FAQ – General

How do I select the most appropriate electrometer mode?

Princeton Applied Research

AMETEK

Subject: Instrument Properties – Electrometer Mode

Introduction

In the broad field of electrochemistry potentiostats are used to measure batteries, sensors, and corrosion cells, among other cell varieties. These cells may respond quickly or slowly and generate high or low currents, sometimes both in a single experiment.

Princeton Applied Research potentiostats are designed with flexibility to tailor their function to specific applications and cells. These options are selectable within the *Advanced Panel* of VersaStudio under *Instrument Properties*, as shown in **Figure 1**. This note addresses the Electrometer Mode setting and is part of a series intended to educate users on the function of the various *Instrument Properties* so that the best measurement can be acquired.

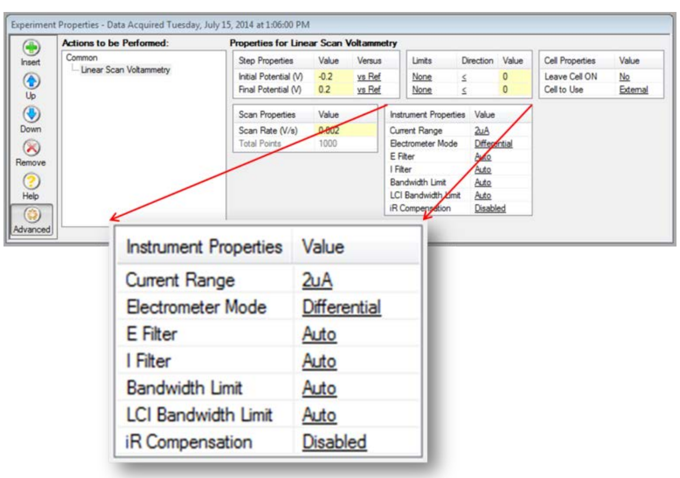

Figure 1: *Experiment Properties* window in VersaStudio showing the *Advanced* panel where the *Instrument Properties* settings can be selected.

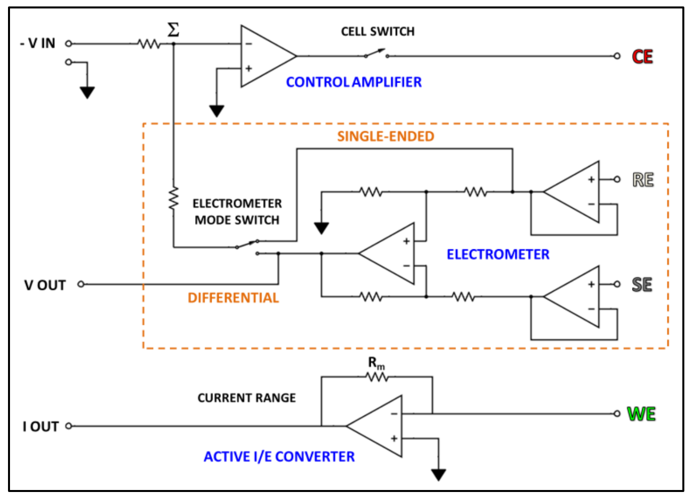

Figure 2: Potentiostat block diagram. V IN is the requested voltage and V OUT is the measured voltage recorded by the software. The dashed box encompasses the electrometer.

Consider the simplified block diagram of a potentiostat in **Figure 2**. There are 3 main components, each with a specific function. The **electrometer** measures the voltage between the sense electrode (SE) and reference electrode (RE) and reports this as V OUT, which is the voltage recorded in the software. The **electrometer** is also responsible for inputting the cell voltage into the control amplifier, which will be described in detail below. The **control amplifier** maintains the user requested potential (V IN) between the working electrode (WE) or SE and RE by supplying power to the counter electrode (CE). This polarization of the sample results in current flowing between the CE and WE at a rate that satisfies the electrochemistry of the system. These two components, in conjunction with the cell, define the control loop. The final component is the **I/E converter**, which measures the current between the CE and WE by converting current to an output voltage dependent on the size of R_m.

