ROTATING DISC AND RING-DISC TECHNIQUES+

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INTRODUCTION

In kinetic studies of electrode processes, uniformity of the concentration gradients along the electrode surface and quantitative information concerning these gradients are necessary. In many instances the rotating disc electrode technique provides an effective means for realizing these requirements. Furthermore this technique allows the surface concentration of reactants and products to be varied in a controlled manner through changes in the rotation rate and hence can be used to determine the reaction orders through the dependence of the current on the rotation rate without the necessity of varying the bulk concentrations.

An important extension of the rotating disc technique is the ring-disc configuration which consists of a disc surrounded by a closely placed concentric ring with its surface in the same plane and separated from the disc by a thin insulating sleeve. The rotating ring-disc electrode is well suited to the study of electrode reactions involving unstable products or intermediates. Species produced electrochemically on the disc are monitored electrochemically on the ring as the liquid spirals out from the disc across the surface of the ring. The concentration of the species in question, averaged over the surface of the ring, can be determined in most instances by one of the following procedures:

1. Maintain the ring potential at a value such as to reverse the process leading to the formation of the species of interest and measure the ring current.

2. Construct the ring of a metal which is favorable for the completion of the overall electrode process yielding the intermediate in question on the disc or for the further oxidation or reduction of the product. Maintain the ring at a fixed potential favorable for such or scan through an appropriate range of potentials and measure the ring current.

Both the rotating disc and ring-disc techniques have already found substantial use in kinetic studies but also offer promise for analysis when solid electrodes are required.

THEORY

The problem of mass transport by convective diffusion to a rotating disc electrode has been solved by Levich (1) for the case of a perfectly smooth, horizontal disc of infinite radius rotating at a constant angular velocity in an infinite liquid under conditions of laminar flow. In practice, a disc electrode can effectively meet these requirements if 1) the radius is very large compared to the momentum boundary layer thickness, 2) all other surfaces within or bounding the liquid are at a distance large compared to the radius of the rotating surface, 3) surface irregularities on the disc are small compared to the momentum boundary

+ Some of the experimental aspects of the paper are based on research supported by the Office of Naval Research.

layer thickness, 4) the rotation rate for the particular disc is below the critical Reynolds number for the onset of turbulence [i.e., $Re = (r^2 \omega/\nu) < 10^5$ where r = overall radius of the disc, ω = angular rotation rate, ν = kinematic viscosity].

According to Levich, the effective thickness of the Nernst transport boundary layer is

$$\delta = 1.80\ aD^{1/3}\nu^{1/6}/\omega^{1/2} \qquad [1]$$

where D is the diffusion coefficient of the reacting species in $cm^2\ sec^{-1}$, a is a dimensionless constant, and all other quantities are in cgs units. The term a in eq. [1] was originally designed as 0.8934 by Levich using an approximation to the integration. Gregory and Riddiford (2) carried out the graphical integration in a more accurate manner and found for D/ν values less than 4×10^{-3} that a can be calculated to within 1% by the empirical equation

$$a = 0.8934 + 0.316\ (D/\nu)^{0.36} \qquad [2]$$

The second term is only a few percent at the most for aqueous solutions and hence is really necessary only for rather accurate work--probably more accurate than most rotating disc electrode configurations permit. Newman (3) also has reported a corrected value for a.

Eq. [1] yields the following expression for the diffusion current density i in A/cm^2

$$i = 0.55a^{-1}zFD^{2/3}\nu^{-1/6}\omega^{1/2}[C(\infty) - C(o)] \qquad [3]$$

or

$$i_D = 0.554a^{-1}zFD^{2/3}\nu^{-1/6}\omega^{1/2}[C(\infty)] \qquad [4]$$

where i_D is the limiting current density, zF is the number of coulombs of charge transferred per mole of diffusing species, and $C(\infty)$ and $C(o)$ are the concentrations of the diffusing reactant in the bulk and at the electrode surface, respectively, in moles cm^{-3}.

