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POTENTIAL DISTRIBUTION FOR DISK ELECTRODES IN AXISYMMETRIC CYLINDRICAL CELLS

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Potential Distribution for Disk Electrodes in Axisymmetric Cylindrical Cells

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Abstract

A cylindrical cell useful for rotating-disk studies has been analyzed for its primary resistance. Values of the resistance are given for a large number of cell configurations. The resistance calculations permit the simpler resistance formulas for infinite cells to be applied to the design of finite cells.

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Key Words: resistance, primary current distribution.

An axisymmetric cylindrical cell is a convenient one for use with a rotating disk or ring-disk electrode. A counterelectrode could naturally occupy the opposite end of the cell and be a mercury pool or a stationary disk. Newman (1) computed the primary current distribution for a disk electrode surrounded by an infinite insulating plane with the counterelectrode being the entire hemisphere at infinity. The effects of mass transfer and kinetics were included in a later paper for a similar cell (2). A carefully designed disk and cell can approach conditions which allow calculations for infinite cells to be applied to finite laboratory sized cells without correction. Previous recommendations for constructing electrodes and cells have been made based upon hydrodynamic and mass transfer considerations (13,14,15). Sawyer and Roberts (16) give some advice on locating the reference electrode in a cell. However, the effect of cell size on the potential distribution does not seem to have been considered, even though the potential mapping experiments of Angell, Dickenson, and Greif (12) around various rotating disk electrode mantles were performed in cells small enough to affect the distribution. The isopotential surfaces they mapped were found to be in qualitative agreement with Newman's result (1). Miller and Bellavance (10) performed single and double probe mapping experiments in a cell which also affected the measurements but found good agreement with the theory.

Better insight into these experiments can be gained by computing the effect of the cell walls. Current interrupters have been shown to measure a resistance corresponding to a primary distribution (23).

To interpret accurately the meaning of the resistance, the effect of the cell must be included. Controlled potential electrolysis requires careful design of cells to minimize potential variation across the working electrodes and has been previously treated by Newman and Harrar (11). The effect of cell walls on current and potential distributions have been investigated for several planar geometries (4,17,18). Drossbach (5) has analytic solutions for cylindrical cells which have working and counterelectrodes of equal diameter. The solutions are infinite series which were developed in a cylindrical coordinate system. A large number of terms would be necessary to describe accurately the behavior of the field near the electrodes. The following treatment can be easily extended to the case of Drossbach and should give better results with fewer terms.

The disk and cell treated are shown in Fig. 1. A working electrode of radius r_d occupies some fraction of the upper plane of the cell. The remaining area between the edge of the disk and the cell wall, and the vertical cell walls of height h, are considered to be insulators. The bottom of the cell is composed entirely of a counterelectrode of radius r_c. A method of superposition is developed to solve Laplace's equation for the cell in Fig. 1 where both the working and counterelectrodes have uniform potential distributions. Thus, the primary current and potential distributions are obtained for the cell.

