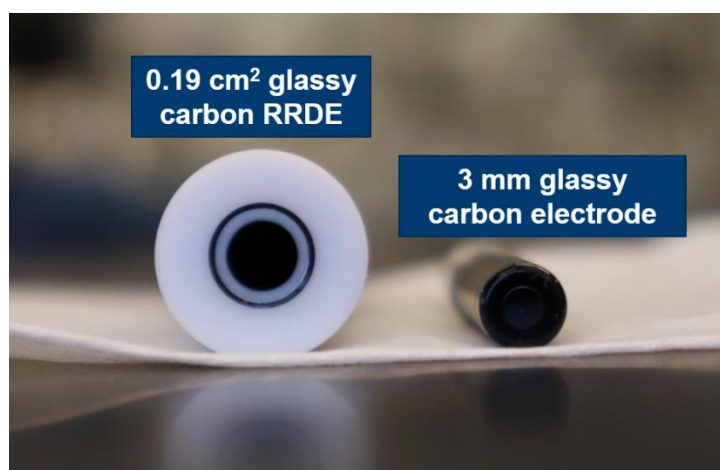
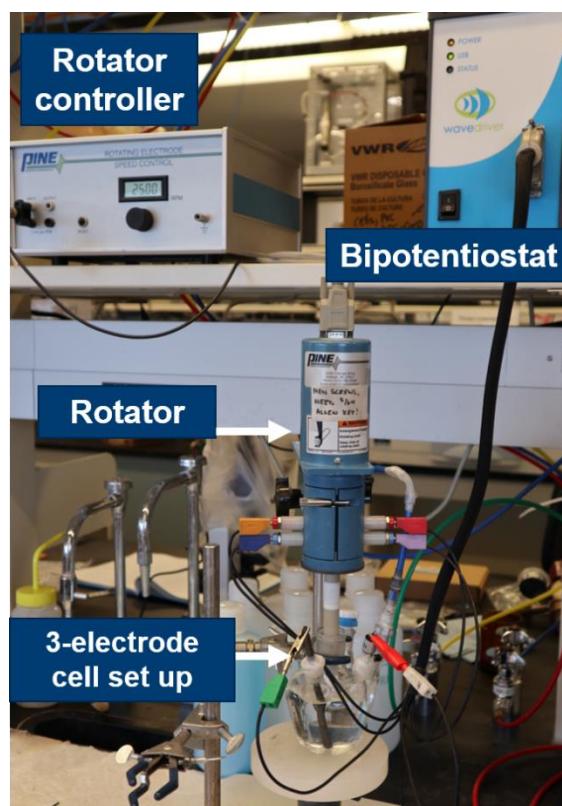


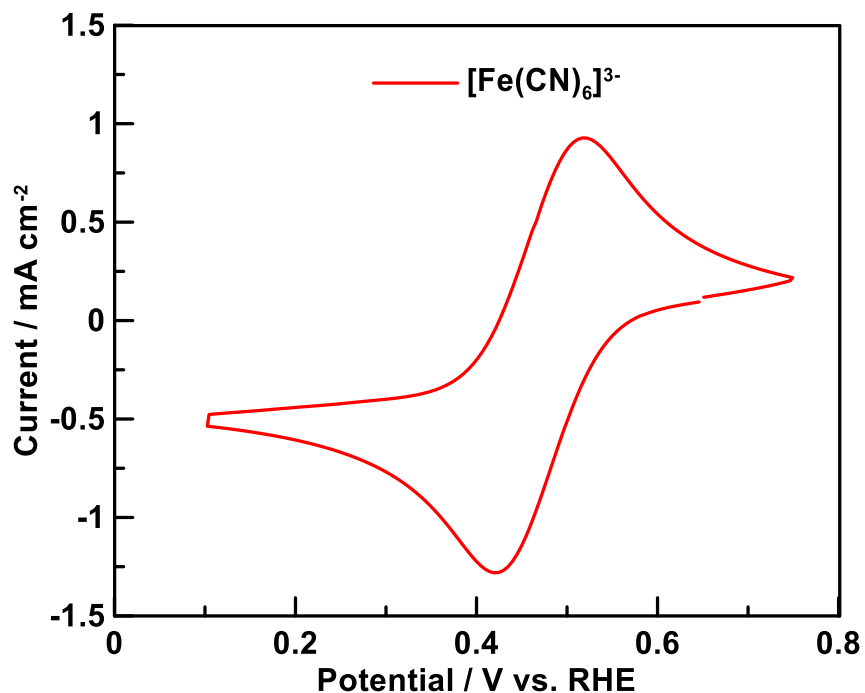
## A new spin on electrochemistry in the undergraduate lab



