2×10^2	7.663×10^4
10^2	10^{-2}	3	1.5×10^2	2×10^4	7.664×10^3
10^4	10^{-3}	3	1.5×10^4	2×10^6	7.668×10^2
10^6	10^{-4}	3	1.5×10^6	2×10^8	7.671×10^1
10^8	10^{-5}	3	1.5×10^8	2×10^{10}	7.672×10^0
10^{10}	10^{-6}	3	1.5×10^{10}	2×10^{12}	7.675×10^{-1}

Figure 6. Complex-plane plot of the dimensionless faradaic impedance as calculated from the perturbation analysis for $\hat{k}_b = 10^x \text{ s}^{-1}$, and $x = 0$ to 10.

shifted: the high-frequency, complexing-reaction impedance decreases, and the low-frequency convective-diffusion loop increases (because of the different scale for the dimensionless complex-plane plot). The frequency dependence of the maxima and minimum in the imaginary part of the faradaic-impedance of each curve is summarized in table 2.

Similar results are illustrated on a Bode plot in figure 7. Here, only the magnitude of the dimensionless faradaic impedance $|Z_F|$ is given as a logarithmic function of frequency for different values of Δ . As Δ decreases, again the homogeneous reaction resistance decreases, and the impedance limit R' , seen as the arrest on the Bode plot, approaches zero. Finally, the complex-plane and Bode-plot results and table 2 imply that the faradaic impedance of a rotating disk is a useful means for determining the homogeneous rate constant $\hat{k}_b$. The frequency $K'_{\max} = 2\Delta^{-2}$ or $K_{\min} = 1.5\Delta^{-2}$ or the magnitude of the impedance R' (the latter perhaps in dimensionless form to eliminate the effect of electrode kinetic parameters) can be used for this purpose.

5. Discussion of Results

In this paper, the frequency response of a particular electrode reaction with a coupled chemical reaction has been investigated. The rate of the homogeneous complexing reaction that follows the electrochemical dissolution reaction has been shown, using both complex-plane and Bode plots, to affect significantly the resulting faradaic impedance. We examine next results of the theoretical treatments of the E, C_i reaction mechanism by employing the "zone diagram" given by figure 8, a log-log plot of the reciprocal of the dimensionless perturbation parameter squared, Δ^{-2} , versus the

Figure 7. Bode plot of the magnitude of the dimensionless faradaic impedance *versus* frequency K for different values of the perturbation parameter Δ .

Figure 8. Reaction-zone diagram showing important behavior of the dimensionless perturbation parameter Δ^{-2} and frequency K .

dimensionless frequency K . The $E_r C_i$ reaction diagram defines the regions of applicability of the various analytic solutions given in the text and the appendices, where the different limiting-case zones are clearly illustrated on this map for both high and low values of K and Δ^{-2} .

The perturbation analysis, presented in the text, is valid for $\Delta \rightarrow 0$ or large $\hat{k}_b$; therefore, the region where these solutions (impedance equation 32 and the complex function 27) are valid covers the top half of the figure. At low to moderate frequencies ($K < K_{\min}$) and $\log \Delta^{-2} \gg 2$ ($\hat{k}_b \gg 10^0$), a clear separation of the outer and the thin inner (homogeneous reaction zone) regions exists and was illustrated in figure 4. For this limiting case, the homogeneous reaction behaves like a boundary condition to the outer region, where convection is important and the homogeneous reaction is equilibrated. Thus, the low-to-moderate-frequency, outer region approximation to equation 27 (equation A6) yields the impedance function equation A7.

At high frequencies ($K \gg K_{\max}$), the boundary-layer thickness is governed by the Warburg line in figure 4. This implies that convection is not important, and the impedance is dictated by diffusion and the rate of the homogeneous reaction. Thus, the high-frequency inner solution approximation (A9) is applicable. Additionally, this solution is a good high-frequency approximation for all $\hat{k}_b$. Finally, the overlapping region of the high and moderate-frequency solutions for $\Delta \rightarrow 0$ is enclosed by a line parallel and to the right of the $K_{\max}$ line and the $K_{\min} = 1.5\Delta^{-2}$ line.

