

Electrochemical Instrumentation for Electrical Engineers

Peter Rieke, March 22, 2025

The Conductivity of Solid Materials

Consider how one would measure the resistivity or conductivity of a material, say, for arguments sake, a chunk of carbon. First one cuts or machines it to get a measurable cross section and a defined length. See Figure 1. One then wraps the bar with four wires, preferably platinum or gold, with a known separation especially between the two center electrodes. After applying a known current to the device from the two outer electrodes one measures the voltage drop across the inner electrodes. Knowing the material area and length between the two inner electrodes, the resistivity ($\text{ohm}\cdot\text{m}$) or conductivity (S/m) can be calculated. Full characterization might include temperature and current dependence. (or stress or radiation or the phase of the moon or whatever the boss wants.)

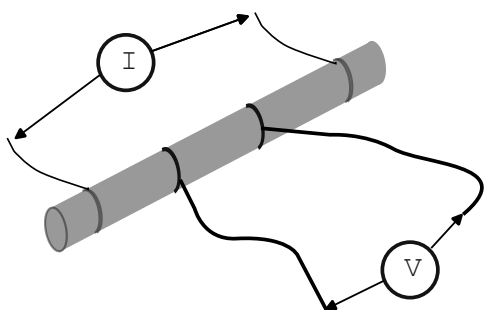


Figure 1 Conceptual 4-Probe Conductivity Apparatus

On carbon, the tightly wound platinum wire contact to the carbon is “ohmic.” There will be a voltage drop across the contact interface depending upon the difference in Fermi energy of the electrons in each material.

Simplistically speaking the Fermi energy is the energy required to remove an electron from the material to a far distance, i.e. a vacuum. The concept applies to metals, semiconductors, insulators, molecules and atoms. Metals form a pool of electrons kinda like the water level in a bucket. Semiconductors have a Fermi energy between the valence and conduction bands while atoms or molecules have an ionization energy.

For metals like carbon and platinum, this voltage across the interface is similar to that of a transistor P/N junction except this interfacial voltage does not depend upon current, or at least not strongly, over modest currents of a few amps or less. From the voltmeter’s perspective, the voltage drops across the

two voltage probe interfaces are equal and opposite. The voltmeter sees no voltage if no current is applied to the current electrodes. Ideally the voltage probes carry no current and there should be no resistive voltage drop through the interface or the wires.

Now suppose we want to measure the resistivity of liquid mercury. One then has to build a cell, I'd use a glass, ceramic or plastic tube, or other chemically compatible and insulating material, to contain the mercury as well as embed the platinum wires in the tube at known spacing. Add the mercury and take a data point. No problems we get the same kind of behavior we see with the carbon material. We see that the conductivity is constant over the typical current range we are interested in. Eventually, at high currents, we can drive it in to a non-linear behavior. But from an engineering perspective we are interested in the linear region where the I-V curve is straight with a constant slope that is our desired conductivity.

The Conductivity of Aqueous Solutions

Now fill the same cell with saltwater. Oddly, the voltage applied to the current electrodes increases to maintain a desired set current and then at about 1.2V gasses start to form at the current electrodes which are oxygen at the positive electrode and hydrogen at the negative electrode. (See the Electrochemistry for Electrical Engineers paper still in preparation)

Per Wikipedia, English chemists William Nicholson and Johann Wilhelm Ritter succeeded in separating water into hydrogen and oxygen by electrolysis in 1800. Hence electrochemistry was born. An observant scientist of the early 1800's might well ask what are the gasses, how much is created per unit of current and can you control the rate at which the gas is generated? First thing you observe is that the two inner voltage probes, which we now called "Reference" electrodes, are giving crappy results. Eventually the mercury calomel and silver chloride reference electrodes are created and the voltage behavior of these electrodes starts to behave. I'm being flippant about over 100 years of research but we need to get somewhere else for now.

Electrochemistry – A Focus on the Interface Not the Material Bulk

Back to those bubbles that form on the electrodes. We want to measure the current-voltage dependence ACROSS one, not both, of those current supply electrode surfaces. Halleluia, the magical "Working" electrode is born. All praise the working electrode. We can do so by connecting one of the platinum reference electrodes to the wire connected to the electrode surface we are interested in. And, POOF, we now only have three wires as two of them are redundant and connected to the working electrode, we still have one reference electrode but let's move it close to the working electrode surface – can't touch mind you – but a couple of millimeters away. And separated by salt water. The remaining current providing electrode gets renamed as the "Counter" electrode. And then promptly gets ignored and even physically isolated so any gas or other Redox products that might form on its surface can't get near the all-star Working electrode. A salt-bridge or ceramic membrane or even a paper filter will work. Cell and Reference electrode design becomes an art form.

Our two reference electrodes are now one metallic wire connected to the working electrode – which we typically ignore, and one reference electrode that is immersed in solution. This reference electrode is no longer just a wire. It is typically a metal covered with a salt that forms a constant voltage between the wire and the solution. For example, a silver wire can be coated with an AgCl layer in a KCl solution. If the coated wire is kept in contact with a KCl solution of constant composition (saturated is an easy choice), the voltage drops across all the interfaces will be constant. Electrochemists often represent this assembly by the notation $\text{Ag}|\text{AgCl}|\text{KCl}(\text{sat.})$. By putting the AgCl coated Ag wire in a glass tube, plugging one end with a porous glass frit and filling the tube with KCl, one produces a probe whose interfaces have constant potential differences that don't change significantly more or less independent of what solution this assembly is placed in.

