ELECTROCATALYSIS OF VARIOUS REACTIONS

General Schedule and Comments (this text is the same text that was in the Lab 2 document)

In general, the format for this class 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 Bio-Logic potentiostat using the EC-Lab software on a PC laptop
3. Perform experimental procedure(s), while being assisted by the TA and the Professor
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 section until this is complete.)

Since your discussion section is short (110 minutes) and we want to cover as much as possible, please use your time wisely by getting started promptly and working efficiently. NOTE: You will need to save or print procedures and reference publications/files before you attend the hands-on discussion sections. This will help you to become acquainted with the experiments and more importantly, will allow you to stay connected to the potentiostat as you run the experiments, because there are sometimes issues when the Internet and the potentiostat are used simultaneously.

Introduction

Thus far in this course you have performed 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 transport 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 perform three reactions (ferricyanide/ferrocyanide redox chemistry, $H_2$ evolution via proton reduction, and $O_2$ evolution via water oxidation) and 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 kinetic parameters.
Safety

To each hands-on discussion section you must bring 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. Attendance at these hands-on discussion sections are mandatory so please do not get a grade of a zero due to improper lab attire. While in lab you will need to wear gloves, which we will supply as nitrile gloves. In addition, do not touch the electrodes while a potential bias is being applied between them, especially the counter electrode. The acidic and basic electrolyte solutions used in this activity are corrosive and/or caustic and therefore, please use caution when handling them, especially when vigorously stirring. If skin or eye contact occurs, immediately flush with copious amounts of water for at least 15 minutes and notify the TA/Professor.

Procedures

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

Tools/materials needed: ~50 mL beaker, stir bar, rubber bands, 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 [Fe⁷⁺/II(CN₆)₃⁴⁻] 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.
   a. OCV: for 30 seconds, recording the potential every second
   b. CV: with vigorous stirring, 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 (share channels/data): $E_{DC} = E_{oc}$, $E_{AC} = 10$ mV, 0.1 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, silica glass slide with a photoresist covered gold working electrode (~2 cm x 0.5 cm), Ag/AgCl (KCl sat’d) reference electrode, carbon cloth or carbon rod counter electrode, aqueous nickel–iron catalyst precursor electrolyte solution (0.1 M NiNO$_3$ + 1.0 M KNO$_3$), aqueous electrolyte solution of 1 M KOH, high-purity water

1. Take the photoresist covered gold slide and use a Q-tip dipped in acetone to wipe away the photoresist, making the exposed gold square. Make a 0.5 cm x 0.5 cm gold working electrode, using a ruler to measure the actual dimensions of the exposed surface area.
2. Expose some more gold on the opposite side of the gold electrode, which will act as the contact for the working electrode.
3. 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 gold electrode is fully immersed in the electrolyte. Perform the following electrochemical measurements to electrodeposit the electrocatalyst.
   a. OCV: for 30 seconds, recording the potential every second
   b. CP: pass ~2 mA/cm$^2$ for ~120 sec, recording the potential every second
4. Gently wash the Ni$_x$Fe$_y$O$_z$H catalyst covered gold electrode in high-purity water to rinse off precursor species and loosely bound materials.
5. 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$_x$Fe$_y$O$_z$H catalyst covered gold electrode is fully immersed in the electrolyte. Perform the following electrochemical measurements.
   a. OCV: for 30 seconds, recording the potential every second
   b. CV: **with vigorous stirring**, 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 (**share channels/data**): $E_{DC} = E_{oc}$, $E_{AC} = 10$ mV, 0.1 MHz – 0.1 Hz, 10 pt/decade

**Assignment** *(combined between this and the prior week’s activity; due Tuesday, May 28, 2019 at the start of the lecture class)*; in the meantime, begin to analyze your data as Tafel plots (log|$I$| vs $E$), because for the next assignment you will be required to interpret your data in the context of electron-transfer kinetics and related information that we discussed during the lecture classes.