

Application Area: Fundamental

Basic overview of the working principle of a potentiostat/galvanostat (PGSTAT) – Electrochemical cell setup

Keywords

Potentiostat, galvanostat, PGSTAT, electrochemical cell, reference electrode, counter electrode, working electrode

Summary

A basic overview of the working principle of a potentiostat/galvanostat is presented. Depending on the application, the connections of the instrument to the electrochemical cell can be (or must be) set up in different ways. Below, the three commonly used electrochemical cell setups are discussed together with the role of the electrodes used in electrochemical measurements.

Basic principle of a potentiostat/galvanostat (PGSTAT)

A basic diagram of a PGSTAT is presented in Figure 1.

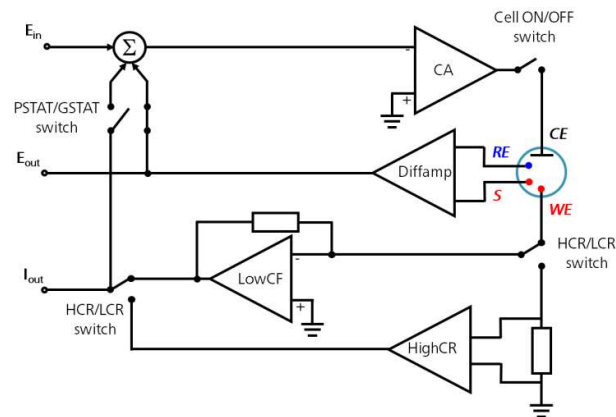


Figure 1 – Basic diagram of a potentiostat/galvanostat

In *potentiostatic mode*, a potentiostat/galvanostat (PGSTAT) will accurately control the potential of the *Counter Electrode* (CE) against the *Working Electrode* (WE) so that the potential difference between the working electrode (WE) and the *Reference Electrode* (RE) is well defined, and corresponds to the value specified by the user. In *galvanostatic mode*, the current flow between the WE and the CE is controlled. The potential difference between the RE and WE and the current flowing between the CE and WE are continuously monitored.

By using a PGSTAT, the value specified by the user (i.e., applied potential or current) is accurately controlled, anytime during the measurement by using a negative feedback mechanism, which is illustrated in Figure 1.

As can be seen from the diagram, the CE is connected to the output of an electronic block, which is called *Control Amplifier* (CA). The control amplifier forces current to flow through the cell. The value of the current is measured using a *Current Follower* (LowCF) or a *Shunt* (HighCR), for low and high currents, respectively. The potential difference is measured always between the RE and S with a *Differential Amplifier* (Diffamp). Depending on the mode the instrument is used (potentiostatic or galvanostatic) the PSTAT/GSTAT switch is set accordingly.

The signal is then fed into the *Summation Point* (Σ) which, together with the waveform set by the digital-to-analog converter (E_{in}) will be used as an input for the control amplifier.

The cell cables of the Autolab PGSTAT (Figure 2) have a total of five connectors: WE, CE, RE, S and ground. The potential is always measured between the RE (blue) and the S (red). Current and potential are always applied between the WE (red) and CE (black). The ground connector (green) can be used to connect external devices to the same ground of the PGSTAT.

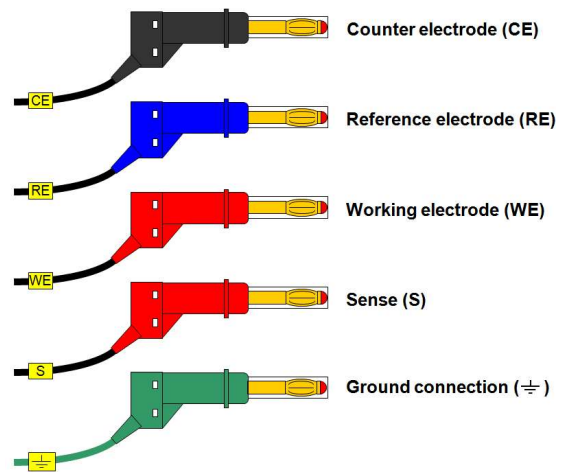


Figure 2 - The connections available on the cell cables of the Autolab PGSTAT and the color code used