At the limiting current, the current density is uniform on the rotating disc even if substantial ohmic voltage drop occurs within the electrolyte in the vicinity of the disc. At currents below the limiting value, however, the current distribution may be considerably greater near the periphery of the disc because of the greater accessibility of the edge than the center as a result of the I-R drop in the solution. Figure 1 indicates the current distribution on the disc according to the treatment of Newman (4) when Tafel kinetics are involved and electrolytic transference of species is considered with the transference number t = 0.5. The parameter N in this figure is defined by the equation

$$N = -\left(\frac{r_o^2\omega}{\nu}\right)^{1/2}\left(\frac{0.5102\nu}{3D}\right)^{1/3}\frac{nZF^2D[C(\infty)]}{RT(1-t)[\kappa(\infty)]} \qquad [5]$$

where r_o is the radius of the disc electrode, n is the number of electrons per molecule or ion of reacting species, $[\kappa(\infty)]$ is the specific conductance in the bulk of the solution, and $Z = -z_+z_-/(z_+ - z_-)$ for an electrolyte consisting of a single salt or Z = - n for solution with a supporting electrolyte. The value of the exchange current density (i_o) does not enter into the calculation provided the local current density is high compared to i_o at all positions on the disc.

In kinetic studies with the rotating disc, it is evident from Figure 1 that substantial errors will be introduced due to non-uniform current distribution unless the parameter N is a relatively low value. Such can be realized through the use of a supporting electrolyte which increases $[\kappa(\infty)]$ in the denominator. For example (4) for copper deposition from a 0.1 M $CuSO_4$ solution on a disc with r_o = 0.25 cm at 300 rpm, N is 79 while with 0.1 M $CuSO_4$ + 1.53 M H_2SO_4 the corresponding value for N

is 1.6 (although it should be noted that the limiting current density has dropped from 79 mA/cm^2 without the H_2SO_4 to 50 mA/cm^2 with the addition of the H_2SO_4 because of the suppression of the transference number from 0.363 to 0). Another approach to reducing the non-uniformity of the current density is to employ a ring-disc electrode assembly with the ring used as a guard by maintaining it at the same potential as the disc with a separate circuit. If the spacing between the disc and ring is very small compared to the radius of the disc and the thickness of the ring, the arrangement is equivalent to examining just that portion of the plot in Figure 1 corresponding to $(r/r_o) \leq r_1/r_3$ where r_1 and r_3 are the radius of the disc and the outside radius of the ring, respectively.

In kinetic studies with the rotating disc technique the dependence of the disc current on the rotation rate provides a relatively simple means (5-7) for determining the reaction order relative to the diffusing species provided a supporting electrolyte is used at a concentration sufficient to ensure a relatively low value for N [high $\kappa(\infty)$] and to avoid appreciable double layer corrections. When the back reaction is negligible, the current density can be expressed as a function of the concentration of a reacting species by the equation

$$i = k[C(o)]^n \qquad [6]$$

where n is the reaction order with respect to the diffusing species and k is a potential-dependent rate-constant. If the rotation rate at a constant potential is increased to a value such that C(0) approaches closely $C(\infty)$, the process will become pure kinetically controlled and the current density then becomes

$$i_L = k\ [C(\infty)]^n \qquad [7]$$

From eq. [3], the actual current density may be expressed as

$$i = B\omega^{1/2}\ [C(\infty) - C(o)] \qquad [8]$$

Let ω_o be defined (see Figure 2) such that

$$i_L = B(\omega_o)^{1/2}\ [C(\infty)] \qquad [9]$$

and the observed current density corresponding to ω_o for a given potential be i_k. From eqs. [6-9],

$$i_k = i_L\left[1 - \left(\frac{i_k}{i_L}\right)^{1/n}\right] \qquad [10]$$

or

$$n = \frac{\log i_L - \log i_k}{\log i_L - \log (i_L - i_K)} \qquad [10a]$$

To apply this equation, only one set of values for i_L and i_k are required. In practice, a series of values is usually obtained to establish the constancy of n and hence the validity of the experiment.

