Perspectives on Newman's Work on Resistance for Flow of Current to a Disk

by Mark E. Orazem and Bernard Tribollet

In the late 1960s, John Newman began publishing a series of papers on the electrical characteristics of a disk electrode embedded in a semi-infinite insulating plane. His work revealed the influence that nonuniform current distributions have on experimental measurements obtained with the rotating disk electrode, commonly used in the electrochemical community. The first paper of this series, published in 1966, showed that the Ohmic resistance of a disk electrode corresponding to the primary current distribution can be expressed as

$$R_e = \frac{1}{4\kappa a} \tag{1}$$

where R_e is the Ohmic resistance with units of Ω, κ is the electrolyte conductivity, and a is the radius of the disk.[1] Newman observed that the Ohmic resistance is not negligible, even when a reference electrode is placed close to the disk. The corresponding primary current distribution was given as

$$i = \frac{2\kappa\Phi_0}{\pi\sqrt{a^2 - r^2}} \tag{2}$$

where Φ_0 is the uniform electrolyte potential at the disk surface. Newman observed that the primary current density tends toward infinity at the periphery of the disk electrode.

This paper has become one of the most heavily cited papers published in the *Journal of The Electrochemical Society*. The number of citations to Ref. 1 is presented in Fig. 1 as a function of the publication year. This paper has received a steady number of citations averaging over 10 per year, which may seem surprising for a paper that is only 1.3 pages in length.

Relevance to Current Research

The popularity of this paper may be attributed, in part, to the fact that Eq. 1 is simple and easy to understand, providing a straightforward functional relationship among the Ohmic resistance, solution conductivity, and radius for a disk electrode. A dimensionless Ohmic resistance can be defined as $R_e\kappa a$, which has a numerical value of ¼.

A second reason for the importance of this work is that the mathematical development required to arrive at Eq. 1 is not immediately obvious. This simple result arose from a transformation from cylindrical coordinates z and r to rotational elliptic coordinates ξ and η, with the transformation given as

$$z = a\xi\eta \tag{3}$$

and

$$r = a\sqrt{\left(1+\xi^2\right)\left(1-\eta^2\right)} \tag{4}$$

Expressed in rotational elliptic coordinates, Laplace's equation for a disk electrode of radius a is separable and can be solved subject to a fixed potential condition on the electrode surface, a zero flux condition on the insulating surface, and a potential tending toward zero far from the disk. Newman presented the correspondence between the coordinate system and the resulting current and potential lines as Fig. 2, indicating that lines of constant potential Φ are also lines of constant ξ. The lines of constant η in Fig. 2 correspond to current lines.

A third reason for the importance of the Ref. 1 is that Eq. 1 provides a correct value for the Ohmic resistance for a disk geometry. In 1970, Newman showed that the Ohmic resistance obtained by use of current interruption was exactly that corresponding to the primary current distribution, given by

FROM:
John Newman, "Resistance for Flow of Current to a Disk" JES, **113**, 501 (1966).

Resistance for Flow of Current to a Disk

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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