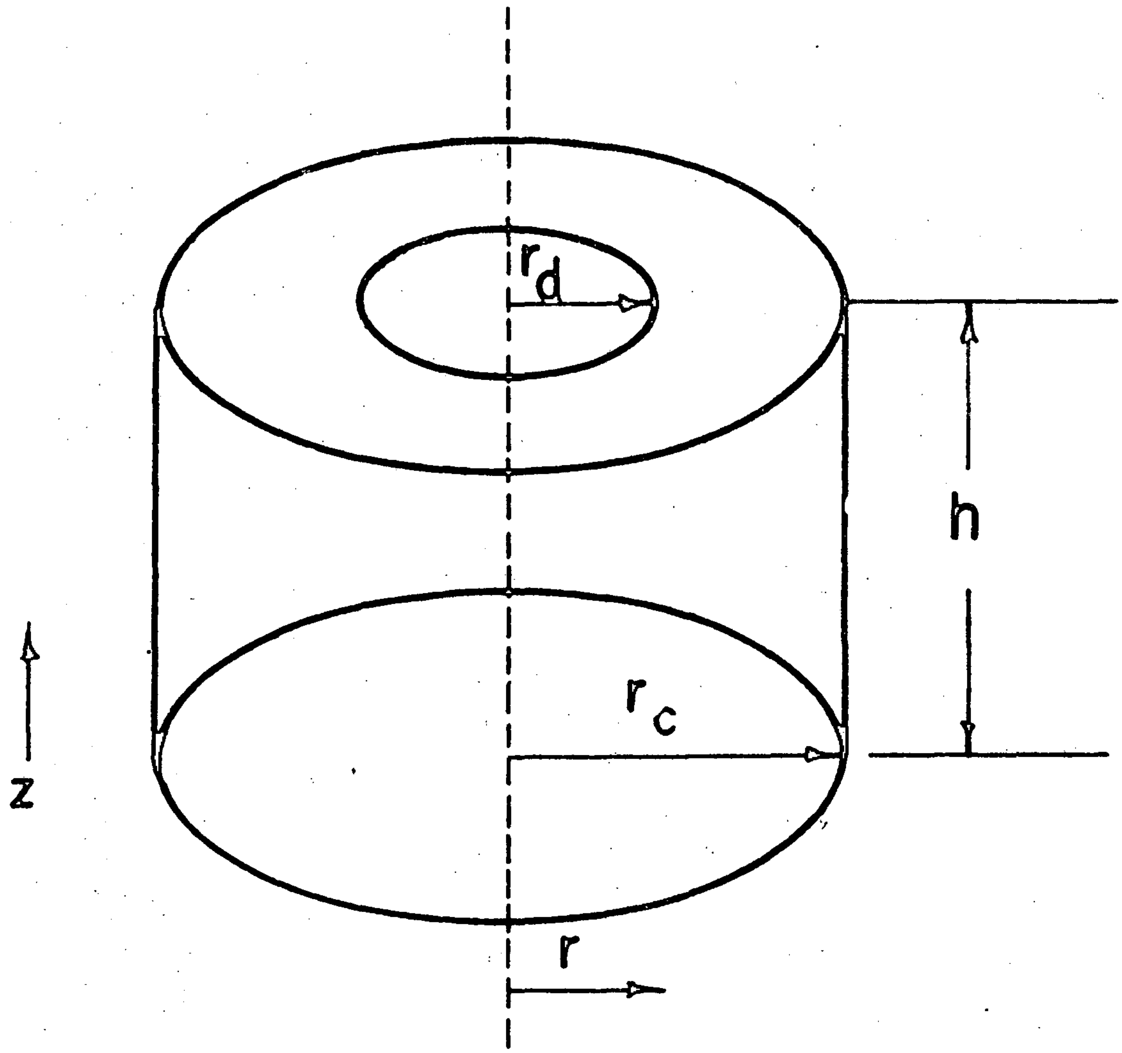

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Figure 1. Axisymmetric cylindrical cell with disk electrodes.

Analysis

The solution for the primary distribution for a disk electrode in an infinite insulating plane was developed by Newman (1) using a classical separation-of-variable technique. Laplace's equation

$$\nabla^2\Phi = 0 \qquad [1]$$

which is the basic governing equation to be solved is linear, so any solution of Eq. [1] may be added to any other solution and the resulting field will satisfy Laplace's equation. Superposition is the technique of adding up simple solutions to Eq. [1] so that a prescribed boundary condition is met. The disk and cell shown in Fig. 1 have a current distribution on the top electrode which is similar to the disk in an infinite plane. An essential similarity is the manner in which the current density becomes infinite as r approaches r_d on the upper electrode. This feature of Newman's solution suggests that a superposition approach to correct the infinite problem to a finite-cell problem would be more advantageous than a finite difference technique. Visualize a cylindrical insulator placed axisymmetrically over the disk in an infinite plane as shown in Fig. 2. The current which flowed to infinity along the plane of the disk is forced to flow along the walls of the insulating cylinder. The open end of the cylinder would then be capped with a counterelectrode. Qualitatively, this is the procedure used to correct the original solution.

To develop this solution quantitatively, a sequence of potential functions which satisfy Eq. [1] will be defined that allow satisfaction