The VersaSTAT and PARSTAT MC family of potentiostats are designed with a virtual ground, or “active”, I/E converter. This design allows users to select between **single-ended** or **differential** electrometer modes. By selecting the electrometer mode, the user is determining how the feedback voltage ($V_{feedback}$, see **Figure 4**) is input into the control amplifier, which is part of the control loop. Regardless of the selected electrometer mode, the digitized potential (V OUT; $V_{measured}$) recorded by the software is always measured in differential mode as the potential difference between the RE and SE. The SE lead must **ALWAYS** be connected. In a typical 2- or 3-electrode configuration (**Figure 3a** and **3b**), the WE is connected directly to the SE and V OUT becomes the potential difference between RE and WE; since $V_{WE} = V_{SE}$. The incorporation of the SE makes differential mode possible.

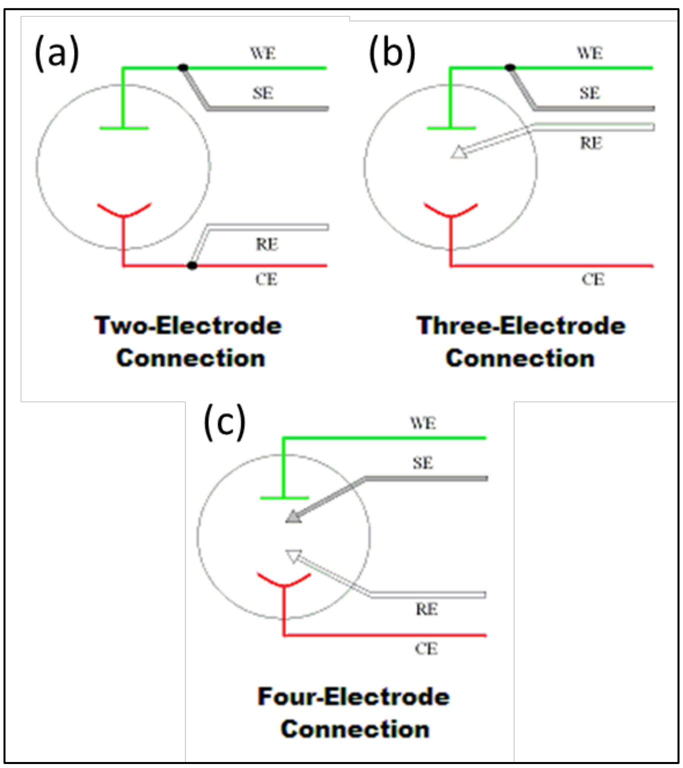

Figure 3: Schematic for two-, three- and four-electrode cell connections.

The difference between the two electrometer modes arises in how the feedback is supplied to the control amplifier via the summing point (Σ). At Σ, -V IN is combined with the feedback potential ($V_{feedback}$) to provide the input for the control amplifier. Note that **Figure 2** indicates that -V IN is used as the input, which denotes the opposite polarity the user requested since an inverting configuration is shown. *In single-ended mode, the $V_{feedback}$ is measured between RE and ground, while in differential mode it is measured between RE and SE.*

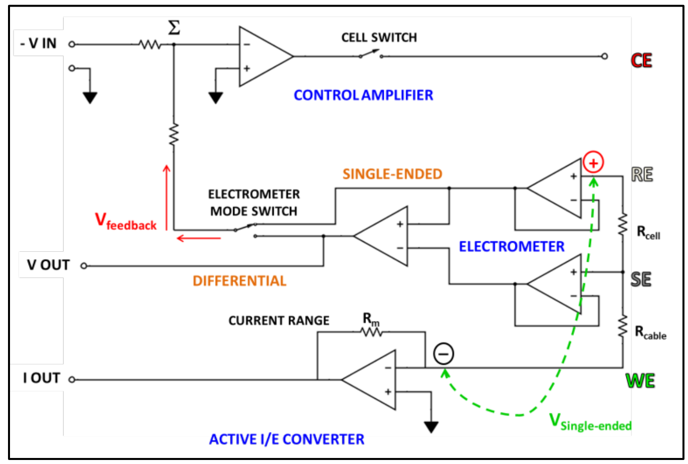

Figure 4: Potentiostat block diagram depicting contributions to the feedback voltage when measured in single-ended mode.

Many of the early generation potentiostats used single-ended electrometers for measuring **both** the voltage at the cell and as the feedback for the control amplifier. Recall that this mode measures the voltage between the RE and ground ($V_{Single\text{-}ended}$, **Figure 4**), but by holding the WE at virtual ground, the measured potential can now be reported as the voltage between the RE and WE.

