Lawrence Berkeley National Laboratory

Recent Work

Title PRIMARY RESISTANCES FOR RING-DISK ELECTRODES

Permalink https://escholarship.org/uc/item/7wk307sb

Author Miksis Jr., Joseph

Publication Date 1975-07-01

Ű

Submitted to Journal of the Electrochemical Society

LBL-4106 Preprint c

PRIMARY RESISTANCES FOR RING-DISK ELECTRODES

Joseph J. Miksis, Jr. and John Newman

July 1975

Prepared for the U. S. Energy Research and Development Administration under Contract W-7405-ENG-48

For Reference

Not to be taken from this room



DISCLAIMER

This document was prepared as an account of work sponsored by the United States Government. While this document is believed to contain correct information, neither the United States Government nor any agency thereof, nor the Regents of the University of California, nor any of their employees, makes any warranty, express or implied, or assumes any legal responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by its trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or the Regents of the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof or the Regents of the University of California.

4

-1-

LBL-4106

Primary Resistances for Ring-Disk Electrodes

Joseph J. Miksis, Jr., and John Newman

Inorganic Materials Research Division, Lawrence Berkeley Laboratory, and Department of Chemical Engineering; University of California, Berkeley 94720

July, 1975

Abstract

A system consisting of a disk electrode, a concentric ring electrode, and a large counterelectrode at infinity has three independent resistance values describing the primary potential difference between any two electrodes when current is passed between any two electrodes. These resistance values are calculated and presented as dimensionless correlations as functions of the ratios of radii of the disk and ring.

Key words: current distribution, potential distribution, Laplace's equation, interrupter techniques

Introduction

A common electrode geometry in electroanalytical and research applications involves a disk electrode and a concentric ring electrode both embedded in an insulating plane and rotated about the axis of the disk. Species produced by an electrochemical reaction at the disk can frequently be detected quantitatively by electrochemical reaction at the ring.^{1,2,3} In some of these applications it is desirable to assess the ohmic potential drop in the solution. For example, to have a controlled electrode potential for the reaction at the disk one needs to know how a current to the disk and a current to the ring separately influence the potential in the solution in the neighborhood of the disk.^{4,5} To ensure that a limiting current is maintained on the ring involves a similar question.⁶

Experimental efforts to answer these questions involve abrupt changes in the current to either the ring or the disk followed by a measurement of the change in potential of both the ring and the disk as shortly thereafter as possible.^{4,5,7} Such rapid changes in potential and current are associated with the primary distributions of potential and current.⁸

Consequently, we can define a mathematical problem in which the potential obeys Laplace's equation,

$$\nabla^2 \Phi = 0$$

(1)

the potential is zero at infinity, and has a uniform value in the solution adjacent to each electrode. Corresponding to a zero current

-2-

00004308153

-3-

density, the normal component of the potential gradient is zero on the insulating annulus between the disk and the ring and on the plane surrounding the ring. This problem excludes consideration of the variation of conductivity within the thin diffusion layer adjacent to the electrodes and effectively regards the change in potential drop to be determined by the bulk of the solution. Also excluded from consideration is the effect of electrode kinetics, it being assumed that the double-layer capacity is sufficiently large that the potential difference across it does not change during the time of the measurement.⁸ (The course of events involving the change of the charge of the double-layer capacity has been examined by Nisancioglu and Newman.^{9,10,11})

The problem thus defined is limited in scope since it involves only the geometry of the system, the conductivity of the solution, and the potentials and currents themselves. The principal result of the model is the expression of the disk and ring potentials in terms of the disk and ring currents:

$$\nabla_{d} = R_{dd}I_{d} + R_{dr}I_{r} , \qquad (2)$$

$$V_r = R_{rd}I_d + R_{rr}I_r , \qquad (3)$$

where I_d and I_r are the total currents to the disk and ring electrodes, respectively, and V_d and V_r are the potentials, presumed uniform, in the solution adjacent to the two electrodes. In the absence of concentration and surface overpotentials, V_d and V_r can be regarded to be the potentials of the electrodes themselves, and this is the usual manner of speaking when discussing primarydistribution problems. Bear in mind that in the applications discussed above these quantities I_d , I_r , V_d , and V_r probably represent instantaneous changes in the electrode currents and the corresponding instantaneous changes in the electrode potentials.