Although the emphasis of this paper has been on small Δ , impedance results are presented in appendix B that are generally applicable over a wider range of the perturbation parameter. Results in table 1 indicated that as $\hat{k}_b$ decreases (or $\Delta > 0.1$),

the perturbation analysis breaks down. In appendix B, a stagnant Nernst-layer approximation is applied such that the resulting equation B2 is valid for any $\hat{k}_j$. The impedance calculated using this expression is reliable in the region on the right side of figure 8 (where it coincides with equation A9) and is approximately valid over the entire frequency range, although not in a rigorous manner.

6. Conclusions

The general Stefan-Maxwell program^[1] accounting for multicomponent diffusion, migration, and convection, in addition to any number of homogeneous and heterogeneous reactions, is a very powerful algorithm for studying the frequency response of the rotating disk. However, when utilizing computer implemented techniques, one must be cautious of numerical inaccuracies that can arise for certain values of the system parameters.

In this paper, the dissolution of a copper rotating disk has been studied. We have shown that a perturbation analysis can be used to elucidate numerical errors that did occur for the case of large, but finite, rate constants of the homogeneous complexing reaction. Introduction of the dimensionless impedance also proved to be very helpful for generalization and elimination of strong and otherwise overriding steady-state factors (like $\bar{V}$ or $\bar{i}_n$). Additionally, the analytic solutions to the simplified governing equations (dilute-solution theory with no migration) have been given for different limiting cases. Results from the perturbation analysis, given in the text, are valid over the entire frequency range for $\Delta \rightarrow 0$. Appendix A gives high and low-to-moderate-frequency approximations to the perturbation-analysis results, again valid for small Δ . Appendix

B gives impedance results, where a Nernst stagnant diffusion layer is used, making the analysis less rigorous. However, the appendix B solution is applicable for a wider range of Δ . These different cases are illustrated using the E, C_i reaction zone diagram, where the regions of validity of the different analytic solutions are given as a function of K and Δ^{-2} .

Finally, the perturbation analysis has been most useful for characterizing the effect of finite rates of the homogeneous reaction on the faradaic impedance spectrum. The theoretical results have helped verify that an additional impedance loop is possible due to the homogeneous complexing reaction. Limiting behavior for asymptotic values of the homogeneous rate constant were presented and provided a window for studying the finite rate cases. The analysis also indicates that the characteristic frequency, $K'_{\max}$, at the maximum in the imaginary part of the high-frequency homogeneous-reaction impedance loop is equal to $2\Delta^{-2}$. Thus, the measured frequency response of an E, C_i reaction mechanism taking place at a rotating disk enables the homogeneous reaction rate constant $\hat{k}_b$ to be determined, independent of the steady-state method previously discussed.^[2] The magnitude of the impedance R' or $K_{\min}$ at the break between the loops can be used in a similar manner. These separate techniques for parameter determination provide an internal check of the proposed reaction mechanism.

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Appendix A - Moderate and High-Frequency Approximations for $\hat{k}_b \rightarrow \infty$

In the text, we justified separating the diffusion-boundary layer into two regions: an inner region where convection is neglected and an outer region, where the homogeneous reaction is treated as being equilibrated. Equations 21 and 22 were obtained by stretching the inner region and neglecting the convective terms. Here, we will present both low-to-moderate and high frequency approximations to these equations in terms of $\tilde{c}_3$ and $\tilde{c}_4$ for large, but finite homogeneous rate constants.

