

Laboratories 8-10
Electrochemical Investigation of SAM's

Laboratory 8 Investigation of the Capacitance of SAMs and Bare Gold

Electrochemical techniques are probably the most sensitive probes of monolayer defects. Infrared spectroscopy, ellipsometry, contact-angle measurements, and QCM studies are all more or less bulk measurements. Cyclic voltammetry (CV) and impedance measurements, however, are extremely sensitive to defects in a monolayer. If 99% of a surface is covered by a well-formed monolayer, most techniques will be representative of that 99%. CV and impedance measurements, however, will immediately recognize the defect areas. (If you'd like to give your boss evidence of a well-formed monolayer, these techniques are not for you.)

Capacitance of Electrochemical Systems

To temper the cutting edge of electrochemistry (I have to admit that the sensitivity of electrochemistry to surface structure can sometimes make it hard to reproduce), we will begin these laboratories with capacitance measurements, as these are closer to bulk-like techniques. For a simple parallel plate capacitor, charge on the capacitor, Q , is proportional to the voltage

$$Q = CV \tag{1}$$

drop across the capacitor, V , as shown in equation 1. C is the capacitance. The simplest description of electrochemical capacitance is the Helmholtz model given by equation 2, where ϵ

$$C = \frac{\epsilon\epsilon_0}{l} \tag{2}$$

is the dielectric constant of the material separating the parallel plates, ϵ_0 is the permittivity of free space and l is the separation between the plates. This model does not adequately describe most electrochemical interfaces as the capacitance depends on both potential and the supporting electrolyte.

The model fails because of several reasons, the most obvious of which is that an electrochemical interface is not a parallel-plate capacitor. Charge on the solution-side can be rather diffuse and even if charge in solution is organized in a sheet parallel to the interface, it is difficult to determine the distance of approach between an ion in solution and the electrode. This distance can vary greatly among different ions. That said, however, the capacitance of an electrode-monolayer-solution system is fairly simple to treat. The distance between the two sheets of charges is well-approximated by the monolayer thickness and the diffuse charge in the solution becomes insignificant. Thus for these monolayers we will use a simple Helmholtz model. The experiments in laboratory 8 will show whether or not the model is valid.

Capacitance is a crucial factor in electrochemical experiments because it gives rise to current during the charging of the capacitor. Rather logically (and without imagination), we term this charging current. To calculate the magnitude of this current, we differentiate equation 1 with respect to t and assume that capacitance is constant (equation 3). (Recognizing that dQ/dt is an expression for current and dV/dt is the potential scan rate, we obtain equation 4.)

$$\frac{dQ}{dt} = C \frac{dV}{dt} \tag{3}$$

$$i = Cv \tag{4}$$

From this very simple derivation, we have an expression for the charging current at steady state when applying a ramping voltage. If there is no possibility for electron transfer between the solution and the electrode this is the only current that we will observe.

Let's now consider the very simple cyclic voltammetry (no redox couple) experiment shown in Figure 1. We apply the potential form shown in the figure. Initially, we have a sharp rise in current because of a sharp change in the voltage ramp. The current then reaches steady state as we are constantly varying the voltage. At reversal of the scan rate, the current changes sign, and when we stop scanning, current goes to zero.

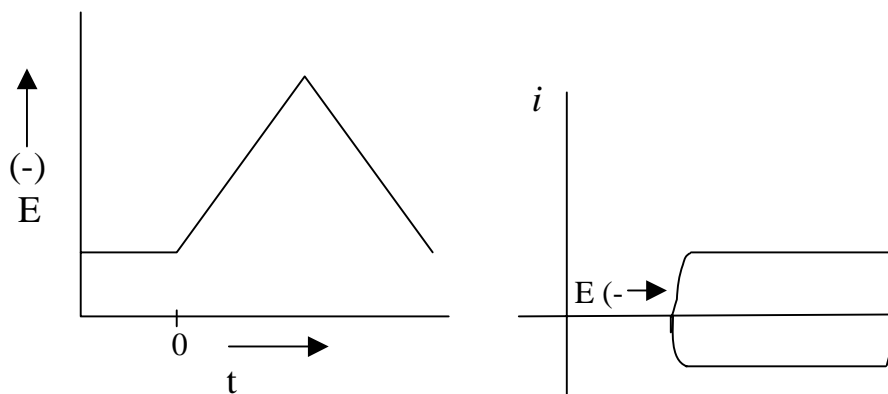


Figure 0. Schematic explanation of a cyclic voltammetry experiment in the absence of a redox couple.