 R_{dd} , R_{dr} , R_{rd} , and R_{rr} are the primary resistances defined by equations 2 and 3 for this ring-disk system. We can attach a physical meaning to them by the following considerations. When there is no ring current, $I_r = 0$, we see that R_{dd} represents the resistance between the disk electrode and a counterelectrode at infinity. This resistance will be lower in the presence of the ring than for the disk alone because current can find a path through the ring electrode to the disk, bypassing some of the resistance of the solution. This is true even though there is no net current to the ring. Under these circumstances, the potential of the ring will take on a definite value to satisfy the condition of no net current to the ring. This value is determined by R_{rd} in equation 3. Thus, R_{rd} is a quantity having the dimensions of a resistance but which yields the potential on the ring due to a current on the disk.

In a similar manner, we see that when there is no disk current, R_{rr} is the resistance between the ring and a counterelectrode at infinity while R_{dr} reproduces the potential on the disk due to a current on the ring. As shown below, $R_{dr} = R_{rd}$.

The geometry of the ring-disk system is defined adequately by the ratio r_0/r_1 of the disk radius to the inner radius of the ring

-4-

004308154

and the ratio r_1/r_2 of the inner and outer radii of the ring. The resistances can be made dimensionless with the conductivity κ of the solution and a characteristic length, which we choose to be the outer radius r, of the ring. Therefore, the results of this study can be presented simply by correlating three dimensionelss resistances $\left(R_{D}^{D} = \kappa r_{2}R_{dd}, R_{D}^{R} = R_{R}^{D} = \kappa r_{2}R_{dr}, \text{ and } R_{R}^{R} = \kappa r_{2}R_{rr}\right)$ as functions of two geometric ratios (r_0/r_1) and r_1/r_2). This simplicity and generality is a further justification for restricting the problem to the primary resistances.

In a subsequent paper from this laboratory,¹² we shall discuss some more complicated behavior of the ring-disk system in which concentration variations and electrode kinetics are considered in order to assess the current distribution on a sectioned electrode (composed of the ring and disk at the same potential) below the limiting current, the collection efficiency of the system when the current distribution on the disk is nonuniform due to the ohmic potential drop in the solution, and the anomolous diffusion coefficient for a redox couple measured by means of the limiting current to a ring electrode with zero current to the disk.

Symmetry of Resistances

Let us consider two cases: case 1 where $I_d=0$ and case 2 where $I_r=0$. For any two functions Φ_1 and Φ_2 , Green's theorem says 13

$$\int \left(\Phi_1 \nabla^2 \Phi_2 - \Phi_2 \nabla^2 \Phi_1 \right) d\mathbf{v}_o = \oint \left(\Phi_1 \nabla \Phi_2 - \Phi_2 \nabla \Phi_1 \right) \cdot \underline{dS} . \tag{4}$$

The integral over the volume V_o is zero here because both Φ_1 and Φ_2 obey Laplace's equation. The surface integral is over the entire area enclosing the volume V_o , which we shall take to be the entire half-space between the plane of the disk and the counterelectrode at infinity. The integral over the insulating surfaces is zero because the normal component of the potential gradient is zero there. The integral over a hemisphere at infinity is zero because each potential is inversely proportional to the radius, the potential gradient is inversely proportional to the square of the radius, and dS is proportional to the square of the radius.

This leaves us with integrals over only the surfaces of the electrodes:

$$\int_{\mathbf{d}} \left(\Phi_1 \nabla \Phi_2 - \Phi_2 \nabla \Phi_1 \right) \cdot \underline{\mathrm{dS}} = - \int_{\mathbf{r}} \left(\Phi_1 \nabla \Phi_2 - \Phi_2 \nabla \Phi_1 \right) \cdot \underline{\mathrm{dS}} .$$
 (5)

Now, by the definition of the primary distributions, the potential adjacent to each electrode is uniform and can be removed from the integral, with the result

-6-

0004308155

$$\mathbf{v}_{d1} \int_{\mathbf{d}} \nabla \Phi_2 \cdot \underline{\mathrm{dS}} - \mathbf{v}_{d2} \int \nabla \Phi_1 \cdot \underline{\mathrm{dS}} = -\mathbf{v}_{r1} \int_{\mathbf{r}} \nabla \Phi_2 \cdot \underline{\mathrm{dS}} + \mathbf{v}_{r2} \int_{\mathbf{r}} \nabla \Phi_1 \cdot \underline{\mathrm{dS}} .$$
(6)

-7-

Furthermore, the integral of the normal component of the potential gradient over the surface of an electrode is proportional to the total current to the electrode. Equation 6 becomes

$$V_{d1}I_{d2} - V_{d2}I_{d1} = -V_{r1}I_{r2} + V_{r2}I_{r1}$$
 (7)

For the cases chosen here, $I_{d1} = 0$ and $I_{r2} = 0$, and this reduces to

$$V_{d1}I_{d2} = V_{r2}I_{r1}$$
 (8)

Substitution of equations 2 and 3 for the electrode potentials, with $I_{d1} = I_{r2} = 0$, yields

$$R_{dr}I_{r1}I_{d2} = R_{rd}I_{d2}I_{r1}$$
 (9)

or

$$R_{dr} = R_{rd}$$
 (10)

Gabrielli <u>et al.</u>⁷ state this result and provide supporting experimental results. Equation 10 could be considered to be an example of the Onsager reciprocal relation.

