Application Note

Introduction to the Rotating Disk Electrode (RDE) and Rotating Ring-Disk Electrode (RRDE)

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The Rotating Disk Electrode (RDE) was conceived with the primary objective of enhancing the study of current density distribution and reducing the influence of the diffusion layer. This innovative electrode was first proposed by Levich in 1942, laying the theoretical foundation for its development. The concept was subsequently experimentally validated by Siver and Kabaonv in 1949, establishing its practical applications in electrochemistry.[1]

By rotating the disk electrode, researchers can manipulate the fluid dynamics around the electrode. This results in a more uniform distribution of current density and reduces the influence of the diffusion layer, enabling more precise analysis. As a result, the RDE is an indispensable tool in modern electrochemical research.

The Rotating Ring Disk Electrode (RRDE) was developed after the Rotating Disk Electrode (RDE) and was first proposed by Frumkin in 1958. At the same time, a theoretical description of solution flow at the RRDE was reported by Levich and Ivanov. The subsequent experimental and mathematical work placed the RRDE technique on a firm theoretical foundation.

The RRDE consists of adding a concentric ring around the RDE. The overall flow pattern at the RRDE initially brings molecules and ions to the disk electrode and the subsequent outward radial flow carries a fraction of these molecules or ions along with productions from the disk electrode to the ring electrode. This flow pattern allows products generated (upstream) by the half reaction at the disk electrode to be detected as they are swept downstream past the ring-electrode. The first reaction to be studied was the Oxygen Reduction Reaction (ORR), in which the dissolved oxygen was reduced on the disk electrode and the hydrogen peroxide (H_2O_2) as the partial reduced product than H_2O was detected by the ring electrode. The number of electrons transferred (n) during the oxygen reduction reaction can be estimated from disk and ring currents.

Theory behind RDE and RRDE

Based on the pioneering work of Levich, subsequent generations of researchers expanded on this foundation, and the rotating disk electrode has since become a mature tool for probing electrochemical reaction kinetics.[2]

The laminar flow at a rotating disk electrode conveys a steady stream of material from the bulk solution to the electrode surface. While the bulk solution far away from the electrode remains well-stirred by the convection induced by rotation, the hydrodynamic layer nearer to the electrode surface tends to rotate with the electrode. While the thickness of the stagnant layer (δ_H) can be mathematically approximated with kinematic viscosity of the solution and the angular rotation rate, it's typically within 300 – 400 µm thickness in an aqueous solution at moderate rotation rate (~1000 RPM).

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Although the mass transport of material from the bulk solution into the stagnant layer occurs by convection due to the stirring generated by the rotating electrode, convection becomes less important when the material enters the stagnant layer and moves closer to the electrode surface. Instead, the final movement of an ion or molecule to the electrode surface is dominated by diffusion across a very thin layer of solution immediately adjacent to the electrode known as the diffusion layer. The thickness of the diffusion layer (δ_F) is about twenty times thinner than the hydrodynamic layer ($\delta_F \approx 0.05\ \delta_H$).

The first mathematical treatment of convection and diffusion towards the cathodic limiting current (i_{LC}) observed at a rotating disk electrode was given by Levich,[2,9] which was derivatized for the anodic limiting current (i_{LA}) as

$$i_{LC} = 0.620nFAD_O^{2/3}\nu^{-1/6}\omega^{1/2}C_O \quad \textbf{(1)}$$

$$i_{LA} = 0.620nFAD_R^{2/3}\nu^{-1/6}\omega^{1/2}C_R \quad \textbf{(2)}$$

, where C_O and C_R are the concentration of the oxidized and reduced form, D_O and D_R are the diffusion coefficient terms for the oxidized and reduced form electrode, A is the active surface area, F = 96485 C/mol is the Faraday constant, ν is the kinematic viscosity of the solution, and ω is the angular rotation rate.

Levich Study and Koutecky-Levich plot

A Levich study is a common experiment performed using a rotating disk electrode in which a series of voltammograms is acquired over a range of different rotation rates. Since the convection of electrolyte maintains the thickness of the diffusion layer (δ_F), a limiting current appears instead of a peak shaped current in static voltammetry.

