the society for solid-state and electrochemical science and technology

Journal of The Electrochemical Society

Resistance for Flow of Current to a Disk

John Newman

J. Electrochem. Soc. 1966, Volume 113, Issue 5, Pages 501-502.
doi: 10.1149/1.2424003

Technical Notes

Resistance for Flow of Current to a Disk

John Newman

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

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 (Fig. 1). 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 rotational elliptic coordinates[1] ξ and η related to cylindrical coördinates by

$$\begin{aligned} z &= a\xi\eta \\ r &= a\sqrt{(1+\xi^2)(1-\eta^2)} \end{aligned} \qquad [1]$$

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 (see Fig. 1, where lines of constant Φ are also lines of constant ξ). In this coördinate system Laplace's equation is

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

and the boundary conditions are

$$\left.\begin{aligned} &\Phi = \Phi_0 \text{ at } \xi = 0 \text{ (on the disk electrode)} \\ &\partial\Phi/\partial\eta = 0 \text{ at } \eta = 0 \text{ (on the insulating annulus)} \\ &\Phi = 0 \text{ at } \xi = \infty \text{ (far from the disk)} \\ &\Phi \text{ well behaved at } \eta = 1 \text{ (on the axis of the disk)} \end{aligned}\right\} \qquad [3]$$

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

$$\Phi = P(\eta)Q(\xi) \qquad [4]$$

The differential equations for P and Q are

$$\begin{aligned} &\frac{d}{d\eta}\left[(1-\eta^2)\frac{dP}{d\eta}\right] + nP = 0, \\ &\qquad \frac{d}{d\xi}\left[(1+\xi^2)\frac{dQ}{d\xi}\right] - nQ = 0 \end{aligned} \qquad [5]$$

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 $n = l(l+1)$ where $l = 0, 1, 2, \ldots$. In order to satisfy the condition on the insulating surface, l must be even. It turns out that the condition $\Phi = \Phi_0$ on the disk can be satisfied simply with the solution for $n = 0$. Integration thus yields

$$\Phi/\Phi_0 = 1 - (2/\pi)\tan^{-1}\xi \qquad [6]$$

Equipotential lines are shown on Fig. 1.

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

$$i = -\kappa\left.\frac{\partial\Phi}{\partial z}\right|_{z=0} = \frac{-\kappa}{a\eta}\left.\frac{\partial\Phi}{\partial\xi}\right|_{\xi=0} = \frac{2}{\pi}\frac{\kappa\Phi_0}{a\eta} = \frac{2\kappa\Phi_0}{\pi\sqrt{a^2-r^2}} \qquad [7]$$

Hence the total current to the disk is

$$I = 2\pi\int_0^a i\,r\,dr = 4\kappa a\Phi_0 \qquad [8]$$

and the resistance is

$$R = \Phi_0/I = 1/4\kappa a \qquad [9]$$

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 $\pi/2 = 1.5708$.

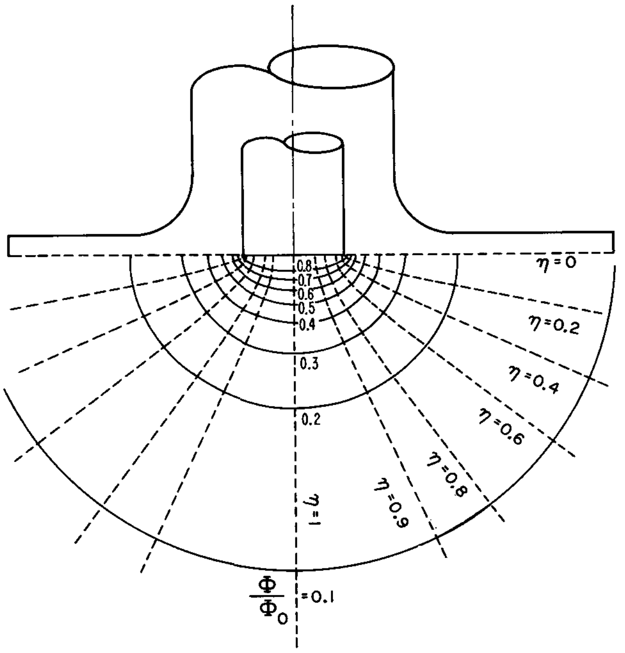

Fig. 1. Current and potential lines for a disk electrode

Table I. Apparent resistance for various probe positions

$a = 0.25$ cm, $\kappa = 0.00872$ (ohm-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] These are related to "oblate spheroidal coördinates" by $\xi = \sinh\mu$ and $\eta = \cos\theta$.

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

Far from the disk the potential approaches

$$\Phi \to 2\Phi_0 a/\pi\rho \text{ as } \rho \to \infty \qquad [10]$$

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 in Table I 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 small uncertainties in the location of the probe. These considerations suggest that it is better to put the probe some distance from the disk.