Analysis

-8-

Newman¹⁴ reviews methods of calculating current and potential distributions in ring or disk geometries. At first we thought that we could treat the ring-disk system as a composite disk of radius r_2 and use the method of separation of variables in rotational elliptic coördinates. Then the current density would be zero on the insulating annulus while the potentials would be specified on the ring and disk, and the coefficients of the series would be determined by trial and error or by matrix inversion so as to satisfy these boundary conditions. However, such a series is inadequate to represent the distributions of potential and current in this system because the current density approaches infinity at the inner edge of the ring and at the edge of the disk. (The coördinate system does allow treatment in a natural way of the infinite current density near the outer edge of the ring, just as it does for the primary distribution near the edge of a disk without a ring.¹⁵)

As an alternative, the currents due to the ring and the disk were treated separately by different methods. First a series of ten cases was defined with prescribed current distributions on the ring. For cases 1 and 3, these current distributions were

$$i_{r1} = \frac{2}{\sqrt{1-x^2}}$$

(11)

and

0004308

$$i_{r3} = \sqrt{\frac{2}{1+x}}$$
, (12)

where

$$x = \frac{2r - r_1 - r_2}{r_2 - r_1} \quad . \tag{13}$$

Case 2 has a zero current density everywhere on the ring but will have a current assigned to the disk as described below. Cases 4 through 10 were assigned the following current distributions on the ring:

$$i_{r,k} = P_{k-4}(x)$$
, (14)

where $P_k(x)$ is the Legendre polynomial.

It was felt that these cases would represent a complete set which could be superposed to reproduce any primary current distribution on the ring electrode. In particular, case 1 has an infinite current density at both the inner and the outer edge of the ring, and the current density approaches infinity in the manner required when an electrode is embedded in an insulating plane, namely, by being inversely proportional to the square root of the distance from the edge. Case 3 involves an infinite current density only at the inner edge of the ring. A superposition of cases 1 and 3 should be able to match the way in which any primary current distribution goes to infinity at the inner and outer edges of the ring. The residual current distribution should be finite over the ring and adequately

represented by a superposition of the remaining cases 4 through 10. For some values of r_0/r_1 and r_1/r_2 where the accuracy of the results was questionable, the number of cases was extended from 10 to 20.

The next step in the procedure is to evaluate the potential distribution on both the disk and the ring due to the current distribution on the ring for each of the cases described above. For this purpose, we use the formula for the potential in the plane of the disk¹⁴

$$\Phi_{o}(\mathbf{r}) = \frac{2}{\pi \kappa} \int_{\mathbf{r}_{1}}^{\mathbf{r}_{2}} \frac{\mathbf{i}(\mathbf{r}') \mathbf{K}(\mathbf{m}) \mathbf{r}' d\mathbf{r}'}{\mathbf{r} + \mathbf{r}'}, \qquad (15)$$

where

$$m = \frac{4rr'}{(r + r')^2}$$
(16)

and K(m) is the complete elliptic integral of the first kind. The evaluation of this integral for the potential distribution on the ring requires care, first of all, because the elliptic integral approaches infinity when r' = r. Additional difficulties are introduced for cases 1 and 3 where the current distribution approaches infinity at the inner or outer edge of the ring.

The potential distributions obtained above will be nonuniform on both the ring and the disk. For each case, the potential can be made uniform on the <u>disk</u> by superposing the potential distribution due to a current distribution introduced on the disk. Here we use rotational elliptic coördinates η and ξ based on the radius r_0 of the disk. The coördinate transformation reads

$$z = r_0 \xi \eta$$
 and $r = r_0 \sqrt{(1 + \xi^2)(1 - \eta^2)}$, (17)

and the solution of Laplace's equation by separation of variables in this coördinate system is 14,16

$$\Phi = \sum_{n=0}^{\infty} B_n P_{2n}(n) M_{2n}(\xi) , \qquad (18)$$

where B_n represents arbitrary coefficients, P_{2n} is again the Legendre polynomial, and $M_{2n}(\xi)$ (called $M_n(\xi)$ is reference 14) is a Legendre function of imaginary argument having properties described earlier. Selection of even Legendre polynomials in equation 18 ensures that the corresponding current distribution is zero in the plane outside the disk; hence, the current distribution is not modified on the ring by superposing a potential distribution of the type in equation 18.