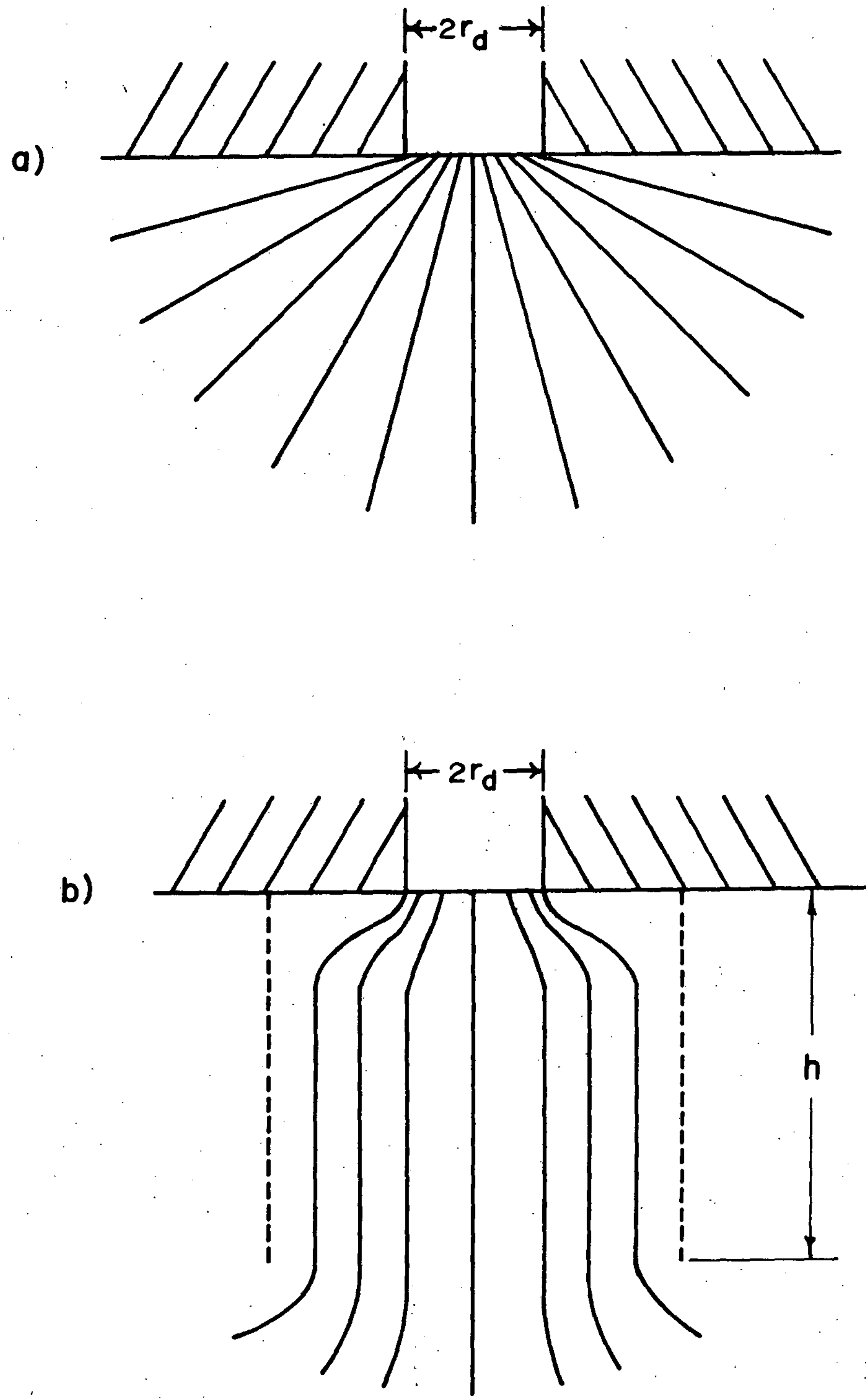

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Figure 2. a) Current lines for a disk electrode in an infinite insulating plane. b) The qualitative effect on the current lines by channelization with an insulating cylinder of height h .

of the boundary conditions of constant potential electrode surfaces and insulating walls of the cell. A natural set of functions to consider are the functions which result from the separation-of-variables solution to Eq. [1] in rotational elliptic coordinates. The first term of the series yields the primary distribution for the infinite plane problem. Newman (2) demonstrated the utility of the remaining terms for computing secondary distributions and for combining into below-the-limiting-current calculation schemes. The orthogonal properties of the terms give powerful leverage in describing potential variations across the disk electrode. Newman (1,19) derives functions

$$\Phi_{n,o} = \frac{I}{4\kappa r_d} P_{2n}(\eta) M_{2n}(\xi) \qquad [2]$$

where η and ξ are related to the coordinate system of Fig. 1 by

$$z = h - r_d \xi \eta$$
$$r = r_d \left[(1 + \xi^2)(1 - \eta^2)\right]^{1/2} \qquad [3]$$

$P_{2n}(\eta)$ are Legendre polynomials (20) and $M_{2n}(\xi)$ are functions which satisfy

$$(1 + \xi^2) \frac{d^2 M}{d\xi^2} + 2\xi \frac{dM}{d\xi} - 2n(2n + 1) = 0 \qquad [4]$$

with boundary conditions

$$M = 1 \text{ at } \xi = 0 \qquad [5]$$

and

$$M \to 0 \quad \text{as} \quad \xi \to \infty \, . \tag{6}$$

The functions $\Phi_{n,o}$ are well behaved at the centerline and give a zero current density on the insulating plane surrounding the disk. They may be superposed to give an arbitrary potential distribution on the disk. With the functions of Eq. [2], the boundary conditions on the upper disk and surrounding plane can be met but not those on the insulating cylinder and the counterelectrode.

These conditions will be met by defining a sequence of corrections which can be added to the functions of Eq. [2] in the following manner

$$\Phi_n = \sum_{j=0}^{k} \Phi_{n,j} \tag{7}$$

k indicates the number of corrections in the sequence. The correction functions indexed by j in Eq. [7] are required to be solutions to Eq. [1] written in cylindrical coordinates

$$\frac{1}{r}\frac{\partial}{\partial r}\left(r\,\frac{\partial \Phi}{\partial r}\right) + \frac{\partial^2 \Phi}{\partial z^2} = 0 \, . \tag{8}$$

The normal component of the current through the walls of the cell can be expressed for the n-th function through the k-th correction as

$$i_{n,k}(r_c,z) = -\kappa \sum_{j=0}^{k} \left.\frac{\partial \Phi_{n,j}}{\partial r}\right|_{r=r_c} \, . \tag{9}$$

Eq. [9] will be used to evaluate the effectiveness of corrections as they are added.