Figure 2 indicates the dependence of the observed current density on rotation rate for several reaction orders. For a first order reaction, the limiting value for the current density at infinite rotation rate (corresponding to i_L) can be obtained by means of the equation

$$\frac{1}{i} = \frac{1}{i_L} + \frac{1}{B[C(\infty)]\omega}1/2 \qquad [11]$$

The rotating disc-ring electrode system has been treated by Ivanov and Levich (8) who have obtained the following relationship for the total ring current when the ring is biased to a potential such as to consume electrochemically all of the

intermediate reaching the ring from the disc:

$$i_r = \frac{n_2}{n_1} \cdot \frac{i_D}{1 + \frac{\kappa\delta_x}{D_x}} \cdot M \qquad [12]$$

where

$$M = 0.8\left[1 - \frac{3}{4}\left(\frac{r_1}{r_2}\right)^3\right]^{1/3} \int_1^{r_3/r_2} \frac{(r/r_2)^2\, dr}{\left[\left(\frac{r}{r_2}\right)^3 - 1\right]^{1/3}\left[\left(\frac{r}{r_2}\right)^3 - \frac{3}{4}\left(\frac{r_1}{r_2}\right)^3\right]} \qquad [12a]$$

and

i_D = current on the disc to generate only the intermediate

κ = rate of conversion of intermediate to final product on the disc (assumed first order in concentration of itnermediate)

n_1 = number of electrons transferred at disc per molecule of reactant converted to intermediate

n_2 = number of electrons transferred at ring per molecule of intermediate

D_x = diffusion coefficient of intermediate

δ_x = diffusion layer thickness for the intermediate

r = radial distance from center of disc

r_1 = radius of disc

r_2, r_3 = inner and outer radii of ring, respectively

This equation carries the assumptions that 1) $(r_2 - r_1) << r_1$, 2) the intermediate does not undergo any homogeneous reaction, and 3) ionic migration can be neglected. The factor M corresponds to the fraction of the total amount of intermediate diffusing away from the disc, which undergoes electrochemical reaction at the ring. While M can be evaluated solely from geometric considerations, such requires a numerical evaluation of the integral in eq. [12a]. Bruckenstein and Feldman (9) have carried out this integration analytically.

Ivanov and Levich indicated that several approximations are made in evaluating the numerical constant in eq. [12a] and that it may be 5% too high. Recently Albery and Bruckenstein (10,11), however, carried out an extensive study of the ring-disc electrode and concluded that the Ivanov-Levich expression for M may be in error by up to 25%, depending on the electrode geometry. Albery and Bruckenstein obtained the following explicit expression for M:

$$M = 1 - F(\alpha/\beta) + \beta^{2/3}[1 - F(\alpha)] - (1+\alpha+\beta)^{2/3}\left\{1 - F[(\alpha/\beta)(1+\alpha+\beta)]\right\} \qquad [13]$$

where

$$\alpha = (r_2/r_1)^3 - 1 \qquad [14a]$$

$$\beta = (r_3/r_1)^3 - (r_2/r_1)^3 \qquad [14b]$$

and

$$F(\theta) = \frac{3^{1/2}}{4\pi} \ln \frac{(1+\theta^{1/3})^3}{1+\theta} + \frac{3}{2\pi} \arctan\left(\frac{2\theta^{1/3} - 1}{3^{1/2}}\right) + \frac{1}{4} \qquad [14c]$$

These authors have tabulated values of M in terms of the parameters r_3/r_2 and r_2/r_1 — a welcome convenience to electrochemists using the ring-disc technique. In an

extensive series of papers, Albery et al. (12-14) have also developed treatments for the current-voltage curves for the ring (11), the effects of first order homogeneous as well as heterogeneous reactions involving the intermediates produced at the disc on the ring current (14), and the shape of the ring current vs. disc current curves during the use of the ring-disc electrode for diffusion layer titrations (13).