In practice, equation 18 is truncated after a finite number of terms, say 20. For each case, the B values are now chosen so that the potential (including that due to the ring current) will be zero on the surface of the disk. Up to this point, case 2 has not been defined or modified. We now require that the potential Φ_0 be equal to unity on the surface of the disk, for case 2, which is equivalent to setting $B_0 = 1$. The superposition of the disk potential function in equation 18 will generate a nonzero net current

-11-

and a uniform potential for the disk for each case.

Next, for each case, we should calculate the potential distribution on the ring due to the current distribution on the disk, and we should add this to the potential distribution previously obtained from the current distribution on the ring. This step involves the use of equation 18 with values of ξ greater than zero since

$$\Phi_{0} = \sum_{n=0}^{\infty} B_{n} P_{2n}(0) M_{2n}(\xi)$$
(19)

in the plane for r greater than r_o . The evaluation of $M_{2n}(\xi)$ has been necessary in earlier work,⁶ and we have introduced refinements here¹⁷ to permit accurate calculation for large values of ξ and n.

The several cases that have been treated now each have prescribed current distributions on the ring and disk, known total currents, a uniform potential on the disk, and a nonuniform but finite potential distribution on the ring. The final step of the procedure is to superpose cases 3 through 10 onto cases 1 and 2, in turn, in such a way that the potential distribution on the ring is made uniform. More cases can be used to attain a higher degree of uniformity.

Cases 1 and 2 now satisfy all the requirements of a primary distribution -- they have uniform potentials on the ring and the disk, and they satisfy Laplace's equation and all the other boundary conditions. Analysis of cases 1 and 2 according to equations 2 and 3 yields values of the resistances R_{dd} , R_{dr} , R_{rd} , and R_{rr} .

-12-

This solution for the primary potential and current distributions by superposition may seem involved and complicated, but it is economical and accurate, and it avoids any trial-and-error calculations. The functions chosen for superposition make special allowance for the geometry of the system and can treat the infinite current densities at the edges of the electrodes even when the insulating annulus is quite thin.

Results

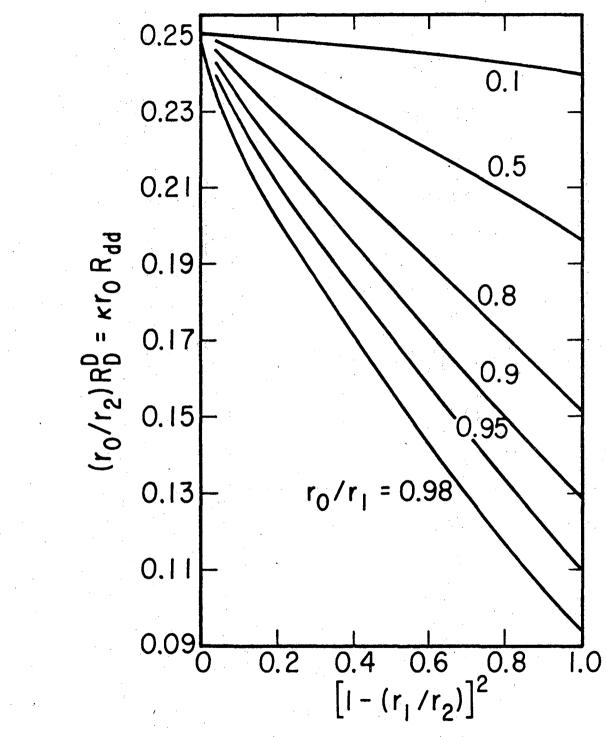
In the computed results, R_{dr} and R_{rd} usually agreed to within 0.01 percent. Certain limiting situations could also be checked to ensure the validity of the results.

Figures 1, 2, and 3 show the values of the three independent resistances as functions of the geometric ratios r_0/r_1 and r_1/r_2 . For a very thin ring, R_{rr} becomes infinite. Consequently, on figure 3 we have added a term which compensates for this and produces a finite limit as r_1 approaches r_2 . An exception is the (unrealistic) limit of a zero gap distance. As r_0 approaches r_1 , the value of $\kappa r_2^R rr$ approaches 0.25, independent of the value of r_1/r_2 .

