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Research Article

Holly M. Fruehwald*, Olena V. Zenkina and E. Bradley Easton

A new spin on electrochemistry in the undergraduate lab

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Abstract: The growing interest in electrochemistry over recent years has sparked an increase in the popularity of various electrochemical techniques, including more advanced methods, that have previously been overlooked in academia and industry. This makes comprehensive hands-on experience in electrochemistry a highly demanded addition to chemistry graduates. However, many students do not receive sufficient training in the theory and experimental design to confidently use and apply various electrochemical techniques throughout their undergraduate, and sometimes even in graduate studies. Here we summarize the theory and practical applications for both rotating disk electrode (RDE) and rotating ring disk electrode (RRDE) techniques. The different modes of operation of rotating ring disk voltammetry, methodologies of data analysis and interpretation as well as the scope of the information that can be extracted from the RDE/RRDE are discussed. Proposed modifications of the laboratory curriculum will allow students to examine and learn valuable information about the reactions on the surface of the electrode/liquid interface. This information will allow chemists to confidently use RDE and RRDE techniques for a wide range of research and development targets. Furthermore, incorporating these techniques into existing chemistry laboratories will help chemistry educators to enrich the undergraduate chemistry curriculum and improve students' learning outcomes.

Keywords: analytical chemistry; chemistry undergraduate laboratories; electrochemistry; graduate education; hydrodynamic voltammetry; rotating disk electrodes.

Introduction

Electrochemistry encompasses a wide range of techniques that have been gaining popularity in recent years due to its versatile applicability in many industries such as transportation (Jaouen et al., 2018), medicine (Silva et al., 2020; Zou et al., 2019), environmental sciences (Janssen & Koene, 2002), industrial processes (Kahyarian, Brown, & Nesic, 2017), and health applications (Heller & Feldman, 2010; Kumar-Krishnan et al., 2016). This is due to the incredibly high sensitivity, relatively low cost, and ease of detection achieved by advances in electrochemical techniques. Consequently, it is becoming increasingly more valuable for chemistry undergraduates and postgraduate researchers to be equipped with the knowledge and hands-on practical experience in various electrochemical techniques. Thus, this manuscript is focused on providing knowledge for laboratory instructors to incorporate hydrodynamic voltammetry into undergraduate labs and graduate laboratory experiments.

***Corresponding author: Holly M. Fruehwald**, Electrochemical Materials Lab, Faculty of Science, University of Ontario Institute of Technology, 2000 Simcoe Street North, Oshawa ON Canada, L1G 0C5, E-mail: holly.fruehwald@ontariotechu.ca. https://orcid.org/0000-0002-4822-4359
Olena V. Zenkina and E. Bradley Easton, Electrochemical Materials Lab, Faculty of Science, University of Ontario Institute of Technology, 2000 Simcoe Street North, Oshawa ON Canada, L1G 0C5, E-mail: olena.zenkina@ontariotechu.ca (O.V. Zenkina), brad.easton@ontariotechu.ca (E.B. Easton). https://orcid.org/0000-0003-1493-0500 (E.B. Easton)

Electrochemistry, in general, has numerous operational modes that allow for the evaluation of the catalytic activity, detection of active catalytic sites and identification of intermediate species, performing reactions, as well as determining and understanding complex reaction mechanisms. A rotating disk electrode (RDE) is a very powerful technique of electrochemical analysis that employs a specialized working electrode connected to a rotator. This type of electrode is most commonly used to analyze reactions under different diffusion conditions. One of its most common applications of a RDE/RRDE is to study the oxygen reduction reaction for fuel cell applications (Fruehwald, Ebralidze, Zenkina, & Easton, 2019; Fruehwald, Ebralidze, Melino, Zenkina, & Easton, 2020).

To control the diffusion of an analyte to an electrode, a constant flow of the analyte to the electrode surface is attained via rotation, which allows for studying of various mass transport processes in the system (Nikolic, Expósito, Iniesta, González-Garcia, & Montiel, 2000). The information from these rotation experiments can be used to obtain valuable kinetic data about the electrochemical reactions that is not accessible by other methods.

Theory

Rotating disk voltammetry is a type of hydrodynamic voltammetry where the working electrode spins at high speeds (Figure 1A). It is used to separate the mass transport effects (i.e. the rate at which an analyte gets from the bulk to the electrode surface): diffusive, and convective components of the current produced by a Faradaic (redox) reaction. Like a traditional working electrode (WE), RDE has a flat WE disk embedded into a non-conductive housing (Figure 1). However, unlike a traditional WE, the RDE is built into a large steel rod that mounts into the electrode rotator. The RDE is secured tightly into the rotator, which uses a motor to spin the electrode at speeds up to 6000 RPM.[1] The contact from the rod to the potentiostat is made by spring-loaded brushes (Figure 1B), which maintain electrical contact while the electrode is rotating at high speeds.

Rotating electrodes operate under the principle of convection, where the rotation of the electrode induces a flux of the analyte to the electrode surface according to Fick's law of diffusion (Figure 2). Thus, the mass transport of the analyte is entirely driven by the influence of the convection of the solution during the rotation of the electrode (Nikolic et al., 2000). The flow of the solution to the electrode is described as laminar flow, meaning that the flow of the electrolyte to the electrode occurs in smooth and steady non-mixable layers (Bard & Faulkner, 2001). The convection of the solution to the electrode leads to a constant diffusion layer thickness (δ) at each rotation rate. From Fick's first law of diffusion, the rate is proportional to the concentration gradient (Wang, 2006):