Moderate Frequencies

For low to moderate frequencies, both the convective terms and the left side of equation 20 can be neglected in this analysis for small values of Δ . With these assumptions, the governing equations, for the inner region and moderate frequencies, are as follows

$$0 = D_3 \frac{\partial^2 \tilde{c}_3}{\partial \bar{\xi}^2} + \frac{D_3 D_4 / D}{1 + \hat{K}^*} (\tilde{c}_4 - \hat{K}^* \tilde{c}_3) \quad (\text{A1})$$

$$0 = D_4 \frac{\partial^2 \tilde{c}_4}{\partial \bar{\xi}^2} - \frac{D_3 D_4 / D}{1 + \hat{K}^*} (\tilde{c}_4 - \hat{K}^* \tilde{c}_3) \quad (\text{A2})$$

Summation of equations A1 and A2 to eliminate the homogeneous-reaction terms on the right yields a solution

$$D_3 \tilde{c}_3 + D_4 \tilde{c}_4 = (D_3 / \hat{K}^* + D_4) P [1 + \bar{\xi} \Delta \theta'(0)] \quad , \quad (\text{A3})$$

where matching of the inner and outer (equation 17) solutions has been applied.

Substitution of A3 into A2 to eliminate $\tilde{c}_3$ yields an equation with the following solution

$$\tilde{c}_4 = \alpha_4 e^{\bar{\xi}} + \beta_4 e^{-\bar{\xi}} + P [1 + \bar{\xi} \Delta \theta'(0)] \quad , \quad (\text{A4})$$

where $\alpha_4 = 0$ so that $\tilde{c}_4$ is bounded at infinity. Since $\partial \tilde{c}_4 / \partial \bar{\xi} = 0$ at $\bar{\xi} = 0$,

$\beta_4 = -P\Delta\theta'(0)$. Equation A3 yields $\tilde{c}_3$, upon substitution of equation A4 for $\tilde{c}_4$, as follows

$$\tilde{c}_3 = -\Delta P\theta'(0) \frac{D_4}{D_3} e^{-\bar{\xi}} + \frac{P}{\hat{K}^*} [1 + \bar{\xi}\Delta\theta'(0)] \quad , \quad (\text{A5})$$

Next, the boundary condition at $\xi = 0$, given by equation 13, gives the constant P , thus enabling equation A5 for $\tilde{c}_{3,0}$ to be written

$$\frac{\tilde{c}_{3,0}}{i_n} = \frac{1}{1 + \hat{K}^*} \frac{\delta}{DF} \left[\frac{-1}{\theta'(0)} + \Delta \hat{K}^* \frac{D_4}{D_3} \right] \quad . \quad (\text{A6})$$

The impedance equation 32 reduces to

$$\mathbf{Z}_F = \frac{\frac{-1}{\theta'(0)} + \Delta \hat{K}^* \frac{D_4}{D_3}}{\Gamma(4/3) + \Delta \hat{K}^* D_4/D_3} \quad (\text{A7})$$

for this limiting case of moderate frequencies. In the limit of $\Delta \rightarrow 0$ ($\hat{k}_b \rightarrow \infty$), $\mathbf{Z}_F$ approaches the normalized dimensionless convective Warburg impedance written in terms of the effective diffusion coefficient D .

High Frequencies

For high frequencies, the $K\Delta^2$ term in equation 20 is significant and must be retained in the perturbation analysis for $\Delta \rightarrow 0$. If convection is neglected in the inner region, then equations 8 and 9 reduce to equations 21 and 22 (using $\tilde{c}_i$ in the place of Θ_i). A solution to this problem is possible by using the two roots with positive real parts of B , B_1 and B_2 , so that

$$\tilde{c}_4 = A_{4,1} e^{-B_1\xi} + A_{4,2} e^{-B_2\xi} \quad . \quad (\text{A8})$$

A solution of this form, yields the following expression for the ac concentration of

species 3

$$\frac{\tilde{c}_{3,0}}{\tilde{i}_n} = \frac{\left[jK + \frac{D_3 D_4}{\Delta^2 D^2 (1 + \hat{K}^*)} \right] \frac{1}{B_1 B_2} + \frac{D_4}{D}}{\frac{D_3 D_4}{D} \frac{F}{\delta} (B_1 + B_2)} \quad (\text{A9})$$