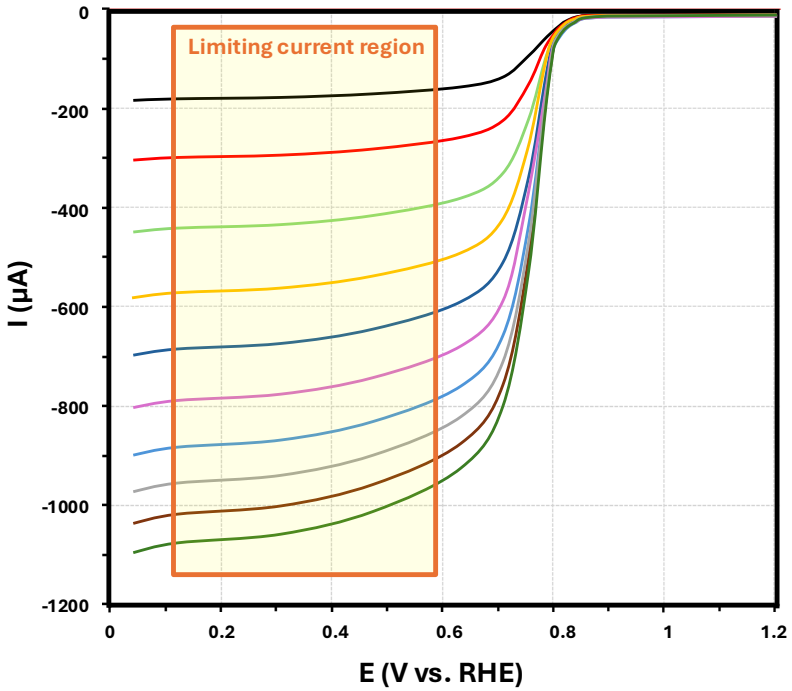


Figure 1. Typical RDE results with different rotational speeds.

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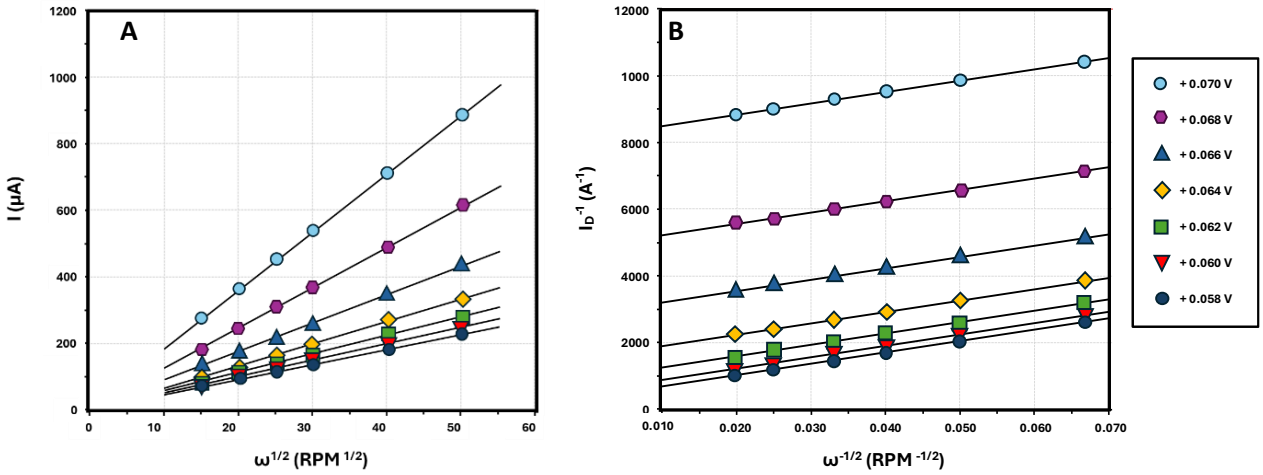


Figure 2. Levich plot (A) and Koutecky-Levich plot (B) derived from results in Figure 1.

