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Mass Transfer to an Eccentric Rotating Disk Electrode

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Abstract

The mass-transfer rate to a rotating disk electrode rotated about an off-center axis is calculated for eccentricities of from zero to 5 electrode radii. An asymptotic form for the transfer rate valid for large eccentricities is also derived and compared to two previous analyses. It is found that mass transfer is not affected until a critical eccentricity is reached and that the asymptotic expression provides a good approximation to the rate of mass transfer even at moderately small eccentricities. The analysis is supported by experimental data on the deposition of copper on several electrodes of eccentricities between 0.66 and 3.94.

Introduction

When the active portion of a rotating disk electrode is offset from the axis of rotation, the Levich formula⁽¹⁾ for the mass transfer rate may no longer be applicable. Riddiford⁽²⁾ implies that exact centering of the active portion is an important design consideration for such electrodes but does not estimate the change in mass-transfer rate due to an eccentricity. More recently Chin and Litt⁽³⁾ have treated the effect of large eccentricities, where the small active portion is located at least several diameters from the center of rotation. Also, Bardin and Dikumar⁽⁴⁾ have attempted an analysis for moderate eccentricities (offsets slightly greater than the electrode radius).

Both of these works are limited in their applicability. Chin's paper is nearly correct for large eccentricities but is inappropriate for only slightly off-center electrodes. Bardin and Dikumar erred seriously in their simplifying assumptions, and their conclusions are incorrect for all eccentricities.

We hope to provide here a more rigorous formulation of the problem and, particularly, to describe the behavior at small eccentricities where the easily developed asymptotic form (for large eccentricities) is not applicable. The small-eccentricity behavior should be found useful in assessing error limits due to machining tolerances in the manufacture of rotating-disk electrodes. Attention is given to large eccentricities for the purpose of completeness only. It seems unlikely that disk electrodes would be operated in this

fashion since the imbalance could be dangerous at high rotation rates.

A little contemplation suggests that the mass-transfer rate is strictly constant until an eccentricity is reached where a fluid trajectory can spiral off the disk electrode and then back onto it. We have sought the value of the eccentricity at this limit as well as the behavior of the mass-transfer rate for somewhat larger eccentricities.

Theory

The laminar flow pattern near a rotating disk has been described by Von Kármán with later improvement (in numerical constants) by Cochran.⁽⁵⁾ Basically, a fluid particle drawn toward the disk near its center spirals outward while approaching the disk and eventually leaves the region of interest. For Schmidt numbers typical of electrolytic solutions, the diffusion layer is very near the disk, and the radial and tangential velocities of the fluid relative to the disk may be adequately expressed as linear functions of the distance from the disk. Cochran found that these velocities are

$$\begin{aligned} v_r &= 0.510r(\omega^3/\nu)^{1/2}z \\ v_\theta - r\omega &= -0.616r(\omega^3/\nu)^{1/2}z \end{aligned} \tag{1}$$

where ν is the kinematic viscosity of the solution and ω is the rotation speed (sec^{-1}).

A fluid particle near the disk will be tracing a path $r(\theta)$, relative to the disk, described by

$$\frac{1}{r} \frac{dr}{d\theta} = \frac{v_r}{v_\theta - r\omega} = -0.828 . \quad (2)$$

Note that this is independent of either r or z within the range of validity of the linear approximations in equation 1. Thus the path followed by any fluid particle near the disk is such that its direction of travel is at an angle α to a ray drawn from the center of rotation (see Figure 1) and

$$\alpha = \cot^{-1}(0.828) = 50.38^\circ . \quad (3)$$

Equation (2) can be integrated to yield the equation for the trajectory passing through the point (r_1, θ_1)

$$r = r_1 \exp [(\theta_1 - \theta) \cot \alpha] . \quad (4)$$

On the other hand, a point on the edge of the electrode is given by

$$r = r_o \sqrt{\epsilon^2 + 1 - 2\epsilon \cos \theta'} . \quad (5)$$

The condition of uniform accessibility, that is, uniform rate of mass transfer, will be maintained for nonzero eccentricities as long as fluid particles spiraling off the electrode never return to or pass over the electrode again. Fluid begins to return to the electrode for an eccentricity at which a trajectory first becomes

tangent to the edge of the electrode. Tangency is given by $\alpha = \beta$, where β is the angle between the edge of the disk and the ray drawn from the center of rotation.