Electrodes used in Electrochemistry

The **counter electrode** (also known as auxiliary electrode), is an electrode which is used to close the current circuit in the electrochemical cell. It is usually made of an inert material (e.g., Pt, Au, graphite, glassy carbon) and usually it hosts the half reaction (of the redox reaction) not under investigation. Because the current is flowing between the WE and the CE, the total surface area of the CE (source/sink of electrons) must be higher than the area of the WE so that it will not be a limiting factor in the kinetics of the electrochemical processes under investigation.

The **reference electrode** is an electrode with a stable and well-known electrode potential and it is used as a point of reference in the electrochemical cell for the potential control and measurement. The high stability of the reference electrode potential is usually reached by employing a redox system with constant (buffered or saturated) concentrations of each participants of the redox reaction. Moreover, the current flowing through the reference electrode is kept close to zero (ideally, zero) which is achieved by employing a very high input impedance on the electrometer ($> 100 \text{ G}\Omega$).

Figure 3 provides an overview of some commonly used reference electrodes.

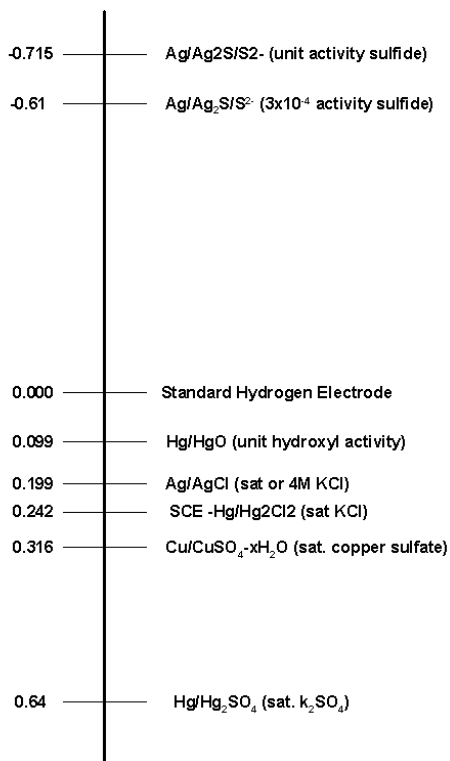


Figure 3 – Potential scale of commonly used reference electrodes (at 25 °C, liquid junction potentials are not considered)

The **working electrode** is the electrode in an electrochemical system on which the half redox reaction of interest is occurring. Common working electrodes can be made of inert materials such as Au, Ag, Pt, glassy carbon (GC), Hg drop, film electrodes etc. For corrosion applications, the material of the working electrode is the material under investigation (which is actually corroding). The size and shape of the working electrode also varies and it depends on the application.

Electrochemical cell setups with Autolab PGSTATS

Two electrode setup

In a two-electrode cell setup (see Figure 4), CE and RE are shorted on one of the electrodes while the WE and S are shorted on the opposite electrode. The potential across the complete cell is measured. This includes contributions from the CE/electrolyte interface and the electrolyte itself. The two-electrode configuration can therefore be used whenever precise control of the interfacial potential across the WE-electrolyte interface is not critical and the behavior of the whole cell is under investigation. This setup is typically used with energy storage or conversion devices like batteries, fuel cells, solar cells, etc. It is also used in measurements of the ultrafast dynamics of electrode processes or electrochemical impedance measurements at high frequencies ($> 100 \text{ kHz}$).