Discussion

The results for R_{dd} can be comprehended in relation to the value $1/4\kappa r_0$ for the primary resistance¹⁵ for a single disk in an insulating plane. The values for the disk resistance, as plotted in

-13-



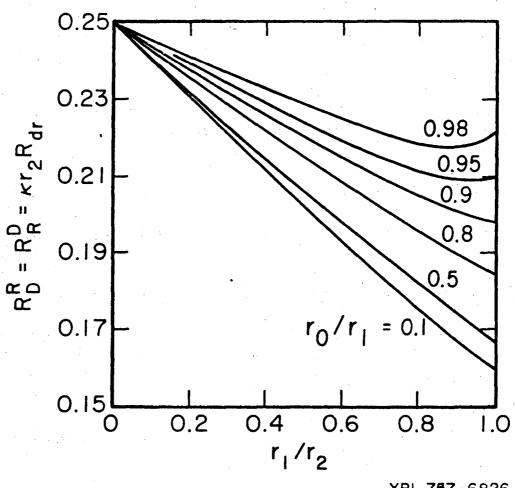
XBL 757-6825

Figure 1. Correlation of the disk resistance.

-14-

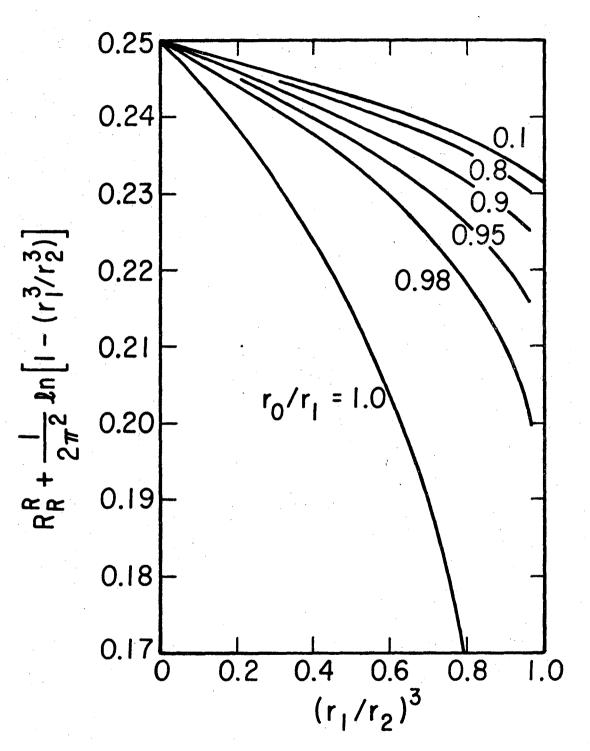
000043 0 8 $(\mathbf{0})$

-15-



XBL 757-6826

Figure 2. Correlation of the interaction resistance.



XBL 757-6827

Figure 3. Correlation of the ring resistance.

-16-

0 0 0 0 4 3 0 8 1 6 0

-17-

figure 1, therefore approach the value 0.25 as the influence of the ring becomes negligible -- either for thin rings $(r_1 \rightarrow r_2)$ or for wide gaps between the ring and the disk $(r_0 << r_1)$. The influence of the ring is always to lower the resistance value $\kappa r_0 r_{dd}^R$ below the value 0.25 because the ring provides an alternative current path which can help the current get from infinity to the neighborhood of the disk. Figure 1 shows how this effect becomes more pronounced for wide rings and narrow gaps.

There are several ways of thinking about the coupling resistances $R_{dr} = R_{rd}$. First imagine a current to the disk with no current to the ring. Then the potential distribution will bear some resemblance to that for a single disk in an insulating plane, and the similarity will become exact in the limit of a thin ring. The ring, in addition to distorting this potential field, will acquire a potential corresponding to the single disk at some radial position r_{\star} which lies between r_1 and r_2 . Since

$$(r/r_{o})^{2} = 1 + \xi^{2}$$
 (20)

on the ring and since

$$M_{o}(\xi) = \frac{2}{\pi} \operatorname{ctn}^{-1}(\xi)$$
, (21)

the potential in the plane at a radial position r_{\pm} due to the primary distribution on a single disk is

$$V_{r} = V_{d} \operatorname{ctn}^{-1}(\xi) = \frac{I_{d}}{2\pi\kappa r_{o}} \sin^{-1}\left(\frac{r_{o}}{r_{\star}}\right)$$
 (22)

This leads to the resistance value

$$\kappa r_2^R r_d = \frac{r_2}{2\pi r_o} \sin^{-1}\left(\frac{r_o}{r_\star}\right) . \qquad (23)$$

This formula becomes rigorous for thin rings when we set r_{\star} equal to r_2 . Thus, the intercept on the right side of figure 2 is known with certainty. The limit for the ordinate is 0.25 for narrow gaps $(r_0 \rightarrow r_1)$ and $1/2\pi = 0.1592$ for wide gaps $(r_0 << r_1)$.