$$J(x,t) = -D\frac{\partial C(x,t)}{\partial x} \tag{1}$$

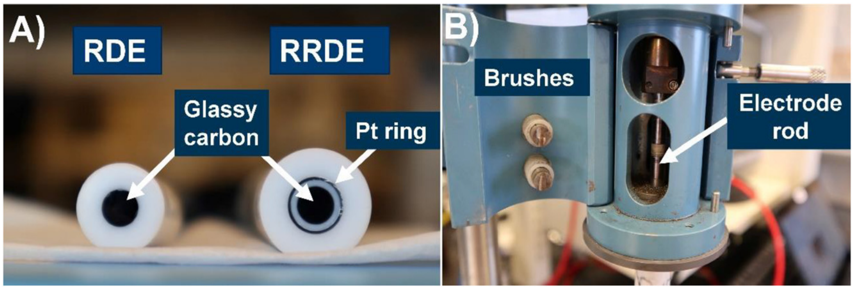

Figure 1: Anatomy of the electrodes and rotator.
A) Image of the two different rotating disks. Left image is a glassy carbon rotating disk electrode (RDE). Right: Rotating ring disk electrode (RRDE) with a glassy carbon disk and platinum ring. B) Image of inside the rotator, depicting the brushes and the rod in the rotator housing.

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[1] The construction of many RDE rods may not allow them to be safely operated at such high speeds, so the users should not exceed the maximum rated speed listed in the safety data sheet provided by the electrode manufacturer.

where J is the flux (mol cm^{-2} s^{-1}), D is the diffusion coefficient (cm^2 s^{-1}), and $\delta C(x,t)/\delta x$ is the concentration gradient (mol L^{-1}) at a distance x and time t (Wang, 2006). The current at the electrode is directly proportional to the flux of the electrolyte at the electrode as well as the surface area (Wang, 2006):

$$i = -nFAJ \tag{2}$$

where n is the moles of electrons, F is Faraday's constant (C mol^{-1}), and A is the surface area (m^2). Combining Eqs. (1) and (2) the current at the electrode becomes:

$$i = nFAD\frac{\partial C(x,t)}{\partial x} \tag{3}$$

Equation (3) essentially states that the current is proportional to the concentration gradient at the electrode surface for each constant rotation rate (Wang, 2006). Thus, the smaller the diffusion layer, the larger the concentration gradient at the electrode. So, faster rotation rates create smaller diffusion layers which leads to a high concentration gradient of electroactive species to the electrode surface, which then produces higher currents.

In a typical redox reaction, oxidized species O, is reduced to R at the surface of the WE as the potential at the WE is scanned towards more negative potentials (more negative than the $E_{1/2}$ of the redox reaction-where the O species would be reduced). This produces a change in the oxidation state of the species. As the potential is scanned towards more positive potentials (more positive than the $E_{1/2}$ of the redox reaction-where the R species would be oxidized), the reverse reaction occurs when species R comes into contact with the WE where it is oxidized back to species O via a change in the oxidation state. The example that will be presented through the manuscript is the potassium (II/III) hexacyanoferrate redox couple ($[Fe(CN)_6]^{4-}/[Fe(CN_6]^{3-}$). This redox process involves the change in the oxidation state of the iron: Fe$^{2+/3+}$. This is the fundamental process that takes place when using a RDE. However, as this is occurring a constant rotation rate is applied (typically in RPM) while the potential at the disk is swept to more negative potentials than the $E_{1/2}$ (reduction). This continues until a limiting current is reached. In other words, the potential is sufficient enough to immediately reduce any species that come in contact with the WE. For example, oxidized species, O, reaches the electrode surface through convection processes during rotation where upon contact with the disk O is converted to reduced species, R. Then R will be diffused away from the disk back to the bulk electrolyte (Figure 2B and C).

At this point, the current is mass transport limited, since alteration of the rotation rate directly affects the convective and diffusive limited current (Bard & Faulkner, 2001). By varying the rotation rate (typically in either revolutions per minute, RPM, or radians per second, rad s^{-1}), the diffusion and convective mass transport currents can be separated through mathematical manipulation of the limiting currents and the alteration of

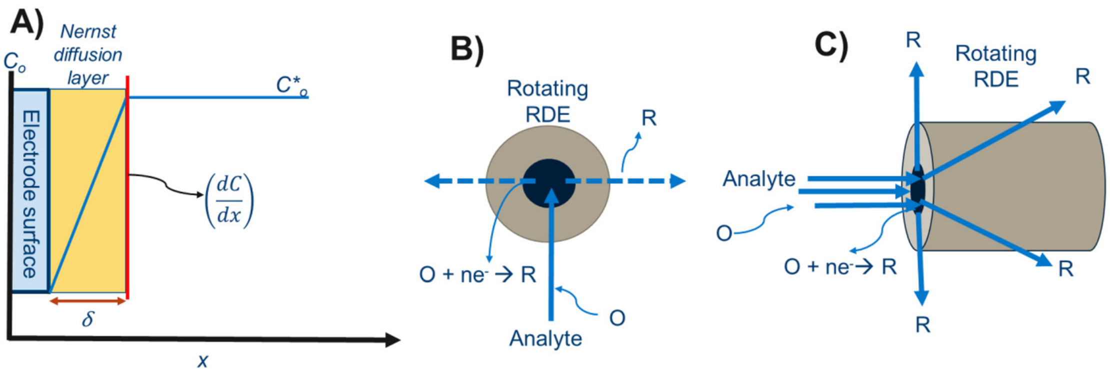

Figure 2: Schematics of the electrochemical processes that occur at the working electrode.
A) Schematic of the Nernst diffusion layer at the electrode surface during hydrodynamic voltammetry for the limiting current. The red line is representing the end of the diffusion layer, the dC/dx region (marked in orange on the image). B) Illustration of the convection pattern at the rotating disk electrode, front view. C) Illustration of the convection pattern at the rotating disk electrode, side view.

