

S2014, BME 101L: Applied Circuits Lab 4

Polarizing and Non-polarizing Electrodes

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1 Design Goal

This lab is not a design lab but a measurement and modeling lab. The goal is to provide equivalent circuits for two different types of electrodes in salt water: stainless steel and silver/silver-chloride.

You will also learn how to make your own silver/silver-chloride electrodes out of fine silver wire.

2 Background

An *electrode* in bioengineering is a transducer that converts between ionic current (generally sodium, potassium, calcium, and chloride ions) in an electrolyte and electron current in a metal wire. The transduction can go either way, using the electrodes to measure ionic current or to create it. (Note: in other fields, the term “electrode” may be used in slightly different contexts, such as converting electron flow in a wire to electron flow in a vacuum, but in this class, we’ll only be using electrochemical electrodes.)

All electrochemical electrodes work through redox reactions. For current to flow, there must be two electrodes, an *anode* and a *cathode*. A *reduction reaction* happens at the cathode, taking electrons from the wire, and an *oxidation reaction* happens at the anode, donating electrons to the wire.

Read the “Electrodes” chapter of Wikipedia book for the course:

http://en.wikipedia.org/wiki/User:Kevin_k/Books/applied_circuits (This “chapter” has ten Wikipedia articles, so leave yourself plenty of time for reading!)

2.1 Polarizable and nonpolarizable electrodes

http://en.wikipedia.org/wiki/Ideally_polarizable_electrode

A *polarizable electrode* ideally has no DC current flow between the electrode and the surrounding electrolyte. The electrode/electrolyte interface behaves like a capacitor. Platinum in NaCl is highly polarizable, but is too expensive for us—we’ll look at stainless steel electrodes, which appear to be moderately polarizable.

A *non-polarizable electrode* has no polarization, that is, current flows freely and the electrode-electrolyte interface behaves like a resistor. A platinum-hydrogen electrode is normally considered a good non-polarizable electrode, but platinum in an NaCl solution (the usual case for bio-electrodes) is highly polarizable. A non-polarizable electrode that can be used in salt solutions is the silver/silver-chloride electrode, which we’ll look at in this lab.

Real electrodes have characteristics that don’t match either ideal, and we’ll try to characterize that non-ideal behavior in this lab. Later on this quarter, we’ll use commercial disposable Ag/AgCl electrodes for the EKG.

Michael R. Neuman’s chapter “Biopotential Electrodes” has further discussion of bio-electrodes:

http://www.fis.uc.pt/data/20062007/apontamentos/apnt_134_5.pdf

A more comprehensive source is *Bioimpedance and bioelectricity basics* by Sverre Grimnes and Ørjan Grøttem Martinsen, particularly Chapters 2 (Electrolytics) and 3 (Dielectrics). These references are more detailed than we need for this course, but are good places to check for more information.

2.2 Stainless steel

http://en.wikipedia.org/wiki/Surgical_steel http://en.wikipedia.org/wiki/Stainless_steel

Surgical steel (such as type 316L stainless steel that the electrodes we'll test are made from) is commonly used for implantable devices, because of its strength, its resistance to corrosion in the body, and very low toxicity. It is not commonly used for electrodes, though, and we'll try to see why in this lab.

Because stainless steel is a complicated alloy, it is not clear what the electrochemical reactions are in salt water. The resistance to corrosion that gives it the "stainless" name comes mainly from a layer of chromium oxide on the surface of the steel. This layer forms naturally in oxidizing conditions, but in reducing conditions it may not form, and the steel behaves differently, corroding much more readily. (The two states are referred to as "passive" and "active" in discussions of the corrosion of stainless steel, and the half-cell potentials are different.)

The most important reactions for stainless steel as an electrode are probably $Fe + 2Cl^- \rightarrow FeCl_2 + 2e^-$, $Fe \rightarrow Fe^{2+} + 2e^-$, and $2H_3O^+ + 2e^- \rightarrow 2H_2 + O_2$, but I'm not certain of that.