EXPERIMENTAL FEATURES

A. Electrode design

Riddiford (15) has reviewed the practical aspects of electrode design and the influence of electrode shape on experimental results. Even though it is recommended to use a bell-shaped electrode (Figure 3A), a cylindrical shaped electrode assembly in which the central portion of the lower surface is the electrode (Figure 3B) is often sufficient. This type of electrode is easily made and suitable for convenient interchange of electrodes which maintain the necessary high purity requirement. In an examination (16) of an electrode of this construction with a diameter of 0.48 cm mounted in a Teflon cylinder (0.96 cm diameter), the limiting current density for the reduction of the I_3^- ion to I^- in a 0.025 M KI_3 + 0.1 M KI solution was found to be proportional to $\omega^{1/2}$ to within 2% for rotation rates from 100 to 18000 rpm. The slope was only 2% higher than the value predicted from eq.[4] using the Gregory-Riddiford value for a or the results of Nelson and Riddiford (17) for this same reduction with an electrode of the bell-shape. In recent years, rotating disc electrodes in cylindrical mounts (Figure 3B) have been used to investigate a number of different electrode reactions in the laboratories at Western Reserve University (e.g., hydrogen oxidation (18), oxygen reduction (16), tin and nickel deposition, various redox couples on semiconductors). In no instance has there been observed any appreciable deviation of the limiting current density from a direct proportional dependence on $\omega^{1/2}$ at rotation rates in the range 100 to 18000 rpm when the limiting current represented pure mass transport control associated with convective diffusion.

In studies with some types of electrodes (e.g., single crystal NiO) at Western Reserve, it has not been possible to fabricate disc-shaped electrodes without unusual difficulty and hence rotating irregular-shaped, flat electrodes mounted in an insulating cylinder have been used. The limiting mass-transport current has been found to be proportional to $\omega^{1/2}$ in the same manner as for the disc electrodes, and in fact, the limiting current densities for a square or near square-shaped rotating electrode are almost the same as for the disc. On occasion, difficulty also has been encountered in obtaining electrodes which are extremely flat and void of pits [e.g., certain types of carbon electrodes (16)]. As long as the irregularities are only of the order of microns in dimension, no deviations of more than a few percent from eq. [4] have been observed with disc electrodes in cylindrical mounts with dimensions similar to those described earlier for rotation rates up to 18000 rpm.

Teflon is probably the best material of construction available for mounting disc and disc-ring electrodes from the viewpoint of maintaining purity of solution. In some cases, however, the electrodes are very fragile and can not be machined to a cylindrical shape (e.g., single crystal graphite, semiconducting single crystal metal oxides). Therefore they can not be press-fitted into Teflon mountings with a sufficiently tight seal. In such instances in the authors' laboratory the electrodes are mounted in Kel-F using a high pressure moulding technique at 300°C.

B. Mechanical system

The basic features of a relatively simple rotating ring-disc system are shown in Figure 4. While both belt drive and direct drive systems have been used, the authors prefer the belt drive because it permits a larger range of rotation rates to be covered with a given motor and the construction of the shaft is simplier and less expensive. For disc and ring-disc electrodes mounted in a cylinder of 1.5-cm diameter or less, a 1/15 HP motor with appropriate pulleys is sufficient for up to

20000 rpm. While a motor control with a feed-back circuit or a variable frequency synchronous motor system is to be preferred for very refined measurements, the authors have found that a simple universal motor with a d.c. field and armature current control provides sufficiently stable rotation rates for most work. Rotation rates in the arrangement shown in Figure 4 are measured by means of a lamp-photocell arrangement connected to a frequency meter with the beam transmitted through a number of equally spaced holes in an aluminum disc attached to the upper part of the shaft. Sealed precision bearings are used to minimize eccentricity in rotation and to prevent any leakage of bearing lubricant. The lead to the disc electrodes extends to the top of the shaft where contact is made by means of a spring-loaded silver-graphite brush. Contact to the ring is made through a slip-ring silver-graphite brush assembly near the top of the shaft. The steel shaft on which the electrode assembly is mounted may be either at ground potential or isolated from ground by supporting the bearing housing on a plastic mounting.

One of the substantial experimental problems in the use of the rotating disc and ring-disc techniques is obtaining a satisfactory seal where the Teflon covered shaft enters the cell. While various types of liquid seals work satisfactorily at rotation rates up to 6000 rpm, at higher speeds they present excessive drag, require cooling, and unless very carefully designed are no longer gas tight. One rather effective technique for preventing gases of the atmosphere from entering the cell around the rotating shaft is to use a relatively long glass or Teflon sleeve around the shaft and then to maintain a slight excess pressure in the gas space above the electrolyte within the cell.