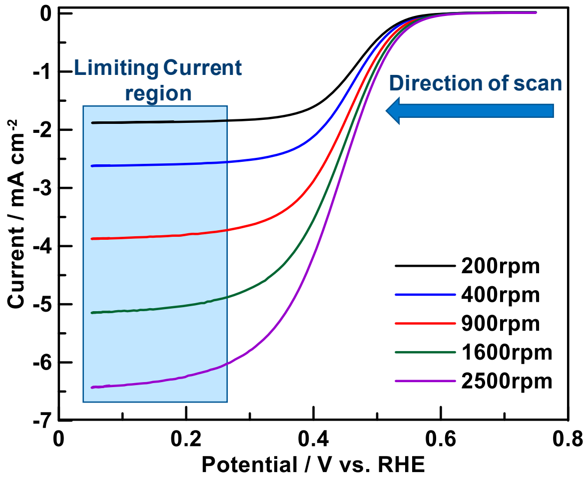

Figure 3: RDE curves from the potassium (II/III) hexacyanoferrate redox couple studied in a N_2 saturated 1 M KNO_3 electrolyte at a scan rate of 10 mV s^{-1} at a temperature of 25 °C.

rotation rate. This enables the researcher to analyze the dependence of the limiting current with respect to the rotation rate, which classically produces a sigmoidal shape (Figure 3).

A rotating ring disk electrode (RRDE) can also be used for similar purposes. This electrode operates similarly to the RDE, but has a second ring-shaped electrode (typically Pt) that surrounds the disk which is separated by a Teflon sheath (Figure 1A, right side). The ring is used to study reactions by performing either collection or shielding experiments, which are extremely beneficial in determining the products or side reactions of various electrochemical processes. This set-up is analogous to the RDE process described above. The addition of the ring creates a second working electrode that could monitor both the oxidation and reduction processes at both electrodes, thus this technique requires a bipotentiostat. Studying the reduction of a species with a RRDE produces a voltammogram identical to the sample curves shown in Figure 3. These results are plotted versus the reversible hydrogen electrode (RHE). This scale is used throughout the manuscript as the potentials change based on the electrolyte used. Calibration to the RHE allows for a direct comparison to the literature examples. To get reliable measurements the effective deaeration of the electrolyte solution before the experiment is crucial since the presence of even trace dissolved oxygen in the electrolyte will alter the redox chemistry of the analyte studied.

Setting up the experiment

Here we will discuss how to calibrate the ring for RRDE tests as well as, the data collection. Throughout the following sections, the potassium (II/III) hexacyanoferrate redox couple ($[Fe(CN)_6]^{4-}/[Fe(CN)_6]^{3-}$) will be used to describe different modes of operation and the subsequent data analysis. A typical cyclic voltammogram of the potassium (II/III) hexacyanoferrate redox couple at a stationary electrode is provided in Figure S3 of the SI for reference.

Data collection

There are two main methods to study reactions by RRDE; collection or shielding experiments.

Collection experiment

When performing a collection experiment, the disk potential is swept linearly while the ring potential is held constant. While rotating the electrode, the disk potential is swept to more negative potentials until a limiting current is reached, such that mass transport limitations are observed. As the species comes into contact with the disk they become reduced. The reduced species are then diffused towards the ring and collected (Figure 4). The ring is held at a sufficiently positive potential so the reduced species are immediately oxidized upon contact with the ring (Zhou, Zheng, Jaroniec, & Qiao, 2016). Thus, the ring regenerates the original analyte. Through this technique, the researcher can monitor both the ring and disk currents as a function of the disk potential (Figure 5).

Calibration of the ring

Proper calibration of the ring is an essential step prior to any RRDE experiment, especially when the collection of a reduced species is important. As part of the calibration, a collection experiment is performed. This is one where the disk potential is varied as the ring potential is held constant. Each manufactured RRDE has a specific

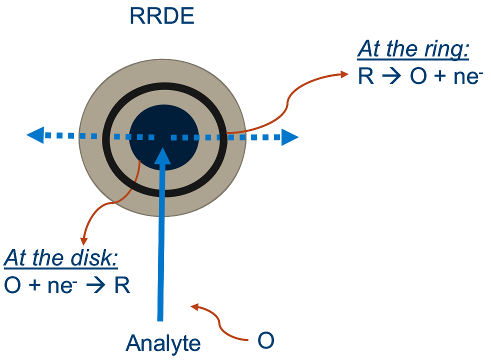

Figure 4: Illustration of the convection pattern at the rotating ring disk electrode.

