

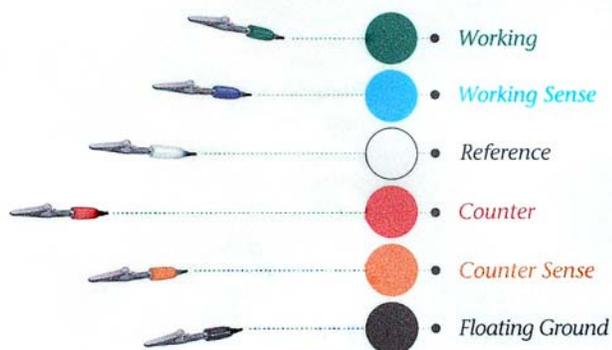
## Two-, Three-, and Four-Electrode Experiments

### Introduction

Electrochemistry uses the control and measurement of a single type of chemical phenomenon with various physical manifestations to study and develop knowledge across a wide array of applications. As such, a large variety of tests have been developed over the years that are good for various studies. Experiments range from simple potentiostatic (chronoamperometry), to cyclic voltammetry (potentiodynamic), to complex AC techniques like impedance spectroscopy. More, each individual technique may have multiple possible experimental setups, often with a best option. This note will be used to discuss one aspect of these setups: the number of electrodes (or probes) used.

### Potentiostat as a Four-Probe Instrument

Gamry potentiostats (as well as some others) are all 4-probe instruments. This means that there are 4 relevant leads that need to be placed in any given experiment. Two of these leads—Working (green) and Counter (red)—carry the current, and the other two—Working Sense (blue) and Reference (white)—are sense leads which measure voltage (potential).



**Figure 1:** Gamry color-coded leads.

Four-probe instruments can be setup to run 2-electrode, 3-electrode, or 4-electrode measurements with just a simple setup change. Understanding why and how to use the different modes can be confusing.

### Electrodes

The discussion of n-electrode mode experiments needs to address what the electrodes are. An electrode is a (semi-)conductive solid that interfaces with a(n) (electrolyte) solution. The common designations are: Working, Reference and Counter (or Auxiliary).

Working electrode is the designation for the electrode being studied. In corrosion experiments, this is likely the material that is corroding. In physical echem experiments, this is most often an inert material—commonly gold, platinum or carbon—which will pass current to other species without being affected by that current.

The Counter or Auxiliary electrode is the electrode in the cell that completes the current path. All electrochemistry experiments (with non-zero current) must have a working – counter pair. In most experiments the Counter is simply the current source/sink and so relatively inert materials like graphite or platinum are ideal, though not necessary. In some experiments the counter electrode is part of the study and the material composition and setup will vary accordingly.

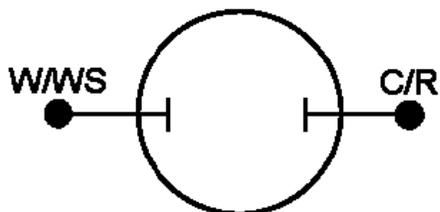
Reference electrodes are, as their name suggests, electrodes that serve as experimental reference points. Specifically they are a reference for the potential (sense) measurements. Reference electrodes should, therefore, hold a constant potential during testing, ideally one which is known on an absolute scale. This is accomplished by first having little or, ideally, no current flow through them, and second by being “well poised” which means that even if some current does flow it will not affect the potential. While many electrodes could be well poised there are several that are very commonly used and commercially available: Silver/Silver Chloride, Saturated Calomel, Mercury/Mercury (mercurous) Oxide, Mercury/Mercury Sulfate, Copper/Copper Sulfate, and more. There are other couples that are often referenced but are not often used today such as the Normal Hydrogen Electrode.

Any conductive material can be used as a reference electrode, but if potential measurements are to be reported that will need to be compared with other systems, use of a non-standard reference will require additional experimentation and explanation.

## Two-Electrode Experiments

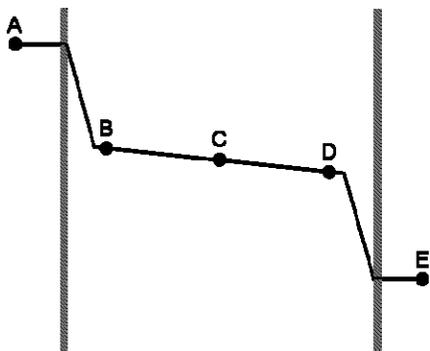
Two-electrode experiments are the simplest cell setups, but often have far more complex results, and corresponding analysis. In a two electrode setup the current carrying electrodes are also used for sense measurement.

The physical setup for two-electrode mode will have the current and sense leads connected together: Working (W) and Working Sense (WS) are connected to a (working) electrode and Reference (R) and Counter (C) are connected to a second (aux, counter, or quasi-/pseudo-reference) electrode. A diagram of 2-electrode cell setup can be seen in Figure 2.



