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The Error in Measurements of Electrode Kinetics
Caused by Nonuniform Ohmic Potential
Drop to a Disk Electrode

by

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Abstract

The error in the exchange current density (i_0) determined at a disk electrode characterized by a nonuniform ohmic potential drop was calculated as a function of the location of the reference electrode. The possible error in i_0 for certain experimental systems can exceed 300%.

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Newman, in his treatment of the current distribution on a rotating disk electrode (1,2), has implied that the nonuniform ohmic potential drop will lead to errors in the determination of kinetic parameters unless special corrections are applied. Because the error will be relatively larger for high exchange current densities and low solution conductivities, linear electrode kinetics have been chosen to assess the magnitude of the effect. The complexity of the results is simplified by restricting the analysis to the same geometry--a disk electrode of radius r_0 in a large insulating plane, with the counter electrode at infinity--and ignoring concentration variations. The apparent surface overpotential is taken to be that measured by a reference electrode, with the ohmic potential drop being determined by interruption of the current. Three particular reference-electrode positions are used to illustrate the effect. The results are qualitatively applicable for other electrode geometries afflicted with a similar nonuniform ohmic potential drop.

Analysis

The potential in solution outside the doublelayer, in the absence of concentration variations, satisfies Laplace's equation

$$\frac{\partial}{\partial \xi} \left[(1 + \xi^2) \frac{\partial \Phi}{\partial \xi} \right] + \frac{\partial}{\partial \eta} \left[(1 - \eta^2) \frac{\partial \Phi}{\partial \eta} \right] = 0 \quad [1]$$

where the rotational elliptic coordinates η and ξ are related to cylindrical coordinates r and z by

$$z = r_0 \xi \eta \quad r = r_0 [(1 + \xi^2)(1 - \eta^2)]^{1/2} \quad [2]$$

(see ref. 3). The boundary conditions adopted for the disk electrode are (1)

$$\frac{\partial \Phi}{\partial \eta} = 0 \quad \text{at} \quad \eta = 0 \quad (\text{on the insulating plane})$$

$$\Phi = 0 \quad \text{as} \quad \xi \rightarrow \infty \quad (\text{far from the disk}) \quad [3]$$

Φ well behaved at $\eta = 1$ (on the axis of the disk)

The solution to Eq. [1] satisfying boundary conditions [3] can be expressed as (1)

$$\Phi = \frac{RT}{F} \sum_{n=0}^{\infty} B_n P_{2n}(\eta) M_{2n}(\xi) \quad [4]$$

where $P_{2n}(\eta)$ is the Legendre polynomial of order $2n$ and $M_{2n}(\xi)$ is a Legendre function with known properties (1).

For sufficiently small current densities (linear polarization), the relationship between the surface overpotential and the local current density is

$$i(r) = i_0 (\alpha_a + \alpha_c) \frac{F}{RT} \eta_s = - \kappa_{\infty} \frac{\partial \Phi}{\partial z} \quad \text{at} \quad z = 0, \quad r \leq r_0 \quad [5]$$

where $i(r)$ refers to the local current density, η_s refers to the local surface overpotential (which is characteristic of the local

current density) and $i_o(\alpha_a + \alpha_c)\frac{F}{RT}$ relates to the local kinetics of the faradaic reaction, taken here to be linear. The local surface overpotential is given by

$$\eta_s = V - \Phi(r,0) \quad [6]$$

where V is the electrode potential (assumed to be uniform) and $\Phi(r,0)$ is the potential in the solution just outside the double layer.

The overpotential measured experimentally usually contains an ohmic contribution which must be removed by either a numerical calculation (1,3) or use of an interrupter technique (4). Newman (5) has shown that the ohmic potential measured by the interrupter technique corresponds to an average potential characteristic of the primary current distribution. A nonuniformly charged double-layer is associated with a non-uniform ohmic potential drop during the passage of current. Immediately after the current is interrupted, the double layer remains charged, and the potential just outside the double-layer changes by a uniform amount over the entire surface of the disk

$$V' - \Phi'(r,0) = V - \Phi(r,0) \quad [7]$$

where primes denote quantities after interruption. The potential at an arbitrary point in the solution is

$$\Phi'(r,z) = \Phi(r,z) - \bar{\Phi}(r,z) \quad [8]$$

where $\bar{\Phi}(r,z)$ represents the local ohmic drop associated with the primary distribution for the same current. The surface overpotential as measured by the current interrupter method with the reference electrode at r,z can be written as

$$\eta_{s,app} = V - \Phi(r,z) - \bar{\Phi}(r,0) + \bar{\Phi}(r,z) \quad [9]$$

It is assumed that one who does not take into account the nonuniform current distribution would calculate an apparent exchange current density, $i_{o,app}$ with the linear polarization expression based on the average current density and apparent surface overpotential:

$$i_{avg} = i_{o,app} (\alpha_a + \alpha_c) \frac{F}{RT} \eta_{s,app} \quad [10]$$