In laboratory 8, you will perform such an experiment with a bare gold electrode and an electrode coated with a SAM. You will calculate the capacitance for both types of electrodes. We will try the experiment with two concentrations of Na_2SO_4 , one concentration of NaCl and two scan rates. If the Helmholtz model is valid, should there be a difference in the capacitive currents for the different situations? We will also ask you to calculate the dielectric constant for the capacitors. A reasonable value for dielectric constants of organic compounds is 2-3. The dielectric constant of water is about 80.

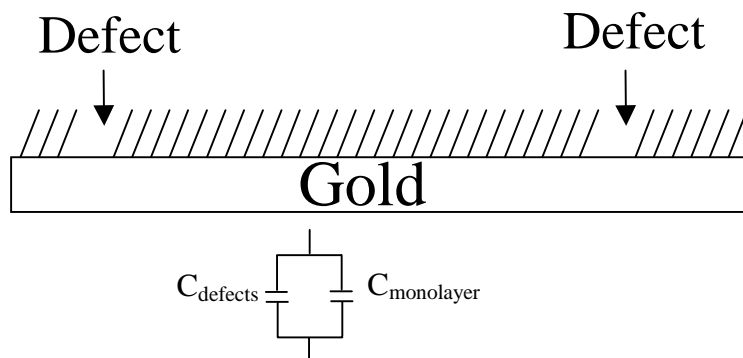


Figure 2. Schematic diagram of a monolayer with defects and its equivalent electrochemical circuit in the absence of electron transfer.

Let's consider for a moment the possibility of defects in the SAM as shown in Figure 2. In the absence of an active redox couple, both defects and monolayer areas will behave as capacitors.

Thus we can consider the electrode-solution interface to be a parallel circuit with capacitors for both defect and monolayer-coated areas as shown. Capacitances add in parallel so the overall monolayer capacitance, C_{total} , is given by equation 5 where C_{m} is the capacitance in monolayer covered areas, C_{dl} is the double layer

capacitance in defect areas, and θ is the fraction of the surface that is covered by the monolayer. If you measure C_{dl} in a separate experiment with a bare gold electrode and estimate C_{m} , it is in

$$C_{total} = C_{dl}(1 - \theta) + C_m\theta$$

principle possible to estimate the surface coverage. In your lab report, comment on whether equation 5 can be used reliably to estimate surface coverage.

In electrochemistry, most quantities scale with area and capacitance is no exception. You should probably carry around in your head the fact that a typical capacitance for an electrochemical interface is $20 \mu\text{F}/\text{cm}^2$. However, as mentioned above, capacitance is often a function of potential and supporting electrolyte.

Electrochemical Instrumentation

For the purposes of this course, we will simply treat potentiostats as black boxes that can apply a potential and measure current. We will discuss briefly the electrode setup. Performance of an electrochemical measurement always requires at least two electrodes, as we have to complete a circuit (Figure 3). The current between the two electrodes as well as the applied potential can be measured. The problem with the configuration in Figure 3 is that there are three regions over which the potential drop occurs: two electrode-solution interfaces and the solution. We only know the potential drop over the whole system, but we are really interested in the single

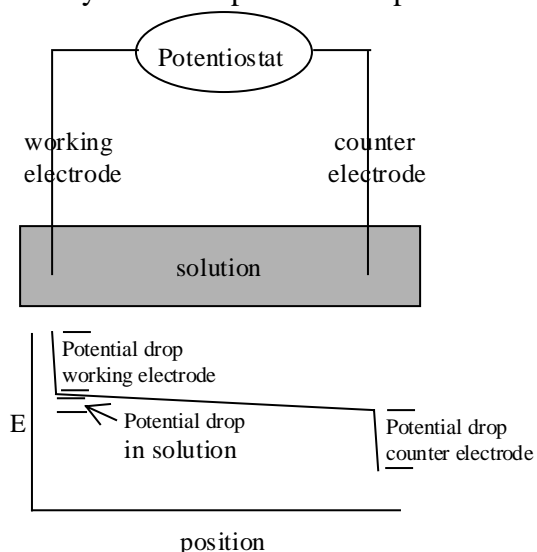


Figure 3. Schematic diagram of a two electrode electrochemical system and the resulting potential drops.

potential drop at our working electrode. For example, when determining the capacitance at a working electrode, we are only concerned with the potential drop at that specific electrode. If we consider the current of the system, the current is equal throughout (we cannot have a buildup of charge). Thus what happens is that the current is constant and the potential drop at any point in the system is that which will maintain the overall current.

One crude way to overcome this problem is to use a high surface area counter electrode. When surface area is high, we don't need large potential drops to produce current. Thus most of the potential drop will occur at the working electrode. The potential drop in the solution is still a problem, but we use a high concentration of supporting electrolyte to minimize solution resistance and hence the potential drop through the solution.