The active I/E converter is responsible for maintaining the WE at virtual ground, as depicted in **Figure 4**. This is a simplified version of the circuit from **Figure 2**, with the addition of R_{cell}, representing the electrochemical cell, and R_{cable}, representing the overall resistance of the WE cell cable. This figure illustrates that $V_{Single\text{-}ended}$ includes the cell voltage and the voltage drop due to the cable. Depending on the electrochemical system under study, this design can improve or diminish the quality of the measurement.

Examples

First consider a low impedance, high current cell, such as a rechargeable battery. The impedance of the cell cable and interconnects contribute more to the overall impedance when measuring low impedance cells. This can lead to incorrect data interpretation or even negatively impact the quality of the data. The high current is also problematic since it results in a larger voltage drop across $R_{cable.}$ This may cause $V_{Single\text{-}ended}$ to be substantially more than the true cell voltage. As part of the feedback loop, this will result in the incorrect voltage being driven by the control amplifier and V OUT will no longer closely match V IN. This effect is illustrated by comparing linear scan voltammetry of a 1 Ω resistor in single-ended and differential modes, as shown in in **Figure 5**. The requested voltage range for V IN was -0.2 to 0.2 V; therefore, the theoretical maximum current is 200 mA (Ohm's Law, V=iR). Clearly the full voltage range is not reached in single-ended (black) mode, but is readily achieved in differential (red) mode.

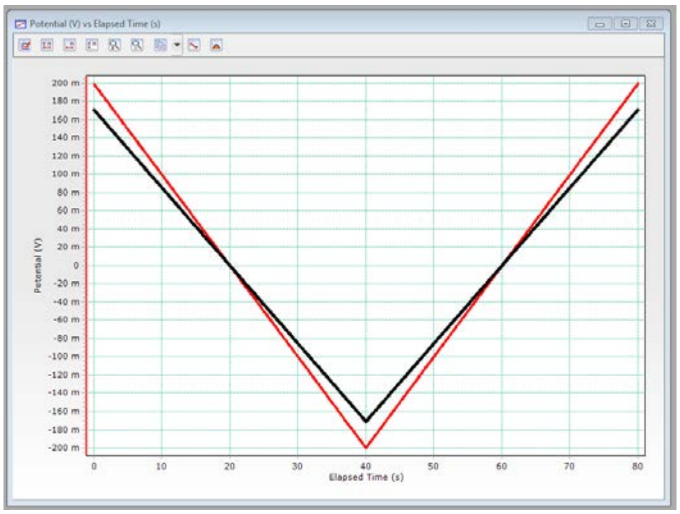

Figure 5: Potential vs. time plot from cyclic voltammetry of a 1 Ω resistor in single-ended (black) and differential (red) mode.

To understand why differential mode is so well suited for high current measurements we return to **Figure 4**. $V_{feedback}$ in differential mode is equivalent to the true cell voltage since the measurement is taken between the SE and RE, which are placed directly across the cell (R_{cell}). For high current cells, the most accurate voltage measurements are obtained using the 4-electrode configuration, as depicted in **Figure 3c,** which **REQUIRES** that differential mode be used. Note that the voltage carrying leads (RE and SE) are closest to the cell and the current carrying leads (WE and CE) are furthest from the cell. This ensures that the voltage is being measured as close to the cell terminals as possible and minimizes errors due to ohmic drop outside the cell.

Let us now consider a low current cell, as is typical with fundamental electrochemical studies and sensors using microelectrodes or ultramicroelectrodes (UMEs). In this scenario, the voltage loss due to the cable will be low (V=iR) and $V_{Single\text{-}ended}$ will approximate the true voltage across the cell, as demonstrated in **Figure 6**. Note that the requested voltage range (V IN from -0.2 to 0.2 V) was applied in both single-ended (black) and differential (red) mode, meaning either mode will provide accurate results.