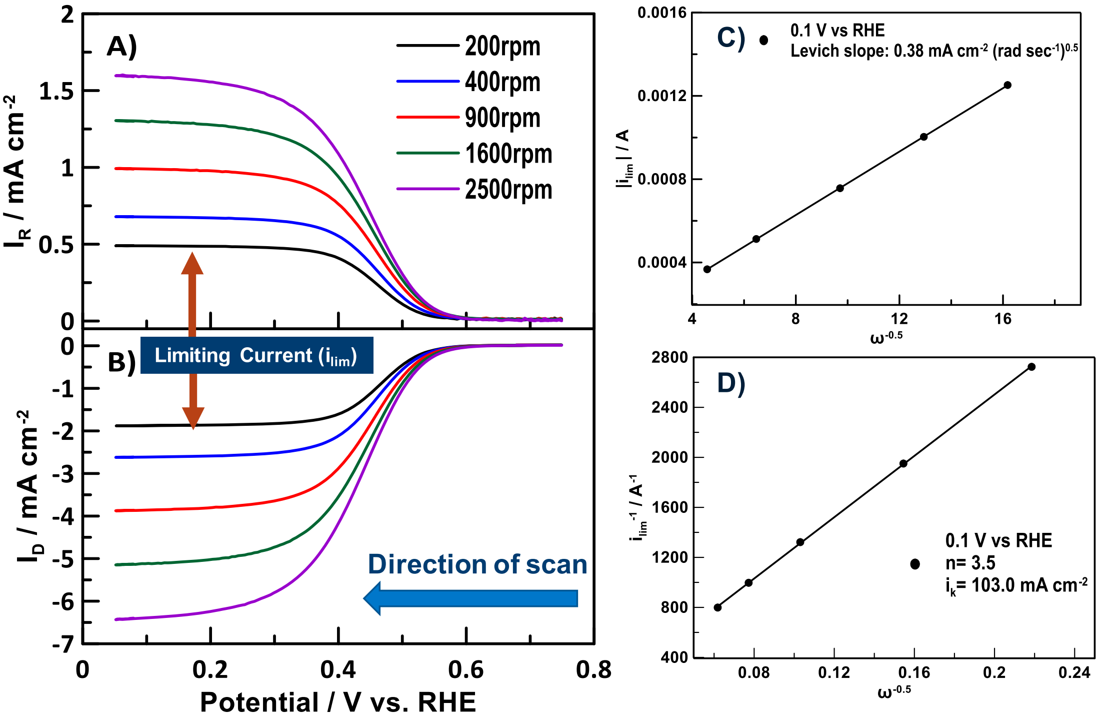

Figure 5: Data analysis from the RRDE experiment with the hexacyanoferrate redox couple.
A) RRDE ring currents from the potassium (II/III) hexacyanoferrate redox couple at a scan rate of 10 mV s^{-1} in 1 M KNO_3 at 25 °C B) RRDE disk currents from the potassium (II/III) hexacyanoferrate redox couple at a scan rate of 10 mV s^{-1} in 1 M KNO_3 at 25 °C C) Levich plot of potassium (II/III) hexacyanoferrate redox couple at 0.1 V vs RHE D) Koutecky-Levich plot of potassium (II/III) hexacyanoferrate redox couple at 0.1 V vs RHE.

collection efficiency (N), which is a measure of how well the ring will collect the reduced species from the disk to oxidize it. N also depends on the distance and separation between the disk and the ring. The determination of the collection efficiency is an important parameter for studying reaction mechanisms. The collection efficiency (Paulus, Schmidt, Gasteiger, & Behm, 2001) is defined as the following:

$$N = -\frac{i_R}{i_D} \tag{4}$$

where i_R and i_D are the limiting currents of the ring and disk respectively. A well-defined electrochemical process is often used for the calibration, classically the potassium (II/III) hexacyanoferrate reaction (Zhou et al., 2016). As the potential is swept negatively, Fe^{3+} species become reduced at the disk:

$$[Fe(CN)_6]^{4-} + e^- \rightleftarrows [Fe(CN)_6]^{3-} \tag{5}$$

The reduced form of Fe^{2+} migrates out to the ring via rotation of the electrode, which is held at a positive enough potential where Fe^{2+} will be oxidized during the diffusion of the species to the ring (Figure 4):

$$[Fe(CN)_6]^{3-} \rightleftarrows [Fe(CN)_6]^{4-} + e^- \tag{6}$$

The measured collection efficiency defines how efficiently the Fe^{2+} generated at the disk is collected and oxidized back to Fe^{3+} at the ring, and this gives the determination of the percentage of species that can be detected at the ring. It is important to note that the area of the ring is considerably smaller than that of the disk. Thus, all of the reduced species produced will not be oxidized at the ring. The size of the ring and the diffusion of the analyte to the ring directly effects how much of a species can be collected at the ring. Typical values of collection efficiency are anywhere from 20 to 40% (Jia, Yin, & Zhang, 2014). The collection efficiency that was calibrated for the RRDE experiments in this manuscript was 0.25, or 25%.

Shielding experiment

The second mode of RRDE analysis is the shielding experiment where the disk potential is held constant while the ring potential is swept. Conceptually, this experiment is the exact opposite of the collection experiment. The shielding experiment is employed to study the reversibility of the reaction at the electrode. In this mode the ring voltammogram is measured at different values of disk potential. The potential at the disk can be changed, and as a result the flux of the oxidized species to the ring could be altered. This can be expressed mathematically by:

$$i_{R,l} = i^0_{R,l} - Ni_D \tag{7}$$

where $i^0_{R,l}$ is the limiting current when there is no disk current, N is the collection efficiency, and i_D is the disk current (Krishnan, Yang, Advani, & Prasad, 2008). The Ni_D term is also referred to as the shielding factor.

Data analysis

Koutecky–Levich analysis

The Levich analysis describes the kinetic contributions at the electrode caused by the flow of the solution to the electrode (Matter, Zhang, & Ozkan, 2006; Sun et al., 2018). The Levich equation can be used to determine the number of electrons transferred (n), which gives important information about the kinetics of the reaction of study, or the diffusion coefficient (D) when one of the parameters is known. A Levich plot is shown in Figure 5C for the $[Fe(CN)_6]^{4-}$/$[Fe(CN)_6]^{3-}$ redox example.

Analysis of the laminar flow of solution using the Levich equations gives a variety of kinetic information when using both RDE and RRDE (Luo et al., 2019; Zhou et al., 2016). The Levich equation takes into account the thickness of the Nernst diffusion layer (Osmieri, Escudero-Cid, Monteverde Videla, Ocón, & Specchia, 2018) (Figure 2A). This diffusion layer is defined as the region that is closest to the electrode surface where the reaction is governed solely by the diffusion of species to the electrode. In this reaction the thickness of the diffusion layer (Sun et al., 2018) is defined as:

$$\delta = 1.61 \times \nu^{0.166} \times D^{0.33} \times \omega^{0.5} \tag{8}$$

where ν is the kinematic viscosity ($m^2\ s^{-1}$); D is the diffusion coefficient ($m^2\ s^{-1}$); and ω is the rotation rate (rad s^{-1}). With RDE, the current density is mass transport controlled, thus the change in concentration of the electroactive species on the surface of the electrode is 0 (due to the analyte concentration being at a steady-state condition), and the limiting current density (Yin & Zhang, 2014) for an RDE is:

$$i_{\text{lev},D} = n \times F \times D \times \frac{C}{\delta} \tag{9}$$

The Levich equation is the combination of Eqs. (8) and (9) (Rahman, Awad, Kitamura, Okajima, & Ohsaka, 2012) to produce:

$$i_{\text{lev},D} = 0.62nFD^{0.67}\nu^{0.166}C\omega^{-0.5} \tag{10}$$

where n is the number of electrons transferred during the reaction, F is Faraday's constant (C mol^{-1}), and C is the concentration of the analyte (mol L^{-1}) (Chen, Higgins, Tao, Hsu, & Chen, 2009).