2.3 Silver/silver chloride

http://en.wikipedia.org/wiki/Silver_chloride_electrode

The electrodes most commonly used in the nanopipette and nanopore labs are Ag/AgCl electrodes. These are relatively cheap to make and are non-polarizing. The reaction is $Ag \rightarrow Ag^+ + e^-$; $Ag^+ + Cl^- \rightarrow AgCl$. Note that both the silver and the silver chloride have low solubility, and so remain on the electrode—the flow of current (electrons in the wire and chloride ions in the solution) affects the ratio of silver to silver chloride on the surface of the electrode.

You will be making your own silver/silver-chloride electrodes by electroplating AgCl onto fine silver wires. Note: "fine silver" refers to silver that is at least 99.9% pure silver—there are many other grades of silver, such as "sterling silver" that is 92.5% silver.

3 Pre-lab assignment

Review your electrochemistry and read up on Ag/AgCl electrodes. Try to find some useful on-line sources other than those mentioned in the background section of this lab handout—be sure to cite them properly in your lab writeup.

Compute the surface area of the electrodes you will use.

- The stainless electrodes are about 2.7cm long to the plastic spacer and 1/8" (3.18mm) in diameter. The spacer should hold them 2cm apart. (I'll bring calipers and a micrometer to lab, so that you can do more careful measurements.)
- The fine silver wire in your kits is 24-gauge AWG (look up the diameter), and you will be folding it around a wire holder that is 4.4mm thick and you will be immersing the wires to a depth of 1cm, 2cm, or 3cm (depending which calibration line you use on the electrode holder), so the length will be 2.44cm, 4.44cm, or 6.44cm.

The first time this lab was done, several students seemed incapable of computing surface area (sometimes computing volume, sometimes claiming surface areas that would require electrodes the size of a laptop to be reasonable). Do sanity checks! Is the surface area you are claiming in the consistent units? How big an area is that?

Make a gnuplot function for computing the magnitude (absolute value) of impedance for a pair of electrodes as a function of frequency and the three parameters R_1, R_2, C_1 . Gnuplot is perfectly capable

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j = sqrt(-1)

# impedance of two impedances in parallel
parallel(z1,z2) = z1*z2/(z1+z2)
# note: there is no need for a "series" function, since that is just
# z1+z2

# impedance of a capacitor of C Farads at f Hz
Z_C(C,f) = 1./(j*2*pi*f*C)

# impedance of an inductor of L Henries at f Hz
Z_L(L,f) = j*2*pi*f*L

# There is no need of a function for resistors, since Z_R(R,f)=R and
# the resistance can just be used directly.

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Figure 1: Some useful assignments and functions for building circuit models in gnuplot.

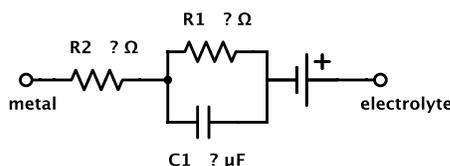


Figure 2: Simplified equivalent circuit for a polarizable electrode. I don't know the half-cell potential—different sources give different redox potentials for stainless steel in salt water. Luckily, for our application the half-cell potentials cancel, because we are using the same materials for both electrodes in the same concentration of electrolyte. R_1 and C_1 should correspond to the electrode/electrolyte interface— R_1 would be infinite for a perfectly polarizing electrode and 0 for a perfectly non-polarizing electrode. R_2 models the bulk resistance of the electrolyte—it should decrease roughly inversely to the concentration of the ions in solution.

of dealing with complex numbers, but you might want to define $j=\text{sqrt}(-1)$ to make the formulas easier to write. Figure 1 has some gnuplot commands that may be useful.