Geometrical considerations then lead to the relation

$$\alpha = \beta = \theta + \theta' - \frac{\pi}{2} \quad (6)$$

for a tangent point on the edge. Since the relationship between θ and θ' is

$$\theta = \tan^{-1} \left(\frac{\sin \theta'}{\epsilon - \cos \theta'} \right) \quad (7)$$

the condition for a tangent point reduces to

$$\theta' = \alpha + \cos^{-1} \left(\frac{\cos \alpha}{\epsilon} \right) \quad (8)$$

after rearrangement using trigonometric identities. This equation shows that no point of tangency exists for $\epsilon < \cos \alpha$. Thus, the critical eccentricity we seek is

$$\epsilon_c = \cos \alpha = 0.6377. \quad (9)$$

For $\epsilon > \cos \alpha$, equation 8 gives two tangent points

$$\theta'_{t1} = \alpha - \cos^{-1} \left(\frac{\cos \alpha}{\epsilon} \right),$$

and

$$\theta'_{t2} = \alpha + \cos^{-1} \left(\frac{\cos \alpha}{\epsilon} \right),$$

(10)

where the principal branch of $\cos^{-1}$ is now to be used.

As $\epsilon \rightarrow 1.0$, it eventually becomes possible for the same trajectory to spiral off the disk, return, spiral off again, and then return once more. Since in this analysis we will not attempt to treat this case, we must determine at what eccentricity this effect begins. At the onset of this behavior, the critical trajectory is one that is tangent to the disk at two points, (r_1, θ'_{t1}) and (r_2, θ'_{t2}) , as shown in figure 2. To determine the eccentricity at which this occurs, we begin with 5 equations in 5 unknowns $(r_1, r_2, \theta'_{t1}, \theta'_{t2}, \epsilon)$. Equation 10 gives two relations for the angles at the tangent points. Equation 5 gives two relations for points on the edge of the electrode. Since the two points must be on the same spiral, equation 4 can be written

$$r_2 = r_1 \exp \left\{ \left[\tan^{-1} \left(\frac{\sin \theta'_{t1}}{\epsilon - \cos \theta'_{t1}} \right) - \tan^{-1} \left(\frac{\sin \theta'_{t2}}{\epsilon - \cos \theta'_{t2}} \right) + 2\pi \right] \cot \alpha \right\} \quad (11)$$

where 2π appears since the trajectory completes a full spiral before the second tangent point is reached. These five equations can be reduced to one equation in ϵ ,

$$\epsilon^2 + 1 - 2\epsilon \cos \left[\alpha + \cos^{-1} \left(\frac{\cos \alpha}{\epsilon} \right) \right] = \left\{ \epsilon^2 + 1 - 2\epsilon \cos \left[\alpha - \cos^{-1} \left(\frac{\cos \alpha}{\epsilon} \right) \right] \right\} \exp \left\{ \left[\pi + \cos^{-1} \left(\frac{\cos \alpha}{\epsilon} \right) \right] 4 \cot \alpha \right\}, \quad (12)$$

which has two solutions

$$\begin{aligned}\epsilon_1 &= 0.998476 \\ \epsilon_2 &= 1.001523\end{aligned}\tag{13}$$

The second solution is significant for calculations with $\epsilon > 1$, since it gives the eccentricity at which fluid begins to pass over the disk only once. Eccentricities between these two critical values will not be treated in this analysis.

The mass-transfer rate to the electrode may now be determined. It should be noted that for eccentricities $0.9985 > \epsilon > 0.6377$, some of the fluid experiences a situation similar to what would occur in a ring-disk system. That is, it spirals off the electrode, passes over an insulating surface, and then spirals over an active surface once more, after which it leaves the region of interest. It seems then that we may calculate the mass-transfer rate for fluid following such a trajectory by determining the radii (r_1, r_2, r_3) at which this fluid (1) leaves the electrode initially, (2) returns to the electrode, and (3) leaves the electrode for the last time, and then use the appropriate formula^(6,7) for mass transfer to a ring-disk electrode which is operated at the limiting current for the same reaction on both the ring and disk. Similarly, for $\epsilon > 1.0015$ one could determine the radii at which a trajectory enters and leaves the electrode surface and use Levich's formula (1) for mass transfer to a ring electrode, with inner and outer dimensions identical to these, to determine the transfer rate along that trajectory. Since each trajectory would have a different ring-disk

