

Experiment 1C

The Rotating Ring-Disk Electrode

Experiment Overview

When one sets the potential of an electrode away from the equilibrium potential, a current flows. The amount a potential deviates away from equilibrium is called the **overpotential**. For a given overpotential, the magnitude of current flow can depend on a number of factors, including the charge transfer rate between solution species and the electrode (called **electrode kinetics**), and **mass transfer** by diffusion, convection, and migration. Positive overpotentials (*i.e.* potentials positive of equilibrium) cause oxidation reactions on the electrode, whereas negative overpotential cause reduction reactions to occur. In this experiment, you will analyze an electrochemical reaction operating in the **mass transfer limited** regime where current flow is limited by the rate of convection (mixing) in the electrochemical cell. Mixing in the system will be induced by rotating the electrode. For a rotating disk electrode (RDE) operated in the mass transfer limited regime, the rate of current flow is described by the **Levich equation**. Experiment 1C will allow you to evaluate the validity of the Levich equation and assess the diffusion coefficient for ferrous and ferric ions in aqueous media. You will also get to use cyclic voltammetry, a technique commonly used to get an overall "survey" of the electrochemical terrain. At the end of this experiment, you should be able to describe the chemistry responsible for all features on the cyclic voltammogram, and quantitatively analyze and predict mass transfer limiting behavior.

Background Theory

Most electrochemical systems with high conductivity electrolytes display current vs. potential curves that look like Fig. 1. Three regions are shown in Fig. 1. The equilibrium potential ($E=E_{eq}$ @ $I=0$) sets the potential scale so we can know whether a given potential will cause an oxidation or a reduction reaction. If the electrode potential is set more positive than the equilibrium value, then an oxidation reaction will occur on the electrode. In ChemE 461, we denote oxidation by a positive current. Conversely, if the electrode is set negative of the equilibrium potential, then a reduction reaction will occur on the electrode, denoted by a negative current. **(Important Note: your textbook uses the opposite convention—positive current to denote reduction, negative current to denote oxidation.)**

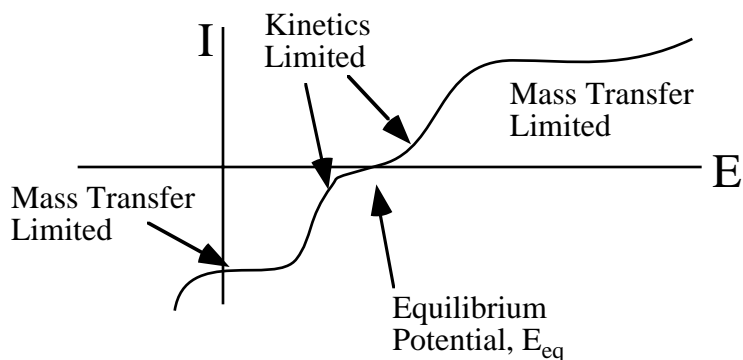


Figure 1. Schematic of typical current vs. potential behavior for an electrochemical system with high conductivity electrolyte.

At large deviations away from equilibrium the current is often determined by the rate of convection in the electrolyte near the electrode, provided the electrolyte is highly conductive.

Since convection determines the rate of current flow in the mass transfer limited regime, all one needs to know is the flow field near the electrode and the diffusivity of the reactant to determine the rate of current flow. One electrode configuration where it is easy to determine the flow field is the rotating disk electrode (RDE). Levich analyzed the flow generated by a rotating disk and showed that the mass transfer limited current should follow the relationship

$$|I_l| = 0.620nFAD^{2/3}\omega^{1/2}\nu^{-1/6}C^* , \quad (1)$$

where $|I_l|$ is the absolute value of the mass transfer limited current (Amps), n is the number of electrons transferred, F is Faraday's constant, A is the electrode area ($= 0.1642 \text{ cm}^2$ for the small disk RRDE), D is the reactant species diffusivity (cm^2/s), ω is the rotation rate of the disk (radians/s), ν is the kinematic viscosity of the electrolyte ($= 0.011 \text{ cm}^2/\text{s}$ for these experiments), and C^* is the bulk composition of reactant (mole/cm^3). Equation (1) is called the [Levich equation](#).