The first type of correction function, $\Phi_{n,1}$, is chosen to eliminate the current near the bottom corner of the cell where the insulating cylinder is normal to the counterelectrode.

$$\Phi_{n,1} = \frac{I}{4\kappa r_d} c_{n,1} \cosh\left(\frac{Q_o(h-z)}{r_c}\right) J_o\left(\frac{Q_o r}{r_c}\right) \qquad [10]$$

Q_o is the first zero of J_o , the Bessel function (20). The constant $c_{n,1}$ is evaluated by requiring Eq. [9] to be zero at $r = r_c$ and $z = 0$, which gives

$$c_{n,1} = -i_{n,o}(r_c,0) \frac{4r_d r_c}{I} [Q_o J_1(Q_o) \cosh (Q_o h/r_c)]^{-1}. \qquad [11]$$

The function in Eq. [10] serves to deflect some of the current from the side wall and onto the bottom of the cell, without disturbing the current distribution on the top surface of the cell.

The remaining current through the cell walls is evaluated by means of Eq. [9] with k equal to 1. A second solution to Eq. [8] is

$$\Phi_{n,2} = \frac{I}{4\kappa r_d} \sum_{\ell=1}^{\infty} c_{n,2,\ell} I_o\left(\frac{\pi(\ell-1/2)r}{h}\right) \sin\left(\frac{\pi(\ell-1/2)z}{h}\right) . \qquad [12]$$

This correction function has zero potential at the bottom of the cell and zero current density at the top. The coefficients $c_{n,2,\ell}$ are evaluated by forcing Eq. [9] to be zero at $r = r_c$ and $0 < z \leq h$ with k equal to 2

$$c_{n,2,\ell} = \frac{8\ r_d}{\pi(\ell - 1/2)\ I\ I_1\left(\frac{\pi(\ell-1/2)r_c}{h}\right)} \int_0^h i_{n,1}(r_c,z)\ \times$$

$$\sin\left(\frac{\pi(\ell-1/2)z}{h}\right) dz\ . \qquad [13]$$

The problem is well behaved because the first correction function was chosen to make it so. Thus Eq. [12] can be truncated after a few terms.

The boundary condition of zero current density along the cylindrical cell walls is now satisfied. The potential along the counterelectrode must now be made uniform. The next correction function must be chosen carefully. The solution to Eq. [8] must have a zero current density along the sides and top of the cell

$$\Phi_{n,3} = K + \frac{I}{4\kappa r_d} \sum_{\ell=1}^{\infty} c_{n,3,\ell} J_o\left(\frac{\Lambda_\ell r}{r_c}\right) \cosh\left(\Lambda_\ell \frac{(h-z)}{r_c}\right) \qquad [14]$$

Λ_ℓ are the zeros of the Bessel function, J_1 (20). The coefficients $c_{n,3,\ell}$ are evaluated by computing Φ_n, Eq. [7], with $k = 2$ and setting

$$\Phi_n(r,0) = -\Phi_{n,3}(r,0) \qquad [15]$$

for

$$0 \leq r \leq r_c\ .$$

The coefficients are

$$c_{n,3,\ell} = - \frac{8\pi\kappa r_d}{I r_c^2 \cosh\left(\Lambda_\ell \frac{h}{r_c}\right)[J_o(\Lambda_\ell)]^2} \int_0^{r_c} \Phi_n(r,0) J_o\left(\frac{\Lambda_\ell r}{r_c}\right) rdr \quad [16]$$

and

$$K = - \frac{8\pi\kappa r_d}{I r_c^2} \int_0^{r_c} \Phi_n(r,0) rdr \quad [17]$$

chosen so that the potential will now be zero on the counterelectrode. All boundary conditions are now satisfied except for a uniform potential across the top disk. The final solution is achieved by summing up all the generated correction functions in the following manner

$$\Phi_{TOTAL} = \sum_{\ell=0}^{m} c_\ell \Phi_\ell(r,z) \quad [18]$$

Φ_ℓ being evaluated from Eq. [7] with $k = 3$ utilizing all of the previously developed constants. The coefficients c_ℓ are found by requiring that the potential Φ_{TOTAL} be constant between zero and r_d along the upper disk. A Gram-Schmidt process is used to compute c_ℓ (22).