For thick rings, it is convenient to think of a zero current on the disk. Then the ring itself will look like a disk, with a small imperfection at the center, and the potential distribution will be nearly that for a disk of radius r_2 in an insulating plane. The small disk of radius r_0 can then sense only one potential, that approximately equal to the potential of the ring $V_r = I_r/4\kappa r_2$. This leads to the limit

$$\operatorname{kr}_{2} \operatorname{R}_{dr} \neq 0.25 \text{ as } \operatorname{r}_{2}/\operatorname{r}_{1} \neq \infty$$
, (24)

independent of the value of r_0/r_1 .

By an analysis of the current deflected from the insulating region for $r < r_1$, one can find a correction to equation 24 for small disks:

-18-

$$\kappa r_2 R_{dr} = \frac{1}{4} - \frac{1}{\pi^2} \frac{r_1}{r_2}$$
 for $r_1 << r_2$ and $r_o << r_1$. (25)

This limiting slope is verified in figure 2.

For rings which are neither thick nor thin, we can use the results in figure 2 to calculate the value of r_{\star} according to equation 23. It turns out that r_{\star} varies from the arithmetic average of r_1 and r_2 for thin rings to a value of $2r_2/\pi$ for thick rings (in order to reproduce the limit in equation 24). This suggests the method of correlation of R_{dr} shown in figure 4. Here a value of r_{\star} is calculated <u>a priori</u>, and the ratio of the left and right sides of equation 23 represents a deviation function which is close to unity. The only advantage of figure 4 over figure 2 is that the scale can be expanded because the minimum and maximum values now differ by a factor of 1.05 instead of a factor of 1.57.

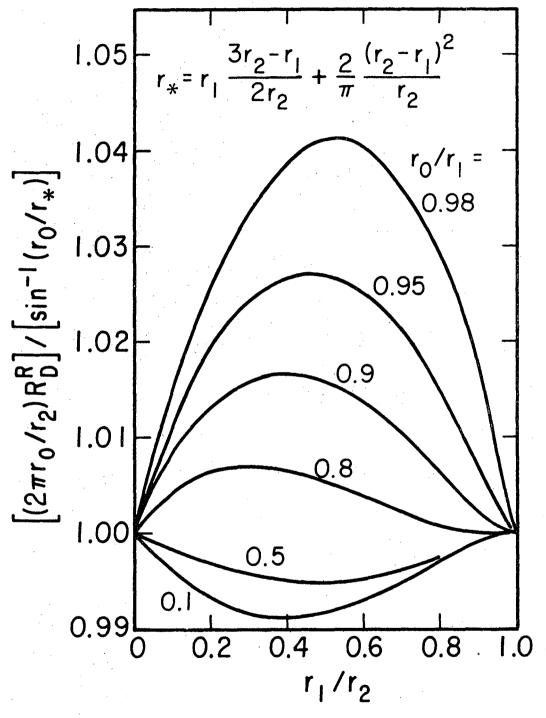
Let us next turn our attention to the ring resistance R_{rr} . For wide rings, it is clear that the resistance value is given by

$$\kappa r_{2}R_{rr} = 0.25$$
, (26)

the value for a single disk of radius r_2 . In the other extreme,

$$<\mathbf{r}_{2}\mathbf{R}_{rr} + \frac{1}{2\pi^{2}}\ln\left(1 - \frac{\mathbf{r}_{1}^{3}}{\mathbf{r}_{2}^{3}}\right) = \frac{\ln 96}{2\pi^{2}} = 0.2312$$
 (27)

for thin rings $(r_1 \rightarrow r_2)$ and small disks $(r_0 << r_1)$.



XBL 757-6828

Figure 4. Correlation of interaction resistance.

-20-

-21-

Figure 3 was plotted so that the small disk case $(r_0 \ll r_1)$ would show clearly these limits. According to this figure, the effect of a nonzero disk is always to lower the ring resistance, because an alternative path is provided between the counterelectrode at infinity and the ring electrode. The correction to equation 27 for small disks is very small, $-(r_0/r_2)^5/45\pi^2$. Thus, we see that the curve for $r_0/r_1 = 0.8$ is already very close to the curve for $r_0/r_1 = 0.1$.

Gabrielli <u>et al</u>.⁷ have measured resistances for four ring-disk geometries. They verified the coupling relationship between R_{rd} and R_{dr} . A comparison between their measurements and our calculated values is made in table 1. For this purpose, $1/\kappa$ was given the value 2.25 ohm-cm for a 2 <u>N</u> sulfuric acid solution. The comparison cannot be regarded as satisfactory. Two experimental values of $\kappa_r_{o}R_{dd}$ are greater than 0.25, which should not be possible. The other two values of $\kappa_r_{o}R_{dd}$ show good agreement. Measured values of the coupling resistance are consistently lower than those calculated. One value of $\kappa_r_2R_{rr}$ is lower than 0.25, which should not be possible. The other measured values of $\kappa_r_2R_{rr}$ are significantly higher than the calculated values.

