

Laboratories 8-10
Electrochemical Investigation of SAM's

Laboratory 9 Investigation of the Permeability of Alkanethiol Monolayers

This lab aims at using electrochemistry to expose the defects (or lack thereof) in self-assembled monolayer films. You will employ two techniques: cyclic voltammetry and electrochemical impedance spectroscopy. Cyclic voltammetry is the workhorse of electrochemistry, but impedance spectroscopy is a less perturbing technique, as only small (5 mV) sinusoidal voltages are applied. In many cases, equivalent circuit models make impedance data simpler to interpret and understand.

Electrochemical Equivalent Circuits and Impedance Measurements

In laboratory 8, we discussed systems in which only charging current occurs. Such a system can be represented as a capacitor. In fact, even in those systems, a solution resistance is present and the equivalent circuit would be a resistor and capacitor in series. We ignored the solution resistance because when current is constant, the potential drop across the solution is also constant. Thus at steady-state, dV/dt is independent of the resistor.

In this lab, we begin to consider systems in which charge transfer can occur between the electrode and solution as shown in Figure 1. This leads us to a more complicated system and the equivalent circuit (Figure 1) now contains solution resistance (R_{soln}), the double-layer capacitance (C_{dl}) and charge-transfer resistance (R_{ct}) in

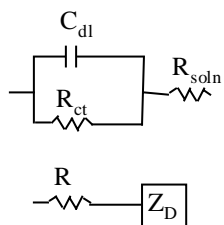


Figure 2. Simplified equivalent circuits for electron transfer processes at high frequencies (top) and low frequencies (bottom).

series with a diffusional impedance (Z_d). (For charge transfer to occur the redox couple must be able to get to the surface, thus the diffusional impedance). The impedance of this circuit is a fairly complicated expression.

Fortunately, by varying frequency, we can simplify the circuit. At high frequency, diffusion is not an issue so we can remove this circuit element as shown in Figure 2. At low frequency, the capacitor behaves as an open circuit, and the circuit becomes diffusional impedance in series with a resistor. (The resistor is actually the sum of the solution resistance and charge-transfer resistance.)

Now that you have some understanding of equivalent circuits, we will consider how to obtain information from them. Normally, we make a plot of the negative of imaginary impedance versus real impedance. Typically this yields a plot such as that shown in Figure 3. High frequencies result in a semicircle region, while low frequencies yield a linear regime. At high frequencies diffusion is not an issue so the circuit becomes that shown at the bottom of Figure 3. We will show in class that such a circuit should yield a semicircular plot. At low

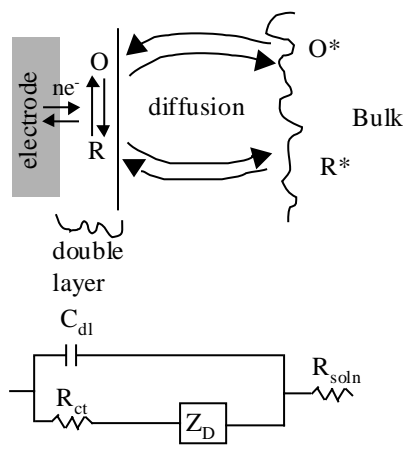


Figure 1. Electrochemical system that includes electron transfer along with its equivalent circuit.

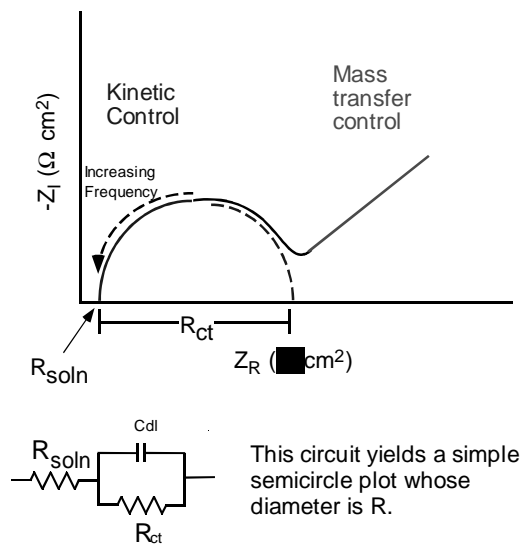


Figure 3. Impedance plot for a typical electrode solution interface when a redox couple is present.

frequencies, the capacitor behaves as an open circuit so the entire system can be described as a resistor in series with diffusional impedance (Figure 2).

