

INTERFACIAL CAPACITIVE CHARGING, UNCOMPENSATED RESISTANCE, AND MASS TRANSPORT LIMITS

General Schedule and Comments *(this text is the same that was presented for Lab 2)*

In general, the format for this “discussion” session will be the same every week and is as follows:

1. Present brief outline of experiments, goals, and updates
2. Break into groups of two or three, set-up work space, and connect to the BioLogic potentiostat using the EC-Lab software on a PC laptop
3. Perform experimental procedure(s), while being assisted by the Instructor
4. If time permits, as a class provide feedback on the activity and recommend other activities
5. Clean-up work space, return items, and store electrodes for subsequent weeks. *(You are not dismissed from the discussion session until this is complete.)*

It is recommended that you read through the procedures and reference publications/files before you watch the experiment video and attend the hands-on discussion sessions. This will help you to become acquainted with the experiment and formulate questions to ask during the discussion session. Being interactive with the videos (i.e. by actively asking yourself questions as to why the experiment is set up in a certain way and why data looks the way it does, etc.) will increase your knowledge and comfort with the techniques shown. This will help with completion of homework assignments and allow you to implement techniques in your own research.

Introduction/Overview

Two weeks ago you learned how to fabricate most of the electrodes that are needed throughout the course and used some of them to perform cyclic voltammetry experiments. This week, you will use these electrodes to perform cyclic voltammetry experiments and chronoamperometry experiments – with varying concentrations of supporting electrolyte – to determine the $R_u C_{dl}$ time constant for charging the double layer (dl) at an electrode|solution interface, the iR_u drop due to uncompensated resistance (R_u) between the WE and RE, and the mass-transport-limited current density at the WE.

Purpose

The purpose of this hands-on discussion activity is to become more familiar with the processes of diffusion, migration, and convection in electrochemical measurements. First, you will determine the RC time constant for charging a carbon button electrode as a function of the concentration of supporting electrolyte. Then, using your platinum microelectrode, you will determine the iR drop in solution between your WE and RE and the mass-transport-limited current density for a Faradaic reaction at your WE as a function of the concentration of supporting electrolyte. This activity will provide you with opportunities to apply conclusions based on the Nernst–Planck equation and will

introduce you to common effects that mass transfer has on rather standard electrochemical experiments.

Safety

For each hands-on discussion session you must bring and wear personal protective equipment consisting of a lab coat and safety glasses/goggles. In addition, at a minimum you must wear closed-toe shoes, pants, and a tee-shirt that covers your entire torso. While in lab you will also need to wear gloves, which we will supply as nitrile gloves. In addition, to reduce the possibility of electric shock to you and your labmates be sure to control the correct channel of the potentiostat and that all persons are away from the experimental apparatus before starting an electrochemical experiment. Moreover, you would not touch the electrodes while a potential bias is being applied between them, especially the counter electrode.

Procedures (*Note: The final experiment in this activity uses electrochemical impedance spectroscopy (EIS); however, channels 1 and 2 are the only channels that have the electronic components necessary to perform EIS measurements. Thus, channel 1 should not be used by any group, except to perform EIS measurements, and channel 2 should be used by a group that has rapidly completed the prior hands-on discussion activities.*)

Part A: Determining the RC time constant at an electrode interface

Tools/materials needed: ~50 mL beaker, stir bar, rubber bands, *polished* carbon button electrode, Ag/AgCl (salt sat'd) reference electrode, carbon cloth counter electrode, aqueous solutions of K_2SO_4 (0.1 mM, 1mM, 10 mM, 100 mM)

- (1) Set-up a three-electrode electrochemical cell in a clean beaker and then fill the beaker with ~15 mL of the most dilute aqueous electrolyte solution (0.1 mM K_2SO_4). Perform the following electrochemical measurements, *without stirring*.
 - a. OCV: for 30 seconds, recording the potential every second
 - b. CA: apply 0.2 V vs RE for ~**60 sec**, recording average current every **0.1 sec**
 - c. Repeat the CA measurement, with stirring
- (2) Replace the solution with the next most concentrated solution (i.e. 1 mM K_2SO_4) and perform the same measurements, but only perform CA for ~**30 sec**, recording every **10 ms**.
- (3) Replace the solution with the next most concentrated solution (i.e. 10 mM K_2SO_4) and perform the same measurements, but only perform CA for ~**5 sec**, recording every **400 μ s**.
- (4) Replace the solution with the most concentrated solution (i.e. 100 mM K_2SO_4) and perform the same measurements, but only perform CA for ~**2 sec**, recording every **200 μ s**.