Therefore, for high frequencies, equation 32 reduces to

$$\mathbf{Z}_F = \frac{\left[jK + \frac{D_3 D_4}{\Delta^2 D^2 (1 + \hat{K}^*)} \right] \frac{1}{B_1 B_2} + \frac{D_4}{D}}{\left[\frac{\Gamma(4/3)}{1 + \hat{K}^*} + \Delta \frac{D_4}{D_3} \frac{\hat{K}^*}{1 + \hat{K}^*} \right] \frac{D_3 D_4}{D^2} (B_1 + B_2)} \quad (\text{A10})$$

This solution yields an infinite Warburg diffusion impedance in the low-frequency limit since convection is not being accounted for. Better agreement with the known low-frequency RDE impedance behavior is obtained by using a solution when all four roots are used (see Appendix B).

Appendix B. Moderate and High-Frequency Approximations for any $\hat{k}_b$

Using all four roots of B yields a solution to equations 21 and 22 (with $\tilde{c}_i$ in the place of Θ_i) of the form

$$\tilde{c}_4 = A_{4,1} \frac{\sinh \left[B_1 [\Gamma(4/3) - \xi] \right]}{\sinh \left[B_1 \Gamma(4/3) \right]} + A_{4,2} \frac{\sinh \left[B_2 [\Gamma(4/3) - \xi] \right]}{\sinh \left[B_2 \Gamma(4/3) \right]}, \quad (\text{B1})$$

where hyperbolic functions are used for convenience only. Equation 21 can be rearranged to give $\tilde{c}_3$ as a function of $\tilde{c}_4$, such that with equation B1 and the boundary condition given by equation 13, the alternating concentration of species 3 at the surface is

$$\frac{\tilde{c}_{3,0}}{i_n} \frac{FD}{\delta} = \frac{\tanh \left(B_1 \Gamma(4/3) \right)}{B_1 (B_2^2 - B_1^2)} \times \quad (\text{B2})$$

$$\left\{ \left(\frac{D^2 jK}{D_3 D_4} + \frac{1/\Delta^2}{1 + K^*} \right) \left[1 - \frac{B_1}{B_2} \frac{\tanh \left(B_2 \Gamma(4/3) \right)}{\tanh \left(B_1 \Gamma(4/3) \right)} \right] - \frac{D}{D_3} B_1^2 \left[1 - \frac{B_2}{B_1} \frac{\tanh \left(B_2 \Gamma(4/3) \right)}{\tanh \left(B_1 \Gamma(4/3) \right)} \right] \right\}$$

This equation yields similar impedance results to the “overall” solution given by equation 27 in the text for large $\hat{k}_b$. In the high-frequency limit, equation B2 simplifies to equation A9 given in appendix A. Equation B2 has greater applicability than the perturbation-analysis solutions, valid only for $\Delta \rightarrow 0$; it is approximately valid for any $\hat{k}_b$.

List of Symbols

a	0.51023
$A_{3,1}, A_{4,1}, A_{4,2}$	coefficients
B_1, B_2	complex roots of B with positive real parts
$\bar{c}_i$	steady-state concentration of species i , mol/cm ³
$\bar{c}_{i,0}$	steady-state concentration of species i at the electrode surface, mol/cm ³
$\bar{c}_{i,\infty}$	steady-state bulk concentration of species i , mol/cm ³
$\tilde{c}_i$	alternating concentration of species i , mol/cm ³
$\tilde{c}_{i,0}$	alternating concentration of species i at the electrode surface, mol/cm ³
D_i	dilute-solution diffusion coefficient of species i , cm ² /s
D	effective diffusion coefficient, cm ² /s
$D_{\max}$	largest diffusion coefficient, cm ² /s
e^-	symbol for the electron
F	Faraday's constant, 96,487 C/equiv
$\bar{i}_n$	steady-state normal current density, A/cm ²
$\tilde{i}_n$	alternating faradaic current density normal to the electrode, A/cm ²
k_a	anodic rate constant for the electrochemical reaction, mol/cm ² ·s

