INTERFACIAL CAPACITIVE CHARGING, UNCOMPENSATED RESISTANCE, AND MASS TRANSPORT LIMITS

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

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

1. Briefly review the experiments, their goals, and any updates to the hands-on activities
2. Break into groups of two or three, set-up each workspace, and make a connection between a laptop running Windows and the BioLogic potentiostat using the EC-Lab software
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 future changes
5. Clean-up each workspace, return items used, 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 and save and/or print procedures and reference publications/files before you watch the experimental pre-lab 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 (e.g. by actively asking yourself questions as to why the experiment is set up in a certain way, why data looks the way it does, etc.) will help to increase your knowledge and comfort with the techniques shown. This will then help you to successfully complete homework assignments and implement techniques in your own research.

Introduction

Two laboratory activities ago you learned how to fabricate most of the electrodes that are needed throughout the course and (ideally) how they can be used 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_uC_{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-transfer-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-transfer-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 evaluate concepts inherent to the Nernst–Planck equation and will introduce you to common observations resulting from mass transport that occur in some common 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 shirt that covers your entire torso, or else you will not be allowed to enter the lab. While in the 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 should never touch any of the electrodes while the potentiostat is applying a potential bias, 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, ideally, 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: ~10 mL beaker, stir bar, stir plate, *polished* carbon button electrode, Ag/AgCl (salt sat'd) reference electrode, carbon cloth counter electrode, aqueous solutions of K_2SO_4 (each containing 0.1 mM, 1 mM, 10 mM, and 100 mM)

(1) Set-up a three-electrode electrochemical cell using a pre-rinsed vial or small beaker half-filled with the most dilute aqueous electrolyte solution (i.e. 0.1 mM K_2SO_4). Perform the following electrochemical measurements, *without stirring*. (Note: Only submerge the cloth portion of your counter electrode in the electrolyte.)
    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 µs**.
(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 µs**.

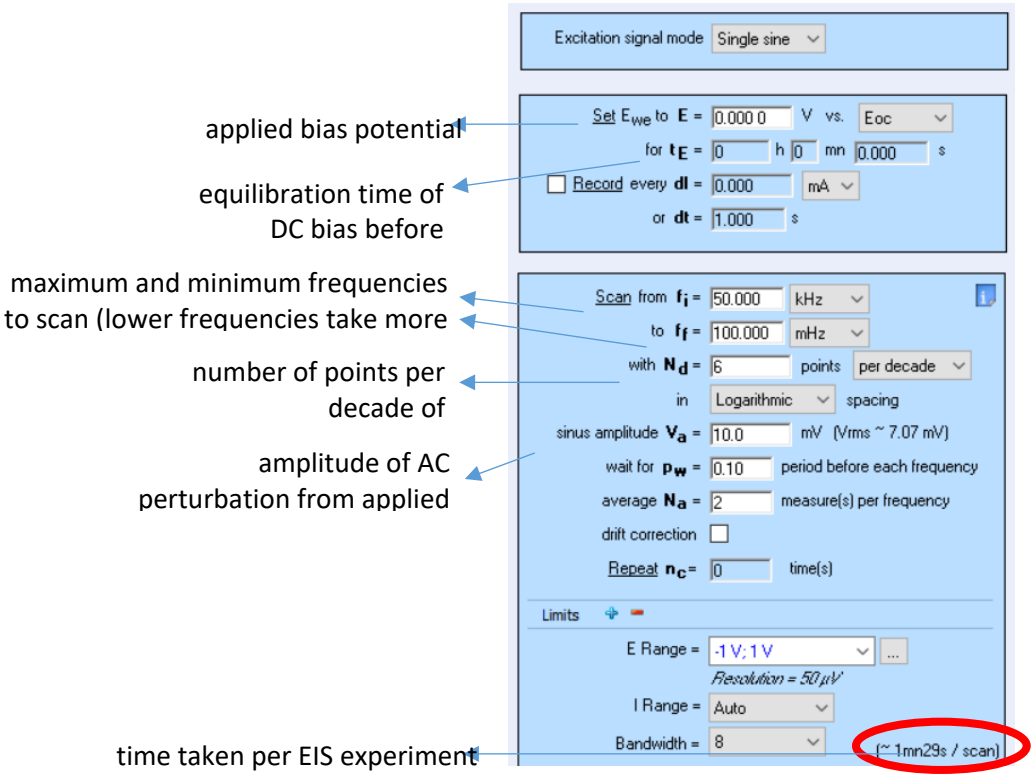
Part B: Determining the *iR* drop in solution and mass-transfer-limited current at an electrode

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

(1) Set-up a three-electrode electrochemical cell using a pre-rinsed vial or small beaker half-filled with aqueous solutions consisting 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, again, 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.*



Assignment 3 – Lab 4 *(combined with next week's activity; due on Wednesday, November 18, 2026 at noon)* (You must show your work for credit on all problems.)

1. Either 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-transfer-limited currents *and* how should it have affected each of the cathodic and anodic mass-transfer-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.