Results

The outlined scheme of computation was programmed and run on a digital computer. The solution was found to converge in most cases with only 2 functions as defined by Eq. [7], and within those functions, the series of Eq. [12] and Eq. [14] could be truncated with 20 terms or less. Resistances for a large number of cell configurations were computed and plotted in Fig. 3 and Fig. 4, where R is made dimensionless with the resistance of a disk electrode with radius r_d in an infinite cell. The electrode dimensions were held constant, and the height of the cylinder was varied in Fig. 3. When r_c/r_d is equal to unity, the upper electrode fills the entire area of the cylinder, and the dimensionless resistance can be computed analytically as

$$4\kappa r_d R = \frac{4h}{r_d \pi} \qquad [19]$$

and is the upper bound for the curves in Fig. 3. As the ratio r_c/r_d becomes larger, the upper disk is shrinking, and the cell appears more like the infinite cell. This is reflected in the trend of the dimensionless resistance towards unity for these curves, except for extremely short cells. The same dimensionless resistance is plotted in Fig. 4 with cells of constant height and varying disk radius. The shorter cylinders in Fig. 4 require a much smaller upper disk electrode to approach the infinite cell resistance. To design a cell for which uncorrected calculations are accurate, values of h/r_d and r_d/r_c must be chosen so that the resistance ratio is close to unity in Fig. 3 or Fig. 4.

Miller and Bellavance (10) reported a resistance and extensive potential mapping for a cell of the configuration shown in Fig. 5a. This cell was modeled in sections as shown in Fig. 5. The idealization assumes that an equipotential plane exists in the cell; resistances are then calculated for both the upper and lower cell. Since most of the potential drop occurs close to the electrode surface, the computed

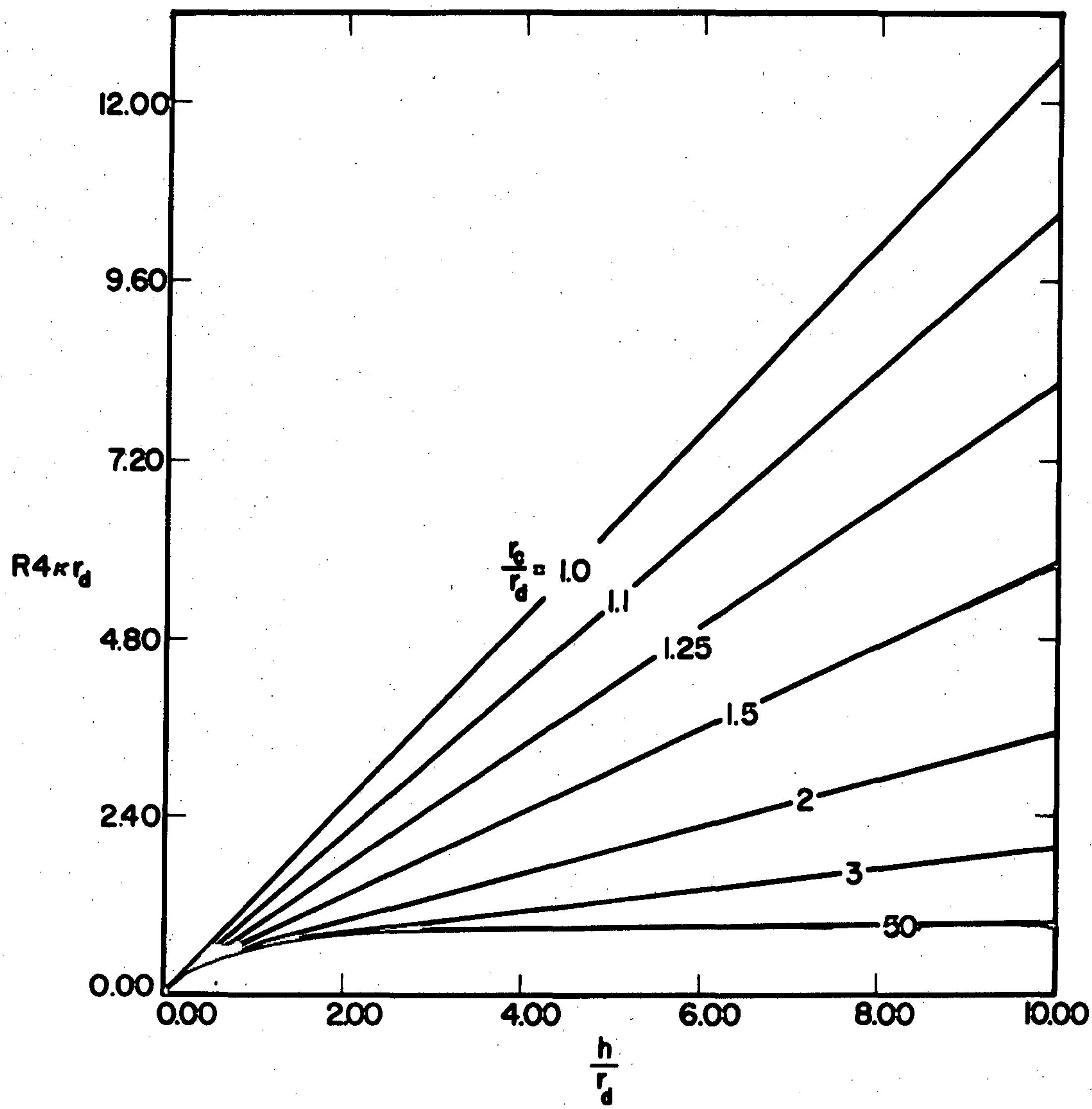

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Figure 3. Resistance of the axisymmetric cell with diameter held constant.

