

FEATURED ARTICLES

The Chalkboard: A Positive Spin on Corrosion Measurements: The Rotating Ring-Disk Electrode

To cite this article: Jamie Noel 2021 *Electrochem. Soc. Interface* **30** 34

View the [article online](#) for updates and enhancements.



The Electrochemical Society
Advancing solid state & electrochemical science & technology

242nd ECS Meeting

Oct 9 – 13, 2022 • Atlanta, GA, US

Abstract submission deadline: **April 8, 2022**

Connect. Engage. Champion. Empower. Accelerate.

MOVE SCIENCE FORWARD



Submit your abstract





ECS Digital Library

The Electrochemical Society's digital library provides you with access to more than 160,000 articles across electrochemistry and solid state science and technology. Publish your next open access article with us to help accelerate scientific discovery and innovation.



Visit iopscience.iop.org/partner/ecs for more information.

THE CHALKBOARD

A Positive Spin on Corrosion Measurements: The Rotating Ring-Disk Electrode

by Jamie Noël

Introduction

Within the inventory of highly sensitive, selective, and broadly useful electroanalytical techniques available nowadays resides a very clever approach to the measurement of reaction rates, including those of certain non-electrochemical reactions, and the simultaneous quantitative identification of reaction products, including short-lived intermediates. Conceived by Alexander Frumkin in 1958¹ and first built by Lev Nekrasov,² the rotating ring-disk electrode (RRDE) was a spin-off of the rotating disk electrode (RDE) for which Benjamin Levich developed the hydrodynamic equations defining the electrochemical response.³ A fascinating account of the development of the RRDE technique by Soviet, American, and British electrochemists during and despite the Cold War can be found in an earlier issue of *Interface*.⁴

What is an RRDE?

The RRDE consists of a ring-shaped electrode encircling and concentric with a disk electrode that is centered on the longitudinal axis of a rotating shaft, as depicted in Fig. 1. The disk is made of a material of interest, and the ring is a stable, relatively inert conductor, such as Pt or Au. An electrically insulating material (commonly polytetrafluoroethylene, PTFE) surrounds and forms a tight seal with the central disk and both sides of the ring so that the two electrodes are not in electrical contact and only the faces of the ring and disk at the butt end of the rotating shaft (i.e., not the sidewalls) contact the electrolyte solution. The requirements that the ring and disk be concentric, centered on the rotational axis of a straight shaft that rotates smoothly with no wobble, and tightly sealed to the insulating shroud in several places demands careful precision machining of these components. These can be purchased from a commercial supplier or custom-made at a capable machine shop. Electrical contact with the potentiostat is made via brush contacts on the rotating shaft, where a solid connection is not possible. The brush contacts connect with the back of either the ring or the disk underneath the insulating shroud to avoid exposure to the electrolyte solution. Usually, the ring and disk each act as independent working electrodes, which then requires the use of a bipotentiostat for electrochemical control and measurement, although certain applications may require electrochemical connection only to the ring. The RRDE system is completed by a drive mechanism with smooth bearings and speed control to rotate the electrodes, an electrochemical cell in which to do the chemistry, and possibly a seal between shaft and cell that enables maintenance of a controlled atmosphere (e.g., anoxic) inside the cell while permitting unhindered rotation of the electrodes.

How does it work?

Exactly like the RDE,⁵ the RRDE rotating in an electrolyte solution causes the solution to be drawn in a laminar flow pattern, first toward the disk surface and then, as it approaches the surface, outward, in a direction parallel to the plane of the disk, at a velocity dependent on the rotation rate, which affords the operator

control over the rate of convective mass transport (Fig. 1). Near the disk, the flow rate of the solution toward the end of the rotating shaft is dependent on the square of the distance, z , from the flat surface, with, of course, a flow rate of zero immediately at that surface. This velocity gradient means that the forced convection set up by the rotation brings solution species close to the surface, but a small mass transport gap remains to be bridged by diffusion, with the diffusion layer thickness, δ , being given by $\delta = 1.61\nu^{1/6}D^{1/3}\omega^{-1/2}$, where ν is the kinematic viscosity of the solution, D the diffusion coefficient of the diffusing species, and ω the angular velocity of rotation in radians/s ($\omega = 2\pi f$, where f is the rotational frequency in Hz). Adjacent to the end of the rotating shaft, a stagnant layer of solution, the Prandtl layer, with thickness $p = 3.6\left(\frac{\nu}{\omega}\right)^{1/2}$, is dragged by the surface (i.e., the radial solution velocity, v_r , of this layer with respect to the butt of the rotating shaft is zero). Beyond the Prandtl layer, the radial velocity of the solution is given by $v_r = 0.51\omega^{3/2}\nu^{-1/2}rz$, where r is the radial distance from the disk center.⁵