APPLICATIONS

The applications of the rotating disc and ring-disc techniques to kinetic studies is well illustrated by recent studies of oxygen reduction on various surfaces with peroxide usually as an unstable intermediate. Some results recently obtained in the authors' laboratory for oxygen reduction using these techniques will be presented as part of the oral presentation of the paper.

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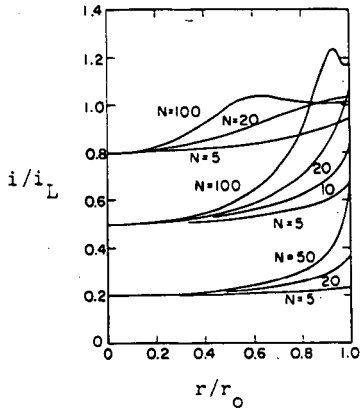

Figure 1. Current distribution on a rotating disc electrode of radius r_o for Tafel kinetics with transfer coefficients of 1/2 and a reaction order of 1, according to Newman (4).

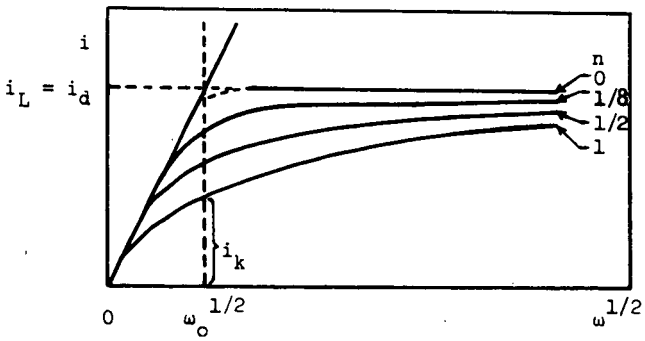

Figure 2. Dependence of current density on rotation rate for various reaction orders [after Frumkin (7)].

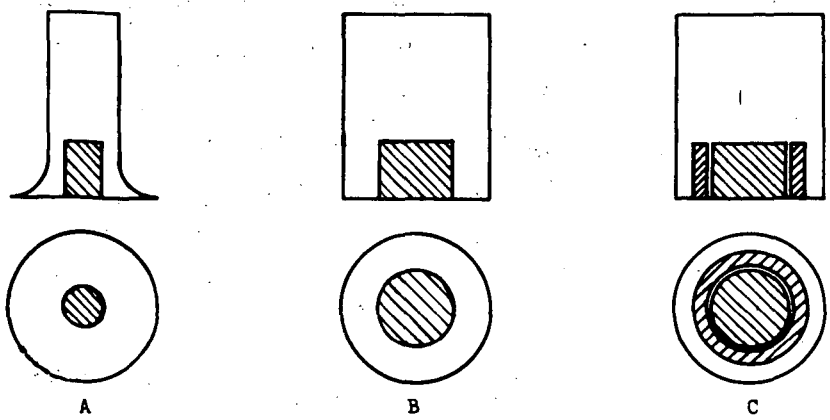

Figure 3. Rotating Disc and Ring-Disc Electrodes.

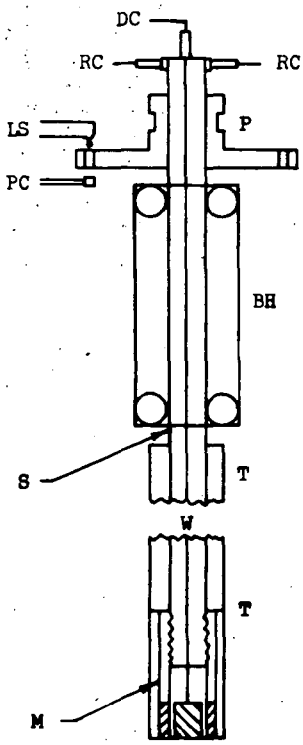

Figure 4. Rotating Ring-Disc Electrode System.

S steel shaft
BH bearings and housing
P pulley
T Teflon insulation
M Metal support
DC disc brush contact
RC ring brush contact
W insulated wire for DC
LS light source
PC photocell