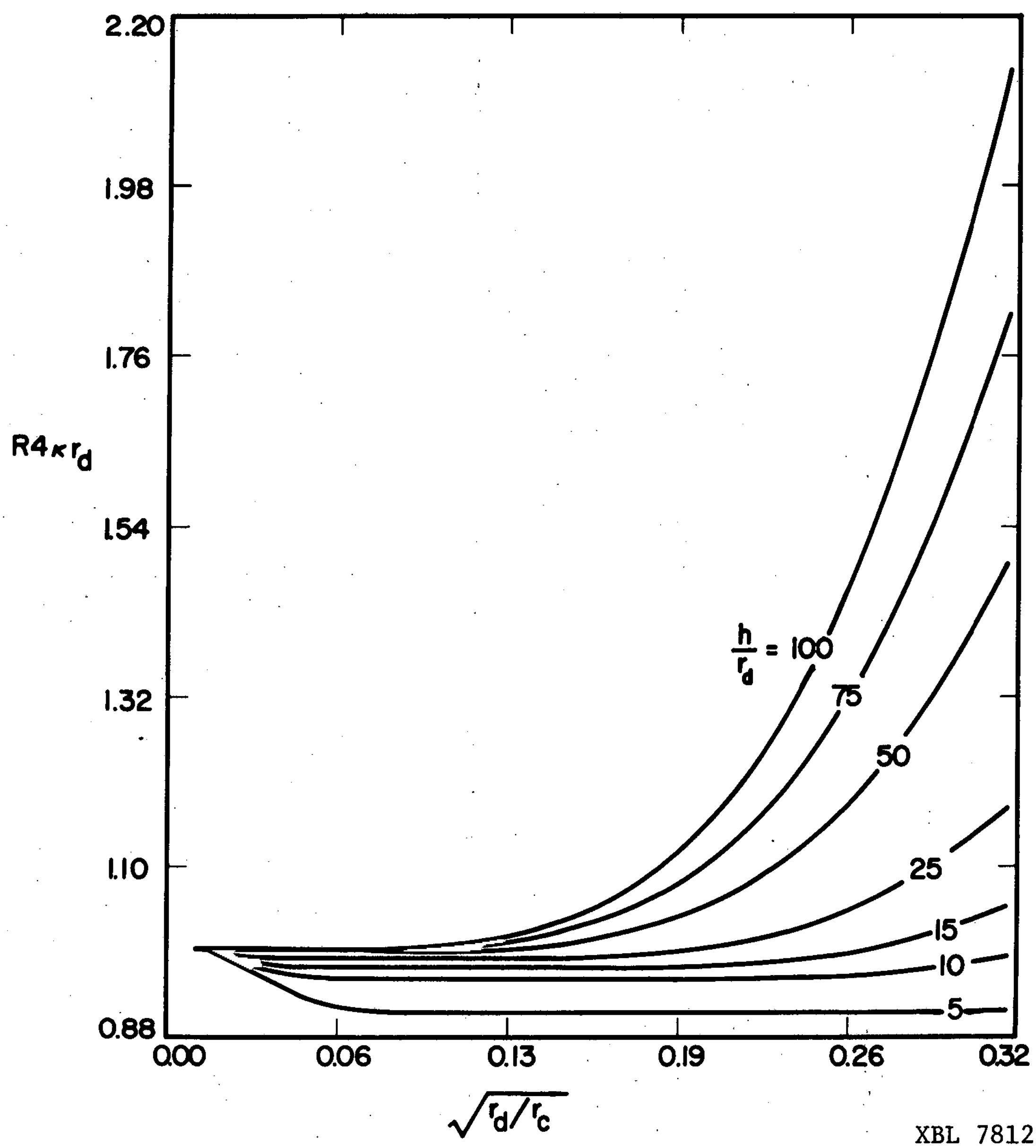

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Figure 4. Resistance of the axisymmetric cell with height held constant.