The Koutecky–Levich equation (KL) can be used to separate the mass transport and the kinetic contributions to the process(es) occurring at the electrode (Levich analysis) while the rotation rate is varied (Treimer, Tang, & Johnson, 2002). This technique uses the limiting current, the regime with no changes in the current as the potential is scanned, where all processes are slower due to mass transport limitation of the kinetics. This is represented by plotting the square root of the rotation rate versus the reciprocal of the current. This yields a linear relationship described by the KL equation (Liu, Li, Ganesan, & Popov, 2009):

$$\frac{1}{i_D} = \frac{1}{i_{\text{lev}}} + \frac{1}{i_k} \tag{11}$$

where i_{lev} is the Levich current, i_D is the limiting disk current, and i_k is the kinetic current. A typical KL plot is shown in Figure 5D (note: the scales are different in the Levich and KL plots due to the KL equation using the reciprocal current while the Levich equation currents are not non-reciprocal). Extrapolating the linear regression analysis will yield kinetic information about the system under investigation. For example, the slope of the line will yield the Levich current, i_{lev} (Wang, Zhang, & Zhang, 2011). Using i_{lev} in Eq. (10), the number of electrons (n) involved in the reaction can be determined, as all other constants can be found from the literature. The number of transferred electrons can be determined at various potentials. Another important parameter that can be extracted is the kinetic current, i_k, which is the current that is not limited by mass transfer effects, essentially the current when there is infinite mass transport (Bard & Faulkner, 2001). The intercept value will give i_k at the given potential. Importantly, the KL analysis method provides only an estimate of the number of electrons transferred. Other methods, specifically RRDE, that utilize the ring data are preferred as a more accurate determination of the number of transferred electrons, especially for applications in the oxygen reduction reaction (Matter et al., 2006).

Mechanistic studies of catalysts for the oxygen reduction reaction

One of the most widespread applications of RRDE is to study the oxygen reduction reaction (ORR). The ORR is the main reaction that occurs at the cathode side of hydrogen fuel cells (FC). This reaction is extensively studied as it is quite sluggish, thus it often requires high loadings of rare and costly metals to catalyze the process and sufficiently drive the reaction. Therefore, to improve the performance and efficiency of FCs, many researchers are trying to minimize the amounts of rare metals (like platinum) in the catalysts or to use non-precious metal catalysts. RRDE is an essential technique for assessing the activity of the catalyst, studying reaction kinetics of the process, and defining major products forming during ORR. For example, the direct conversion of oxygen to water is a four-electron process and is the desired product for a potential FC catalyst candidate. However there is often a by-product, hydrogen peroxide, formed via a two-electron process due to the incomplete conversion of oxygen to water (Scheme 1).

The production of hydrogen peroxide is undesirable, leads to efficiency losses in FCs, and can poison the catalyst (Fruehwald, Ebralidze, Zenkina, & Easton, 2021). Thus, determining the amount of hydrogen peroxide produced during the course of the ORR is a direct measure of the reaction efficiency (the affinity of the system to produce the ideal product for the ORR, water) of new catalysts for FCs. In RRDE, obtaining the ring and disk current data as the potential is scanned provides a reliable method to determine the product distribution, H_2O versus H_2O_2 (Hossen, Artyushkova, Atanassov, & Serov, 2018). Results are normally reported as the percentage of hydrogen peroxide produced which can be determined using the following equation:

$$\%H_2O_2 = 200 \times \frac{i_R/N}{i_D + i_R/N} \qquad (12)$$

where N is the collection efficiency, and i_R and i_D are the absolute values of the ring and disk currents at a given potential (Sun et al., 2018). Plotting the % H_2O_2 produced at varying disk potentials could provide valuable information on how the mechanism can vary under a different applied potential (Figure 6B).

4-electron transfer process

$$O_2 + 4e^- + 4H^+ \longrightarrow 2\,H_2O$$

2-electron transfer process

$$O_2 + 2e^- + 2H^+ \longrightarrow H_2O_2$$

Scheme 1: Equations for the different pathways that can occur during the oxygen reduction reaction.

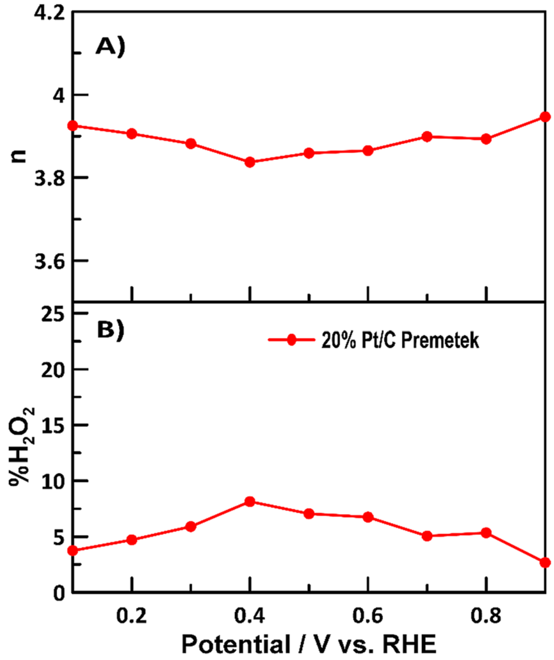

Figure 6: Determination of the number of electrons and % hydrogen peroxide obtained by a 20% Pt/C catalyst. A) Number of electrons transferred from the oxygen reduction reaction studied on a 20% Pt/C Premetek catalyst at 900 rpm in O_2 saturated 0.5 M H_2SO_4 at a scan rate of 10 mV s^{-1}. B) $\%H_2O_2$ from the oxygen reduction reaction studied on a 20% Pt/C Premetek catalyst at 900 rpm in a O_2 saturated 0.5 M H_2SO_4 at a scan rate of 10 mV s^{-1}.