Shabrang and Bruckenstein⁵ analyze their results in terms of equations of the form

and

$$V_d - V_T = R_D I_d + (I_d + I_r) R_C$$

(28)

Table 1. Comparison of calculated resistances with those measured by Gabrielli <u>et al.</u>⁷ for four ring-disk geometries.

r _o /r ₁	r ₁ /r ₂	^{Kr} 2 ^R rr		^{Kr} 2 ^R dr		^K ro ^R dd	
		meas.	calc.	meas.	calc.	meas.	calc.
0.952	0.42	0.244	0.252	0.211	0.228	0.307	0.192
0.968	0.62	0.272	0.261	0.194	0.22	0.217	0.216
0.976	0.82	0.311	0.273	0.189	0.218	0.231	0.238
0.976	0.976	1.213	0.342	0.177	0.219	0.262	0.2495

-22-

$$V_r - V_T = R_R I_r + (I_d + I_r) R_C'$$
, (29)

where $R_{\rm D}$, $R_{\rm R}$, $R_{\rm C}$, and $R_{\rm C}'$ are resistances and $V_{\rm T}$ is the potential of the reference electrode and can be expressed as

$$V_{T} = R_{Aux}I_{d} + R'_{Aux}I_{r} .$$
 (30)

Comparison with equations 2 and 3 shows that we can make the associations

$$R_{dd} = R_{D} + R_{C} + R_{Aux} , \qquad (31)$$

$$R_{dr} = R_{C} + R'_{Aux} , \qquad (32)$$

$$R_{rd} = R_C' + R_{Aux} , \qquad (33)$$

and

$$R_{rr} = R_{R} + R_{C}' + R_{Aux}'$$
 (34)

In view of equation 10, we can write

$$R_{C} - R_{C}' = R_{Aux} - R_{Aux}'$$
 (35)

Shabrang and Bruckenstein take these differences to be zero. Indeed, if the counterelectrode is far away and the reference electrode is moderately far away from the ring-disk system, we can estimate¹⁵

 $R_{Aux} = R'_{Aux} = \frac{1}{2\pi\kappa\rho}$,

(36)

where ρ is the radial position of the reference electrode in spherical coordinates. However, the currents I_d and I_r do not, in general, need to have the same influence on the potential V_T in equation 30; the difference will become accentuated the closer the reference electrode probe is to the ring-disk system.

From figures 1, 2, and 3, we find $\kappa_r_{o}R_{dd} = 0.249$, $\kappa_r_{2}R_{rd} = 0.209$, and $\kappa_r_{2}R_{rr} = 0.3238$ for the geometry of Shabrang and Bruckenstein $(r_{o}/r_{1} = 0.95 \text{ and } r_{1}/r_{2} = 8/8.4)$. R_{D} corresponds approximately to $R_{dd} - R_{dr}$, and R_{R} corresponds approximately to $R_{rr} - R_{rd}$. (Shabrang and Bruckenstein come to a different conclusion.) For the ratio $R_{D}/(R_{D} + R_{R})$, they find values of 0.37, 0.35, 0.34, 0.39, 0.36, 0.34, and 0.31, whereas we calculate 0.366 for the corresponding ratio. (Here, we assume that the labels V_{o}/V_{D} and V_{o}/V_{R} are interchanged in their table III.)

Because of uncertainties in the position of the reference electrode and the conductivity of the solution, we refrain from further comparisons with their data.

From the results of Miller and Bellavance⁴ we deduce an experimental value of $\kappa r_2 R_{rd} = 0.192$. The corresponding value from figure 2 is $\kappa r_2 R_{rd} = 0.206$ for $r_0/r_1 = 0.909$ and $r_1/r_2 = 0.812$.

Conclusion

Computed values of the primary resistances for a ring-disk system, as presented here, should permit estimation of the uncompensated resistances when an attempt is made to control the potentials of the

-24-

-25-

electrodes. There are few geometries for which this information is available.

Discrepancies between calculated and experimental values may lead to refined experiments or to considerations beyond the scope of the primary resistances.

Acknowledgment

This work was supported by the United States Energy Research and Development Administration.

