ELECTROCATALYSIS OF VARIOUS REACTIONS

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

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. As a class, discuss the activity, provide feedback, 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. 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 with using the Internet and the potentiostat 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. 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 (electro)catalysis 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, $\text{H}_2$ evolution via proton reduction, and $\text{O}_2$ evolution via water oxidation) and analyze the observed behavior to determine values for electrocatalytic, and other, 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 the data in order to isolate kinetic processes and quantify kinetic parameters.
Safety

You must bring personal protective equipment to the lab (i.e. lab coat and safety glasses/goggles). You must wear closed-toe shoes, pants, and a tee-shirt that covers your entire torso to be allowed to work in the hands-on discussion sections. These sections are mandatory so please do not get a zero due to improper lab attire. While in lab you will need to wear gloves, which we will supply (nitrile gloves). To reduce the possibility of electric shock to you and lab mates be sure you are working on 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 is being applied between them. *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 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 of 500 mM K$_2$SO$_4$ (1) with 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** 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**

(2) Repeat the procedure for the **acidic** electrolyte solution (with no iron present)

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

**Tools/materials needed:** two 50 mL beakers, stir bar, rubber bands, silica glass with a thin layer of conductive fluorine-doped tin oxide (FTO) working electrode (~1 cm x 1 cm), Ag/AgCl (KCl sat’d) reference electrode, carbon cloth or carbon rod counter electrode, aqueous nickel–iron catalyst precursor electrolyte solution, aqueous electrolyte solution of 1 M KOH

(1) 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 your FTO electrode is immersed in the electrolyte ~0.5 cm deep. Perform the following electrochemical measurements to electrodeposit the electrocatalyst, **without stirring**.

a. OCV: for 30 seconds, recording the potential every second
b. CP: pass 50 μA for ~120 sec, recording the potential every second
(2) Gently dip the FTO electrode in deionized water to rinse it

(3) Set-up a three-electrode electrochemical cell in a clean beaker and then fill the beaker with ~25 mL of the alkaline electrolyte solution making sure that your FTO electrode is only immersed in the electrolyte ~2 – 3 mm deep. 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

Assignment (assigned with last week’s activity; due Tuesday, March 14, 2017 at 8 am PST).

For the next assignment you will be required to interpret your data. Therefore, it is advantageous to plot your data as log|I| vs E and think about your results and discuss them with others in the context of electron-transfer kinetics.