The semicircular region is worth considering further. The left intersection of the semicircle with the x-axis is the value of the solution resistance. The diameter of the semicircle is equivalent to the charge-transfer resistance. At the top of the semicircle, the angular frequency is equal to the reciprocal of $R_{ct}C_{dl}$. Why will explore in class why these relationships hold.

Although diffusional impedance is beyond the scope of this class, it results in a linear region in the plot. Equation 1 describes this region. If one extrapolates the linear region to zero on the x-axis, you get an intercept of $R_{soln} + R_{ct} - 2\sigma^2 C_{dl}$. Assuming that the diffusion coefficients of the oxidized and reduced species are the same and their concentrations are the same, one can calculate the diffusion coefficient from equation 2. Of course you have to obtain values of

$$Z_{Im} = Z_{Re} - R_{soln} - R_{ct} + 2\sigma^2 C_{dl} \quad 1$$

$$\sigma = \frac{RT}{n^2 F^2 A \sqrt{2}} \frac{2}{D^{1/2} C^*} \quad 2$$

R_{soln} , R_{ct} , and C_{dl} to obtain a value of σ . In equation 2, R is the gas constant, T is temperature, n is the number of electrons transferred, A is electrode area, D is the diffusion coefficient, and C^* is the bulk concentration of each of the redox species. By looking at both the linear and semicircular portions of an impedance plot, one can obtain an enormous amount of information about the electrochemical system.

The model that we will use for a monolayer-coated electrode is that of an impermeable film with defects (Figure 4). This is similar to the model in the last laboratory except that in this case we have a redox couple so there will be electron transfer at the defects. We assume that no electron

transfer occurs at the monolayer-coated areas. The equivalent circuit at high frequencies will be that shown in Figure 2 (top) except that the capacitance will actually be the sum of the monolayer and defect capacitances. (The monolayer and double-layer capacitances are in parallel so the total capacitance due to these two parallel capacitors is simply the sum of the two capacitances. See laboratory 8 if you wish to refresh your memory.) To calculate the defect

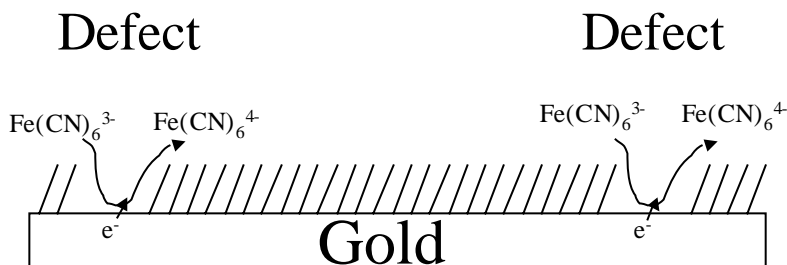


Figure 4. Model of electron transfer at a monolayer that contains defects.

area, we assume that the charge transfer resistance/area in the defects is the same as that at bare gold. This yields equation 3 where θ is the fraction of the surface that is covered by the monolayer, R_{ct}^0 is the charge-transfer resistance of bare gold, and R_{ct} is the charge-transfer

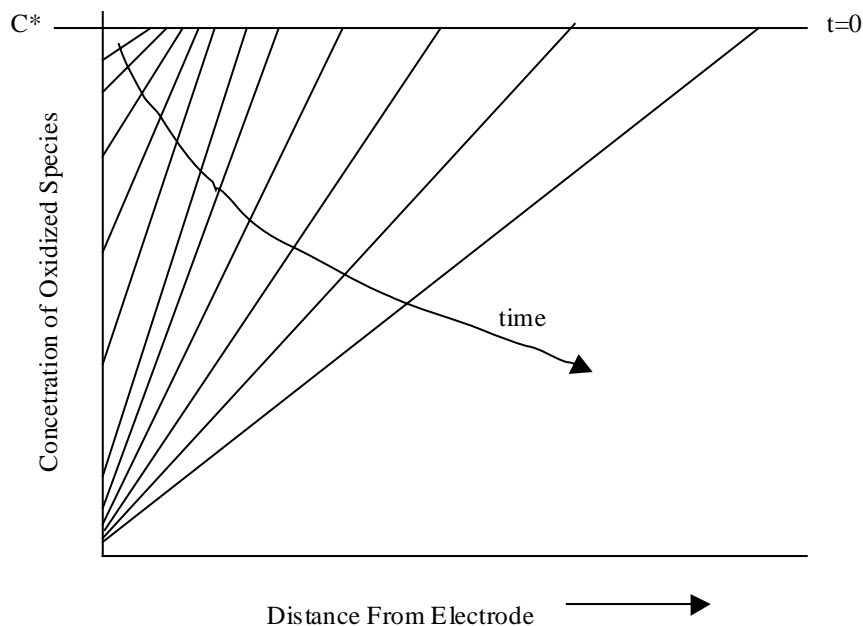
$$(1 - \theta) = \frac{R_{ct}^0}{R_{ct}} \quad 3$$