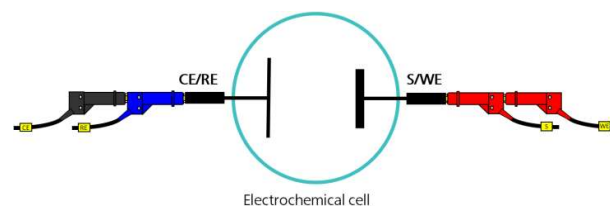


Figure 4 – Schematic view of the 2 electrode setup

Note: to avoid ohmic losses in high current applications, it is recommended to connect the S and RE leads directly to the cell, as indicated in Figure 4.

Three electrode setup

The three-electrode cell setup (Figure 5) is the most common electrochemical cell setup used in electrochemistry. In this case, the current flows between the CE and the WE. The potential difference is controlled between the WE and the CE and measured between the RE (kept at close proximity of the WE) and S. Because the WE is connected with S and the WE is kept at pseudo-ground (fixed, stable potential), by controlling the polarization of the CE, the potential difference between RE and WE is controlled all the time. The potential between the WE and CE usually is not measured. This is the

voltage applied by the control amplifier and it is limited by the compliance voltage of the instrument. It is adjusted so that the potential difference between the WE and RE will be equal to the potential difference specified by the user. This configuration allows the potential across the electrochemical interface at the WE to be controlled with respect to the RE.

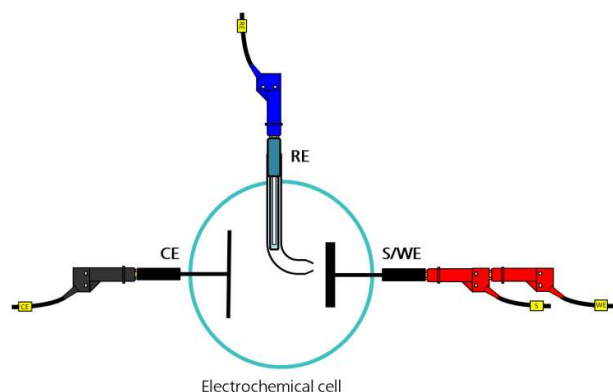


Figure 5 – Schematic view of the 3 electrode setup

To decrease the ohmic losses due to the existence of residual solution between the RE and WE (called *uncompensated resistance*, R_u), a so-called Luggin-Haber (or just Luggin) capillary can be used to bring the RE extremity as close as possible to the surface of the WE (see Figure 5). Since almost no current flows into the reference electrode (typically, the leakage current is a few pA at most), there is little or no voltage drop across the capillary, ensuring that the extremity of the capillary is at a potential very close to the potential of the RE.

Four electrode setup

The four-electrode cell setup (see Figure 6) is used for applications where the potential difference (between RE and S) which occurs because of a passage of a current across a well-defined interface (between WE and CE) needs to be measured. This type of experimental setup is not very common in electrochemistry and usually it is used for measurements of junction potentials between two non-miscible phases or across a membrane, giving the possibility to calculate the resistance of the interface or the membrane conductivity.

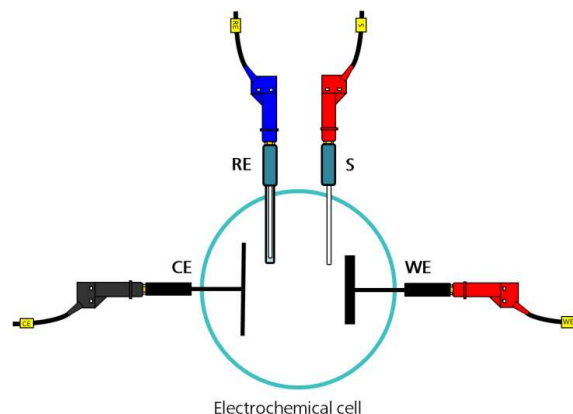


Figure 6 – Schematic view of the 4 electrode setup

References

- (1) A. Bard, L. Faulkner, *Electrochemical Methods – Fundamental and Applications*, 2nd Edition, John Wiley and sons

Date

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For more information

Additional information about this application note and the associated NOVA software procedure is available from your local Metrohm distributor. Additional instrument specification information can be found at www.metrohm.com/en/products/electrochemistry.