Determination of the number of transferred electrons

The number of electrons transferred in the reaction can be determined through KL analysis. This can be done whether using RDE or/and RRDE techniques. However, RDE is not the most accurate way to determine the number of electrons transferred in a reaction. The most accurate methodology comes using RRDE when the data is collected at the ring. During this experiment at the disk, the oxidized species are reduced as the potential is varied. The ring is held at a constant potential to collect any hydrogen peroxide that was formed and determine the number of electrons transferred ($n = 2$ for H_2O_2 or 4 for H_2O) in the reaction (Tan et al., 2017):

$$n = \frac{4i_D}{i_D + \frac{i_R}{N}} \tag{13}$$

where n is the number of electrons transferred, N, is the collection efficiency, and i_R and i_D are the ring and disk currents respectively (Zhang, Wei, Yang, Tavares, & Sun, 2017). Using Eq. (13) the researcher can monitor the changes in the number of transferred electrons as the potential is varied (Figure 6A). Combining the information about the number of transferred electrons, $\%H_2O_2$ produced, and the features of the RRDE disk and ring voltammograms researchers can determine kinetic and mechanistic pathways by which the material under investigation catalyzes ORR.

Implementation and utilization of RRDE technique for undergraduate laboratories

Hands-on experience in voltammetry has become a “must-have” skill for chemistry graduates to be competitive in the job market. Nowadays this technique is heavily applied in both industrial and research settings. In general, the student experience with voltammetric techniques during undergraduate laboratories could be greatly expanded. Notably, this could be done through modification/modernization of the existing laboratory procedures of the chemistry curriculum. For example, in our curriculum (Ontario Tech University, Canada, ON), electrochemistry-based labs are mainly focused on analytical studies involving polarographic techniques and the determination of trace elements in samples. The learning outcomes for students are centered on the basics of voltammetry with the main focus on stationary cyclic voltammetry (CV). The students perform CV by using the classical potassium (II/III) hexacyanoferrate redox reaction and analyze the CVs using the Randles–Sevcik equation. As a result, voltammetry is utilized mainly to demonstrate the dependence of scan rate on the peak currents. Currently, this laboratory is paired with the trace analysis study on an irreversible system, namely the determination of acetaminophen in cough syrup samples. Notably, hydrodynamic voltammetry could be readily incorporated into this procedure by using a RDE as the solid electrode. Then, all previously planned CV experiments could still be performed using the RDE in a stationary mode (no rotation). However, using a RDE in rotation mode, voltammetry experiments using the potassium (II/III) hexacyanoferrate redox couple can be readily performed at different rotation rates that would allow extraction of valuable kinetic data. Notably, a simple addition of RDE measurements at the last step of the existing laboratory will allow students to study the kinetics of this classic redox process. While experimentally it is a very easy upgrade (addition of RDE to instrumental set-up) this results in a significant boost of learning outcomes. Indeed, RDE experiments will enable students to study the same redox couple in the solution and will yield a different voltammetric wave shape depending on the presence of convective mass transport in the system. As a result, students will gain in-depth mechanistic understanding of the kinetics of the system, obtain unique practical skills, and reinforce their knowledge of electrochemical theory.

RDE and RRDE techniques can be further embedded into the undergraduate curriculum to study a wide range of materials for clean energy technologies. As mentioned, the oxygen reduction reaction (ORR) is very commonly explored using hydrodynamic voltammetry for application in fuel cell technologies. Thus, the laboratory session targetting an investigation of the ORR efficiency of the materials for fuel cells could be a valuable addition to the undergraduate chemistry curriculum. This experiment will illustrate the relevance of the RDE technique to the students. Below we propose a plausible laboratory procedure for studying ORR performance of a Pt/C catalytic system that is ready to be directly incorporated into the curriculum.

In the supporting information, we go through the basics of RRDE set up, collection, and analyzing the data for a commercial 20% Pt/C catalyst used in Proton Exchange Membrane Fuel Cells (PEMFC), as well as, provide an experimental procedure to be used in undergraduate labs. Hydrodynamic voltammetry is the electrochemical method of choice to screen catalyst candidates for applications in PEMFCs, especially as ORR catalysts. This technique could provide a simple and effective undergraduate laboratory to study the activity of materials for clean energy systems.

Proposed laboratory experiment

We propose a simple laboratory experiment to study the ability of the material to catalyze the ORR and to define the mechanism of the catalytic transformation for the active catalyst (see SI for detailed laboratory procedure).

First, a proper layer of the catalyst should be created on the electrode. For a 5 mm diameter disk (used in this work) this corresponds to 5 μL. Loadings between 20 and 60 μg cm^{-2} are usually ideal to form thin catalyst layers on the electrode (Zhang et al., 2017). Thick catalyst layers result in transport limitations as the thick and rough catalyst layers could disturb the laminar flow of the electrode, creating turbulence. This is when the flow of the electrolyte to the electrode occurs in non-linear and chaotic layers (Luo et al., 2019). The reference electrode used in the experiment was a Hg/$HgSO_4$ reference that was calibrated to be 0.65 V versus reversible hydrogen electrode (RHE). All potentials were corrected to the RHE scale by adding the Hg/$HgSO_4$ potential to the recorded potential from the measurements. The RHE has been used because of the potential changes based on pH, so it is often used directly in electrolyte solutions (Jerkiewicz, 2020; Smith & Stevenson, 2007). Other common reference electrodes include Hg/HgO, or Ag/AgCl, the difference between reference electrodes is the encompassing potential windows of each of them in different electrolyte and under various temperature conditions. Depending on the electrolyte of choice and the temperature of the measurement, the reference electrode should be chosen carefully. Counter electrodes are used to compensate for the charge produced at the working electrode. These electrodes must have a high surface area so typically carbon-based or platinum wires are ideal because their large surface areas can handle the charges produced well. A graphite rod was used as the counter electrode for all experiments in these manuscripts.

