Laboratories 8-10
Electrochemical Investigation of SAM's

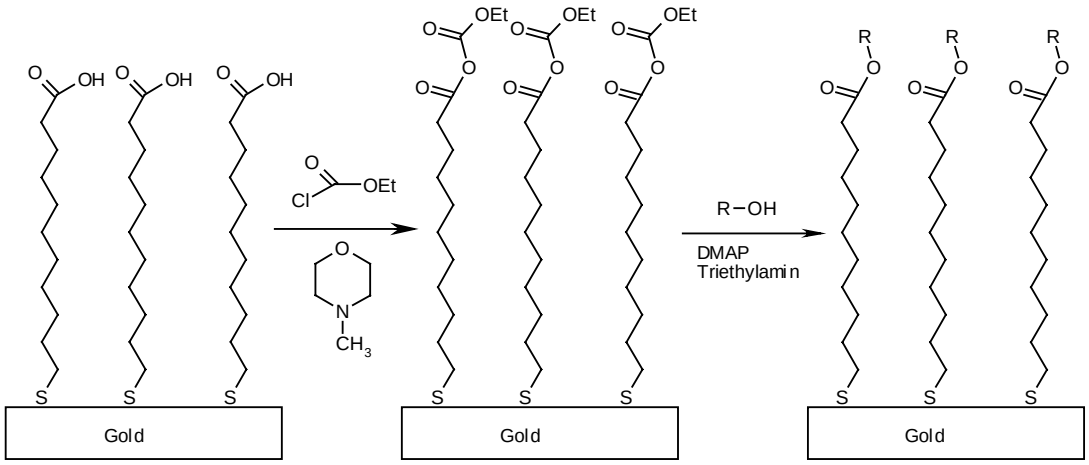
Laboratory 10 Cyclic Voltammery with Immobilized Films

In this laboratory, you will derivatize a self-assembled monolayer to attach a redox couple (ferrocene) to a surface. This will allow us to explore thin-film electrochemistry as well as utilize CV to determine surface coverage. Thin film electrochemistry is much simpler than that with bulk diffusion owing to the absence of mass transfer effects. Below I first describe the derivatization process and then quantitatively discuss Nernstian electrochemistry of thin films.

Derivatization of mercaptoundecanoic acid monolayers

Derivatization of self-assembled monolayers requires a functional group on the surface to which we can link another molecule covalently. The most common groups employed for this purpose are carboxylic acids and alcohols (*e.g.*, mercaptoundecanoic acid and mercaptoundecanol). We can use these groups to form amide or ester linkages to the surface.

In our specific case, we will employ the reaction scheme shown below. After forming a monolayer of mercaptoundecanoic acid, we will activate it using ethyl chloroformate to form a mixed anhydride. An ester linkage to ferrocene methanol will form in the presence of DMAP as a catalyst and triethyl amine as a base. I would expect your reaction yields to range from 30 to 50%. We would like to use FTIR in an attempt to show that the reaction is working. Your TA will run an experiment to show the formation of the anhydride peaks and in the next lab, we will look at the ester formation.



Scheme I. Esterification of a Self-Assembled Monolayer.

We derivatized with ferrocene methanol because it undergoes a reversible, one-electron redox process. Unlike your previous attempts at cyclic voltammetry, you now have a process where the redox couple does not need to diffuse to the electrode. This greatly simplifies cyclic voltammetry as we will see below.

Thin-layer voltammetry

The absence of diffusion effects in thin-layer voltammetry leaves a reaction completely controlled by either thermodynamics (Nernst equation) or kinetics. Let's consider the case where the concentrations in the film obey the Nernst equation (equation 1). In this equation, $E^{o'}$ is the formal potential of the couple and $C_o(t)$ and $C_R(t)$ are the time-dependent concentrations of the

$$E = E^{o'} + \frac{RT}{nF}\ln\frac{C_o(t)}{C_R(t)} \qquad 1$$

oxidized and reduced species, respectively. Note that we don't assume that there is a constant bulk concentration anymore. In this system, we can describe the current in terms of the change in concentration of the oxidized species as shown in equation 2. Here *n* is the number of electrons transferred per mole of reaction, V is the volume of the thin layer cell, *t* is time and F is the Faraday constant. A mass balance of the oxidized and reduced species gives equation 3,

$$i = -n\,F\,V\left[\frac{d\,C_o\,(t)}{dt}\right] \qquad 2$$

where C_{tot} is a constant. Using this mass balance and the Nernst equation, we can obtain an

$$C_O(t) + C_R(t) = C_{tot} \qquad 3$$

expression for $C_O(t)$ as a function of the instantaneous potential, E (equation 4). This expression can be rearranged to yield equation 5. By differentiating equation 5 with respect to *t* and noting that $\upsilon = -\frac{dE}{dt}$, we obtain equation 6, which is our desired expression for current as a function of potential. (We leave the details of the derivation of these equations either as an exercise for the student or the lecturer.)