List of Symbols

B_n coefficients in series 18 for potential I_d disk current, A I_r ring current, A K complete elliptic integral of the first kind m see equation 16 M_{2n} Legendre function of imaginary argument P_k Legendre polynomial

r radial position in cylindrical coördinates, cm

r radius of disk, cm

r₁ inner radius of ring, cm

r₂ outer radius of ring, cm

r, position on ring electrode, cm

 $R_{dd}, R_{dr}, R_{rd}, R_{rr}$ resistances defined by equations 2 and 3, ohm $R_{D}, R_{R}, R_{C}, R_{C}'$ resistances defined by equations 28 and 29, ohm

R_{Aux}, R_{Aux} resistances defined by equation 30, ohm						
$R_D^D, R_D^R, R_R^D, R_R^R$ dimensionless resistances						
S	surface area, cm ²					
v _d	disk potential, V					
Vr	ring potential, V					
1	potential at reference electrode, V					
vo	volume, cm ³					
X	see equation 13					
z	distance from the plane of the disk, cm					
η	rotational elliptic coördinate					
к	conductivity of the solution, $ohm^{-1} - cm^{-1}$					
ξ	rotational elliptic coördinate					
ρ	radial position in spherical coördinates, cm					
Φ	potential in the solution, V					

-26-

-27-

References

1. A Frumkin, L. Nekrasov, B. Levich, and Ju. Ivanov. "Die Anwendung der rotierenden Scheibenelektrode mit einem Ringe zur Untersuchung von Zwischenprodukten elektrochemischer Reaktionen." Journal of Electroanalytical Chemistry, 1, 84-90 (1959).

W. J. Albery and S. Bruckenstein. "Ring-Disc Electrodes.
 Part 2. -- Theoretical and Experimental Collection Efficiencies."
 <u>Transactions of the Faraday Society</u>, 62, 1920-1931 (1966).

3. William H. Smyrl and John Newman. "Ring-Disk and Sectioned Disk Electrodes." Journal of the Electrochemical Society, 119, 212-219 (1972).

4. Barry Miller and Maria I. Bellavance. "Measurement of Current and Potential Distribution at Rotating-Disk Electrodes." <u>Journal of</u> the Electrochemical Society, 120, 42-53 (1973).

5. Mani Shabrang and Stanley Bruckenstein. "Equivalent Circuit for the Uncompensated Resistances Occurring at Ring-Disk Electrodes." Journal of the Electrochemical Society, 121, 1439-1444 (1974).

6. William H. Smyrl and John Newman. "Detection of Nonuniform Current Distribution on a Disk Electrode." <u>Journal of the Electrochemical</u> <u>Society</u>, <u>119</u>, 208-212 (1972).

7. C. Gabrielli, M. Keddam, and H. Takenouti. "Étude de la répartition du potentiel a la surface d'une électrode a disque-anneau." Journal de Chimie Physique, 69, 737-740 (1972).

8. John Newman. "Ohmic Potential Measured by Interrupter Techniques." Journal of the Electrochemical Society, <u>117</u>, 507-508 (1970). 9. Kemal Nişancioğlu and John Newman. "The Transient Response of a Disk Electrode." <u>Journal of the Electrochemical Society</u>, <u>120</u>, 1339-1346 (1973).

10. Kemal Nişancioglu and John Newman. "The Transient Response of a Disk Electrode with Controlled Potential." <u>Journal of the</u> <u>Electrochemical Society</u>, 120, 1356-1358 (1973).

11. Kemal Nişancioğlu and John Newman. "The Short-Time Response of a Disk Electrode." <u>Journal of the Electrochemical Society</u>, <u>121</u>, 523-527 (1974).

12. Peter Pierini and John Newman. "Potential Distribution within Axisymmetric Cells." in preparation

Francis B. Hildebrand. <u>Advanced Calculus for Applications</u>,
 p. 293. Englewood Cliffs, N.J.: Prentice-Hall, Inc., 1962.

14. John Newman. "The Fundamental Principles of Current
Distribution and Mass Transport in Electrochemical Cells," pp. 321-334.
Allen J. Bard, ed., <u>Electroanalytical Chemistry</u> (New York: Marcel
Dekker, Inc., 1973), <u>6</u>, 187-352.

15. John Newman. "Resistance for Flow of Current to a Disk." Journal of the Electrochemical Society, 113, 501-502 (1966).

16. John Newman. "Current Distribution on a Rotating Disk below the Limiting Current." <u>Journal of the Electrochemical Society</u>, <u>113</u>, 1235-1241 (1966).

17. Joseph J. Miksis, Jr. <u>Primary Resistances for Ring-Disk</u> <u>Electrodes</u>. M.S. thesis, University of California, Berkeley, in preparation. LEGAL NOTICE

This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Energy Research and Development Administration, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately owned rights. TECHNICAL INFORMATION DIVISION LAWRENCE BERKELEY LABORATORY UNIVERSITY OF CALIFORNIA BERKELEY, CALIFORNIA 94720

-

•