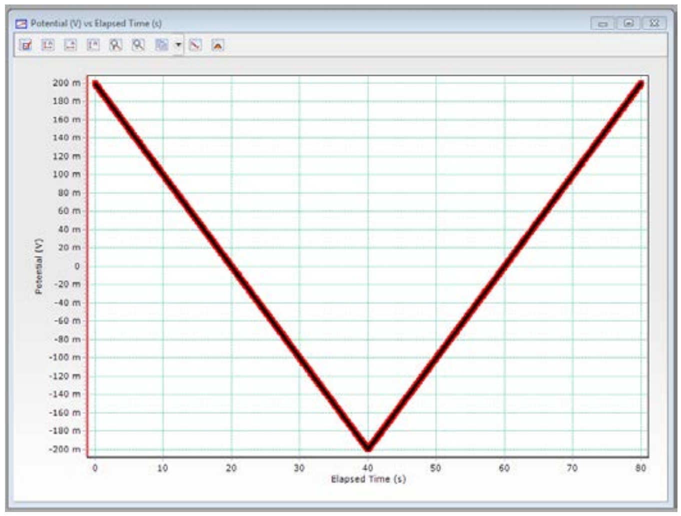

Figure 6: Linear scan voltammetry of a 100 kΩ resistor in single-ended (black) and differential (red) mode

A typical corrosion cell will also generate low currents; however, these cells are often highly capacitive. Capacitive cells can lead to oscillations that appear in the results as "noisy" data. This is especially problematic in differential mode as shown in **Figure 7**, which compares the potential vs. time plots for linear scan voltammetry on a 100 μF capacitor in single-ended and differential modes.

When performing an experiment in differential mode, if you notice oscillations in your data, the experiment should be repeated in single-ended mode in an attempt to minimize these oscillations. If this approach is successful check that the voltage you requested is being applied accurately. In other words, verify that the voltage drop across the cell cable is not substantially impacting the feedback voltage, $V_{Single\text{-}ended}$. In the example in **Figure 7**, the requested voltage range, 0.34

to 0.43 V, was applied in single-ended mode. This is evident by overlaying the potential vs. time data from both modes and suggests the experiment should be run in single-ended mode to obtain the highest quality results.

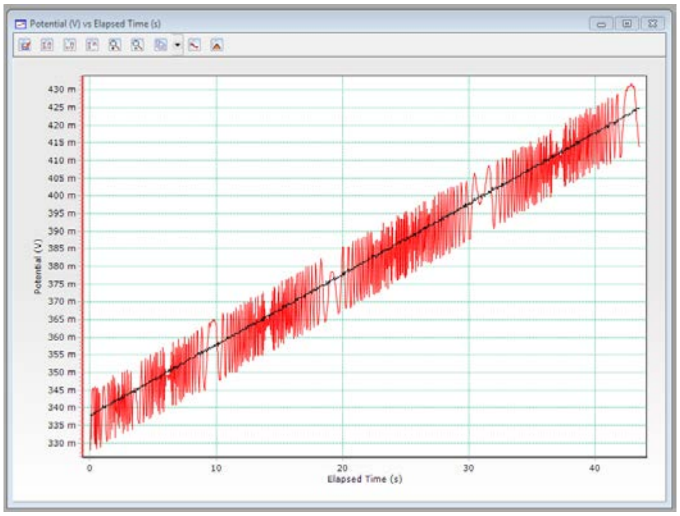

Figure 7: Potential vs. time plot from Linear scan voltammetry of a 100 μF capacitor in single-ended (black) and differential (red) mode

Summary

The following key points should be used as a guide for selecting the appropriate electrometer mode whenever running a new experiment.

- Differential electrometer mode –
  - Best suited for high currents (200 mA range and higher) and/or low impedance cells.
  - Works with all electrode configurations and MUST be used for 4-electrode configurations.
  - Most accurate results, regardless of current
- Single-ended electrometer mode –
  - Ideal when measuring low currents on highly capacitive cells (large samples) or any cell experiencing oscillations.
  - Can reduce oscillations, but accuracy of the feedback voltage is dependent on the current magnitude being measured.

If you are unsure about which mode is best, we suggest you run the experiment using the default electrometer mode. Currently, each Action in VersaStudio defaults to the electrometer mode deemed the most appropriate for that type of experiment and the cells typically studied by the experiment. This setting is designated as "Auto", which can be used as a starting point. If the results show non-ideal behavior as detailed in this document, then the user should refer to the guidelines for selecting the appropriate electrometer mode and may find it useful to run a typical experiment in both modes and then compare the results.