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Resistance for Flow of Current to a Disk

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The total current to an equipotential disk imbedded in an infinite, insulating plane is $I = 4\kappa a\Phi_o$, where κ is the conductivity, a is the disk radius, and Φ_o is the potential of the disk relative to infinity.

In order to obtain the concentration and activation overpotential for a rotating disk electrode it is necessary to subtract from the measured overpotential the ohmic potential drop between the reference electrode probe and the disk. The ohmic drop for a small disk is concentrated in the solution near the disk. Rather than try to put the probe from a reference electrode very near the surface and thus distort the potential and velocity distributions, one can estimate the ohmic drop from the resistance between a disk imbedded in the surface of an insulator and a counter electrode at infinity. This procedure does not account for deviations from the primary current distribution.

For the purpose of calculating the potential distribution from Laplace's equation, we use elliptic coördinates* ξ and η related to cylindrical

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* These are related to "oblate spheroidal coördinates" by $\xi = \sinh \mu$ and $\eta = \cos \theta$.

coördinates by

$$z = a\xi\eta$$

$$r = a\sqrt{(1+\xi^2)(1-\eta^2)}$$

where a is the radius of the disk, z is the normal distance from the disk, and r is the distance from the axis of symmetry. In this coördinate system Laplace's equation is

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

and the boundary conditions are

$\Phi = \Phi_o$ at $\xi = 0$ (on the disk electrode).

$\partial\Phi/\partial\eta = 0$ at $\eta=0$ (on the insulating annulus).

$\Phi = 0$ at $\xi = \infty$ (far from the disk).

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

To obtain a solution by the method of separation of variables we set

$$\Phi = P(\eta)Q(\xi) .$$

The differential equations for P and Q are

$$\frac{d}{d\eta}\left[(1-\eta^2)\frac{dP}{d\eta}\right] + nP = 0, \quad \frac{d}{d\xi}\left[(1+\xi^2)\frac{dQ}{d\xi}\right] - nQ = 0 ,$$

where n is the separation constant. The solutions of these equations are Legendre functions. In order to have well behaved solutions, n is restricted to values $n = \ell(\ell+1)$ where $\ell = 0, 1, 2, \ldots$. In order to satisfy the condition on the insulating surface, ℓ must be even. It turns out that the condition $\Phi = \Phi_o$ on the disk can be satisfied simply with the solution for $n = 0$. Integration thus yields

$$\Phi/\Phi_o = 1 - (2/\pi)\tan^{-1}\xi .$$

The current density at the disk surface can then be evaluated as follows:

$$i = -\kappa\left.\frac{\partial\Phi}{\partial z}\right|_{z=0} = \frac{-\kappa}{a\eta}\left.\frac{\partial\Phi}{\partial\xi}\right|_{\xi=0} = \frac{2}{\pi}\frac{\kappa\Phi_o}{a\eta} = \frac{2\kappa\Phi_o}{\pi\sqrt{a^2-r^2}} .$$

Hence the total current to the disk is

$$I = 2\pi \int_0^a i \; r \; dr = 4\kappa a \Phi_0 \; ,$$

and the resistance is

$$R = \Phi_0 / I = 1/4\kappa a \; .$$

This result agrees satisfactorily with that of Gröber[1] for the analogous heat conduction problem. The resistance of a hemisphere of radius a mounted on an insulating plane is easily calculated to be $1/2\pi\kappa a$. Hence the resistance of the disk is greater than that of a hemisphere by a factor of $\pi/2 = 1.5708$.

For a 0.1 M copper sulfate solution and a 0.5 cm (dia.) disk the above formula gives $R = 114.7$ ohms since $\kappa = 0.00872 \; (\Omega\text{-cm})^{-1}$ for this solution at 25°C[2].

Far from the disk the potential approaches

$$\Phi \rightarrow 2\Phi_0 a/\pi\rho \quad \text{as} \quad \rho \rightarrow \infty$$

where ρ is the distance from the center of the disk in spherical coördinates. This formula can be used to estimate the error for the situation where the reference electrode is not at infinity and the potential field is distorted by the walls of the cell.

The ohmic resistance of the solution is tabulated below for several possible locations of the probe from the reference electrode. These show that even with the probe only half a millimeter from the surface, the resistance is by no means negligible. Far from the disk the resistance is not very sensitive to the location of the probe. These considerations suggest that it is better to put the probe some distance from the disk.

Apparent Resistance for Various Probe Positions

$a = 0.25$ cm, $\kappa = 0.00872\ (\Omega\text{-cm})^{-1}$

r cm	z cm	R ohm	probe position
0	0.05	14.48	below the disk
0	0.1	27.78	below the disk
0	2.5	107.43	below the disk
2.5	0	107.39	beside the disk
2.7	0	107.93	beside the disk
∞	∞	114.7	at infinity

1 Heinrich Gröber. Die Grundgesetze der Wärmeleitung und des Wärmeüberganges. Berlin: Julius Springer Verlag, 1921.

2 B. Fedoroff. "Contribution a l'étude des sulfates simples et doubles de quelques métaux de la série magnésienne." Annales de Chimie, ser. 11, 16, 154-214 (1941).

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