(or ring only, for $\epsilon > 1.0015$) analogue, it would be necessary to section the surface of the electrode into thin strips following the trajectories (shaded on figure 3) and determine, via the above method, the transfer rate to each. In the following discussion, details are presented only for the case $\epsilon > 1.0015$, which can be compared easily to previous treatments. The analysis for $0.6377 < \epsilon < 0.9985$ is similar except that the more complicated expression for mass transfer to a ring-disk system must be substituted for Levich's equation for transfer to a ring electrode only.

For a ring electrode with the active portion between r_1 and r_2 , the Levich formula for mass transfer to a segment of width $d\theta$ is

$$dj = (r_2^3 - r_1^3)^{2/3} \frac{Dc_\infty}{2\Gamma(4/3)} \left(\frac{0.510v}{3D} \right)^{1/3} d\theta . \quad (14)$$

The total mass transfer to the disk will be given by this equation integrated between the two tangent points θ_{t1} and θ_{t2} . Upon changing the independent variable from θ to θ' and dividing by the rate of mass transfer to a centered disk electrode of equal area (j_{disk}), we find

$$j/j_{\text{disk}} = \frac{1}{2\pi} \int_{\theta'_{t1}}^{\theta'_{t2}} \left(\frac{r_2^3}{r_1^3} - 1 \right)^{2/3} \left[\epsilon \frac{\cos(\theta' - \alpha)}{\cos \alpha} - 1 \right] d\theta' . \quad (15)$$

Given θ'_1 , the quantity r_2/r_1 can be determined by simultaneous solution of equations 4 and 5. This must be done numerically due to the

complexity of these equations. As a test of this numerical procedure, one can verify the identity

$$2\pi = \int_{\theta'_{t1}}^{\theta'_{t2}} \left(\frac{r_2^2}{r_1^2} - 1 \right) \left[\epsilon \frac{\cos(\theta' - \alpha)}{\cos \alpha} - 1 \right] d\theta' \quad (16)$$

which results from calculating the area of the electrode.

The asymptotic behavior as $\epsilon \rightarrow \infty$ is of some interest since it shows clearly the differences between this analysis and those of Chin and Litt and Bardin and Dikumar. As $\epsilon \rightarrow \infty$,

$$\begin{aligned} \frac{r_1}{r_0} &\rightarrow \epsilon - \cos \theta' , \\ \frac{r_2}{r_0} &\rightarrow \epsilon + \cos(\theta' - 2\alpha) , \\ \theta'_{t1} &\rightarrow \alpha - \frac{\pi}{2} , \\ \theta'_{t2} &\rightarrow \alpha + \frac{\pi}{2} , \end{aligned} \quad (17)$$

and with $x = \sin(\theta' - \alpha)$, equation 15 becomes

$$\begin{aligned} j/j_{\text{disk}} &\rightarrow \frac{1}{\pi} \left(\frac{36\epsilon}{\cos \alpha} \right)^{1/3} \int_0^1 (1 - x^2)^{1/3} dx \\ &= \frac{1}{\sqrt{\pi}} \left(\frac{9\epsilon}{2 \cos \alpha} \right)^{1/3} \frac{\Gamma(4/3)}{\Gamma(11/6)} = 1.027 \epsilon^{1/3} \end{aligned} \quad (18)$$

correct to the largest order in ϵ . The method of Bardin and Dikumar would lead to

$$j/j_{\text{disk}} \rightarrow \frac{1}{\sqrt{\pi}} \left(\frac{9\epsilon}{2}\right)^{1/3} \frac{\Gamma(4/3)}{\Gamma(11/6)} = 0.884 \epsilon^{1/3} \quad (19)$$

while Chin and Litt obtain an expression equivalent to

$$j/j_{\text{disk}} \rightarrow \frac{3}{2\pi^{1/6}} \left(\frac{\epsilon}{3 \cos \alpha}\right)^{1/3} = 0.998 \epsilon^{1/3} . \quad (20)$$

The differences arise from different schemes for segmenting the electrode before applying the ring analogy. Bardin and Dikumar took the streamlines to be radially outward from the center of rotation (figure 4). Chin and Litt approximate the circular electrode by a square of equal area, but with the proper angle given to the spiral streamlines. Thus we conclude that the shape approximation used by Chin and Litt introduces less than a 3% error in the asymptotic transfer rate, but the neglect of the fluid trajectory by Bardin and Dikumar yields a 14% error.