Note that different reference electrode chemistries will have different potential drops. So, when reporting an I-V curve for our Working electrode, one must specify the type reference electrode that was used. In summary, our four-probe resistance measurement experiment has become a three-electrode experiment and one of the voltage probes becomes chemically intricate.

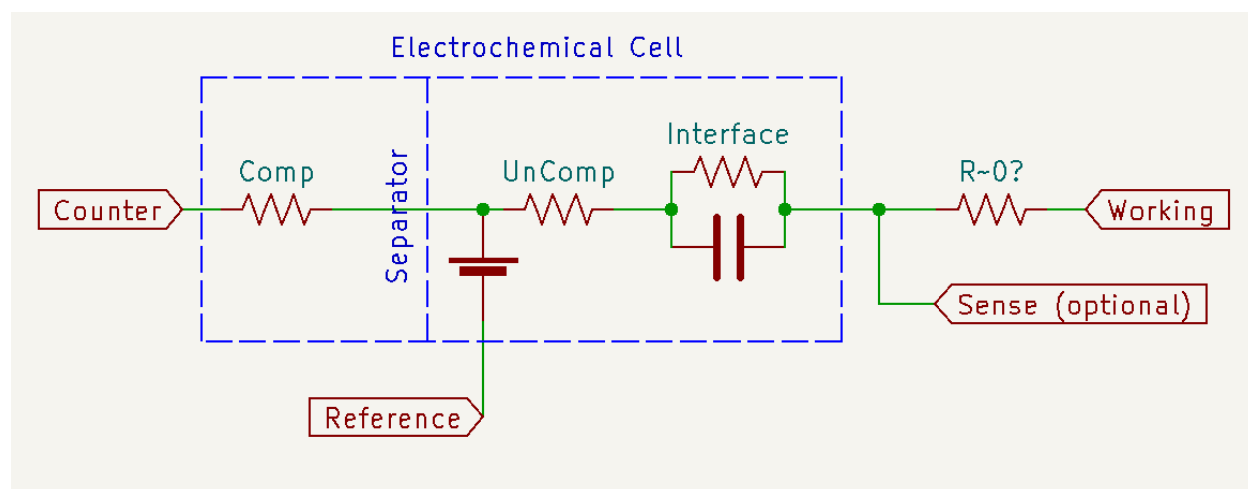


Figure 2 Schematic of an Electrochemical Cell

Fig. 2 shows a summary of the electrochemical cell and the wire connections. Note the Sense electrode is optional unless there is for some reason a lot of resistance in the working electrode wire. The cell, containing the electrochemical solution, is outlined in blue. Often the counter electrode is isolated from the other components by a membrane or separator such as a glass frit or even a piece of filter paper. The Reference electrode is represented as a battery as there is a voltage drop across the electrode that depends upon the particular chemistry used in the reference electrode. The Working electrode interface is represented as a resistor and a capacitor. In reality the I-V characteristics of this interface are highly nonlinear, frequency dependent and show a high degree of hysteresis. Since one measures the voltage drop between the Reference and Working/Sense connectors, the "Compensated" resistance between the Counter electrode and the Reference electrode is immaterial provided the power supply can apply sufficient voltage and current. However, the "Uncompensated" resistance is part of the voltage measurement and we can keep this small by placing the Reference electrode close to the surface of the Working electrode.

The Potentiostat/Galvanostat

The circuit diagram above is basically a feedback loop on the Control Amplifier. Current or Potential information is feed back to the Control Amp via the selector switch. The Control Amplifier is a summation amplifier which adjusts its output voltage to ensure that $V_{in} = -V_{fb}$. Ha, you see. It turns out the Counter electrode is actually the brains behind the operation. We must elevate its lowly status. All hail the Counter electrode.

One can select the feedback voltage from two sources. In the potentiostatic mode, feedback comes from the Instrument amp that outputs the difference between RE and SE, i.e. the voltage drop across the Working electrode. These should be high impedance inputs that do not draw significant current. The Galvanostatic mode feedbacks a voltage proportional to the current. Gains can be varied for both the RE/SE voltage and WE current amplifiers.

The working electrode is at virtual ground. This is important and one can find in the literature example where the Working electrode is not at ground. For example, the Current Amp might be replaced with a resistor and an instrument amp used to measure the voltage drop across that resistor. The Working electrode would then be held at voltages significantly above ground. In environmental monitoring, other sensors, boat hulls and even the actual earth may act as current sinks that could affect the measured current. In the laboratory, where the cell is isolated from ground, the design is less important.

The actual circuit diagram is more complex as we need to amplify signals to varying degrees or buffer the signals for high input impedance or dampen unwanted noise. But those are things that EEs know about and should be able to design. I will prepare as some point a summary of the circuits that I have built and comment on what is most important. Spoiler alert – the choice of op-amps and low impedance capacitances are critical.

Our ultimate goal is to use the above circuit to interface to a wide variety of sensors. Many sensors do not require 4 test leads while others do. A pH electrode is a zero-current, voltage-measurement device and because the current is zero, we need neither the Counter or Working electrodes. A resistive temperature sensor (RTD) connected to a Wheatstone Bridge is a 4-electrode device. A conductivity sensor uses an AC current excitation and measures the resulting AC voltage output. Hence it needs 4-electrodes also. A turbidity sensor is basically a photodiode and hence the current is measured when held at constant potential. This can be done with 2 wires. However, a light source is needed, such as an LED, and we may need additional power leads for some sensors.

The main objective is to simplify the electrical components associated with a sensor that must be placed in our test media and provide a universal interface to all types of sensors. We will talk more about the Universal Sensor Interface concept at a later date.