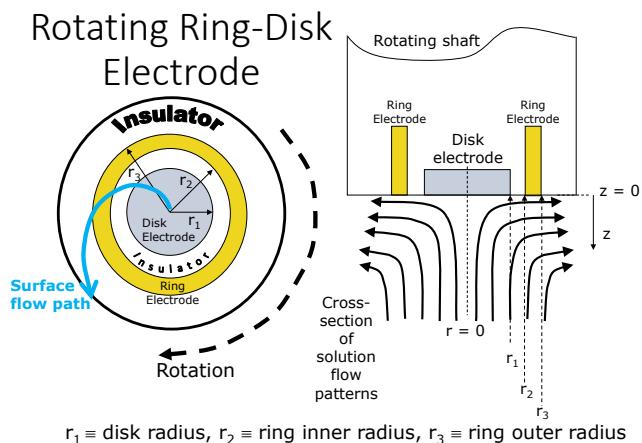


FIG. 1. End-on and cross-sectional views of a rotating ring-disk electrode showing the locations of the disk, ring, and insulating components on the rotating shaft, the critical dimensions of the RRDE, and the solution flow patterns.

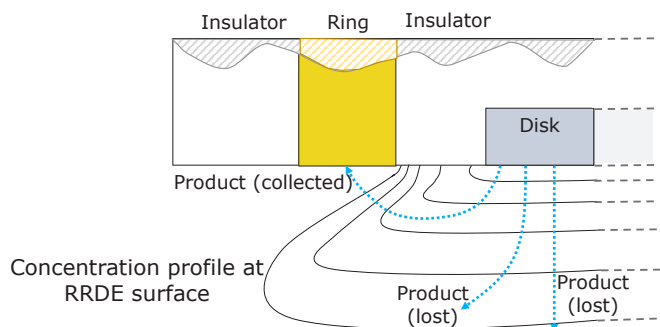


Fig. 2. Cut-away cross-sectional view of an RRDE operating in collection mode and the near-surface concentration profile of reaction products released from the disk surface, including possible trajectories of individual particles that could lead them to reaction at the ring electrode or out into the bulk solution where they will be lost to the RRDE.

This arrangement is crucial to the function of the RRDE. It means that chemical species produced at the disk electrode have little chance of diffusing along the Prandtl layer from disk to ring (too narrow a region for diffusion over such a long distance), and there is no chance of species traveling inward (upstream) from the ring to disk. Instead, they will diffuse away from the disk surface, eventually reaching the radially flowing layers of the solution and being swept away from the disk and over the ring, on their way off the butt of the rotating shaft (Fig. 2). As the solution flows past the ring, some of the products from the disk diffuse back through the Prandtl layer to the ring electrode surface, where they are oxidized or reduced, depending on the ring electrode potential and the nature of the chemical species. Thus, the ring could be used as an analytical detector for redox-active species produced at the disk. This mode of RRDE operation is known as “collection mode” (there is also a “shielding mode” in which the disk is set to consume redox-active species from the bulk solution, and the ring detects any residual species that get by the disk in unreacted form, as well as a “reaction mode” in which reactive species produced at the disk and other species of complementary reactivity produced at the ring meet and react together near the inner radius of the ring, such as in “ring-of-fire” electrochemiluminescence).^{6,7} The ring, however, only collects a fraction of the species produced at the disk; the rest are lost to the bulk solution. Therefore, for the RRDE technique to be made quantitative, the collection efficiency of the ring, N , must be known. The mathematics required to determine it are rather difficult and eluded Frumkin, Levich, and others until electrochemical math whiz John Albery finally provided a solution for the differential equations involved⁸ (not reported here in the interest of conserving space). Fortunately, the collection efficiency depends only on the geometry of the RRDE (radius of the disk and inner and outer radii of the ring) and is therefore constant for each RRDE regardless of other experimental variables. Moreover, the efficiency is easily and accurately measurable experimentally under appropriate conditions, ($N = \frac{i_R}{i_D}$, where i_R is the current measured at the ring and i_D the disk current).