The currents measured during a Levich study are usually plotted against the square root of the rotation rate on a graph called a Levich plot. As predicted by the Levich equation, the limiting current increases linearly with the square root of the rotation rate with a slope of $0.620nFAD^{2/3}\nu^{-1/6}C$ and y- intercept at zero.

Based on a rearrangement of the Levich equation in terms of the reciprocal current, an alternate method of presenting the data of the Levich equation in terms of the reciprocal current is called a Koutecky-Levich plot. As straight lines from plotting the reciprocal current (i_L^{-1}) against the reciprocal root of the angular rotation rate ($\omega^{-1/2}$), the intercept equals to the reciprocal kinetic current

$$i_L^{-1} = i_K^{-1} + \left(\frac{1}{0.620nFAD^{\frac{2}{3}}\nu^{-\frac{1}{6}}C}\right)\omega^{-1/2} \qquad \textbf{(3)}$$

Empirical Collection Efficiency of RRDE

Compared to RDE, adding the ring electrode allows the user to collect species produced on the disk. In more detail, with Rotating Ring Disk Electrode (RRDE), products generated at the disk are convectively transported to the ring, where they are directly detected (with minimal time delay between product generation and detection).

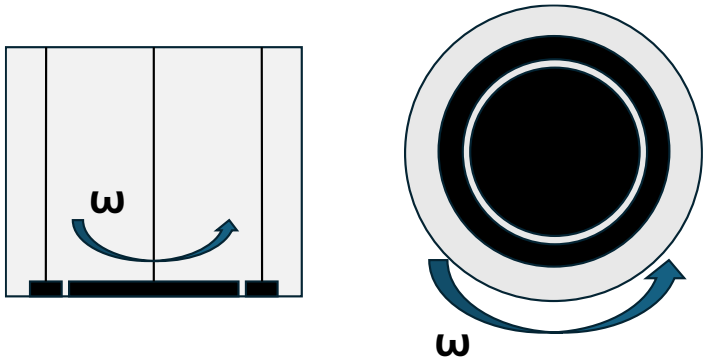


Figure 3. Structural diagram of a typical RRDE.

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The cathodic limiting current observed at the disk (i_{DISK}) is a measure of how much X is being "generated" at the disk electrode; at the mean meantime, the anodic limiting current at the ring (i_{RING}) is a measure of much X is being "collected" at the ring electrode. Therefore, the ration of the ring current to the disk current under these conditions is called the apparent collection efficiency (N).

$$N = -i_{RING} \,/\, i_{DISK} \quad \textbf{(4)}$$

In practice, the ferrocyanide/ferricyanide half reaction is widely employed for measuring collection efficiency since it is a simple, single-electron and [36] The typical RRDE tests are carried out in an electrolyte of 10 mM potassium ferricyanide ($K_3Fe(CN)_6$) and potassium nitrate (KNO_3) as supporting electrolyte with rotation rates between 500 and 2000 RPM. Initially, both the ring and the disk electrodes are held at a sufficiently positive potential that no reaction occurs. Reduction of ferricyanide to ferrocyanide at the disk occurred with slowly potential swept (~50 mV/sec) towards more negative potentials.

$$Fe(CN)_6^{3-} + e^- \rightarrow Fe(CN)_6^{4-} \quad \textbf{(5)}$$

The generated ferrocyanide generated is swept outward (radially) away from the disk electrode and toward the ring electrode. Some (but not all) of the ferrocyanide generated at the disk travels close enough to the ring electrode that is oxidized back to ferricyanide.

$$Fe(CN)_6^{4-} \rightarrow Fe(CN)_6^{3-} + e^- \quad \textbf{(6)}$$

The measured ratio of the ring limiting current to the disk limiting current is empirical collection efficiency. As the rotation rate increases, both the disk and the ring currents increase since both the anodic and cathodic limiting currents are proportional to the square root of the rotation rate, the empirical collection efficiency is expected to be independent of the rotation rate.

When a molecule or ion is oxidized or reduced at an electrode, there are usually competing pathways towards different productions. If these pathways lead to an electrochemically active chemical species that can be detected by the ring, it is possible to determine which pathway is favored.