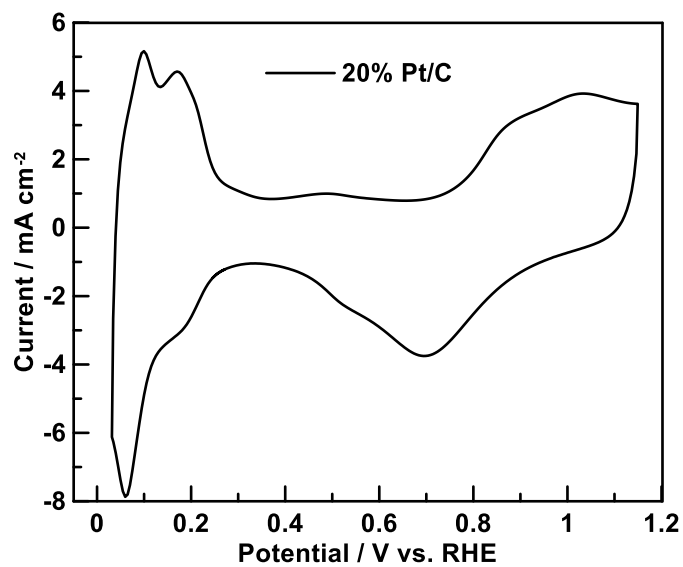
**Figure S1.** Image visually showing the difference between a rotating ring disk electrode (RRDE) (Pine Research Instruments) and a 3 mm glassy carbon electrode (CH Instruments).



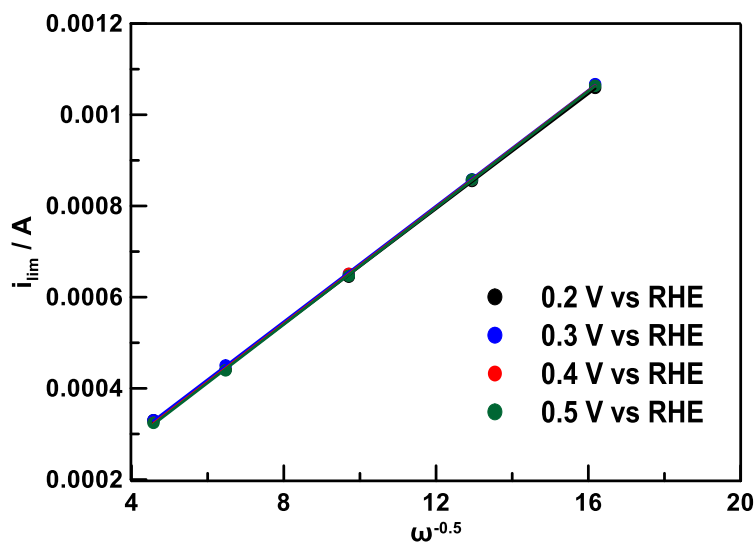
**Figure S2.** Image of the complete RDE set up used.



**Figure S3.** Cyclic voltammogram of iron (II) hexacyanoferrate (III) redox couple in 1 M KNO<sub>3</sub> electrolyte purged with N<sub>2</sub> at a scan rate of 50 mV s<sup>-1</sup>.