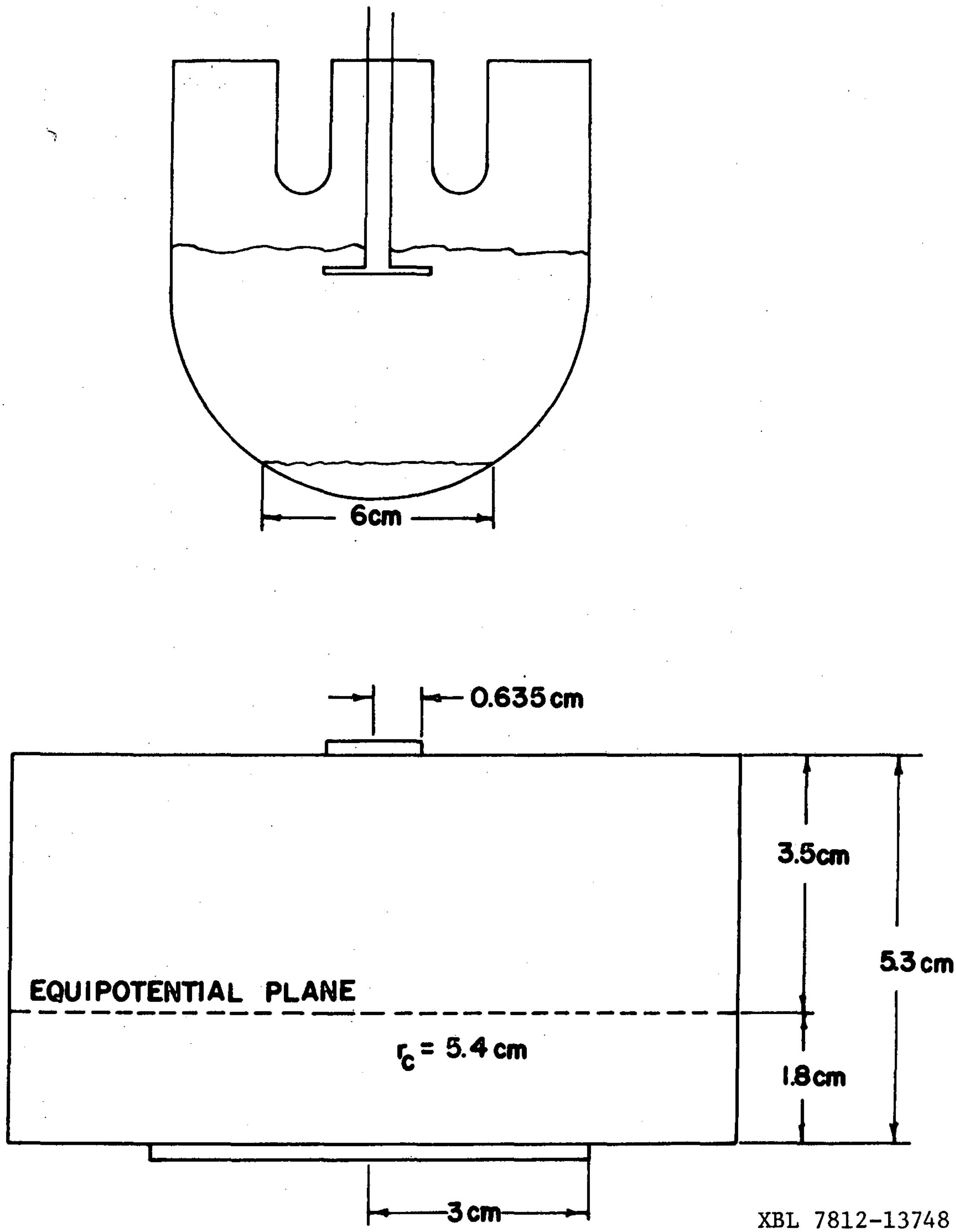

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Figure 5. The upper cell is that of Miller and Bellavance. The lower cell is the idealization used by Pierini and Newman. (Not to scale.)

resistance is relatively insensitive to the location of the equipotential plane in the cell model. The results using the dimensions of Fig. 5 give a resistance of 11.32 ohms which can be compared to the reported value of 11.35 ohms and contrasted with the value of 11.03 ohms for the disk electrode in an infinite cell. In particular, the effect of the geometry of the cell walls and the counterelectrode is adequate to account for the departure of the interrupter resistance from the infinite-cell value and no support can be found for the computation of a resistance value based on the area average of the potential of the solution adjacent to the electrode, as suggested by Nanis (7,9).

Isopotential lines for the cell of Fig. 5 are mapped in Fig. 6. The potential lines close to the electrodes are quite similar to those plotted in Fig. 1 of Newman (1) for the disk electrode in an infinite cell. The effect of the cell walls is exhibited most strongly by the bending of potential lines near the wall of the cell. The bending of the potential lines and the presence of the counterelectrode explains the deviation of Miller and Bellavances' interrupter resistance from the calculated resistance as suggested by Newman (23).

This technique of superimposing solutions to Laplace's equation to satisfy boundary conditions appears to be complicated and unwieldy when compared to finite difference techniques. However the computer program is straightforward and the resulting calculations take into account correctly the nature of the infinite current density at the edge of the smaller disk. The results of the calculations will be useful to design finite rotating disk cells which give results in agreement with the simpler calculations for an infinite cell, thus eliminating the need for the more detailed computations.