resistance of the monolayer-coated electrode. You can determine the R_{ct} values from the diameters of the semicircles. As you can see, impedance provides a rather straightforward method for estimating the surface coverage. Note, however, that we made several assumptions.

Cyclic Voltammetry

You were already exposed to cyclic voltammetry in laboratory 8, but now we add a redox couple and the situation becomes much more complicated. In fact, we are going to ignore charging current for a while and assume that current is due to electron transfer. Electron-transfer rates depend on two things: the kinetics of electron transfer and the amount of the redox species that can reach the surface. For $\text{Fe}(\text{CN})_6^{3-/4-}$, the kinetics of electron transfer are reasonably fast, so we will assume at least for the moment that at the surface, the concentrations of $\text{Fe}(\text{CN})_6^{3-}$ and $\text{Fe}(\text{CN})_6^{4-}$ can be described by the Nernst equation. Even with this assumption, faithful reproduction of the voltammogram requires an analytical solution to two differential equations. Thus we will give you a qualitative feel for cyclic voltammetry and introduce quantitative aspects without proof. (The details of CV simulations can be found in *Anal. Chem.*, **1964**, 36, 706 and *Anal. Chem.* **1965**, 37, 1351.)

First for the qualitative, pictorial explanation. If we assume that concentrations at the surface are governed by the Nernst equation, the concentration of the oxidized species at the surface will decrease as the potential becomes more negative. (See Figure 5). A lower concentration at the surface gives a higher concentration gradient (at least initially) so according to Fick's law of diffusion (the equation in Figure 5), we will have more flux to the surface and hence a higher cathodic current. As we



$$i = nFAJ \quad J = -D(dC/dx) \cong D(C^* - C_{x=0})/\Delta x$$

Figure 5. Crude concentration profiles at different time in a CV experiment (only the negative scan is shown). The equations are approximate forms of the current for the system.

continue to make the potential more negative, the concentration at the surface will eventually go to zero. Simultaneously, the area that is depleted of the oxidized species will increase and the concentration gradient will begin to decrease. As the concentration gradient decreases, we will have less flux to the surface and current will begin to decrease. All of this will result in a current-voltage curve that looks like that in Figure 6.

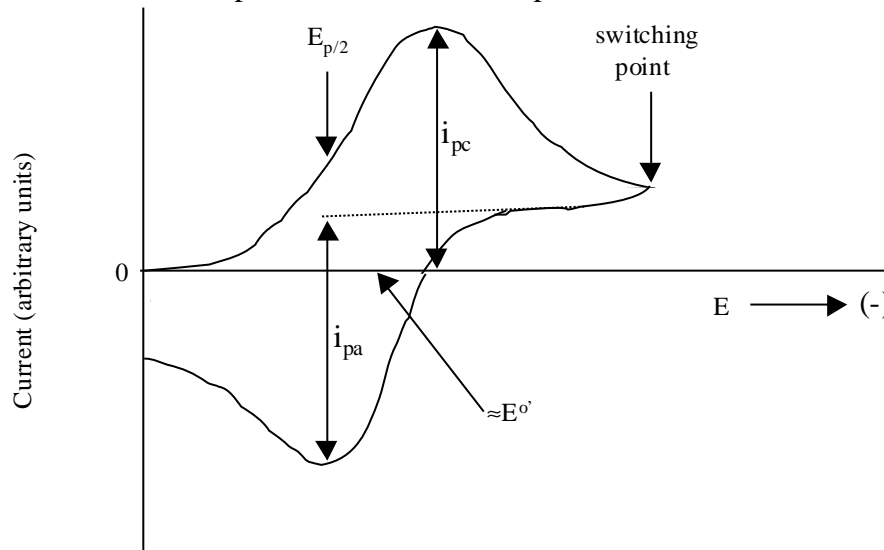


Figure 6. Shape of a cyclic voltammogram for a Nernstian electrochemical reaction.