The ORR was studied in 0.5 M H_2SO_4 and voltammograms presented here were recorded at 10 mV s^{-1}. All of the RRDE curves presented in the subsequent Figures have had the background currents subtracted (Janßen et al., 2018). It is important to perform a cyclic voltammogram of the Pt/C catalyst in N_2-purged electrolyte to provide some electrochemical cleaning of the Pt surface prior to main experiments (Figure S4). Also, a proper background scan in the absence of O_2 should be performed so that the charging currents can be properly accounted for in our analysis. For more detailed information about the preparation of electrodes and electrode materials please see Elgrishi et al. (2018).

In the ORR, oxygen is dissolved in the electrolyte and flows to the disk via the rotation of the electrode. As it reaches the electrode, oxygen is reduced from O_2 to H_2O via a four-electron transfer process (Fruehwald et al., 2019; Hossen et al., 2018). Thus, it is important to maintain a solution that is saturated with O_2. However, not all O_2 molecules will be directly reduced to H_2O, and a two-electron undesirable by-product, H_2O_2 is often produced (Zhang et al., 2017). Using the RRDE collection experiment, the ring is held at a potential (1.2 V vs. RHE) where any H_2O_2 that is produced from the reaction is detected and measured (Figure 7A). In essence, the ring is behaving like an amperometric H_2O_2 sensor. RRDE is a powerful characterization technique for studying the ORR mechanisms as the researcher can quantify the amounts of peroxide that is produced and provides some insight into the electron transfer process occurring over the course of the reaction.

Using the data from Figure 7 and Eqs. (10) and (11) a KL plot can be made to determine an estimate of the number of transferred electrons and the kinetic currents associated with the material at a given potential (Figure 8). The limiting currents were plotted versus the scan rate at various potentials. It was calculated that

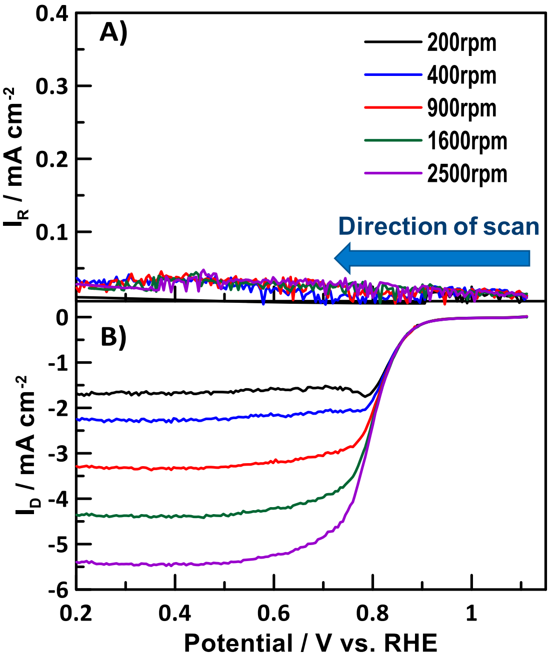

Figure 7: Plotted RRDE data from the ORR using a 20% Pt/C catalyst. A) RRDE ring currents from the oxygen reduction reaction studied on a 20% Pt/C Premetek catalyst in O_2 saturated 0.5 M H_2SO_4 at a scan rate of 10 mV s^{-1}. B) RRDE disk currents from the oxygen reduction reaction studied on a 20% Pt/C Premetek catalyst in a O_2 saturated 0.5 M H_2SO_4 at a scan rate of 10 mV s^{-1}.

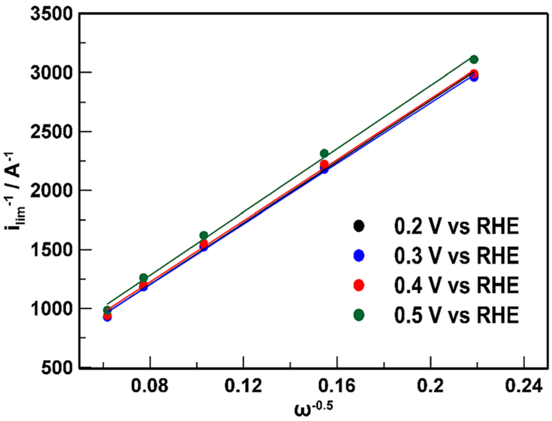

Figure 8: Koutecky–Levich plots of the 20% Pt/C catalyst at different potentials.

the number of electrons transferred was four, which is expected for the 20% Pt/C Premetek catalyst as there were limited ring currents detected (due to the low ring currents measured). This indicated that the Pt/C is catalyzing the ORR through the ideal direct four-electron pathway.

A Levich plot can also be made using the limiting current plotted against the square root of the rotation rate in rad s^{-1} at different potentials (Figure S5). Theoretical Levich slopes for Pt/C material are well reported in the literature, thus comparing the slope obtained in this work to literature reports will aid to determine the reaction kinetics. For example, Rahman et al. (2012) reported a theoretical Levich slope of 0.34 mA cm^{-2} (rad s^{-1})$^{-0.5}$ for a four-electron transfer process using Pt/C catalyst in H_2SO_4. The Levich slope of the 20% Pt/C catalyst in Figure S5 yielded a slope of 0.32 mA cm^{-2} (rad s^{-1})$^{-0.5}$, indicating it follows a four-electron transfer process. Using the data collected by the student and the theoretical slopes, further insights into the reaction mechanism of the catalyst under investigation can be determined. Ultimately the student can use the Levich slopes to further help identify the major products of the reactions.