**Figure S4.** Cyclic voltammogram of 20% Pt/C catalyst in N<sub>2</sub> purged 0.5 M H<sub>2</sub>SO<sub>4</sub> electrolyte at a scan rate of 50 mV s<sup>-1</sup>.



**Figure S5.** Levich plot of 20% Pt/C catalyst O<sub>2</sub> saturated 0.5 M H<sub>2</sub>SO<sub>4</sub> studied at different potentials vs reversible hydrogen electrode (RHE).

### **Further Experimental Details about the ORR studied**

The experiments were performed using a Pine Instruments rotator (model AFPC2) with the Pine WaveDriver 20 bipotentiostat (Figure S2). The experiments were performed on a glassy carbon RRDE (diameter= 5 mm, area = 0.19625 cm<sup>2</sup>) with a platinum ring. A commercial 20% Pt/C Premetek catalyst was used to perform the ORR. Prior to deposition of the catalyst, the electrode was polished with an aluminum slurry to remove any contaminants that might have accumulated on the electrode prior to ORR measurements. A catalyst ink was made by adding 10 mg of the 20% Pt/C material with 400  $\mu$ L of a 50:50 deionized water and isopropyl alcohol mixture, and 100  $\mu$ L Nafion<sup>®</sup>. The water and alcohol were used to disperse the catalyst and the Nafion<sup>®</sup> was used as a proton conductor. The ink was sonicated in an ultra-sonic bath to create a good dispersion of the ink. A volume of ink was deposited on the electrode using a micropipette to obtain a Pt loading of 60  $\mu$ g cm<sup>-2</sup>.

**Table S1.** Pre-survey results before completion of the laboratory experiment.

| Question   | Survey Answers |   |   |
|--|----------------|---|---|
| How confident are you in your practical electrochemical techniques? (scale of 1-5, 1 least confident and 5 most confident) | 4              | 2 | 4 |

|   |       |    |     |
|---|-------|----|-----|
| How confident are you in your knowledge of the theory behind hydrodynamic voltammetry (scale of 1-5, 1 least confident and 5 most confident)          | 2     | 2  | 1   |
| How confident are you in your technical skills to perform hydrodynamic voltammetry techniques? (scale of 1-5, 1 least confident and 5 most confident) | 3     | 1  | 2   |
| As of today, do you feel as if you have learned enough about hydrodynamic voltammetry to confidently apply it in a work or research setting?          | Maybe | No | Yes |

**Table S2.** Post-survey results after completion of the laboratory experiment.

| Question   | Survey Results |     |  |
|--|----------------|-----|--|
| Did this laboratory session effectively reinforce the hydrodynamic voltammetry techniques you learned in the lecture?                          | Yes            | Yes | Yes  |
| Have you fully understood the goals and targets of the experiment?   | Yes            | Yes | Yes  |
| Have you obtained new hands-on experience that you feel would be useful for your future career?  | Yes            | Yes | Yes  |
| Did you enjoy this experiment?   | Yes            | Yes | Yes  |
| Did this experiment meet your expectations of the learning objectives?   | Yes            | Yes | Yes  |
| Were you having technical trouble setting up the experiment?   | No. No issues  | No  | No. The set up was fairly straightforward and only required minimal assistance.                      |
| Were you having issues understanding the background behind the experiment, or troubles to analyze and interpret the results of the experiment? | No             | No  | No. The information in the lab manual was very clear on how to analyze the data and the analysis was |

---

|  |   |   |  |
|--|---|---|--|
|  |   |   | covered in the lecture period.   |
| Is there anything that you feel this experiment lacked?  | No  | No  | No. This experiment fully informs students about the method of hydrodynamic voltammetry, and provided needed context/ practical application. |
| Do you think you can apply what you learned here to a new situation or in a new context?                   | Yes   | Yes   | Yes  |
| Do you feel you now have sufficient background knowledge and technical skills on hydrodynamic voltammetry? | Yes   | Yes   | Yes  |
| Please rate your experience with the lab overall (scale of 1-5, 1 least impressed and 5 most impressed)    | 5   | 5   | 4  |
| Would this be worthwhile to complete as an independent study project?                                      | Maybe   | Yes   | Yes  |
| Any other comments of feedback to add to your overall experience with the lab?                             | The lab was very simple yet was still able to introduce the topic in a clear way and made understanding the concepts and how it can be applied a lot easier | The introduction and procedure was easier to understand and easy to follow. | Shortening some of the waiting time would make the lab slightly more enjoyable.  |

