Experiment 1B

Electrode Kinetics

Experiment Overview

When one sets the potential of an electrode away from the equilibrium potential, a current flows. The amount a potential deviates away from equilibrium is called the overpotential. For a given overpotential, the magnitude of current flow can depend on a number of factors, including the charge transfer rate between solution species and the electrode (called electrode kinetics), and mass transfer by diffusion, convection, and migration. Positive overpotentials (*i.e.* potentials positive of equilibrium) cause oxidation reactions on the electrode, whereas negative overpotential cause reduction reactions to occur. In this experiment, you will explore the regime where electrode kinetics limit the current flow. For the kinetics-limited regime, current flow is often described by the Butler-Volmer equation or the linearized Butler-Volmer equation. Experiment 1B will allow you to evaluate kinetic rate parameters for a reaction using a linearized Butler-Volmer rate law.

Background Theory

Most electrochemical systems with high conductivity electrolytes display current vs. potential curves that look like Fig. 1. Three regions are shown in Fig. 1. The equilibrium potential ($E=E_{eq}$ @ $I=0$) sets the potential scale so we can know whether a given potential will cause an oxidation or a reduction reaction. If the electrode potential is set more positive than the equilibrium value, then an oxidation reaction will occur on the electrode. In ChemE 461, we denote oxidation by a positive current. Conversely, if the electrode is set negative of the equilibrium potential, then a reduction reaction will occur on the electrode, denoted by a negative current. (Important Note: your textbook uses the opposite convention—positive current to denote reduction, negative current to denote oxidation.)
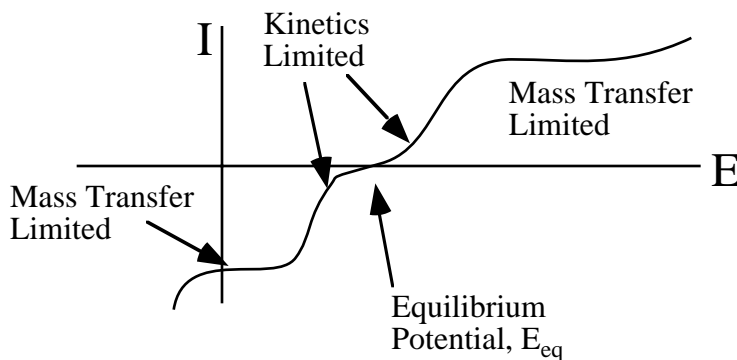

Figure 1. Schematic of typical current vs. potential behavior for an electrochemical system with high conductivity electrolyte.

At modest deviations away from equilibrium the current is often determined by the charge transfer kinetics at the electrode. While at large deviations from equilibrium, the rate that reactant is transported by convection and diffusion often limits the current. (If the conductivity of the electrolyte is not high, then ionic migration often dictates the current flow.)

The deviation away from equilibrium is called the overpotential (η),

$$\eta = E - E_{eq} . \tag{1}$$

Within the kinetics-limited regime, a common form for the current-potential relationship is called the Butler-Volmer Equation

$$j = j_o (e^{(1-\alpha)nf\eta} - e^{-\alpha nf\eta}) , \tag{2}$$

where j is the current density (current per unit area, A/cm^2), j_o is the exchange current density (A/cm^2), α is the transfer coefficient, n is the number of electrons transferred, and f= F/RT. Equation (2) can be written in terms of total current, I, as the class text does, simply by multiplying both sides by the area. Equation (2) can be linearized when $\alpha nf\eta \ll 1$, to get the expression

$$j = j_o nf\eta . \tag{3}$$

Equations (2) and (3) only hold for the region where the current is less than or equal to $\approx$10% of the mass transfer limited current. At higher fractions of the mass transfer limiting current, the rate of reaction is influenced by both the mass and charge transfer rates (called mixed control).

Experimental Procedure

This experiment will use sulfate-based electrolyte with 10 mM Fe^{+2} and Fe^{+3} in 1 M H_2SO_4. The reaction occuring on the electrode is

$$Fe^{+3} + e^- = Fe^{+2} , \tag{4}$$

where the sulfuric acid acts as an inert component that raises the conductivity of the electrolyte (sulfuric acid is called the supporting electrolyte). The reaction will proceed in the forward or backward direction, depending upon which direction the potential of the electrode is biased away from equilibrium (i, the sign of the overpotential). All potentials will be measured relative to a saturated calomel electrode (SCE) as the reference. In this experiment, you are going to determine the exchange current density for reaction (4) by fitting experimental data to Eq. (3).

Acquiring high quality data suitable for a kinetic analysis requires an extremely clean electrode. Any impurities in the electrolyte that adsorb to the electrode will likely alter the rate of charge transfer across the interface. Therefore, we will employ an electrochemical cleaning step prior to collecting the data point. One way to try variations on this experiment is to neglect electrode cleaning, and see how that affects the results.