What can it do?

With the ring electrode potential held constant at a value at which it will oxidize or reduce a chemical species of interest generated at the disk electrode at the mass-transport-limited rate, one can accurately quantify the rate of production of such species at the disk by measuring the current at the ring. The disk potential can be scanned or held constant during the measurement, depending on the experiment objectives. This flexibility opens many opportunities for innovative experiments to access data that are difficult to obtain by other means. For example, depending on the size of the gap between disk and ring,

the rotation rate, and other factors, the transit time between disk and ring for chemical species may be milliseconds,⁹ allowing for the detection of short-lived reaction intermediates. In fact, one of the original and most reported uses of the RRDE is to probe the oxygen reduction reaction (ORR) to determine whether the mechanism proceeds via a direct, 4-electron pathway, or by two 2-electron steps, with hydrogen peroxide as an intermediate.¹⁰⁻¹⁴ This determination is accomplished by setting the ring electrode at a potential at which H_2O_2 will be oxidized back to oxygen and then watching for a ring current indicating H_2O_2 oxidation as dissolved oxygen is reduced at the disk electrode polarized to different potentials under various conditions, as illustrated schematically in Fig. 3.

Use in Corrosion

The RRDE is a valuable tool in corrosion science. In addition to enabling studies of the cathodic half-reactions that comprise half of the overall corrosion process,^{14,15} such as the oxygen reduction mentioned above, RRDE techniques can contribute to understanding materials dissolution and corrosion product film formation. Using a disk electrode made of a material of interest, one can employ the ring to detect and quantify the release of soluble species from the disk occurring as a result of its degradation during free corrosion or under electrochemical polarization. This approach may provide key information about the oxidation state of the species dissolving from

(continued on next page)

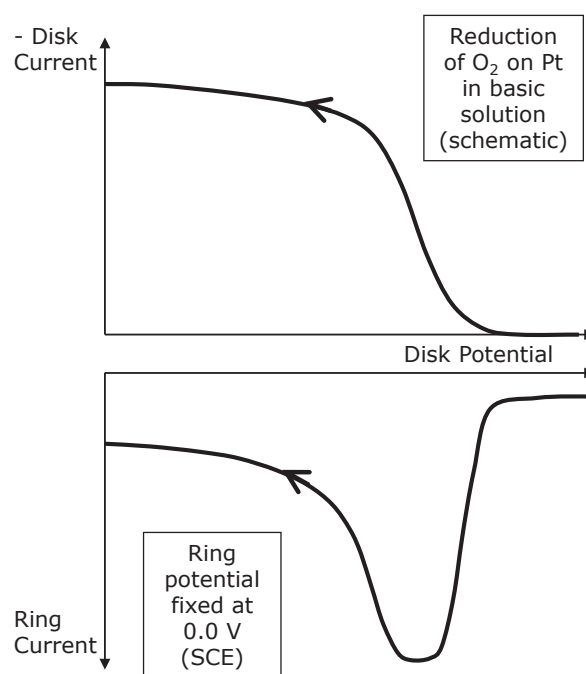


Fig. 3. Schematic illustration of the current response of the disk (upper panel) and ring (lower panel) currents to a sweep of the disk potential through a range over which the reduction of dissolved oxygen molecules occurs in basic solution. The ring potential is held constant at a value at which H_2O_2 , an intermediate species in the oxygen reduction reaction, is oxidized back to oxygen and protons (be careful of the sign conventions in this figure). The ring current has a peak, because even though the production of H_2O_2 at the disk increases as the potential decreases, the rate of H_2O_2 consumption by reduction to water at the disk itself, before it can get to the ring, increases as well.