Equation [7] shows that the current density becomes infinite at the edge of the disk, a general characteristic of the primary current distribution where electrode polarization is ignored. This is in marked contrast to the uniform current density predicted by Levich (3) on the basis of mass transfer limitations. At currents below the limiting current both factors, ohmic drop in the solution and mass transfer limitations near the disk, influence the current distribution, which will then finally neither be uniform on the disk nor infinite at the edge of the disk. We have formulated this more general problem and expect to report results for the rotating disk in the near future.

Acknowledgment

This work was supported by the United States Atomic Energy Commission, under Contract W-7405-eng-48.

Manuscript received Dec. 6, 1965; revised manuscript received Jan. 31, 1966.

Any discussion of this paper will appear in a Discussion Section to be published in the December 1966 JOURNAL.

REFERENCES

1. Heinrich Gröber, "Die Grundgesetze der Wärmeleitung und des Wärmeübergangeses," Julius Springer Verlag, Berlin (1921).
2. B. Fedoroff, *Annal. Chim.*, **16**, 154 (1941).
3. B. Levich, *Acta Physicochim. U.R.S.S.*, **17**, 257 (1942).

Preliminary Evaluation of Ceria-Lanthana as a Solid Electrolyte for Fuel Cells

David Singman

Power Supply Branch, Harry Diamond Laboratories, Washington, D. C.

Solid electrolytes which are oxygen-ion conducting offer attractive possibilities for the construction of fuel cells capable of electrochemical oxidation of hydrogen and various hydrocarbons. Aqueous electrolyte fuel cells are limited to low current densities by activation polarization. The life of fused salt electrolyte cells is limited by corrosion. A solid electrolyte fuel cell utilizing a mixture of 85 mole % ZrO_2 and 15 mole % CaO was reported by Weissbart and Ruka (1). Although this cell is relatively unaffected by activation polarization, its output is resistance limited to operation near 1000°C because the specific conductance of the solid solution is 0.02 ohm^{-1} cm^{-1} at 1000°C and 0.002 ohm^{-1} cm^{-1} at 800°C (2).

A solid solution of 85 mole % ceria-15 mole % lanthana having higher conductivity has been reported by Croatto and Mayer (3). As is shown in Fig. 1, curves I and II, the conductivity of ceria-lanthana at 800°C is approximately equal to calcia-zirconia's conductivity at 1000°C. Oxygen ion conductance should occur in ceria-lanthana solid solution according to the concepts of Wagner (4) and Kingery (5) because fluorite lattice having anion vacancies exists (6). If the conduction is 95% or more ionic, this electrolyte may be suitable for fuel cell use because as much as 5% electronic conduction may be tolerated (7). Consequently, preliminary investigations were made of this electrolyte to determine its suitability in fuel cells.

Experimental

Initially, 99.9% pure (minimum) cerium oxide and a purified grade of lanthanum nitrate hexahydrate, 98% pure, were used as starting materials. A higher grade of purity of nitrate, 99.997% pure, was later used.

The mixed oxide was prepared by conversion of ceric oxide to an aqueous solution of the nitrate, addition of lanthanum nitrate solution, evaporation to dryness, and ignition of the residue. X-ray intensity measurements indicated that the solid solution had fluorite structure (8). Wafers were molded from the fine powder. After being hydraulically pressed at 10,000 lb/in. and ignited for several hours at 1000°C, the disks had the following dimensions: 2 cm diameter and 0.1 cm thickness. Porous platinum electrodes, 1.4 cm in diameter, were formed on the faces which had been ground smooth and parallel.

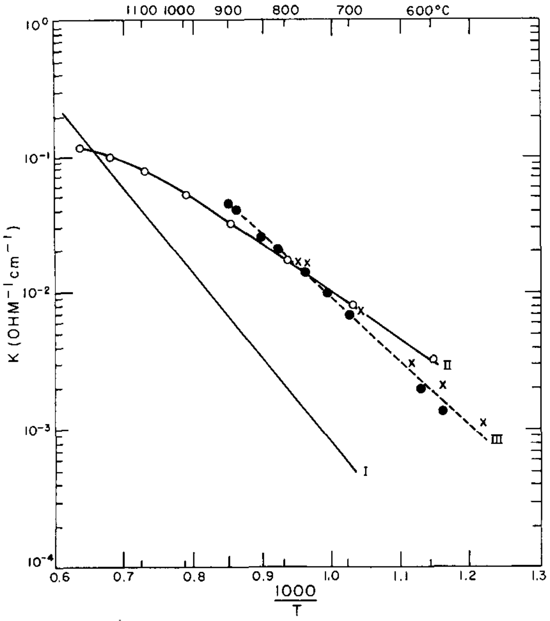

Fig. 1. Comparison of electrical conductivity of calcia-zirconia and ceria-lanthana.

Curves	Electrolyte	Workers
I	Calcia-zirconia	Kingery *et al.* (12)
II	Ceria-lanthana	Croatto and Mayer (3)
III	Ceria-lanthana	This laboratory