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

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

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

The differential equations for P and Q are

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

$$\frac{d}{d\xi}\left[(1+\xi^2)\frac{dQ}{d\xi}\right] - nQ = 0 \quad [5]$$

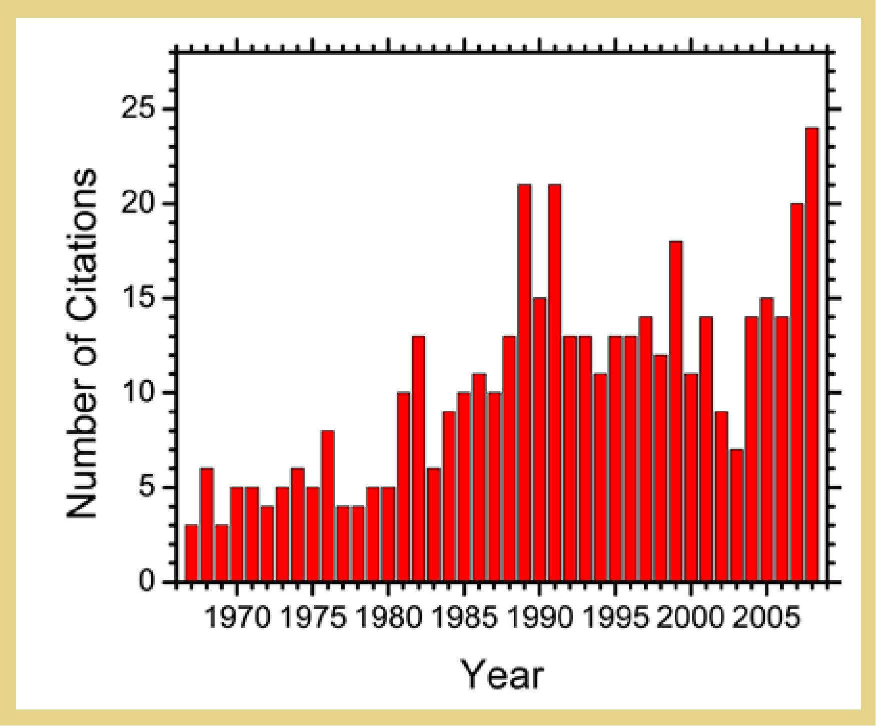

Fig. 1. *The number of papers citing Ref. 1 as a function of the year the paper was published.*

analyze the high-frequency asymptote for impedance data collected for a solid oxide fuel cell. Schmidt *et al.*[14] use Eq. 1 for the study of anodes in solid oxide fuel cells, and Razniak and Tomczyk[15] used Eq. 1 in their study of cathodes in solid oxide fuel cells. Fleig *et al.*[16] invoke Eq. 1 in their study of the impedance response of solid oxide fuel cells.

General theory for disk electrodes.—Frateur *et al.*[17] provided an experimental and computational verification of the influence of geometry-induced local current and potential distributions on local and global impedance spectra. This manuscript cites Ref. 1 as providing limiting behavior, but leans more heavily on Newman's subsequent paper on frequency dispersion in impedance measurements.[3] Antohi and Scherson[18] provide an alternate calculation to that provided by Newman[3] for the global impedance response of disk electrodes. Ref. 1 is invoked as describing the mathematical formulation for the primary distributions. In their calculations of the transient response of micro-electrodes, Behrend et al.[19] cite Newman[1] for his calculation of the primary resistance and associated current distributions, but their calculations were not placed into the context of Newman's subsequent papers describing the time dependence of potential and current distributions.[3,20,21]

Eq. 1.[2] In an analysis of the influence of nonuniform current and potential distributions on the transient and impedance response of a disk electrode, Newman demonstrated that high-frequency asymptote for the real part of the impedance can be represented by Eq. 1.[3] Thus, the remarkably simple result developed in Ref. 1 is general, has profound meaning, and is experimentally observed.

Electrochemical applications.—Martinez *et al.*[22,23] cite the use of Eq. 1 for the Ohmic resistance to a disk sensing electrode on a cement substrate. Bek *et al.*[24] cite the use of Eq. 1 for the Ohmic resistance to a microelectrode. Evans *et al.*,[25] Stiles *et al.*,[26] and Hansen *et al.*[27] cite the use of Eq. 1 for the Ohmic resistance to disk electrodes. Tomczyk *et al.*[28] referred to Ref. 1

Citing Publications in 2008

The 24 papers published in 2008 that cite Ref. 1 amply illustrate the breadth of the reach of Newman's work.

Micro-electrodes.—Eckhard and Schuhmann invoke the expression in a review of AC techniques for micro-electrodes.[4] Ahuja *et al.*[5] invoke the relevance of the primary current distribution given by Eq. 1 on a disk electrode. Boika *et al.*[6] use Newman's work[1,3] to calculate the potential gradient (caused by the Ohmic drop) in solution around a disk microelectrode polarized with an alternating voltage. Cantrell *et al.*[7] extended the work of Newman to account for overpotential-dependent formulations of both resistive and capacitive interfacial components in finite-element models of platinum disk and cone electrodes. Amatore *et al.*[8,9] cite Ref. 1 in their investigation of the effect of uncompensated solution resistance on steady-state and transient voltammograms at disk micro-electrodes. Chen *et al.*[10] take advantage of the radial dependence of the Ohmic resistance to develop an approach for spatially-resolved ohmic microscopy. Cho *et al.*[11] use Eq. 1 in their study of the dependence of the impedance of embedded single cells on cellular behavior.