the disk surface¹⁶⁻²⁰ or allow the identification and quantification of individual components dissolving from an alloy,²¹⁻²⁵ oxide,^{26,27} or even a polymer.²⁸ For example, the dissolution of magnetite, Fe_3O_4 , an oxide containing both ferrous and ferric ions, was deconvoluted to determine the relative amounts of Fe(II) and Fe(III) released under open-circuit conditions and at different applied potentials to quantify the contributions of congruent dissolution and reductive dissolution mechanisms to the overall process as a function of potential, as can be seen in Fig. 4.²⁷ Additionally, a comparison of the disk current with that of the ring (with corrections for collection efficiency) can provide information about the fraction of corrosion products dissolving into the solution vs. those being incorporated into a solid deposit on the electrode surface (e.g., oxide film formation), or even probe localized corrosion (e.g., pitting).²⁹

In some ways, the RRDE could be considered a low-tech forerunner of the clever AESEC (atomic emission spectroelectrochemistry) technique developed in the laboratory of Kevin Ogle at Chimie ParisTech,³⁰ in which an inductively-coupled plasma-atomic emission spectrometer (or ICP-mass spectrometer in some adaptations) analyzes the output from an electrochemical flow cell to identify and quantify metal-containing species released from a material undergoing corrosion or degradation under electrochemical polarization. However, rather than being replaced by AESEC, the RRDE is clearly

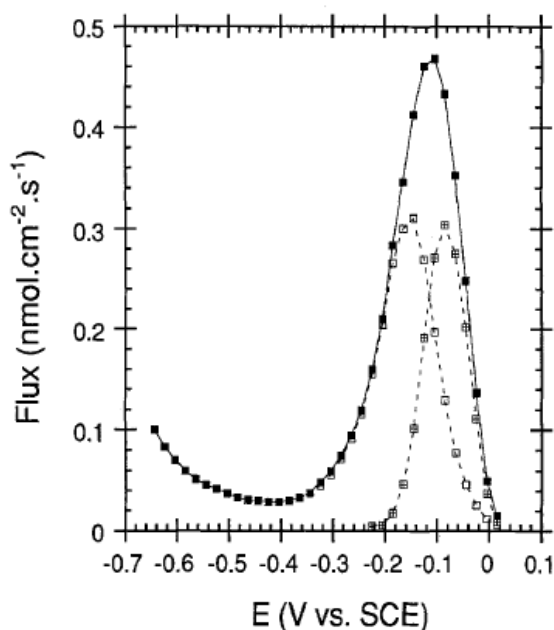


FIG. 4. Dissolution fluxes of Fe(II) (□) and Fe(III) (⊕) as a function of applied potential on a magnetite disk, converted from measured ring electrode currents acquired on an RRDE consisting of a magnetite disk and Au ring exposed to 0.1 M KClO_4 + 1 mM EDTA at pH 3.0, a temperature of 20°C, and a rotation rate of $\omega = 209$ radians/s. The total Fe dissolution flux (■) is also given. Congruent dissolution of magnetite (i.e., without redox conversion of Fe ions in the mixed oxidation state oxide) can be seen to occur at a potential $E \sim -0.09$ V/SCE where the number ratio of Fe(II) to Fe(III) ions released is 1:2; this is also (by necessity) the open circuit potential of the magnetite in this solution. However, the solid curve shows that magnetite dissolves fastest in this solution at $E \sim -0.11$ V/SCE, where a small amount of reductive dissolution enhances the process. (Figure published in reference 27.)

a complement to it because the RRDE has some sensitivity to the chemical state of species emitted by the disk material, whereas the ICP atomizes everything that enters and allows one to determine only the elements present and the total amount of each. Additionally, the ability of the RRDE to probe reactive intermediates is unavailable in AESEC.