$$C_o(t) = \frac{C_{tot}\,\exp\left[\frac{nF}{RT}\left(E - E^{o'}\right)\right]}{1 + \exp\left[\left(\frac{nF}{RT}\right)\left(E - E^{o'}\right)\right]} \qquad 4$$

$$C_o(t) = C_{tot}\left[1 - \frac{1}{1 + \exp\left[\left(\frac{nF}{RT}\right)\left(E - E^{o'}\right)\right]}\right] \qquad 5$$

$$i = \frac{n^2\,F^2\,\upsilon\,VC_{tot}}{RT}\;\frac{\exp\left[\frac{nF}{RT}\left(E - E^{o'}\right)\right]}{\left[1 + \exp\left[\frac{nF}{RT}\left(E - E^{o'}\right)\right]\right]^2} \qquad 6$$

Consider equation 6 briefly. It is symmetric about $E^{o'}$. When the potential is very negative of $E^{o'}$, there will be no current because the exponential will go to zero. When the potential is far positive of $E^{o'}$, the will be no current because the squared term in the denominator will force the expression to zero. The peak current occurs at $E=E^{o'}$ and is described by equation 7. A typical voltammogram is given in Figure 1.

$$i = \frac{n^2 F^2 v V C_{tot}}{4RT} \qquad 7$$

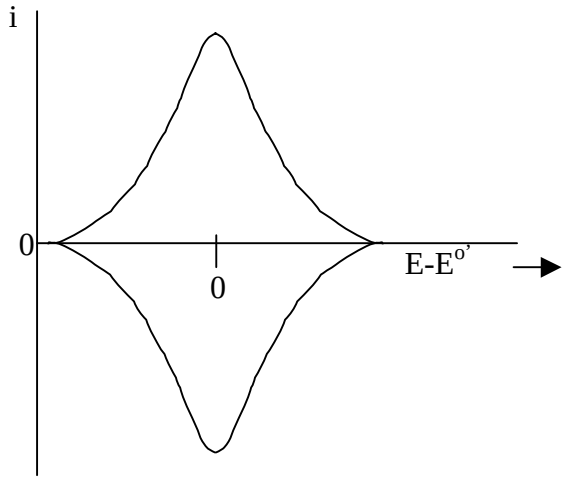


Figure 1. Shape for a reversible thin-layer voltammogram.

The above derivation is really for an electrochemical cell with a very small volume (hence the V term in the equation). Our system is a little bit different in that we have a single layer on the surface and we really would have no idea what to use for a volume for this system. To get a similar expression for the monolayer, we can simply replace VC_{tot} with ΓA where Γ is the surface coverage (moles/cm^2) and A is the electrode area.

In all of the above derivations, we assumed Nernstian behavior at the surface. This is not always the case. When kinetics become an issue, the voltammograms are no longer symmetric and peak splitting occurs. We will not treat these systems in class, although your system may not be completely Nernstian.

Whether a system is reversible or not, we can determine surface coverage from a thin-layer voltammogram. To do this, we integrate the i-e curve and divide the integral by the scan rate. By dividing by the scan rate, you are in effect integrating an i-t curve. Because current is in units of C/sec, the area found in the integration has units of Coulombs. To convert this quantity to moles/area on the surface, we simply divide by *n*FA. Thus this simple experiment will allow you to determine your surface coverage.

Specific Procedure

Perform steps 10 and 11 of laboratory 9 (Actually your time may be better spent doing that in the middle of the lab.)

1. Remove the two MUA monolayers and rinse them with ethanol and water. Measure the thickness of the layers.
2. *Note: The following chemical procedures should be done in the hood.* Immerse each slide in 10 mL of dried DMF. Add 100 µL of N-methyl morpholine followed by 100 µL of ethyl chloroformate. Mix gently. After adding the chloroformate, wait 10 minutes. Rinse the slide with ethyl acetate and dry with N_2. Have the TA measure a spectrum of the film. It should contain anhydride peaks.

3. Assuming that the IR spectrum looks good, immerse the slide in 10 mL of CH_2Cl_2 solution containing 0.1 M ferrocene methanol, 28 mg of 4-(dimethylaminopyridine), and 70 μL of triethylamine. Leave the slide in solution for 1 hour.
4. After 1 hour, rinse copiously with CH_2Cl_2 and EtOH. Have the TA measure the IR spectrum again. Measure the thickness of the film ellipsometrically. You may want to restrict yourself to wavelengths below 500 nm. (Why?)
5. Put the slide in the electrochemical sample holder and immerse it in 1.0 M Na_2SO_4. Run a cyclic voltammogram at 20 mV/sec over a potential range from 600 mV to -100 mV. Try it again with a scan rate of 100 mV/second. Finally repeat the 20 mV/second run. Try this voltammetry at two different spots on the same slide.
6. On your own time, calculate the surface coverage.
7. Immerse the other derivatized slide in 0.1 M HCl in EtOH. Rinse with EtOH and rerun the Ir spectrum. Remeasure thickness. Can you think of a way to estimate yield from the IR spectra?