Given below are operating procedures for making the experiments run. You should always be prepared to modify the instrument settings and experimental conditions to improve the results you get. Don't hesitate to "play around" and figure out how the instruments work. You will have plenty of time with this experiment. If you are concerned that you might break something, or don't understand the interplay between instrument and experiment, then ask for assistance.

ELECTRODE CLEANING USING THE PAR 363 POTENTIOSTAT WITH COMPUTER CONTROL (Starting with everything but the power turned OFF)
(1) Carefully immerse Pt working electrode, Pt counter electrode, and SCE Reference Electrode in electrolyte, making sure to keep Pt working electrode from bumping against the cell sides or bottom. Make sure the CELL switch on potentiostat is OFF before doing this.
(2) Connect the Platinum Working Electrode to the Green Lead. The elctrode should have a 0.5 cm diameter Pt disk at the end. Check to make sure that is the electrode you have.
(3) Connect the SCE Reference Electrode to the lead with micro banana plug
(4) Connect the Pt Counter electrode to the Red Lead
(5) Start the stirrer motor and set to a moderate level of mixing. Make sure the Working Electrode is close to the stir bar so you have good mixing near the electrode surface.
(6) On potentiostat, set the MODE switch to CONTROL E, set the METER to I ±1V f.s., set the CURRENT RANGE to 1 mA, and set the INITIAL POTENTIAL to 0.000. Make certain the BNC connector from the computer D/A board is plugged into the EXTERNAL INPUT on front of potentiostat.
(7) On the computer screen, set CONTROL TYPE to POTENTIOSTAT, set DISK CURRENT CONVERTER to 1 mA/V, set SWEEP TYPE to CYCLIC VOLTAMMOGRAM, set EQUILIBRIUM POTENTIAL to +430, set SWEEP MAXIMUM to +1675, set SWEEP MINIMUM to –275, set CV SWEEP RATE to 100, set NUMBER OF SWEEPS to 20, set SAVE EVERY Nth to 20.
(8) Run Computer Program
(9) After you verify source curve on computer, turn CELL ON on potentiostat
(10) Cleaning protocol will run for about 13 minutes. The data saved on disk can be used to see how clean the electrode was, and to determine what the mass transfer limiting current is for the stirred beaker.
(11) Turn CELL to OFF.
(12) Disconnect the BNC cable from the EXTERNAL INPUT on front of potentiostat.
(13) Quickly proceed to the next steps. Once cleaning is finished, the electrode immediately begins to slowly accumulating gunk on the surface, which can affect the reproducibility of the results.

After cleaning the electrode, you should immediately determine the equilibrium potential of the system as accurately as possible. Make sure the meter button is set to display current (1 V equals ±CURRENT RANGE setting on potentiostat). To do this, first set the INITIAL POTENTIAL to +0.450, and set CURRENT RANGE to 1 mA. Then, turn CELL to ON and make changes to the INITIAL POTENTIAL value until the meter reads 0. Next, set CURRENT

RANGE to 100 µA and tweak the INITIAL POTENTIAL until the meter is nulled again. Finally, set CURRENT RANGE to 10 µA and tweak the INITIAL POTENTIAL until the meter is nulled again (if it is sufficiently stable for you to do this). Once the meter is nulled, the value showing on the INITIAL POTENTIAL is your equilibrium potential. Now you are ready to make a kinetic measurement.

KINETIC MEASUREMENTS USING THE PAR 363 POTENTIOSTAT

(1) Set CURRENT RANGE on potentiostat to 1 mA
(2) Set a digital voltmeter (DVM) to measure D.C. Volts and plug it into the CURRENT MONITOR on front of the Potentiostat. The output from the CURRENT MONITOR is a potential, where the measured potential is related to the current by the CURRENT RANGE setting (*e.g.,* measuring ± 0.5 volts means the actual current is $\pm 0.5*$CURRENT RANGE setting) If you deem it more convenient, you can just use the Meter on the front of the potentiostat instead of the DVM (make sure it is set to measure I).
(3) Check to make sure the initial reading is nearly zero, if not tweak Initial Potential to get it as close as possible.
(4) Change INITIAL POTENTIAL in increments of ± 0.005 and write down the reading from the meter or DVM. If the meter deflects only a tiny bit, change CURRENT RANGE to 100 µA and repeat.
(5) Repeat items (1)-(4) until you have data that goes from 0.075 V below equilibrium to 0.075 V above equilibrium.
(6) Return INITIAL POTENTIAL to equilibrium, and repeat procedure but this time get more data within $\pm$ 15 mV of the equilibrium potential (e.g., make smaller increments as you change potential away from equilibrium.
(7) Turn CELL to OFF.

There are all kinds of variations you will now have time to complete. For example, let the Working Electrode sit for different amounts of time after cleaning, and then retake the the kinetic measurements. Are they the same? Do they change in a systematic manner? Can you repeat the cleaning cycle and recover your initial results? Doe scleaning longer change the results further? Take time to explore some or all of these questions.