k_c	cathodic rate constant for the heterogeneous electrochemical reaction, cm/s
$\hat{k}_f^*$	forward rate constant for the homogeneous complexing reaction, 1/s
$\hat{k}_b$	backward rate constant for the homogeneous complexing reaction, 1/s
K	dimensionless perturbation frequency
$K_{\max}$	dimensionless frequency at the maximum in the imaginary part of the low-to-moderate-frequency, outer faradaic impedance loop (characteristic of convective diffusion)
$K_{\min}$	dimensionless frequency at the minimum in the imaginary part of the inner and outer faradaic impedance loops (characteristic of the homogeneous reaction)
$K'_{\max}$	dimensionless frequency at the maximum in the imaginary part of the high-frequency, inner faradaic impedance loop (characteristic of the homogeneous reaction)
$\hat{K}^*$	thermodynamic equilibrium constant for the homogeneous complexing reaction
n	number of electrons involved in electrode reaction
n_j	number of mesh points used in Stefan-Maxwell model
$\tilde{N}_i$	alternating molar flux of species i , mol/cm ² ·s
$p = \omega/\Omega$	dimensionless frequency
P	integration constant, mol/cm ³
R	universal gas constant, 8.3143 J/mol·K
R_p	polarization resistance, $\Omega \cdot \text{cm}^2$
R'	resistance characteristic of the homogeneous reaction, $\Omega \cdot \text{cm}^2$
R_0	mass-transfer resistance, $\Omega \cdot \text{cm}^2$

s_i	stoichiometric coefficient of species i in the electrode reaction
T	absolute temperature, K
v_z	axial component of the velocity to a rotating disk, cm/s
$\bar{V}$	steady-state kinetic driving force (electrode potential relative to given reference electrode placed just outside double layer), V
$\tilde{V}$	alternating kinetic driving force (electrode potential relative to given reference electrode placed just outside double layer), V
z	normal distance from surface, cm
Z_F	complex faradaic impedance, $\Omega \cdot \text{cm}^2$
$Z_F^{(MF)}$	low-to-moderate frequency approximation for the complex faradaic impedance, $\Omega \cdot \text{cm}^2$
Z_F	dimensionless complex faradaic impedance
$ Z_F $	magnitude of the dimensionless complex faradaic impedance

Greek symbols:

α_4	constant in equation A4 for $\tilde{c}_4$
β_4	constant in equation A4 for $\tilde{c}_4$
β	symmetry factor
$\Gamma(4/3)$	0.89298, the gamma function of 4/3
δ	characteristic diffusion layer thickness, cm
$\bar{\delta}$	$\Gamma(4/3)\delta$, Nernst stagnant diffusion-layer thickness, cm
$\hat{\delta}$	homogeneous reaction thickness, cm

Δ	perturbation parameter (dimensionless homogeneous reaction thickness)
$\frac{-1}{\theta'(0)}$	dimensionless convective-diffusion impedance function
θ	dimensionless ac-concentration function for a rotating disk
Θ_3, Θ_4	ac-concentration functions, mol/cm ³
ν	kinematic viscosity, cm ² /s
ξ	dimensionless axial distance for rotating-disk convective-diffusion equation
$\xi_{\max}$	maximum dimensionless axial distance
ξ_{δ}	dimensionless diffusion-layer thickness
$\bar{\xi}$	stretched dimensionless axial distance (inner region) for rotating-disk convective-diffusion equation
$\hat{\tau}$	time constant of the homogeneous reaction, s
τ_{MT}	mass transfer (convective-diffusion) time constant, s
Φ	electrostatic potential, V
χ	dummy variable
ω	perturbation frequency, rad/s
Ω	angular rotation speed of disk, rad/s

subscripts:

a	anodic
b	backward reaction
c	cathodic

- 0 just outside the diffuse part of the double layer
- ∞ in the bulk electrolyte, where there are no concentration variations
- 3 cuprous ion
- 4 copper chloride complexed species

superscripts:

- steady-state conditions
- alternating conditions

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