---

## **Laboratory Experiment: Determining the Kinetics of Electrocatalysts for Energy Applications**

### Learning objectives:

- 1) Reinforce hydrodynamic voltammetry concepts learned in lecture
- 2) Learn practical skills surrounding the use of rotating disk electrodes
- 3) Improve the ability to analyze and discuss the experimental data collected

### Introduction

Clean energy technologies have been becoming increasingly more popular industrially and research-wise due to the impacts of climate change on our environment. A representative example of such a clean energy device is the proton exchange membrane fuel cells (PEMFCs). These are devices that utilize chemical energy in the form of hydrogen and oxygen and convert it into electrical energy, with water being the only waste product. The cathode side of the PEMFC, where the oxygen reduction reaction (ORR) occurs is the most problematic one since it involves sluggish reactions that require high loadings of expensive and rare materials. Thus, minimizing or replacing the use of those materials is heavily demanded by industry and challenging the research minds.

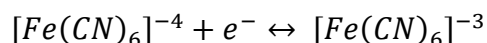
Hydrodynamic voltammetry is the major method to study the ORR. This is a voltammetric technique that involves a working electrode that is rotated at high speeds, referred to as a rotating disk electrode (RDE). Using this type of electrode the kinetic, diffusion, and convective components of a faradaic (redox) reaction can be separated. 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. Thus, mass transport is entirely driven by the influence of the convection of the solution during the rotation of the electrode, one where current is proportional to the concentration gradient at the electrode surface for each constant rotation rate. This creates a diffusion layer at the surface of the electrode. The smaller the diffusion layer, the larger the concentration gradient at the electrode is.

In this experiment a rotating-ring disk electrode is used, which operates similarly to the RDE described, but has a second ring-shaped electrode (typically Pt) that surrounds the disk which is separated by a Teflon sheath. This creates a second working electrode in the 3-electrode set up.

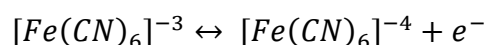
The RRDE electrode needs to be calibrated before the measurements. As part of the calibration, a collection experiment is performed. For this experiment, the disk potential is varied as the ring potential is held constant. Each RRDE has a specific collection efficiency ( $N$ ), which is a measure of how well the ring will collect the reduced species from the disk to oxidize it. The collection efficiency is defined as the following:

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

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 ferricyanide reaction. As the potential is swept negatively,  $Fe^{3+}$  species become reduced at the disk:



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 :



From there, a collection experiment will be performed on a commercial 20% Pt/C catalyst to determine the effectiveness of this catalyst for the ORR. While rotating the electrode, the disk potential is swept cathodically until a limited current is reached, such that mass transport limitations are observed. As the redox-active species come into contact with the disk they become reduced and then radiated towards the ring and collected. The ring is held at a sufficiently positive potential so the reduced species are immediately oxidized upon contact with the ring. Thus, the ring regenerates the original analyte.

## Data analysis

The flow of the solution can be analyzed using the Levich equation to give a wide range of valuable kinetic information when using the RRDE. With rotating electrodes, the current density is mass transport controlled, thus the concentration of the electroactive species on the surface of the electrode is 0, and the limiting current density for an RDE is:

$$i_{lev,D} = 0.62nFD^{0.67}v^{0.166}C\omega^{-0.5}$$

Where  $D$  is the diffusion coefficient ( $m^2s^{-1}$ );  $n$  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 ( $mol L^{-1}$ ),  $n$  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 ( $mol L^{-1}$ ), kinematic viscosity ( $m^2s^{-1}$ ); and  $\omega$  is the rotation rate ( $rad s^{-1}$ ). Overall, the Levich analysis describes the kinetic contributions at the electrode, as well as, can also be used to determine the number of electrons transferred ( $n$ ) or the diffusion coefficient ( $D$ ) when one of the parameters is known.