From the collection experiment the number of electrons transferred and the %H_2O_2 formed can be determined using Eqs. (11) and (12). We determined the number of transferred electrons over a wide range of potentials so that the product distribution of the reaction could be monitored as it proceeds (Figure 6).

Interestingly, we see that the number of electrons transferred ($n = 4$) stays almost constant within the potential window that is correlating well with the results from the KL analysis. As we monitor the formation of H_2O_2 (%) (Figure 6B) we see that the amount of peroxide remains relatively low (below ca. 10%). This shows that while the major pathway is the direct conversion of O_2 to H_2O, there is a minor two-electron reaction pathway that is responsible for the formation of small amounts of H_2O_2. With RRDE techniques the extent of conversion of the O_2 to either H_2O or H_2O_2 can be determined through data processing (Matter et al., 2006).

Results of test pilot laboratory

Using the information reported in this manuscript, we have created a laboratory experiment protocol to incorporate hydrodynamic voltammetry into the undergraduate laboratory. This procedure, is included in the SI. We tested this experiment on a small cohort of students who had just recently completed a 3rd-year instrumental analytical chemistry course. In the laboratory section of this course, the students performed their first electrochemistry experiment using the hexacyanoferrate redox couple with a stationary electrode. Notably, the students learn the main principles of hydrodynamic voltammetry as part of the instrumental chemistry lectures, but they were not getting practical experience with this technique. The proposed laboratory experiment will allow 3rd-year students to build on their recent laboratory experience with the stationary electrodes, by introducing a rotating electrode technique for acquiring a wide variety of kinetic information about the system. Similar to the undergraduate laboratory style at our institution, the students were given a copy of the procedure (included in the SI), a 3-h time limit, and the required equipment and chemicals. The Teaching Assistant was present in the lab to monitor the process and provide additional help when requested, but mainly the experiment was completed independently by the students.

On average it took the students 2 h and 28 min to complete the experiment. We are satisfied with the timing of this experiment as this fills the scheduled laboratory time with some extra time left for discussing the data analysis. We assessed the students' knowledge and confidence in electrochemistry and hydrodynamic voltammetry before and after the completion of the experiment. The results are presented in Tables S1 and S2. From the students' responses before the experiment, we see that the majority indicated a lack of confidence and gaps in their knowledge of hydrodynamic voltammetry. Interestingly, the majority of students were somewhat confident in their overall experience in electrochemical techniques, just not in hydrodynamic voltammetry.

Upon completion of the proposed electrochemical voltammetry laboratory experiment, the students had an overwhelmingly positive response on their experience with the experiment and associated learning outcomes. After the technique was incorporated into the pre-existing undergraduate laboratory session, the students that participated in the pilot project noted that this laboratory experiment significantly reinforced their pre-existing theoretical knowledge about the technique that they had learned in the lectures. The students highly rated this experiment and were feeling that the resulting experience will be beneficial for their future careers and were ready to apply this technique in new situations or contexts. One student mentioned that the experiment effectively demonstrate the practical applications of the RDE/RRDE technique. With electrochemistry techniques becoming increasingly more prevalent in industry and research, early incorporation of voltammetric techniques in the undergraduate laboratory curriculum is very beneficial to the students learning and their confidence once they graduate and go to the workforce. The overwhelmingly positive reviews of this experiment show the desire of the students to learn a variety of electrochemical methods for modern applications, such as the studies of the ORR performance/mechanistic pathways of the catalytic trannsformations and/or processes in fuel cells. The students went as far as to mention that this experiment would be worthwhile to perform as an independent study project for a component of their third-year laboratory course. Overall, the increase in confidence and knowledge in hydrodynamic voltammetry techniques, combined with the high level of students' satisfaction from the proposed laboratory experiment, shows that the abovementioned technique is a valuable addition to the undergraduate chemistry curriculum that will allow students to get an extended set of electrochemistry skills that are highly demanded by modern employers, that will be very beneficial to the future students' careers.

Modifications to this laboratory design

While this example highlights a standard catalyst for the ORR, this experiment can be modified to include materials that have different amounts of Pt to study how this will affect the main reaction mechanism. This can even be extended to other potential catalysts for the ORR, such as non-precious metal catalysts (eg. commercially available catalysts from Pajarito Powder), or carbon-free catalysts. Overall, hydrodynamic voltammetry experiments reported here aim to give students and/or researchers a fundamental understanding of the applications and uses of electrochemistry in real-world settings with a focus on green energy solutions. This topic is relevant to future technologies for clean energy applications (Hurst et al., 2019).

Conclusions

In conclusion, with growing interest in electrochemistry, there is a need for detailed information about the various common electrochemical techniques. Due to the ease of analysis, relatively low-cost instrumentation, and high sensitivity the electrochemical techniques are gaining popularity and are becoming more commonly used in industrial and academic applications. Thus, the distilling of knowledge and providing sufficient hands-on training to students and researchers is essential and highly demanded by employers in academia and industry. This work introduces the concept of the rotating disk and rotating ring disk electrode, compares different modes of operation to access various kinetic, and mechanistic information for the system under study. Using the information presented here, chemistry students and postgraduates can confidently use rotating disk electrochemical techniques and extract all relevant data to reveal the mechanism of the reactions they study.

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Supplementary Material: Supporting information includes photos of different glassy carbon electrodes compared to a RDE, as well as a photo of the RDE/RRDE set up. Cyclic voltammograms of the potassium (II/III) hexacyanoferrate redox couple and 20% Pt/C catalyst are included along with the Levich plot of the 20% Pt/C catalyst. The experimental procedure is included for an undergraduate laboratory design as well as students' rating on the experiment.

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