The difference between Eq. [5] and [10] is a consequence of the nonuniform ohmic drop to the disk electrode which is unavoidably contained in Eq. [10]. Substitution of Eq. [4] and [9] into Eq. [10] gives an expression for the error one might expect in the exchange current density

$$i_o / i_{o,app} = \frac{\pi J}{4} \left[\frac{4\kappa_{\infty} r_o V}{I} - 1 - \sum_{n=1}^{\infty} \frac{B_n}{B_o} P_{2n}(\eta) M_{2n}(\xi) \right] \quad [11]$$

where

$$J = (\alpha_a + \alpha_c) \frac{F r_o i_o}{RT \kappa_{\infty}}$$

$$B_o = \frac{F}{RT} \frac{I}{4\kappa_{\infty} r_o}$$

and the B_n values have been determined in ref. (1). Equation [11] is valid for any arbitrary position of the reference electrode.

Let us now examine three special cases. With the reference electrode at infinity, Eq. [11] can be expressed as

$$i_o/i_{o,app} = \frac{\pi J}{4} \left[\frac{4\kappa_{\infty} r_o V}{I} - 1 \right] \quad [12]$$

With the reference electrode adjacent to the working electrode

$$i_o/i_{o,app} = i(r)/i_{avg} \quad [13]$$

a general result applicable to other geometries as well. Placing the reference electrode close to the working electrode decreases the ohmic potential drop, but it also permits the extremes in the error for the exchange current density. Near the center, $i(r)$ has its smallest value, and the error can be expressed as

$$i_o/i_{o,app} = \frac{\pi J}{4} \left[\frac{4\kappa_{\infty} r_o V}{I} - \sum_{n=0}^{\infty} \frac{B_n}{B_o} \right] \quad [14]$$

Near the edge, $i(r)$ has its largest value, and

$$i_o/i_{o,app} = \frac{\pi J}{4} \left[\frac{4\kappa_{\infty} r_o V}{I} - \sum_{n=0}^{\infty} \frac{B_n}{B_o} P_{2n}(0) \right] \quad [15]$$

With the reference electrode farther from the surface, the error can actually be expected to lie between these extremes. Figure 1 contains the numerical results of the error in the exchange current density for

several positions of the reference electrode as a function of the dimensionless exchange current density J . For the values of J considered, the error in i_0 can range from -50 to more than 300%.

Discussion and Conclusions

The most important result of the paper is that serious errors in the measurement of electrode kinetic parameters (i.e., i_0) can result from an electrode which is characterized by a nonuniform current distribution. The magnitude of this error depends on the position of the reference electrode relative to the working electrode. For the cases shown in Figure 1, the errors associated with nonuniform current distribution are smallest when the reference electrode is located far from the disk. However, decreasing the error in this manner increases the ohmic drop which must be compensated for by an interrupter technique. Under certain experimental conditions, the compensated ohmic potential can be as large as 90% of the total measured overpotential, with a consequent decrease in the accuracy of the surface overpotential. There are cell designs (6,7) which provide a uniform primary current distribution over the surface of the electrode and at the same time position the reference electrode in the plane of the working electrode in such a manner as not to disturb the local current distribution. Also, the use of a spherical electrode, as pointed out by Newman (2), can be used to eliminate current distribution problems.

A second result of this work is that for the reference electrode positions shown in Figure 1, one needs only to measure the value of J for the system in question to assess the degree of error

in i_0 . For other reference electrode positions, Eq. [11] can be evaluated to assess the error in i_0 . The results in this paper can be used qualitatively to assess the error for configurations other than the disk electrode. Equation [13] can be used on any electrode system provided that $i(r)$ is known.

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Nomenclature

B_n	coefficients in series for potential
F	Faraday's constant, coulomb/equiv
i	normal current density at electrode surface, amp/cm ²
i_o	exchange current density, amp/cm ²
$i_{o,app}$	apparent exchange current density, amp/cm ²
i_{avg}	average current density, amp/cm ²
I	total current to the disk, amp
J	dimensionless exchange current density (see Eq. [11])
M_{2n}	a Legendre function
P_{2n}	Legendre polynomial of order 2n
r	radial coordinate, cm
r_o	radius of disk, cm
R	universal gas constant, joule/mole - deg
T	absolute temperature, °K
V	potential of metal disk electrode, volt
z	normal distance from disk, cm
z_i	charge number of species i
α_a, α_c	parameters in kinetic expression (see Eq. [5])
η	elliptic coordinate (see Eq. [2])
η_s	surface overpotential, volt
$\eta_{s,app}$	apparent surface overpotential, volt
κ_∞	conductivity of bulk solution, mho - cm ⁻¹
ξ	elliptic coordinate (see Eq. [10])
Φ	electrostatic potential, volt
$\bar{\Phi}$	ohmic drop, volt

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Figure 1

Correction in i_o Determination for Linear Polarization for Various Positions of the Reference Electrode Relative to the Disk Electrode.

Curve A approaches 0.5 for large J , while Curve C approaches infinity.

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