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An Asymptotic Solution for the Warburg Impedance of a Rotating Disk Electrode

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Abstract

The Warburg impedance of a rotating disk electrode is treated by a regular-perturbation expansion valid for large alternating-current frequencies. This solution agrees well with the exact numerical solution, the error in the Warburg impedance being less than 2% for a dimensionless frequency of 10.

Key Words: Warburg impedance, rotating disk

Introduction

When an electrode is subjected to an alternating current, the concentration on the surface and thus the concentration overpotential vary in a time-dependent manner. This variation gives rise to what is known as the Warburg impedance. Early studies of the frequency dependence of this impedance were made around the start of the century by Warburg.[1] More recently,[2] the impedance of a rotating disk electrode was studied, and numerical results presented for large Schmidt numbers. We investigate here the asymptotic behavior of the Warburg impedance for large frequencies.

It is assumed in the treatment of the problem that the Schmidt number is large and that radial convection and diffusion are negligible. The radially-dependent problem is currently being studied at this laboratory.[3] It is further assumed that dilute-solution theory, with constant transport and thermodynamic properties, is applicable, and that there is an excess of supporting electrolyte so that migration effects are negligible.

Mathematical Formulation

The dimensionless, time-varying equation of convective diffusion is given by

$$\frac{\partial^2 c}{\partial \zeta^2} + 3\zeta^2 \frac{\partial c}{\partial \zeta} - \frac{\partial c}{\partial t^*} = 0 \qquad (1)$$

where c is the concentration of reactant, $\zeta = y\sqrt{\Omega/\nu}\,(a\nu/3D)^{1/3}$ is a dimensionless distance from the disk, $a = 0.51023$ is a constant,[4] and $t^* = t\Omega D(a\nu/3D)^{2/3}/\nu$ is a dimensionless time. We may express the concentration as a sum of its steady and time-varying contributions

$$c = \bar{c} + \tilde{c} \, . \tag{2}$$

The steady problem was first treated by Levich.[5] For an alternating current of frequency ω, the time-varying concentration may be expressed as†

$$\tilde{c} = Ae^{jKt^*}\Theta \tag{3}$$

where $K = \omega\nu(3D/a\nu)^{2/3}/\Omega D$ is a dimensionless frequency. Substitution into the convective diffusion equation yields the complex equation

$$\Theta'' + 3\zeta^2\Theta' - jK\Theta = 0 \tag{4}$$

subject to the boundary conditions

$$\Theta = 1 \text{ at } \zeta = 0 \, , \; \Theta \to 0 \text{ as } \zeta \to \infty \, . \tag{5}$$

The Warburg impedance is related to the concentration overpotential by the expression

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†Strictly speaking, one takes the real part of such complex expressions: $\tilde{c} = \mathrm{Re}\left\{Ae^{jKt^*}\Theta\right\}$.

$$Z_w = \frac{\tilde{\eta}_c}{\tilde{i}} = \frac{RT\sqrt{\nu/\Omega}}{n^2F^2\bar{c}_0 D\Theta'(0)} \left(\frac{3D}{a\nu}\right)^{1/3} \tag{6}$$

where $\tilde{\eta}_c = RT\tilde{c}_0/nF\bar{c}_0$ is the time-varying concentration overpotential (valid for $\tilde{c}_0 << \bar{c}_0$) .

Asymptotic Solution

We are concerned here with the behavior of equations 4 and 5 for large K . This system appears to comprise a singular-perturbation problem;[6] however, a closer examination shows that the solution is regular for large K if we modify the variables. If we let

$$\Theta = \exp\{-(jK)^{3/4}Y(x)\} \tag{7}$$

and

$$x = \zeta/(jK)^{1/4} \tag{8}$$

equations 4 and 5 become

$$(Y')^2 - 3x^2Y' - 1 = Y''/(jK)^{3/4} \tag{9}$$

$$Y = 0 \text{ at } x = 0 \text{ , } \mathrm{Re}\{(jK)^{3/4}Y\} \to \infty \text{ as } (jK)^{1/4}x \to \infty \text{ .} \tag{10}$$

Y can evidently be expanded in a regular expansion in $K^{-3/4}$

$$Y = Y_0(x) + (jK)^{-3/4}Y_1(x) + (jK)^{-3/2}Y_2(x) + 0(K^{-9/4}) \text{ .} \tag{11}$$