As we reverse the voltage, we still have a layer depleted of the oxidized species, but the surface concentration

begins to rise so current decreases further. Finally, we reach a region where anodic current begins to dominate (Figure 6). Then we begin to go through similar concentration profiles for the reduced species. We will achieve a peak current and then current will decrease as the depletion layer for the reduced species increases.

That was a very qualitative description of CV. Nicholson and Shain performed quantitative simulations of CV in 1964 and the field of electrochemistry changed in a major way. All reversible voltammograms look the same and the typical shape is that shown in Figure 6. The quantitative simulations show several things for a Nernstian system. The peak current in a cyclic voltammogram containing only one species is described by equation 4 (25 °C) where i_p is the peak current, n is the number of electrons transferred, A is the electrode area, D is the diffusion coefficient of the species, ν is the scan rate and C^* is the bulk concentration of the species. The distance between E_p and the point where current is half that at E_p , $E_{p/2}$, is $56.5/n$ mV at 25 °C, where n is the number of electrons transferred. Note that for a Nernstian system,

$$i_p = (2.69 \times 10^5) n^{3/2} A D^{1/2} \nu^{1/2} C^* \quad 4$$

E_p should be independent of scan rate, but i_p will depend on the square root of scan rate. Another useful piece of information is that the separation of anodic and cathodic peaks is about $(59/n)$ mV at 25 °C. If the diffusion constants for the oxidized and reduced species are very similar, the value of E_o' can be estimated from the average of E_{pa} and E_{pc} , where E_{pa} is the potential of the anodic peak current and E_{pc} is the potential of the cathodic current. Thus in your experiments you will use CV to estimate the value of E_o' for the $\text{Fe}(\text{CN})_6^{3-/4-}$ couple. You will need that value for your impedance measurement. You will also use the peak current to estimate the diffusion coefficient for $\text{Fe}(\text{CN})_6^{3-}$. One other characteristic of a reversible system is the i_{pa} and i_{pc} are the same, but i_{pc} has to be determined as shown in Figure 6.

Completely Nernstian systems are difficult to find as electron transfer between an electrode and a couple is often quite slow. You can make a system behave more like a Nernstian system by slowing down the scan rate. With less current flowing, the kinetics have a better chance of being Nernstian.

However, as electrodes foul (or are coated with monolayers), systems become more sluggish and are apt to show some kinetic control. Fortunately, Nicholson and Shain have

Table I. Peak Separation as a Function of the Variable ψ	
ψ	$n(E_{pa}-E_{pc})$
10	61
7	63
6	64
5	65
4	66
3	68
2	72
1	84
0.75	92
0.5	105
0.35	121
0.25	141
0.10	212

treated such cases as well as Nernstian cases. What happens is that as kinetics become slower and slower, peaks begin to split. We don't see a simple $(59/n)$ mV separation anymore. In fact, the peak separation is a function of the rate constant for electron transfer, k^o . The table below gives some values of the dimensionless parameter ψ as a function of peak splitting. Using the formula for ψ (equation 5), one can calculate the value of the rate constant k^o if diffusion coefficients are known. The values of k^o do not depend heavily on α , and we will estimate it as 0.5. In this equation, D_O and D_R are the diffusion coefficients of the oxidized and reduced species, respectively, and v is the scan rate.

$$\psi = \frac{\left(\frac{D_o}{D_R}\right)^{\alpha/2} k^o}{\left[D_o \pi v \left(\frac{nF}{RT}\right)\right]^{1/2}} \quad 5$$

For a totally irreversible system (peak separations are usually greater than 300 mV) yet another method of determining the value of the rate constant applies. I simply state the equations without proof. Using equation 6, you can plot $\ln(i_p)$ versus $E_p - E^{o'}$ at different scan rates. The slope of the plot will be $-\alpha n_a f$ and the intercept will be proportional to k^o . In this equation, i_p is the peak current, C_o^* is the bulk concentration of the oxidized species, E_p is the peak potential and $E^{o'}$ is the formal potential.

$$i_p = 0.227 n F A C_o^* k^o \exp\left[-\frac{\alpha n_a F}{RT} (E_p - E^{o'})\right] \quad 6$$

You may ask why we went through all of that. First of all, it shows some of the power of cyclic voltammetry to give different pieces of information. Second, you need to use it in order to employ CV in determining electrode coverage. The rate constant is proportional to the electrode area. Thus you can use equation 7 to estimate electrode coverage from the CV data. In this equation, θ is the fractional surface coverage and k_{coated}^o and k_{bare}^o are the rate constants at

$$1 - \theta = \frac{k_{coated}^o}{k_{bare}^o} \quad 7$$

monolayer-coated gold and bare gold, respectively. You will want to compare the coverage values determined using impedance and CV.