Experimental Procedure

This experiment will use sulfate-based electrolyte with 20 mM Fe^{+2} and Fe^{+3} in 1 M H_2SO_4 . The reaction that will be occurring on the electrode is



where the sulfuric acid acts as an inert component that raises the conductivity of the electrolyte (sulfuric acid is called the supporting electrolyte). The reaction will proceed in the forward or backward direction, depending upon which direction the potential of the electrode is biased away from equilibrium. All potentials will be measured relative to a saturated calomel electrode (SCE) as the reference. In this experiment, you are going to use cyclic voltammetry (linear sweep of the potential from one end of the potential range to the other end) to get current vs. potential curves that resemble Fig. 1 (what are there differences, and why are they there?). The diffusivity of ferrous and ferric ions will be determined by fitting data from the mass transfer limited region of the cyclic voltammogram to Eq. (1). The mass transfer limited current data should be plotted in classic Levich plot form, with $|I_l|$ plotted against $\omega^{1/2}$.

Given below are operating procedures for making the experiments run. You should always be prepared to modify the instrument settings and experimental conditions to improve the results you get. Don't hesitate to "play around" and figure out how the instruments work. You will have plenty of time with this experiment. If you are concerned that you might break something, or don't understand the interplay between instrument and experiment, then ask for assistance.

The first step to getting good voltammetry data is to make sure you start out with a clean electrode. We will use an electrochemical cleaning procedure to clean the electrode.

ELECTRODE CLEANING USING THE PINE BIPOTENTIOSTAT

(Starting with everything but the power turned OFF)

- (1) Carefully immerse Pt rotating ring disk electrode (RRDE), Pt counter electrode, and SCE reference electrode in electrolyte, making sure to keep Pt disk electrode from bumping against the cell sides or bottom. Make sure the ELECTRODES switch on potentiostat is set to DUMMY. Make sure the blue banana plug labelled IN on the potentiostat is disconnected.
- (2) Connect the Pt RDE to ELECTRODE K1 on the potentiostat.
- (3) Connect the SCE Reference Electrode to ELECTRODE REF on the potentiostat
- (4) Connect the Pt Counter electrode to ELECTRODE CE on the potentiostat
- (5) On potentiostat, set the MODE switch to POTENTIOSTAT, set the SWEEP RATE to 1000, set the MILLIVOLTS PER SECOND toggle to 0-999.9, set the AUTO toggle to ZERO, set the UPPER LIMIT to +1675, set the LOWER LIMIT to -0275, set STOP AT LIMIT toggle to middle position, set K1 OFFSET VOLTAGE to OFF, set K1 SWEEP VOLTAGE toggle to ON, set the K1 ELECTRODE CURRENT CONVERTER to 1 mA/V.
- (6) On the MSRX Speed Control, turn power on and set RPM to 1000
- (7) On potentiostat, set AUTO toggle to ON, and turn ELECTRODES switch to NORMAL.
- (8) Let system run for about 15 minutes to clean the electrode.
- (9) Set ELECTRODES to DUMMY

Now you are ready to collect good cyclic voltammetry data. This part of the experiment will be run under computer control.

CYCLIC VOLTAMMETRY USING THE PINE BIPOTENTIOSTAT UNDER COMPUTER CONTROL (Starting with everything set-up after cleaning)

- (1) On potentiostat, set the MODE switch to POTENTIOSTAT, set the SWEEP RATE to 500, set the MILLIVOLTS PER SECOND toggle to 0-999.9, set the UPPER LIMIT to +1675, set the LOWER LIMIT to -0275, set STOP AT LIMIT

toggle to middle position, set K1 OFFSET VOLTAGE to OFF, set K1 SWEEP VOLTAGE toggle to ON, set the AUTO toggle to ZERO, set the K1 ELECTRODE CURRENT CONVERTER to 1 mA/V.

(2) On the MSR Speed Control, set RPM to 0000.

(3) On the computer, set DISK CONTROL to RRDE #1 or #2 depending on specific station, set CONTROL TYPE to POTENTIOSTAT, set DISK CURRENT CONVERTER to 1 mA/V, set SWEEP TYPE to CYCLIC VOLTAMMOGRAM, set EQUILIBRIUM POTENTIAL to +430, set SWEEP MAXIMUM to +1675, set SWEEP MINIMUM to -275, set CV SWEEP RATE to 50, set ROTATOR SPEED TYPE to CONSTANT, set MEAN SPEED to 400, set NUMBER OF SWEEPS to 2, set SAVE EVERY Nth to 2.

(4) Run Computer Program

(5) After you verify source curve on computer, set AUTO toggle to ON and turn ELECTRODES switch to NORMAL on potentiostat. If they are already set that way, leave them.