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 while the rotation rate is varied. This technique uses the limiting current, the regime with no changes in the current over time, 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:

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

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,  $i_{lev}$ . Using  $i_{lev}$  in the equation above, the number of electrons ( $n$ ) involved in the reaction can be determined, as all other constants can be found from 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.

As mentioned, 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 ( $H_2O$ ) is a 4-electron process and is the desired product for a potential PEMFC catalyst candidate. However, there is often a by-product, hydrogen peroxide ( $H_2O_2$ ) formed via a 2-electron process due to the incomplete conversion of oxygen to water.

Obtaining the ring and disk data provides a reliable method to determine the product distribution of  $H_2O$  vs  $H_2O_2$  for a catalyst. Results are normally reported as the percentage of hydrogen peroxide produced which can be determined using the following equation:

$$\%H_2O_2 = 200 \times \frac{i_R/N}{i_D + i_R/N}$$

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.

We can also use the ring and the disk currents to determine the number of electrons transferred in the reaction:

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

In this experiment, you will observe the product distribution of a PEMFC catalyst by combining the information about the number of transferred electrons,  $\%H_2O_2$  produced, and the features of the RRDE disk and ring voltammograms to determine the kinetic and mechanistic pathways by which the 20% Pt/C material can catalyze ORR.

## Procedure

### *Part I: Calibration of the ring*

1 M  $\text{KNO}_3$  and 10 mM  $\text{K}_3\text{Fe}(\text{CN})_6$  will be provided to you.

1. Add 50 mL of the 1 M  $\text{KNO}_3$  and 150 mL of the 10 mM  $\text{K}_3\text{Fe}(\text{CN})_6$  to the electrochemical cell
2. Using the aluminum slurry provided, polish the rotating ring disk electrode surface by making a figure 8 pattern on the polishing pad a few times with the electrode surface
3. Rinse the electrode with deionized water and carefully dry the electrode surface
4. Place the graphite counter electrode, and  $\text{Hg}/\text{HgSO}_4$  electrode into the cell.  
Place the RRDE electrode into the rotator and secure with the screws. Lower the RRDE electrode into the electrochemical cell so that the glassy carbon surface is submerged in the solution
5. Purge the solution with nitrogen gas for 10 mins.
6. Turn off the gas.
7. In the Aftermath software, run a cleaning CV with the following parameters:

|                   |         |
|-------------------|---------|
| Segments          | 31      |
| Initial potential | 0 mV    |
| Upper potential   | 100 mV  |
| Lower potential   | -600 mV |
| Final potential   | 0 mV    |
| Sweep rate        | 50 mV/s |

8. Turn on the rotator and set it to 2500 RPM
9. Once the CV is complete run the RRDE measurement using the following parameters:

|          |   |
|----------|---|
| Segments | 6 |
|----------|---|

|                   |         |
|-------------------|---------|
| Initial potential | 0 mV    |
| Upper potential   | 100 mV  |
| Lower potential   | -600 mV |
| Final potential   | 0 mV    |
| Sweep rate        | 10 mV/s |
| Ring potential    | 0.83 mV |

10. Run the RRDE using the parameters from step 8 at 1600, 900, 400, and 200 RPM.
11. When complete, remove the electrodes from the cell and rinse them well with deionized water
12. Discard the solution in the electrochemical cell into the appropriate waste and rinse the cell well with deionized water

### *Part II: Preparation of Pt/C catalyst electrode*

*While partner 1 is calibrating the ring, partner 2 can start preparing the catalyst ink for the ORR*