Cyclic Voltammetry versus Impedance Spectroscopy

Both impedance spectroscopy and cyclic voltammetry have their place. Impedance spectroscopy is extremely useful for studying corrosion mechanisms and electrode coverage for two reasons. First the data are often easy to interpret in terms of simple equivalent circuits. Second, the use of a small sinusoidal voltage has little effect on the film. This could be particularly important in characterizing monolayers as the wide potential window in cyclic voltammetry could contribute to desorbing the monolayer.

Cyclic voltammetry is perhaps best suited for determining the mechanism of electrochemical reactions. It often allows determination of the number of electrons transferred, E_o' , whether a couple undergoes multiple oxidation/reduction steps, and whether there are other species in the solution that participate in the electrochemical process. Although it is generally not used in corrosion studies, it is such a widespread technique that we felt the need to introduce it into this course. It will also prove to be an interesting tool in our next lab, which involves synthesizing electroactive monolayers.

Procedure

1. Clean 2 gold-coated substrates using the plasma cleaner and determine the complex refractive index of one of them.
2. Immerse the slide for which you determined n and k in 0.0001 M octadecanethiol in ethanol for 30 minutes. Remove it from solution and rinse copiously with ethanol.
3. While you are waiting, for the monolayer to form, begin your experiments on bare gold. Place the gold electrode in the electrochemical holder. Using the techniques you learned last week, put the gold slide, reference electrode, and counter electrode in a solution of 0.005 M $\text{Fe}(\text{CN})_6^{3-}$ in 1.0 M Na_2SO_4 . Open the CV application and run the CV from 0.5 to -0.2 V at 100 mV/second. Run the same CV at 10 mV/second. Note the peak splittings. Is the reaction reversible? Does it become more or less reversible at the higher scan rate? At home, calculate the diffusion coefficient of $\text{Fe}(\text{CN})_6^{3-}$ assuming that the reaction is reversible.
4. Next put the same gold electrode in a solution containing 0.005 M $\text{Fe}(\text{CN})_6^{3-}$ and 0.005 M $\text{Fe}(\text{CN})_6^{4-}$ in 1 M Na_2SO_4 . Select the impedance spectroscopy technique. Utilize a 5 mV sinusoidal voltage and use a frequent range of 0.1 Hz to 10^5 Hz. (Don't go to lower frequencies because the experiment will take too long.) Run the experiment with the center voltage being E_o' determined from CV. At home, calculate the diffusion coefficient for $\text{Fe}(\text{CN})_6^{3-}$, the solution resistance, and the charge transfer resistance.
5. Depending on which is ready first, use either the monolayer you prepared today or the one you started preparing last week. Run the CV as above. If the peak splitting is greater than 300 mV, you may want to employ scan rates of 300, 100, and 10 mV/second. Repeat the first scan after the others to make certain that you are not altering the monolayer during the experiment. At home, use electrochemical theory to calculate the rate constants for the reaction and eventually the coverage of the electrode. Use a value of 2.6×10^{-2} cm/sec as the rate constant for $\text{Fe}(\text{CN})_6^{3-}$ at a bare electrode.
6. If the monolayer in 5 did not change significantly during the voltammetry, use the same spot and perform the impedance experiment described in 4. If the monolayer did appear to change, use a different spot on the same slide. At home, determine the solution resistance, R_{ct} , and the film capacitance. How does this value of the capacitance compare with the value

you determined in the last laboratory? Using the R_{ct} value of the bare gold, what fraction of the surface is covered by the monolayer? If you were unable to determine R_{ct} for bare gold, use a value of $2 \Omega\text{cm}^2$.

7. Repeat the CV and ac impedance (steps 5 and 6) measurements with the remaining monolayer. Make similar calculations. Do the two monolayers seem to differ?
8. Finally, clean two substrates with the plasma cleaner. Measure the appropriate optical constants. Immerse them in a solution of 0.001 M Mercaptoundecanoic acid in ethanol.
9. You are finished for today, but there is probably a lot of thinking to do.