Variations on the RRDE

Barry Miller^{31,32} recognized that the ring electrode could be made into a simultaneous multi-component detector that would be particularly useful for corrosion studies by splitting it into two or more electrically independent arc electrodes, as illustrated, for the simplest case, in Fig. 5. This represented a substantial expansion in the utility of the RRDE. For instance, the magnetite dissolution study discussed above²⁷ was performed by conducting the same experiment twice—once with the ring set to detect the release of species containing ferrous ions and again with the ring set to reduce any released ferric species to ferrous. The measurements could have been completed in half the time, with greater reliability (no concerns about the reproduction of identical experimental and disk surface conditions), had a split-ring-disk electrode been available. The split-ring-disk electrode depicted in Fig. 5 would require a tripotentiostat to control and measure from its three independent working electrodes, and the capture efficiency of each ring component would decline in proportion to its smaller surface area. Further variations of this sort, such as an RRDE with two concentric split rings³³ (that is oddly reminiscent of a biplane) are possible but would require a multipotentiostat capable of servicing the required number of working electrodes.

Conclusions

Though it is approaching its 65th birthday, the RRDE is not ready to be retired and remains an excellent option in the repertoire of electrochemists and corrosion scientists. The *Journal of The Electrochemical Society* and other publications offer many accounts of innovative applications of the RRDE and its offshoots, which are also excellent fodder for provoking ideas for more novel RRDE

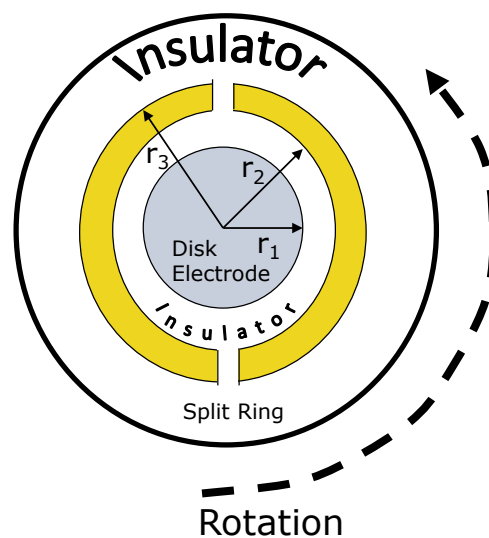


FIG. 5. Schematic representation of the working end of a split-ring RRDE. The disk and each of the arc electrodes derived by splitting the ring are electrically independent working electrodes. This device, therefore, must be operated using a tripotentiostat.

approaches. Helpful training on the theory and practice of RRDE electrochemistry and other electrochemical techniques is also available through some of the technical short courses offered by The Electrochemical Society at its biannual meetings. ■

© The Electrochemical Society. DOI: 10.1149.2/2.F04212IF

About the Author



DR. JAMIE NOËL, ASSISTANT PROFESSOR OF CHEMISTRY, WESTERN UNIVERSITY

Education: B.Sc., M.Sc. Guelph; Ph.D. Manitoba

Research Interest: Studies of the degradation of nuclear fuel and container materials for permanent disposal of nuclear fuel waste.

Work with Students: A research group of 25 graduate and undergraduate students,

postdoctoral fellows, and research scientists conducting experimental research on corrosion aspects of copper, carbon steel, uranium dioxide, stainless steels, nickel alloys, and other materials.

Research Partners: The Nuclear Waste Management Organization; the Swedish Nuclear Fuel and Waste Management Company; the National Cooperative for the Disposal of Radioactive Waste; the Nuclear Waste Management Organization of Japan; Imperial Oil.

Pubs & Patents: 50 refereed conference proceedings papers, 20 commercial reports, 5 book chapters, coauthored 100+ refereed journal articles. Associate Editor, *CORROSION Journal*.

Awards: ECS R. C. Jacobsen and Lash Miller Awards and the Western University Faculty of Science Distinguished Research Professorship (twice).

Work with ECS: ECS Corrosion Division Chair, ECS Education Committee Chair, Short Course Instructor (Fundamentals of Electrochemistry) at ECS biannual meetings.