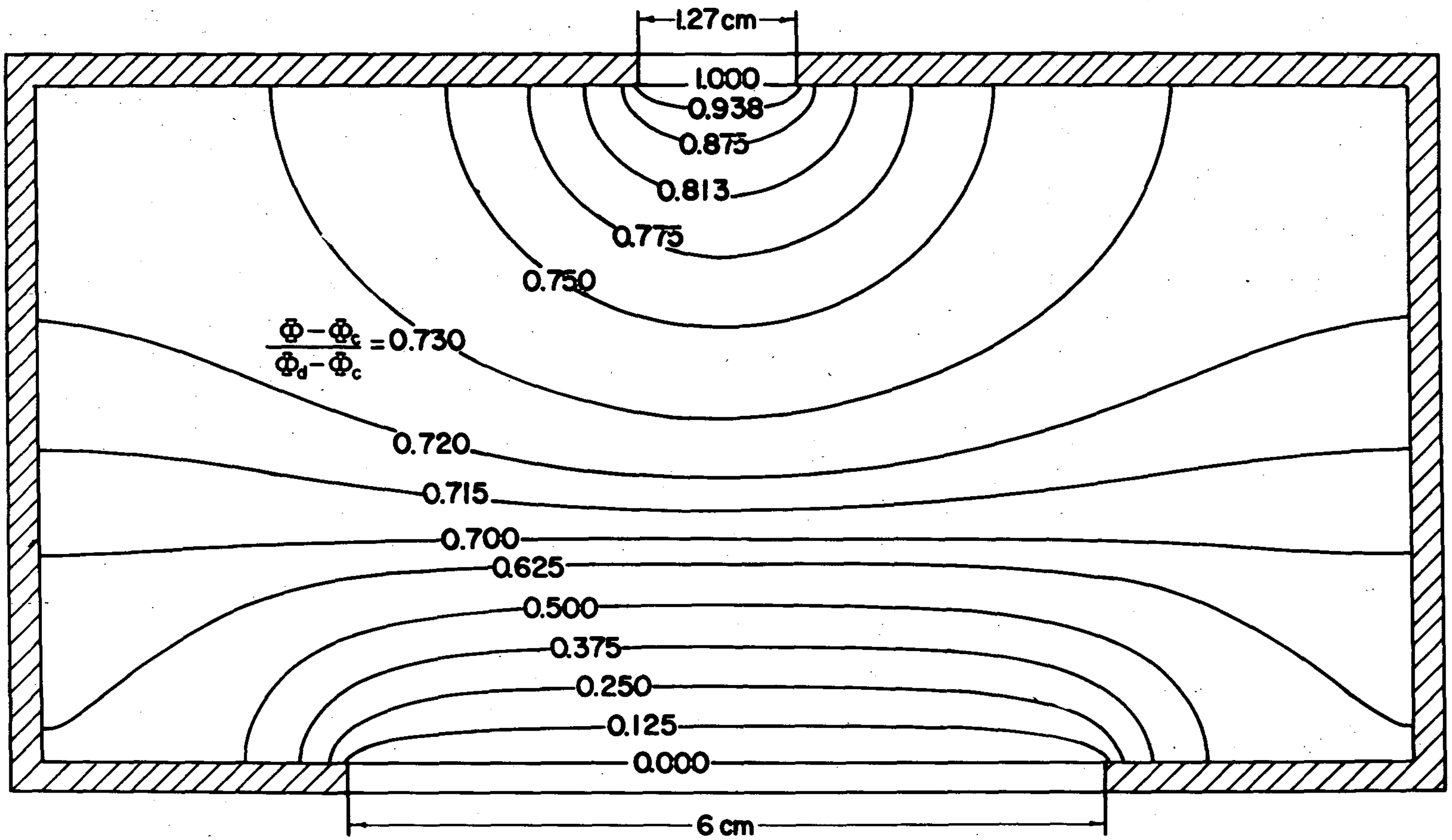

Figure 6. Potential distribution in the cell of Miller and Bellavance for the idealized cell.

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List of Symbols

$c_{n,1}; c_{n,2,\ell}; c_{n,3,\ell}$	constants associated with potential functions.
h	vertical height of cell, cm.
i	current density, A/cm^2.
I	total current, A.
I_o	modified Bessel function of the first kind of order 0.
I_1	modified Bessel function of the first kind of order 1.
j,k,ℓ	indices.
J_o	Bessel function of the first kind, of order 0.
J_1	Bessel function of the first kind of order 1.
K	constant of Eq. [17].
M_{2n}	Legendre function, see Eq. [4].
P_{2n}	Legendre polynomial.
Q_o	first zero of J_o , $Q_o = 2.404825558$.
r	radial coordinate, cm.
r_c	radius of counterelectrode, cm.
r_d	radius of working electrode, cm.
R	total resistance of cell, ohms.
z	vertical coordinate, cm.

ξ,η rotational elliptic coordinates.

Φ potential in cell, V.

Φ_n see Eq. [7], corrected function, V.

$\Phi_{n,i}$ correction terms, V.

Λ_ℓ zeros of J_1.

κ electrical conductivity, mhos/cm.

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