Part B: Determining the iR drop in solution and mass-transport-limited current at an electrode

Tools/materials needed: ~50 mL beaker, stir bar, rubber bands, *polished* platinum microelectrode, Ag/AgCl (salt sat'd) reference electrode, carbon cloth counter electrode, aqueous solutions of K_2SO_4 each with 0.5 mM ferricyanide/ferrocyanide (0 mM, 1 mM, 10 mM, 100 mM)

- (1) Set-up a three-electrode electrochemical cell in a clean beaker and then fill the beaker with ~15 mL of deionized water containing salts of 0.5 mM $[Fe^{III}(CN)_6]^{3-}$ and 0.5 mM $[Fe^{II}(CN)_6]^{4-}$. Perform the following electrochemical measurements, *with vigorous stirring*. *Note:* Stir just beneath the microelectrode surface to obtain the best data and only submerge the cloth portion of your counter electrode in the electrolyte.
 - a. OCV: for 30 seconds, recording the potential every second
 - b. CV: sweep between -100 mV and 600 mV vs RE at a scan rate of 10 mV/s for several reproducible sweeps
- (2) Repeat the procedure for each of the other three aqueous electrolyte solutions, in increasing order of concentration of K_2SO_4 .
- (3) For the final condition that used aqueous 100 mM K_2SO_4 , stop stirring, and then perform a potentiostatic electrochemical impedance spectroscopy (PEIS) measurement using the parameters shown in the image below.

Excitation signal mode: Single sine

Set E_{we} to $E = 0.0000$ V vs. E_{oc}

for $t_E = 0$ h 0 mn 0.000 s

Record every $dl = 0.000$ mA

or $dt = 1.000$ s

Scan from $f_i = 50.000$ kHz to $f_f = 100.000$ mHz

with $N_d = 6$ points per decade

in Logarithmic spacing

sinus amplitude $V_a = 10.0$ mV ($V_{rms} \sim 7.07$ mV)

wait for $p_w = 0.10$ period before each frequency

average $N_a = 2$ measure(s) per frequency

drift correction

Repeat $n_c = 0$ time(s)

Limits

E Range = -1V:1V

Resolution = 50 μ V

I Range = Auto

Bandwidth = 8

(~ 1mn29s / scan)

applied bias potential

equilibration time of DC bias before experiment

maximum and minimum frequencies to scan (lower frequencies take more time)

number of points per decade of frequencies

amplitude of AC perturbation from applied DC bias

time taken per EIS experiment

Assignment 3 – Lab 4 (combined with next week's activity; due on Monday, November 6, 2023 at noon) (You must show your work for credit on all problems.)

1. Using the data provided to you for Lab #4, or your own data if your laboratory experiments were successful, do the following.
 - a. Part A: CA Data
 - i. Submit one plot of your CA data containing four different labeled datasets each obtained for a different concentration of supporting electrolyte and each containing the no stirring and stirring condition for the given concentration. Transform the y -axis to a logarithmic scale, which is straightforward to do using Excel or EC-Lab.
 - ii. Explain why we expect the trends in the datasets plotted in **part i** to be linear, indicating the process that is responsible for this linear behavior.
 - b. Part B: CV and EIS Data
 - i. For each CV dataset, indicate which one or two processes are likely dictating the slope of the data near the x -intercept and whether the concentration of supporting electrolyte is influencing the slope of the data.
 - ii. For the CV data obtained using the smallest concentration of supporting electrolyte, the current at extreme polarization biases was not solely limited by diffusive mass transport. What type of flux also contributed to these mass-transport-limited currents and how should it have affected each of the cathodic and anodic mass-transport-limited currents?
 - iii. For the CV data obtained using the largest concentration of supporting electrolyte, explain the cause of the significant positive shift in the value of the x -intercept in comparison to the other conditions measured. Also, using the EIS data, approximate the value of the high-frequency x -intercept of the Nyquist plot (*Google it*) as the series resistance in your cell and using that value and the CA data measured using the same concentration of supporting electrolyte, approximate the value of the interfacial capacitance.