Each electrode/electrolyte interface could be modeled with the circuit show in Figure 2. The two electrode-electrolyte interfaces are in series, back-to-back, so the half-cell potentials cancel (assuming the same electrolyte concentration at both electrodes). Because we are canceling out the half-cell potentials, we can lump the two electrode-electrolyte interfaces together, and just model the whole electrode-electrolyte-electrode system as a resistor in series with a parallel arrangement of a capacitor and resistor. This is the standard model used for EKG measurements, for example. Note that in real EKG applications, the salt concentrations on the skin may vary from electrode to electrode, so the half-cell potentials may not be identical—EKGs have to be able to handle a DC component that is large compared to the signal of interest.

Make another gnuplot function that models the magnitude of impedance with a power law: $|Z| = af^b$. You will use these two functions for fitting models to your data.

Do some plotting of the functions with different parameters, so that you get a feel for what each parameter does to the shape of the curve. You will probably have to give gnuplot some initial values for fitting your data, so it would be a good idea to have some feeling for what the parameters mean.

4 Parts, tools, and equipment needed

Parts for this lab from kit:

- alligator clip leads
- resistors
- 1 foot fine silver wire 24 gauge (for Thursday lab)
- 2 EKG electrodes (for Thursday lab)

Tools for this lab:

- (optional) calipers
- (optional) micrometer

Equipment in lab:

- function generator
- two multimeters
- cups for salt water (3 per station)
- secondary containment tubs
- sponges in case of spills (there'd better not be any!)
- paper towels
- stock NaCl solutions (1M, 0.1M, 0.01M, 0.0001M) (about 75ml/setup, or 1l of each)
- stainless steel electrodes (Tuesday)
- electrode holders for silver wire (Thursday)
- NaCl solution for electroplating (1l of 1M) (Thursday)

5 Procedures

Warning: salt water and expensive electronics equipment do not play nicely together. All liquids must be kept contained in the secondary containment tubs throughout the lab. Do not remove the cups from the tubs!

5.1 Characterizing stainless steel electrodes

Immerse the electrodes in 1M NaCl solution, up to the plastic spacer, as shown in Figure 3, so that you have a known area of electrode submerged. You can rest the alligator clips on the rim of the cup to help stabilize the electrodes.

First, measure the DC resistance of the electrodes with the ohmmeter.

Next, connect a voltmeter across the electrodes, an ammeter in series, and the whole thing to the function generator, so that you can simultaneously measure the RMS AC voltage and current.

Actually, the ammeters we have only measure RMS current up to 5kHz, and we want to go to higher frequencies than that, so you'll need to replace the ammeter with a 1Ω or 10Ω resistor and a voltmeter, as the voltmeter function is pretty accurate to 50kHz, and usable up to 1MHz. Measure the resistor you



Figure 3: Stainless steel electrodes made from 1/8" 316L stainless steel welding rod.

are using with the ohmmeter function of the multimeter, as the resistors in your kit are not exactly the resistance that they are labeled with, and the meters are more accurate than the labeling.

Be sure to draw a schematic of your setup!

Measure the RMS voltage and RMS current for several frequencies from 3Hz to 300kHz. You should measure at several frequencies per decade, roughly uniformly spaced in log space (say, 3, 5, 7.5, 10, 15, 20, 30, . . . , 3E5). Sorry, you'll have to record this by hand, as we don't have the time to set up the equipment with LabView and automate the test. It may help to have one person making the measurements and calling out the numbers to their partner who records the numbers in a file.

Plot the magnitude of the impedance (V/I) as a function of frequency (use a log scale for frequency!). Fit both your models to the data. Which is the better fit?

Repeat the measurements for the other salt concentrations, and make one plot with all sets of data points and both models for each of the concentrations. (If this plot gets too cluttered, do the RC modeling and the power-law modeling on separate plots.)

Which parameters change a lot with concentration? which only a little? If you were to use these electrodes to measure the conductivity of the solution, what frequency would you want to measure at, and why?