For example, the oxygen reduction reaction (ORR) in aqueous solution typically proceeds via two major pathways: (1) the direct four-electron reduction from O_2 to H_2O (n = 4, Eq. 7), and (2) the two-electron reduction from O_2 to hydrogen peroxide (H_2O_2, n = 2, Eq. 8).

$$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O \quad \textbf{(7)}$$

$$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2 \quad \textbf{(8)}$$

As shown in Figure 4, the cathodic current from oxygen reduction was observed on disk electrode when swept negatively to about +0.8V vs. RHE and reached a plateau at potentials more negative than +0.6V. The potential on ring electrode was set at constant +1.4V vs. RHE to oxidize any hydrogen peroxide that is produced by oxygen reduction on the disk electrode.

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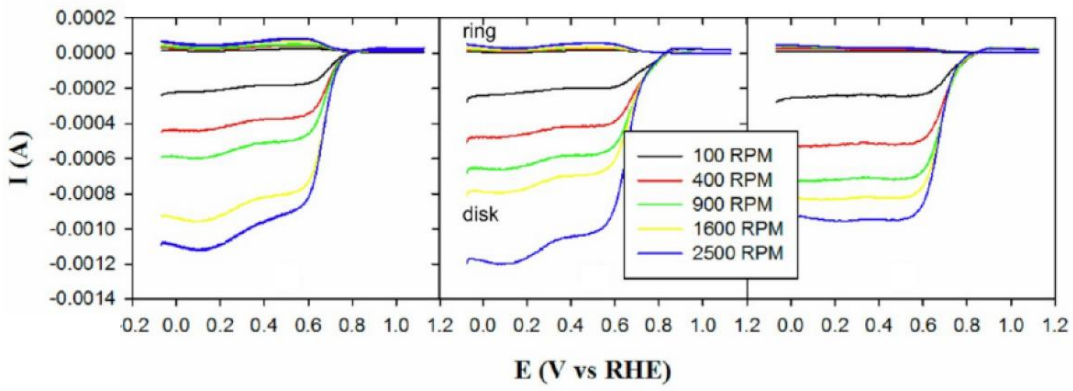


Figure 4. Experimental RRDE results for oxygen reduction reaction. Reproduced from Ref. [4] by permission of ACS.

The voltametric currents collected at the ring electrode were about an order of magnitude lower than disk current, indicating that only a minimal amount of peroxide intermediates were produced during oxygen reduction. The number of electron transfer (n) in oxygen reduction was calculated as 3.45, 3.72 and 3.60 with equation **(7)**.

$$n = \frac{4i_{DISK}}{i_{DISK} + \frac{i_{RING}}{N}} \quad \textbf{(7)}$$

Summary

The Rotating Disk Electrode (RDE) and Rotating Ring-Disk Electrode (RRDE) have become essential tools in modern electrochemical research, enabling precise investigation of reaction kinetics, mass transport, and mechanistic pathways. Their ability to control fluid dynamics and detect intermediate species has greatly advanced our understanding of complex electrochemical processes, such as the oxygen reduction reaction. The empirical data and theoretical models developed using RDE and RRDE have laid a strong foundation for both academic research and industrial applications.

AMETEK offers the 636A Rotator for RDE, RRDE, and RCE with rotational speeds up to 11,000 RPM and the PARSTAT 3000A-DX Bipotentiostat features hardware synchronization. The combination of 636A Rotator and PARSTAT3000A-DX Bipotentiostat provides a powerful platform for studying electrode reaction kinetics. In addition, a wide selection of electrodes is available for routine analytical tasks using RDE and RRDE.

As electrochemical technologies expand into fields like energy conversion, environmental monitoring, and advanced materials, RDE and RRDE are poised to play a pivotal role in driving new discoveries and supporting the development of next-generation solutions.

Summary – RDE and RRDE have become foundational tools in electrochemistry, supporting advancements in energy conversion, catalysis, environmental monitoring, and materials science. AMETEK offers the 636A Rotator and PARSTAT3000A-DX Bipotentiostat for electrochemical mechanism studies.

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