Substituting this expansion into equation 9 and equating terms of equal order in K, we obtain relatively simple differential equations for Y_0, Y_1, Y_2, etc. Solving these, we have that $Y_0'(0) = 1$ and $Y_2'(0) = 3/4$, while odd terms give no contribution to $Y'(0)$. The concentration derivative on the surface of the disk is thus given by

$$\Theta'(0) = -\sqrt{jK}\, Y'(0) = -\sqrt{jK} + 3j/4K + 0(K^{-5/2}) \tag{12}$$

so that we may write

$$\mathrm{Re}\left\{\frac{1}{\theta'(0)}\right\} = \frac{4K(2\sqrt{2}\ K^{3/2})}{16K^3 - 6\sqrt{2}\ K^{3/2} + 9} \tag{13}$$

$$-\mathrm{Im}\left\{\frac{1}{\theta'(0)}\right\} = \frac{4K(2\sqrt{2}\ K^{3/2} - 3)}{16K^3 - 6\sqrt{2}\ K^{3/2} + 9} . \tag{14}$$

These latter expressions may be used to evaluate the real and imaginary parts of the Warburg impedance (see equation 6).

Results and Discussion

Figure 1 shows $1/\Theta'(0)$ plotted on the complex plane with the dimensionless frequency K as a parameter. The exact numerical solution is shown along with the asymptotic solution represented by equations 13 and 14. These results are summarized in Table 1. Also shown in the table is the impedance of a stagnant Nernst diffusion layer[7]

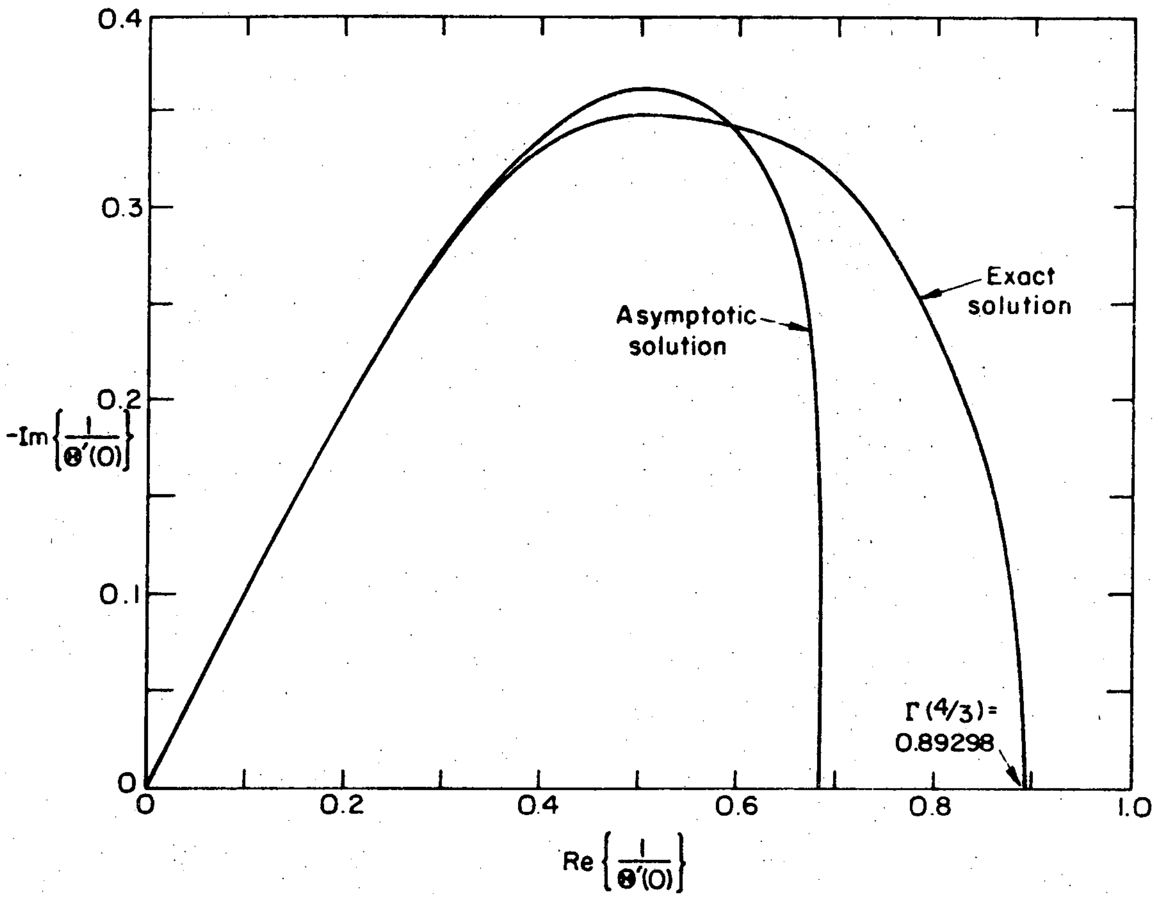

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Figure 1. The complex $1/\bar{\Theta}'(0)$ plane showing the asymptotic and exact numerical solutions.

