GAMRY INSTRUMENTS

APPLICATION NOTE

Two-, Three-, and Four-Electrode Experiments

Introduction

Electrochemical experiments range from simple potentiostatic (chronoamperometry), to cyclic voltammetry (potentiodynamic), to complex AC techniques such as impedance spectroscopy. Moreover, each individual technique may have multiple possible experimental setups, often with a best option. This note discusses one aspect of these setups: the number of electrodes (or probes) used.

Potentiostat as a Four-Probe Instrument

Gamry potentiostats (and some others) are all 4-probe instruments. This means that there are four 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).

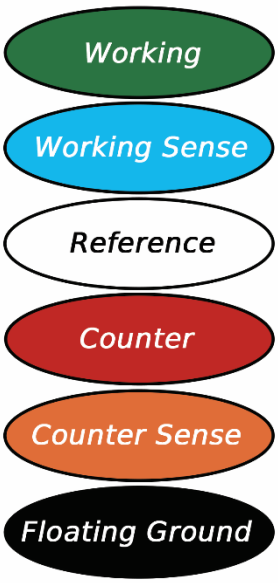


Figure 1: Gamry color-coded leads.

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

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 probably the material that is corroding. In physical-electrochemistry experiments, this is most often an inert material—commonly gold, platinum or carbon—which passes 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 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, so the material composition and setup 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 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 does 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 typically 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 need to be compared with other systems, use of a non-standard reference requires 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 has 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. See Figure 2 for a diagram of a 2-electrode cell setup.

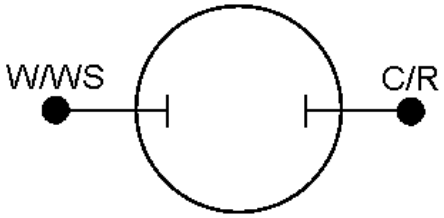


Figure 2: Two-electrode cell setup.

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 a map of the whole-cell potential looks like Figure 3, then a 2-electrode setup has the Working Sense lead at point A and the Reference lead at point E, and so measures the voltage drop across the whole cell.

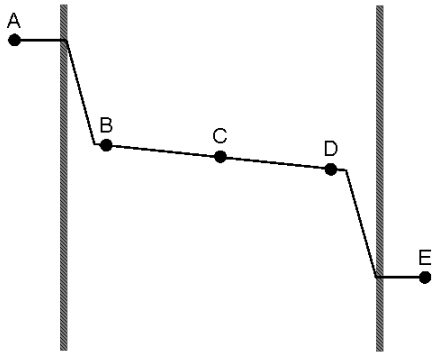


Figure 3: Measured (sample) potential map across a whole cell. The Working lead is at point A and the Counter lead is at point E.

Two-electrode setups are used in a couple of general cases. One is where measurement of the whole cell voltage is significant, for example electrochemical-energy devices (e.g., batteries, fuel cells, supercapacitors). 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 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: see Figure 4).

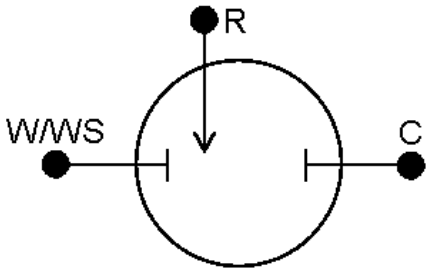


Figure 4: 3-electrode cell setup.

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 is the most common setup used in electrochemical experimentation*.

There is a second case of the three-electrode setup worth explaining. The Interface 5000 potentiostat can measure the voltage difference between the counter sense and reference for some experiments while simultaneously measuring the voltage difference between the reference and working sense. In this instance, you would connect the counter and counter sense to the counter electrode, the reference to the reference electrode, and the working and working sense to the working electrode. In this particular setup you get both half cells in addition to the full cell in a single experiment.

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 (see Figure 5).

Four-electrode setups measure 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.

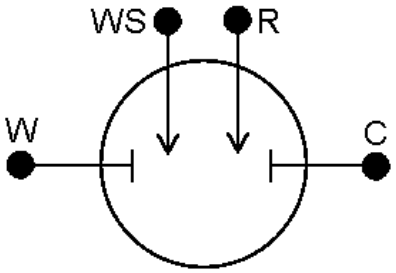


Figure 5: 4-electrode cell setup.

The most common use of this setup is to measure impedance across some solution-phase interface, such as a membrane or liquid-liquid junction. This setup can 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 are a special instance. In ZRA mode, the Working and Counter electrode leads are shorted together inside the instrument, i.e., there is zero 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 electrode is not critical in this experiment, but can act as a "spectator" electrode to the Working-Counter coupling.

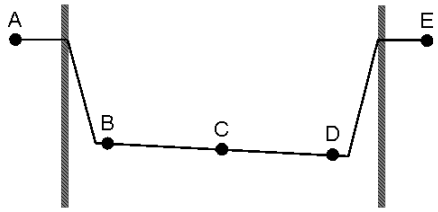


Figure 6: Measured potential map across a ZRA mode Cell. W/WS at A, C/CS at E. Note that this is not an accurate potential map within the Helmholtz layers. B and D represent closest measurable approaches.

ZRA mode redraws Figure 3 as Figure 6. Now the potential at A equals the potential at E. The reference could be at position B, C, or D. The Reference in solution picks 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.

Application Note *Rev. 3.0 9/5/2019 © Copyright* 1990–2015 Gamry Instruments, Inc.

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