The most common method used to isolate a potential drop to the electrode interface of interest is to use a reference electrode. An ideal reference electrode is designed to have the current voltage behavior shown in Figure 4. The potential drop between the reference electrode and the solution is essentially constant. In reality the potential drop shows a small dependence on current. However, when we employ reference electrodes, we seldom (unless someone hooks up wires to the potentiostat incorrectly) pass a significant current through them. Thus the potential drop across a reference electrode is constant.

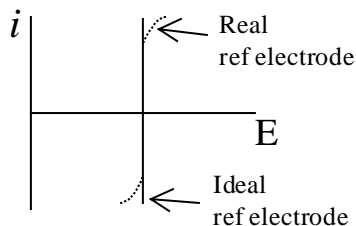


Figure 4. Current-voltage characteristics of ideal (solid line) and real (dashed line) reference electrodes.

When we use a reference electrode, we measure only the potential drop between the working and reference electrode (Figure 5). We measure current between the working and counter electrode. (As the potential measurement between the working and reference draws a miniscule current, it does not affect the current measurement between the working and counter electrode.) We are still measuring a potential drop across two electrode-solution interfaces, but at least one is constant. Thus any change in potential occurs at the working electrode. For your differential capacitance measurements, you are only concerned with the change in voltage so this works out fine. Even when a redox-couple is present, we still can measure only the change in potential across the working electrode. This turns out not to be a huge disadvantage.

You may be thinking that there is still some potential drop in the solution between the working and reference electrode. This is true. We again use a high concentration of supporting electrolyte to minimize solution resistance. We also position the reference electrode so that it is as close to the working electrode as possible. Sometimes one tries to compensate for the solution resistance, but those methods can be risky and they are beyond the scope of this course. The best thing is to minimize resistance.

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 0.001 M octadecanethiol in ethanol for 30 minutes. Remove it from solution and rinse copiously with ethanol.
3. While waiting for the monolayer to form, place the other clean gold slide in the electrochemical holder. We use the holder because it provides a reproducible surface area. The challenge in using such a holder is that the o-ring may disrupt the monolayer structure in that region. We will check this in the next lab period.
4. Connect the reference electrode to the white lead and immerse it in 0.1 M Na_2SO_4 . Connect the platinum wire electrode to the red lead and immerse it behind the reference electrode.

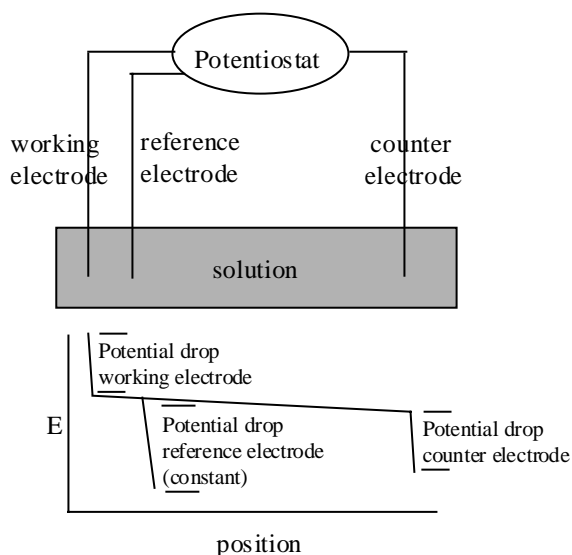


Figure 5. Schematic diagram of a three electrode system and the accompanying potential drops.

5. Place a drop of water on the active part of the working electrode (gold slide) to avoid formation of an air bubble. Now connect this electrode to the green lead and immerse it in front of the reference electrode.
6. Open the cyclic voltammetry technique in the software and set the potential range to go from 0.4 V to -0.1 V. Set the scan rate to 100 mV/second. Run the voltammogram and save the file. The calculation of capacitance is fairly straightforward so go ahead and do it right away.
7. Set the scan rate to 10 mV/second and determine capacitance.
8. Repeat steps 6 and 7 using 1 M Na_2SO_4 as the electrolyte.
9. Repeat steps 6 and 7 using 0.1 M KCl as supporting electrolyte.
10. While still in KCl solution, run a voltammogram from 0.7 V to -0.5 V. Why does this make a difference in your CV?
11. Once your monolayer is formed, determine the thickness of the layer and do the same capacitance determinations that you did in steps 6-9. If you are well prepared, you can quickly estimate the dielectric constant of the monolayer. Think about the assumptions and errors in calculating ϵ .
12. Monolayers can be unstable in solution so redo the capacitance measurement of the monolayer in 0.1 M Na_2SO_4 to see if anything has changed.
13. Clean a third gold substrate with the plasma cleaner and determine its n and k values. Immerse the substrate in 0.001 M octadecanethiol in ethanol and leave it for the next lab.