Table 1. Solutions for the real and imaginary parts of $1/\Theta'(0)$.

	asymptotic solution		exact solution		Nernst layer solution	
K	$\mathrm{Re}\left\{\frac{1}{\Theta'(0)}\right\}$	$-\mathrm{Im}\left\{\frac{1}{\Theta'(0)}\right\}$	$\mathrm{Re}\left\{\frac{1}{\Theta'(0)}\right\}$	$-\mathrm{Im}\left\{\frac{1}{\Theta'(0)}\right\}$	$\mathrm{Re}\left\{\frac{1}{\Theta'(0)}\right\}$	$-\mathrm{Im}\left\{\frac{1}{\Theta'(0)}\right\}$
1.5	0.65758	0.27793	0.72406	0.30195	0.75500	0.28926
2.0	0.56637	0.35398	0.64160	0.33934	0.67925	0.33682
3.5	0.40549	0.33980	0.45610	0.34736	0.48538	0.37104
5.0	0.33041	0.29907	0.35557	0.31151	0.36695	0.34060
7.5	0.26468	0.25101	0.27346	0.25876	0.26868	0.27945
10	0.22729	0.21967	0.23143	0.22396	0.22266	0.23537
20	0.15905	0.15716	0.15999	0.15812	0.15656	0.15788
50	0.10015	0.09985	0.10030	0.10000	0.10004	0.10001
100	0.07075	0.07067	0.07079	0.07072	0.07071	0.07071

$$\frac{1}{\Theta_N'(0)} = \Gamma\left(\frac{4}{3}\right) \frac{\tanh\sqrt{j\omega\delta^2/D}}{\sqrt{j\omega\delta^2/D}} = \frac{\tanh\left(\Gamma\left(\frac{4}{3}\right)\sqrt{jK}\right)}{\sqrt{jK}} \tag{15}$$

where the Nernst diffusion-layer thickness δ is taken to be

$$\delta = \Gamma\left(\frac{4}{3}\right)\sqrt{\frac{\nu}{\Omega}}\left(\frac{3D}{a\nu}\right)^{1/3} . \tag{16}$$

At large K the asymptotic expansion agrees well with the exact solution, the error in the Warburg impedance for $K = 10$ being less than 2% for both real and imaginary parts. As K decreases, the asymptotic solution departs radically from the exact solution. It should be pointed out that it is in the region of intermediate to large values of K that the Nernst diffusion-layer approximation is most in error in predicting the Warburg impedance. It appears, therefore, that the asymptotic expansion developed here offers an improved approximate solution in this region of K.

Summary

A regular-perturbation expansion valid for large alternating-current frequencies has been developed to predict the Warburg impedance of a rotating disk electrode. This asymptotic solution compares favorably with the exact solution and offers an improvement over the Nernst diffusion-layer approximation in the region of intermediate to large K.

Acknowledgment

Charles M. Mohr assisted in the numerical calculations for the Nernst diffusion-layer and exact solutions. This work was supported by the United States Atomic Energy Commission.

Nomenclature

a	0.51023
A	amplitude of the time-varying concentration, mole/cm^3
c	concentration of reactant, mole/cm^3
$\bar{c}$	steady concentration of reactant, mole/cm^3
$\tilde{c}$	time-varying concentration of reactant, mole/cm^3
c_∞	bulk concentration of reactant, mole/cm^3
D	diffusion coefficient, cm^2/sec
F	Faraday's constant, 96,487 coulomb/equiv
$\tilde{i}$	normal alternating-current density at electrode surface, amp/cm^2
j	$\sqrt{-1}$
K	$\omega\nu(3D/a\nu)^{2/3}/\Omega D$, dimensionless frequency
n	number of electons produced when one reactant ion or molecule reacts
R	universal gas constant, 8.3143 joule/mole-deg
t	time, sec
t^*	$t\Omega D(a\nu/3D)^{2/3}/\nu$, dimensionless time
T	absolute temperature, °K
Sc	ν/D , Schmidt number
x	see equation 8
y	normal distance from the disk, cm
Y	see equation 7
Y_m	expansion functions (see equation 11)
Z_W	Warburg impedance, ohm

$\Gamma(4/3)$	0.89298, the gamma function of 4/3
δ	$\Gamma(4/3)\sqrt{\nu/\Omega}\,(3D/a\nu)^{1/3}$, Nernst diffusion-layer thickness
ζ	$y\sqrt{\Omega/\nu}\,(a\nu/3D)^{1/3}$, dimensionless distance normal to the disk
$\tilde{\eta}_c$	time-varying concentration overpotential, volt
Θ	complex, dimensionless, time-varying concentration
ν	kinematic viscosity, cm^2/sec
ω	frequency of alternating current, rad/sec
Ω	rotation speed of disk, rad/sec

Subscripts

$(\ )_0$	( ) evaluated at the electrode surface

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