**Figure 2:** 2-electrode cell setup

Two-electrode experiments measure the whole cell, that is, the sense leads measure the complete voltage dropped by the current across the whole electrochemical cell: working electrode, electrolyte, and counter electrode. If the whole cell potential map looks like Figure 3, then 2-electrode setup will have the Working Sense lead at point A and the Reference lead at point E, and so measure the voltage drop across the whole cell.

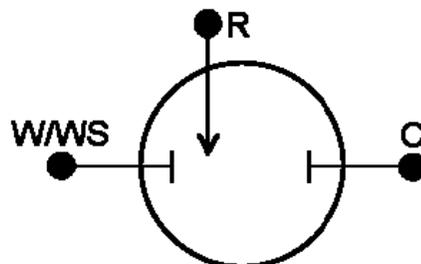


**Figure 3:** Measured (sample) potential map across a whole cell. The Working lead is at point A and the Counter lead at point E.

Two-electrode setups are used in a couple general cases. One is where measurement of the whole cell voltage is significant, for example electrochemical energy devices (batteries, fuel cells, super caps). The other is where the counter electrode potential can be expected not to drift over the course of the experiment. This is generally in systems which exhibit very low currents and/or relatively short timescales and which also have a well poised counter, e.g. a micro working electrode and a much larger silver counter electrode.

## Three-Electrode Experiments

In three electrode mode, the Reference lead is separated from the Counter and connected to a third electrode. This electrode is most often positioned so that it is measuring a point very close to the working electrode (which has both Working and Working Sense leads attached). A diagram of a 3-electrode cell setup can be seen in Figure 4.



**Figure 4:** 3-electrode cell setup

In Figure 3 the sense points are located at A and—roughly—B. Three-electrode setups have a distinct experimental advantage over two electrode setups: they measure only one half of the cell. That is, the potential changes of the working electrode are measured independent of changes that may occur at the counter electrode.

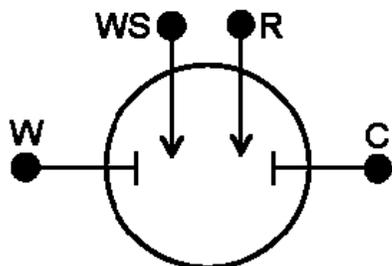
This isolation allows for a specific reaction to be studied with confidence and accuracy. For this reason, 3-electrode mode the most common setup used in electrochemical experimentation.

## Four-Electrode Experiments

In four-electrode mode the Working Sense lead is decoupled from the working electrode, as was (and in addition to) the Reference lead. A diagram of a 4-electrode setup can be seen in Figure 5.

Four-electrode setups are measuring potential along the B-D line in Figure 3, where there may be some “obstruction” at C. This setup is relatively uncommon in electrochemistry, though it does have its place. In 4-electrode mode the potentials for any electrochemical reactions that are occurring at the working (and

counter) electrode(s) are *not* being measured. What is being measured is the effect of an applied current on the solution itself or some barrier in that solution.



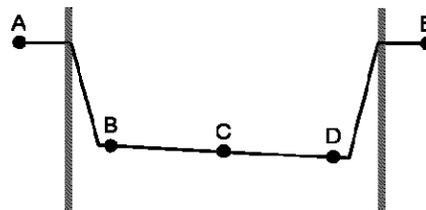
**Figure 5:** 4-electrode cell setup

The most common use of this setup is for measuring impedance across some solution phase interface, such as a membrane or liquid-liquid junction. This setup may also be used to make very accurate measures of solution resistance or the resistance across the surface of some material (solid state cells).

### Special Case Setup: ZRA Mode

Zero Resistance Ammeter (ZRA) experiments do provide a special setup instance. That should be briefly mentioned. In ZRA mode the Working and Counter electrode leads are shorted together, i.e. there is 0 net voltage dropped across the whole cell. For Gamry instruments, the setup is similar to the 3-electrode setup (Figure 4) with an extra, orange Counter Sense

(CS) lead connected to the counter (see Figure 1). The Reference is not critical in this experiment, but can be added to act as a “spectator” electrode to the Working-Counter coupling.



**Figure 6:** Measured potential map across a ZRA mode Cell. W/WS at A, C/CS at E. Note that this is not an accurate potential map within the Helmholtz layers. B and D represent closest measurable approaches.

ZRA mode would redraw Figure 3 as Figure 6 above. Now the potential at A would equal the potential at E. The reference could be at position B, C, or D. The Reference in solution will pick up slightly different potentials based on position, current flow and solution resistance.

ZRA mode is used for galvanic corrosion, electrochemical noise and a handful of specialized experiments.

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