Solid-state systems.—Simonsen *et al.*[12] use Eq. 1 in an application for solid-state electrochemistry. Lee *et al.*[13] use Eq. 1 to

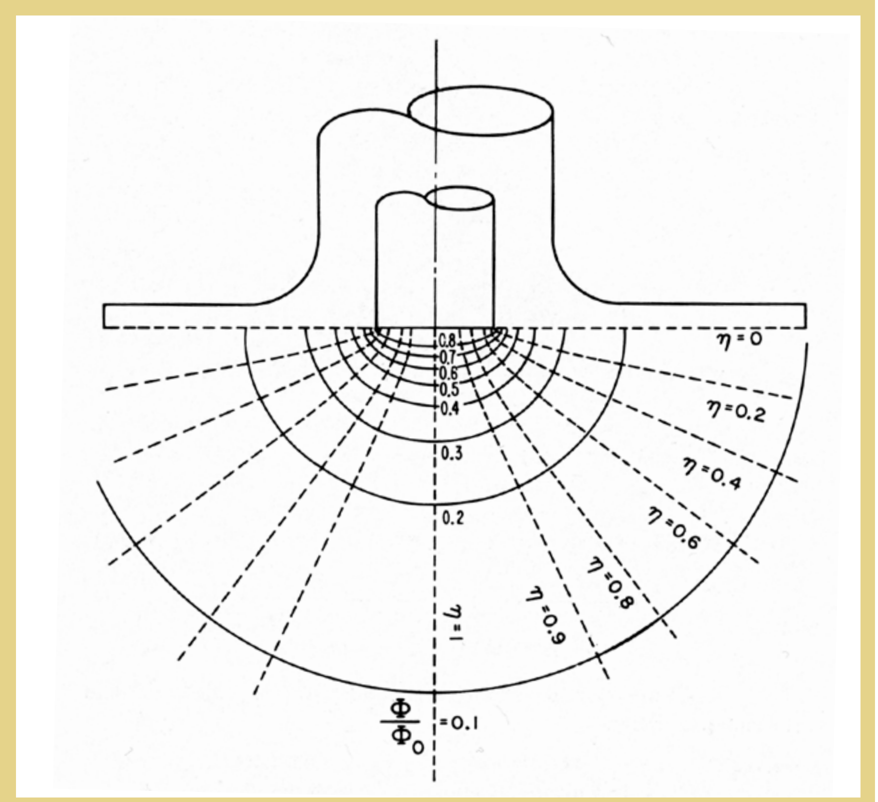

Fig. 2. *The current and potential lines for a disk electrode. (Taken from Newman[1] and reproduced with permission of The Electrochemical Society.)*

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in their investigation of the oxygen electrode reaction at the Pt/Nafion® interface using disk-shaped electrodes. Mendez *et al.*[29] use Eq. 1 in their development of a mechanistic model for the electro-polishing process on a flat electrode.

Conclusions

The fundamental studies of the disk electrode pioneered by Newman in the late 1960s have provided a foundation for electrochemical research. The body of work should probably be taken as a whole, since Ref. 1 represents a limiting behavior for an electrode system that is described in greater detail in subsequent works. Nevertheless, his work on the Ohmic resistance for a disk under primary current distribution yielded a simple, nontrivial, and correct expression that is as relevant today as it was in 1966.

About the Authors

Mark Orazem is Professor of Chemical Engineering at the University of Florida. He obtained his doctorate in 1983 from the University of California, Berkeley under the direction of John Newman. Orazem is an ECS Fellow and serves as Associate Editor for the *Journal of The Electrochemical Society.* He is the President-Elect of the International Society of Electrochemistry. He has over 130 refereed publications and has co-authored, with Bernard Tribollet, a textbook on impedance spectroscopy, which is sponsored by ECS and published by John Wiley & Sons.

