

ELECTROCATALYSIS OF VARIOUS REACTIONS

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

Thus far in the hands-on discussion sessions you have seen how we perform measurements where the resulting currents were not limited by electron-transfer kinetics across the electrode–solution interface, and instead were often limited by iR drop or diffusive mass transfer in solution. This week you will perform experiments that intentionally operate, at least in part, under conditions where the current is limited by the kinetics of electron transfer across the electrode–solution interface.

Purpose

The purpose of this hands-on discussion activity is to become more familiar with scenarios where electrocatalysis dominates the observed current–potential behavior and the data can be analyzed by the Current–Overpotential equation, Butler–Volmer equation, and Tafel plots. You will measure the effects of three reactions (ferricyanide/ferrocyanide redox chemistry, H_2 evolution via proton reduction, and O_2 evolution via hydroxide/water oxidation) and you will analyze the observed behavior to determine values for electrocatalytic parameters. This activity will provide you with a better understanding of the limiting regimes observed during measurement of electrocatalytic behavior and how to analyze and correct measured data in order to isolate behavior due to kinetic processes and quantify approximate kinetic parameters.

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, do not touch the electrodes while a potential bias and/or an electronic current is being applied between them, especially the counter electrode. Caution: The acidic and basic electrolyte solutions used in this activity are corrosive and/or caustic and therefore, you should use caution when handling them, especially when vigorously stirring. If skin or eye contact occurs, you should immediately flush them with copious amounts of water for at least 15 minutes and notify someone.

Procedures

Part A: Analysis of redox shuttle and hydrogen evolution electrocatalysis at platinum

Tools/materials needed: ~50 mL beaker, stir bar, platinum microelectrode working electrode, Ag/AgCl (KCl sat'd) reference electrode, carbon cloth or carbon rod counter electrode, aqueous electrolyte solution containing 500 mM K₂SO₄ and (1) 10 mM [Fe^{III/II}(CN)₆]^{3-/4-} and (2) at pH 1

- (1) Set-up a **three-electrode** electrochemical cell in a clean beaker and then fill the beaker with ~25 mL of the **iron-containing** aqueous electrolyte solution. Perform the following electrochemical measurements, **with vigorous stirring**.
 - a. OCV: for 30 seconds, recording the potential every second
 - b. CV: sweep between -0.2 V and 0.7 V vs RE at a scan rate of 10 mV/s for several reproducible sweeps, *and then expand the scan window to -1.2 V vs RE for several more reproducible sweeps*
 - c. PEIS: $E_{DC} = E_{oc}$, $E_{AC} = 10$ mV, 1 MHz – 0.1 Hz, 10 pt/decade
- (2) Repeat the procedure in step #1 for the pH 1 aqueous electrolyte solution, with no iron present.
- (3) Dilute this solution by a factor of 10 with high-purity water and repeat the procedure.
- (4) Dilute this solution by another factor of 10 with high-purity water and repeat the procedure again.

Part B: Analysis of oxygen evolution at a Ni–Fe oxide electrocatalyst

Tools/materials needed: two ~50 mL beakers, stir bar, ~ 4 cm x 2 cm piece of FTO glass, parafilm, Ag/AgCl (KCl sat'd) reference electrode, carbon cloth or carbon rod counter electrode,

aqueous nickel–iron catalyst precursor electrolyte solution (0.1 M Ni^{II}SO₄ + 2 mM Fe^{II}SO₄), aqueous electrolyte solution of 1 M KOH, high-purity water

- (1) Take the FTO glass and wrap a portion of it with parafilm so that a controlled rectangular area of 2.0 cm x 1.5 cm is exposed. Use a ruler to quantify the actual geometric dimensions of the exposed region.
- (2) Set-up a **two-electrode** electrochemical cell in a clean beaker and then fill the beaker with ~25 mL of the **Ni–Fe-containing** electrolyte solution making sure that the exposed part of your FTO glass electrode is fully submerged in the electrolyte. Perform the following electrochemical measurements to electrodeposit the electrocatalyst, **without stirring**.
 - a. OCV: for 30 seconds, recording the potential every second
 - b. CP: pass -2 mA/cm² for ~120 sec, recording the potential every second
- (3) Gently wash the FTO electrode that is covered in Ni_xFe_yO_zH catalyst in high-purity water to rinse off precursor species and loosely bound materials.
- (4) Set-up a **three-electrode** electrochemical cell in a clean beaker and with clean electrodes then fill the beaker with ~25 mL of the **alkaline** electrolyte solution making sure that the exposed part of your Ni_xFe_yO_zH catalyst-covered FTO electrode is fully submerged in the electrolyte. Perform the following electrochemical measurements, **with vigorous stirring**.
 - a. OCV: for 30 seconds, recording the potential every second
 - b. CV: sweep between -0.2 V and 0.7 V vs RE at a scan rate of 10 mV/s for several reproducible sweeps
 - c. PEIS: $E_{DC} = E_{oc}$, $E_{AC} = 10$ mV, 1 MHz – 0.1 Hz, 10 pt/decade

Assignment 4 – Lab 7 (combined with last week's activity; due on Monday, November 27, 2023 at noon) (You must show your work for credit on all problems.)

1. Using the data provided to you for Lab 7, or your own data if your laboratory experiments were successful, do the following.
 - a. Part A: H₂ Evolution CV Data
 - i. Submit a Tafel plot of your data obtained in the presence of iron and label each region where the observed current was dominated by electrocatalysis or mass transfer. Also, what redox reaction(s) occurred near $E_{app} = -1.2$ V?
 - ii. Submit one Tafel plot of your data containing three different labeled datasets for H₂ evolution. Also, calculate the Tafel slope and the exchange current density for your data obtained during H₂ evolution at pH 1.
 - b. Part B: O₂ Evolution CV Data
 - i. Submit a Tafel plot of these data and indicate on the plot the theoretical reversible standard-state potential for the O₂ evolution reaction. Also, explain whether electrodeposition of Ni_xFe_yO_zH could have been performed using a three-electrode setup.