(6) The experiment will run for about 3 minutes, at the end you will be asked to save the file, include 400rpm in name.

(7) Repeat items (3) – (6), but changing the MEAN SPEED in software from 400 to 900, then from 900 to 1600, then from 1600 to 2500, then from 2500 to 3600.

Also make sure you save the file name with the correct rpm of the experiment that was just completed.

(11) Set ELECTRODES to DUMMY on potentiostat.

Collection Experiments with the Rotating Ring–Disk Electrode

Your textbook gives an excellent overview of the rotating ring-disk electrode in §9.4 and describes the theory for collection experiments in §9.4.2. Briefly, you will be determining the collection efficiency of two different ring-disk electrodes, and you will also test whether the rotation rate has a substantial effect on the collection efficiency.

Experimental Procedure

This experiment will use sulfate-based electrolyte with 20 mM Fe⁺³ in 1 M H₂SO₄. The reaction on the disk electrode is the reduction of ferric ion to ferrous ion,



where the sulfuric acid acts as an inert component that raises the conductivity of the electrolyte (sulfuric acid is called the supporting electrolyte). The reaction will proceed at the mass transfer limited rate by holding the potential well negative of the equilibrium potential. All potentials will be measured relative to a silver chloride (AgCl) or saturated calomel reference electrode (SCE). On the ring electrode, we will set the potential sufficiently positive so ferrous ion generated at the disk will get oxidized at the mass transfer limited rate at the ring electrode according to the reaction



Since there is no ferrous ion in the bulk solution, all the ring current should be due to ferrous generated at the disk. If we know how much ferrous is generated (the disk current), and how much ferrous is collected at the ring (the ring current), we can calculate the collection efficiency for the system.

The two RRDE's used in these studies have: (1) a platinum disk of radius 2.29 mm, the platinum ring has a inner radius of 2.46 mm and an outer radius of 2.69 mm, and (2) a platinum disk of radius 2.81 mm, the platinum ring has a inner radius of 3.12 mm and an outer radius of 3.96 mm. Using theory presented in the textbook (Eqs. 9.4.16 & 9.4.17), compute the expected collection efficiency for these two ring-disk electrodes (check it twice since the equation is quite convoluted) and compare it to your experimental results.

Given below are operating procedures for making the experiments run. You should feel free to experiment with the instrument settings and experimental conditions to see how changing them affects the kind of results you get.

The first step to getting good data is to make sure you start out with a clean electrode. Follow the electrochemical cleaning procedure described above for both the ring and disk electrodes.

Now you are ready to get some collection efficiency data.

COLLECTION EFFICIENCY USING THE PINE BIPOTENTIOSTAT

(Starting with everything as set-up after cleaning)

(1) On the potentiostat, toggle the AUTO switch to ZERO, set the K1 ELECTRODE SWEEP VOLTAGE to OFF, set the K2 ELECTRODE SWEEP VOLTAGE to OFF, set the K1 ELECTRODE OFFSET VOLTAGE to -0050, set the K2 ELECTRODE OFFSET VOLTAGE to +1150. Decide on the appropriate K1 and K2 CURRENT CONVERTER SETTINGS based on your results from the prior experiments.

(2) On the potentiostat, set ELECTRODES to NORMAL

(3) On the potentiostat, set METER SELECT to I1, and record value from meter. The disk current is Meter Value*K1 Current Converter Setting. If the meter is not working properly, use a digital voltmeter (DVM). The DVM should be set to DC Volts, with the Red (+) lead plugged into the I1 banana plug and the Black (-) lead plugged into the DC Common banana plug on the potentiostat.

(4) On the potentiostat, set METER SELECT to I2, and record value from meter. The ring current is Meter Value*K2 Current Converter setting. If the meter is not working properly, use a digital voltmeter (DVM). The DVM should be set to DC Volts, with the Red (+) lead plugged into the I2 banana plug and the Black (-) lead plugged into the DC Common banana plug on the potentiostat.

- (5) On the MSRX Speed Control, set RPM to 1600.
- (6) Repeat steps (3) – (4)
- (7) Change RPM to 2500
- (8) Repeat steps (3) – (4)
- (9) Change RPM to 3600
- (10) Repeat steps (3) – (4)
- (11) Set ELECTRODES to DUMMY on potentiostat.
- (12) Repeat procedure for the other RRDE electrode.