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References

1. J. S. Newman, *J. Electrochem. Soc.*, **113,** 501 (1966).
2. J. S. Newman, *J. Electrochem. Soc.*, **117,** 507(1970).
3. J. S. Newman, *J. Electrochem. Soc.*, **117,** 198 (1970).
4. K. Eckhard and W. Schuhmann, *Analyst*, **133,** 1486 (2008).
5. A. K. Ahuja, M. R. Behrend, J. J. Whalen, III, M. S. Humayun, and J. D. Weiland, *IEEE T. Bio-Med. Eng.*, **55,** 1457 (2008).
6. A. Boika and A. S. Baranski, *Anal. Chem.*, **80,** 7392 (2008).
7. D. R. Cantrell, S. Inayat, A. Taflove, R. S. Ruoff, and J. B. Troy, *J. Neural Engineering*, **5,** 54 (2008.
8. C. Amatore, A. Oleinick, and I. Svir, *Anal. Chem.*, **80,** 7947 (2008).
9. C. Amatore, A. Oleinick, and I. Svir, *Anal. Chem.*, **80,** 7957 (2008).
10. Y. Chen, A. Belianinov, and D. Scherson, *J. Phys. Chem. C*, **112,** 8754 (2008).
11. S. Cho, M. Castellarnau, J. Samitier, and H. Thielecke, *Sensors*, **8,** 1198 (2008).
12. V. L. E. Simonsen, L. Norskov, and K. K. Hansen, *J. Solid State Electrochem.*, **12,** 1573 (2008).
13. B.-K. Lee, J.-Y. Lee, H.-Y. Jung, J.-H. Lee, and J.-H. Hwang, *Solid State Ionics*, **179,** 955 (2008).
14. M. S. Schmidt, K. V. Hansen, K. Norrman, and M. Mogensen, *Solid State Ionics*, **179,** 1436 (2008).
15. A. Razniak and P. Tomczyk, *Materials Science-Poland*, **26,** 195 (2008).
16. J. Fleig, H. R. Kim, J. Jamnik, and J. Maier, *Fuel Cells*, **8,** 330 (2008).
17. I. Frateur, V. M.-W. Huang, M. E. Orazem, N. Pébère, B. Tribollet, and V. Vivier, *Electrochim. Acta*, **53,** 7386 (2008).
18. P. Antohi and D. A. Scherson, *Electrochem. Solid-State Lett.*, **11,** F9 (2008).
19. M. R. Behrend, A. K. Ahuja, and J. D. Weiland, *IEEE T. Bio-Med. Eng.*, **55,** 1056 (2008).
20. K. Nisancioglu and J. S. Newman, *J. Electrochem. Soc.*, **120,** 1356 (1973).
21. K. Nisancioglu and J. S. Newman, *J. Electrochem. Soc.*, **120,** 1339 (1973).
22. I. Martinez, C. Andrade, N. Rebolledo, V. Bouteiller, E. Marie-Victoire, and G. Olivier, *Corrosion*, **64,** 107 (2008).
23. I. Martinez, A. Castillo, and C. Andrade, *J. Nucl. Mater.*, **373,** 226 (2008).
24. R. Y. Bek, L. I. Shuraeva, L. I. Skvortsova, T. P. Aleksandrova, and V. A. Tarasova, *Russ. J. Electrochem.*, **44,** 493 (2008).
25. L. A. Evans, M. Petrovic, M. Antonijevic, C. Wiles, P. Watts, and J. Wadhawan, *J. Phys. Chem. C*, **112,** 12928 (2008).
26. R. L. Stiles, R. Balasubramanian, S. W. Feldberg, and R. W. Murray, *J. Am. Chem. Soc.*, **130,** 1856 (2008).
27. K. K. Hansen, *J. Appl. Electrochem.*, **38,** 591 (2008).
28. P. Tomczyk and S. Zurek, *Pol. J. Chem.*, **82,** 1891 (2008).
29. J. Mendez, R. Akolkar, T. Andryushchenko, and U. Landau, *J. Electrochem. Soc.*, **155,** D27 (2008).