5.2 Electroplating silver wire with AgCl

Wrap the silver wire around the electrode holder as shown in Figure 4. Use alligator clip leads to connect the electrodes through an ammeter to a power supply.

Put the electrode holder upright in a cup within the secondary containment tub, and carefully add 1M NaCl solution until it is past the shoulders but not deep enough for the alligator clips to touch the solution. Turn on the power with a very low voltage, and gradually increase the voltage until you have a current of about 1mA for each square centimeter of area for one wire (you did precompute the area of the wire in the pre-lab, didn't you?). After a couple of minutes you should have a fairly uniform grey coating of AgCl on the positive wire. Time how long you do the plating! Remember to record in your notes how long and at what current you did the plating, so that someone else could replicate it.

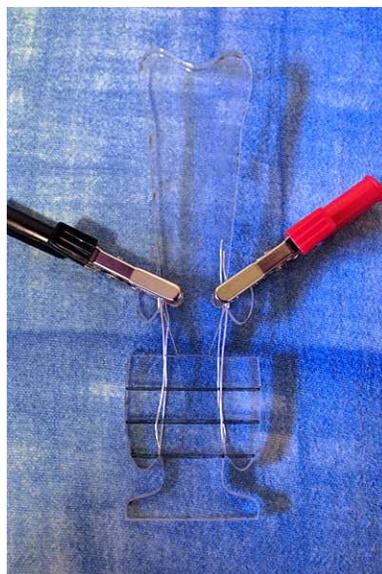


Figure 4: Holder showing wire wrapped around it. Cut the silver wire into two pieces 6" long. Wipe any finger grease off of it with a paper towel. Wrap one wire around the left ear, through the left armpit, and back up around the ear again. Do the same with the other wire on the right ear. (Note: the wire in this picture is about 7" long—you'll have no loose ends with a 6" wire.)

Reverse the polarity and plate the other wire also. Note that as you are plating the other wire, you are unplating the first wire, so you want to run the second plating only half as long as the first—that way you'll end up with more or less equal plating on both electrodes.

If your coatings are mottled, try wiping finger grease off with a paper towel and plating some more. If you were doing this lab with real biological samples, the wires would probably be cleaned with acetone or other organic solvent, and rinsed with deionized water, both before and after plating.

There is another method for producing the AgCl layer, by immersing the fine silver wires in chlorine bleach, but bleach is a bit too hazardous for a lab that has no sink and no eyewash station nearby. The electroplating method supposedly produces a thicker, more uniform coating of AgCl anyway.

5.3 Characterizing Ag/AgCl electrodes

Immerse the plated electrodes in 1M NaCl (preferably not the same solution as used for electroplating, which may be somewhat depleted of Cl^- ions), up to one of the calibrated lines on the electrode holder (1cm, 2cm, 3cm at the shoulders). It may be easiest to hold the holder upright in the cup first, and gradually pour in liquid.

Do the same characterization experiments with the Ag/AgCl electrodes that you did with the stainless steel electrodes.

5.4 Characterizing EKG electrodes

Take two of the disposable EKG electrodes and stick them together face-to-face, trying to seal them together all the way around. Clip alligator leads onto them and try to characterize the EKG electrodes the same way you did the home-made Ag/AgCl electrodes. Note that you don't have any concentration here to vary, as the electrodes come with their own gel electrolyte in little sponges over the Ag/AgCl electrodes.

6 Demo and writeup

Your report should include the schematic diagram of the equivalent circuit for each type of electrode, the plots and fits of the magnitude of electrode impedance, and your interpretation of the results. The writeup should be understandable by another bioengineer who has not read this assignment.

Some things to discuss:

- Which models fit the data best?
- What electrodes would you use and what frequency would you use if you were trying to measure the concentration of salt water electronically?
- How would you modify the measurement technique to get the full complex impedance, rather than just the magnitude of it?

7 Design Hints

Since this is a measurement lab, rather than a design lab, the main things to think about are how to make and record the large number of measurements efficiently.