Website: <https://www.uwo.ca/chem/people/faculty/noel.html>

 <https://orcid.org/0000-0003-3467-4778>

References

1. O. A. Petrii and S. Fletcher, *The Frumkin Era in Electrochemistry*. In *Electrochemistry in a Divided World*, F. Scholz, Ed., Springer International Publishing, Switzerland (2015).
2. A. N. Frumkin and L. N. Nekrasov, *Dokl. Akad. Nauk SSSR*, **126**, 115 (1959).
3. V. G. Levich, *Acta Physicochim. U.R.S.S.*, **17**, 257 (1942).
4. F. Dalton, *Electrochem. Soc. Interface*, **25**, 50 (2016).
5. A. J. Bard and L. Faulkner, *Electrochemical Methods: Fundamentals and Applications*, 2nd Ed., Wiley, New York (2008). See Chapter 9.
6. J. T. Maloy, K. B. Prater, and A. J. Bard, *J. Am. Chem. Soc.*, **93**, 5959 (1971).
7. J. T. Maloy and A. J. Bard, *J. Am. Chem. Soc.*, **93**, 5968 (1971).
8. W. J. Albery, *Trans. Faraday Soc.*, **62**, 1915 (1966).
9. K. B. Prater and A. J. Bard, *J. Electrochem. Soc.*, **117**, 207 (1970).
10. J. Maruyama, M. Inaba, and Z. Ogumi, *J. Electroanal. Chem.*, **458**, 175 (1998).
11. S. Beyhan, N. E. Şahin, S. Pronier, J.-M. Léger, and F. Kadırgan, *Electrochim. Acta*, **151**, 565 (2015).
12. W. Chen, L. W. Liao, J. Cai, Y.-X. Chen, and U. Stimming, *J. Phys. Chem. C*, **123**, 29630 (2019).
13. I. S. Filimonenkov, S. Y. Istomin, E. V. Antipov, G. A. Tsirlina, and E. R. Savinova, *Electrochim. Acta*, **286**, 304 (2018).
14. K. G. Boto, and L. F. G. Williams, *J. Electroanal. Chem. Interfacial Electrochem.* **77**, 1 (1977).
15. M. Sharon and S. Ghosh, *J. Solid State Electrochem.*, **4**, 52 (1999).
16. H. Zhang and S. M. Park, *J. Electrochem. Soc.*, **141**, 718 (1994).
17. R. Kotz, S. Stucki, D. Scherson, and D. M. Kolb, *J. Electroanal. Chem.*, **172**, 211 (1984).
18. M. Umeda, Y. Kuwahara, A. Nakazawa, and M. Inoue, *J. Phys. Chem. C*, **113**, 15707 (2009).
19. S. Joiret, M. Keddām, X. R. Novoa, M. C. Perez, C. Rangel, and H. Takenouti, *Cement & Concrete Composites*, **24**, 7 (2002).
20. S. H. Cadle, *J. Electrochem. Soc.*, **121**, 645 (1974).
21. J. Li, W. Sun, B. Hurley, A. A. Luo, and R. G. Buchheit, *Corr. Sci.*, **112**, 760 (2016).
22. J. I. Gardiazabal and J. R. Galvele, *J. Electrochem. Soc.*, **127**, 259 (1980).
23. L. Gal-Or, S. Brucrenstein, and J. M. Carter, *J. Biomed. Mater. Res.*, **12**, 1 (1978).
24. S. L. F. A. da Costa, S. M. L. Agostinho, and K. Nobe, *J. Electrochem. Soc.* **140**, 3483 (1993).
25. R. G. Buchheit, M. A. Martinez, and L. P. Montes, *J. Electrochem. Soc.*, **147**, 119 (2000).
26. F. Fenini, K. K. Hansen, and M. B. Mogensen, *J. Electrochem. Soc.*, **166**, C3159 (2019).
27. D. S. Mancey, D. W. Shoosmith, J. Lipkowski, A. C. McBride, and J. J. Noël, *J. Electrochem. Soc.*, **140**, 637 (1993).
28. D. E. Stilwell and S. M. Park, *J. Electrochem. Soc.*, **136**, 688 (1989).
29. F. Huet, M. Keddām, X. R. Novoa, and H. Takenouti, *J. Electrochem. Soc.*, **140**, 1955 (1993).
30. K. Ogle, *Corrosion*, **75**, 1398 (2019).
31. B. Miller, *J. Electrochem. Soc.*, **116**, 1117 (1969).
32. B. Miller and M. I. Bellavance, *J. Electrochem. Soc.*, **119**, 1510 (1972).
33. S. Haupt and H. H. Streblov, *J. Electroanal. Chem.*, **216**, 229 (1987).