1. Create a catalyst ink by adding together in a vial 10 mg of the 20% Pt/C commercial Premetek catalyst, 200  $\mu$ L deionized water, 200  $\mu$ L isopropyl alcohol, and 100  $\mu$ L of the provided 5% Nafion solution.
2. Cap the vial and ultra-sonicate this ink for 15 minutes
3. While the ink is sonicating prepare the RRDE electrode and cell
4. Add 200 mL of the provided 0.5 M  $\text{H}_2\text{SO}_4$  to the 250 mL electrochemical cell
5. Purge this solution with nitrogen gas
6. Using the aluminum slurry provided, polish the rotating ring disk electrode surface by making a figure 8 pattern on the polishing pad a few times with the electrode surface

7. Rinse the electrode with deionized water, dry it, and clamp it with the glassy carbon side facing up
8. Once the ink is finished sonicating use a suitable Eppendorf pipette to deposit 5  $\mu\text{L}$  onto the glassy carbon surface
9. Be sure to only coat the glassy carbon surface, if the ink spreads onto the ring or to the surrounding Teflon section, remove the ink from the electrode with a Kim wipe (Kimberly-Clack wipe) and repeat steps 6-8
10. After deposition either dry the electrode with a heat gun on a gentle heat setting or let it air dry
11. Once the film is fully dry inspect it to make sure that there are no cracks and there is a smooth film on the surface. If not, repeat steps 6-10
12. Once the film is prepared place the RRDE in the rotator and secure it with the screws. Lower it into the cell along with the graphite counter electrode and the  $\text{Hg}/\text{HgSO}_4$  reference electrode and connect the leads

### *Part III: ORR measurements*

1. Open the corresponding Aftermath software and select the CV experiment
2. Turn off the nitrogen gas and run a CV with the following parameters to clean the surface of the electrode:

|                   |          |
|-------------------|----------|
| Segments          | 31       |
| Initial potential | 0 mV     |
| Upper potential   | 500 mV   |
| Lower potential   | -620 mV  |
| Final potential   | 0 mV     |
| Sweep rate        | 200 mV/s |

3. Once the CV is complete, perform a background RRDE scan in  $\text{N}_2$  saturated solution using the following parameters:

|                   |         |
|-------------------|---------|
| Segments          | 5       |
| Initial potential | -615 mV |
| Upper potential   | 500 mV  |
| Lower potential   | -620 mV |
| Final potential   | -615 mV |
| Sweep rate        | 10 mV/s |
| Ring potential    | 500 mV  |

4. Once completed, vigorously purge the solution with O<sub>2</sub> for 20 minutes.
5. When purging is complete turn down the O<sub>2</sub> purging to a gentle flow
6. Turn on the rotator and set the RPM to 2500
7. Run a RRDE scan using the same parameters in step 3
8. Repeat steps 6-7 using 1600, 900, 400, and 200 RPM

## Data Analysis

1. Using the data from part 1 determine the collection efficiency of the RRDE used in this experiment
2. Plot the current vs potential for both the ring and disk measurements at the varying rotation rates for part 1 and part 3
3. Using the data from the ring and disk currents at 900 RPM from part 3 calculate the number of electrons transferred and the %H<sub>2</sub>O<sub>2</sub> produced at 0.2, 0.3, 0.4, 0.5, 0.6 , and 0.7 V vs RHE
4. Plot the data calculated from question 3 as a function of potential
5. Create a Koutecky-Levich plot from the data obtained at 0.3 V vs RHE
6. Compare the number of electrons transferred from the ring data to the KL plot for the 20% Pt/C catalyst

## Questions

1. Create a Levich plot from the data obtained from the 20% Pt/C. Look in the literature and determine if the slope obtained from this catalyst compares to either a 2 or 4 electron pathway?
2. Determining the number of electrons transferred and %H<sub>2</sub>O<sub>2</sub> are important parameters for determining if the material would be a good candidate for PEMFC applications. What do the numbers you have calculated tell you about the product distribution? Would this be a good catalyst for the ORR?
3. What are the benefits of using a rotating electrode over a stationary electrode?