Experimental Technique

The mass-transfer rates for centered and eccentric electrodes were determined for electrodeposition of copper onto copper electrodes. The solution used was .008 M CuSO_4 in 1.5 M H_2SO_4 . The rotating disk electrodes were fabricated from plexiglass, drilled and fitted with short sections of 0.25 inch copper rod and polished with first emery paper then wet crocus cloth. Limiting current curves were

recorded at three rotation speeds for electrodes of eccentricities 0.00, 0.66, 0.88, 2.13, 2.94, and 3.94. The ratios j/j_{disk} were then calculated for each electrode and rotation speed by dividing the total current by that of the centered disk at the same rotation speed. To minimize the effect of temperature variations, the centered electrode was used for every third run, and these results used to calculate the transfer ratios for the non-centered electrodes used in the preceding and following runs.

Results

The experimental results are given in figure 5 along with the numerical results, the large eccentricity asymptote (equation 18), and the analytical and experimental results of Bardin and Dikumar. The data emphasize the importance of sectioning the electrodes along streamlines in order to use the Levich equation for ring electrodes to predict the mass-transfer rate. Our data disagree significantly with those of Bardin and Dikumar, due, perhaps, to their use of quite small electrodes (~ 1mm in diameter). This small size might make accurate determination of the eccentricity difficult and would tend to emphasize edge effects. The data gathered by Chin and Litt support this analysis also, since they correlated well with their theoretical analysis, which differs from the present analysis by only 3 percent at the large eccentricities at which their experimental work was conducted ($\epsilon > 9$).

Although, as previously noted, this analysis fails in a limited region about $\epsilon = 1$, the curves for the results for $\epsilon < 1$ and $\epsilon > 1$ can be joined with no apparent discontinuity at $\epsilon = 1$, as shown on figure 5.

The close agreement between the numerical and asymptotic (analytic) results is somewhat surprising in view of the fact that curvature of the trajectories was ignored in the asymptotic analysis and becomes pronounced as ϵ becomes small. It appears that the formula

$$\frac{j}{j_{\text{disk}}} = 1.027 \epsilon^{1/3} + 0.044 \epsilon^{-5/3} \quad (21)$$

will be accurate to within 1.0 percent for $\epsilon > 0.8$. The exponent $-5/3$ is justified by an extension of the asymptotic analysis.

Acknowledgments

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List of Symbols

C_{∞}	bulk concentration of reactive species (gm/cm^3)
D	diffusion coefficient of reactive species (cm^2/sec)
j	mass flux to electrode (gm/sec)
j_{disk}	mass flux to a centered electrode (gm/sec)
O	center of rotation
O'	center of electrode
r	radial coördinate from center of rotation (cm)
r_o	radius of electrode (cm)
v_r, v_{θ}	velocity components relative to the disk (cm/sec)
z	coördinate normal to disk (cm)
α	angle of fluid trajectories near disk
β	angle between edge of disk and ray from O
ϵ	offset of center of rotation
ϵ_c	critical offset for non-uniform accessibility
θ	angular coördinate from center of rotation
θ'	angular coördinate from center of disk
ν	kinematic viscosity of solution (cm^2/sec)
ω	rotation speed of disk (sec^{-1})

XBL 7412-7667

Figure 1. Nomenclature for offset disk electrode.

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Figure 2. Trajectory for eccentricity at which analysis fails.

XBL 7412-7669

Figure 3. Partitioning scheme for ring-disk analogy ($\epsilon < 1$).

(a) Bardin and Dikusar

(b) Chin and Litt

(c) This Paper

XBL 744-5957

Figure 4. Comparison of partitioning schemes ($\epsilon > 1$).

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Figure 5. Mass-transfer ratio j/j_{disk} versus eccentricity for an off-center rotating disk electrode.

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