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

$$R_e = \frac{1}{4\kappa a}$$  \hspace{1cm} (1)

where $R_e$ is the Ohmic resistance with units of $\Omega$, $\kappa$ 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

$$i = \frac{2k\Phi}{\pi\sqrt{a^2 - r^2}}$$ \hspace{1cm} (2)

where $\Phi$ 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 $\frac{1}{4}$.

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 $\xi$ and $\eta$, with the transformation given as

$$z = a\xi\eta$$ \hspace{1cm} (3)

and

$$r = a\sqrt{(1+\xi^2)(1-\eta^2)}$$ \hspace{1cm} (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 $\Phi$ are also lines of constant $\xi$. The lines of constant $\eta$ 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
Eq. 1. 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. Thus, the remarkably simple result developed in Ref. 1 is general, has profound meaning, and is experimentally observed.

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. Ahuja et al. invoke the relevance of the primary current distribution given by Eq. 1 on a disk electrode. Boika et al. use Newman’s work to calculate the potential gradient (caused by the Ohmic drop) in solution around a disk microelectrode polarized with an alternating voltage. Cantrell et al. 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. 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. take advantage of the radial dependence of the Ohmic resistance to develop an approach for spatially-resolved ohmic microscopy. Cho et al. 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. use Eq. 1 in an application for solid-state electrochemistry. Lee et al. use Eq. 1 to analyze the high-frequency asymptote for impedance data collected for a solid oxide fuel cell. Schmidt et al. use Eq. 1 for the study of anodes in solid oxide fuel cells, and Razniak and Tomczyk use Eq. 1 in their study of cathodes in solid oxide fuel cells. Fleig et al. invoke Eq. 1 in their study of the impedance response of solid oxide fuel cells.

Electrochemical applications.—Frateur et al. 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. Antohi and Scherson provide an alternate calculation to that provided by Newman 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. cite Newman 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.

Electrochemical applications.—Martinez et al. cite the use of Eq. 1 for the Ohmic resistance to a disk sensing electrode on a cement substrate. Bek et al. cite the use of Eq. 1 for the Ohmic resistance to a microelectrode. Evans et al., Stiles et al., and Hansen et al. cite the use of Eq. 1 for the Ohmic resistance to disk electrodes. Tomczyk et al. referred to Ref. 1

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

Fig. 2. The current and potential lines for a disk electrode. (Taken from Newman and reproduced with permission of The Electrochemical Society.)
in their investigation of the oxygen electrode reaction at the Pt/Nafion® interface using disk-shaped electrodes. Mendez et al.20 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 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 Mark Orazem, a textbook on impedance spectroscopy, which is sponsored by ECS and published by John Wiley & Sons.

Bernard Tribollet is Director of Research at the Centre National de la Recherche Scientifique (CNRS) and Associate Director of the Laboratoire Interfaces et Systèmes Électrochimique at the University of Pierre and Marie Curie. He obtained his doctorate in 1978 under the direction of Israel Epelboin and worked at the Laboratoire Electrochimie et Catalyse at the University of Paris VI. He left France in 1981 as a visiting scientist. Tribollet has worked at the University of Montreal and the Ecole Polytechnique de Montreal, Canada. In 1986 he returned to France to become Professor of Electrochemistry at the University of Paris XI, Orsay. He was the Director of Research at the Centre National de la Recherche Scientifique (CNRS) and Associate Director of the Laboratoire Interfaces et Systèmes Électrochimique at the University of Paris XI, Orsay. He is the author of over 200 refereed journal publications and refereed chapters in books. He is the author of a textbook on electrochemistry, which he has sponsored by ECS and published by John Wiley & Sons.

References