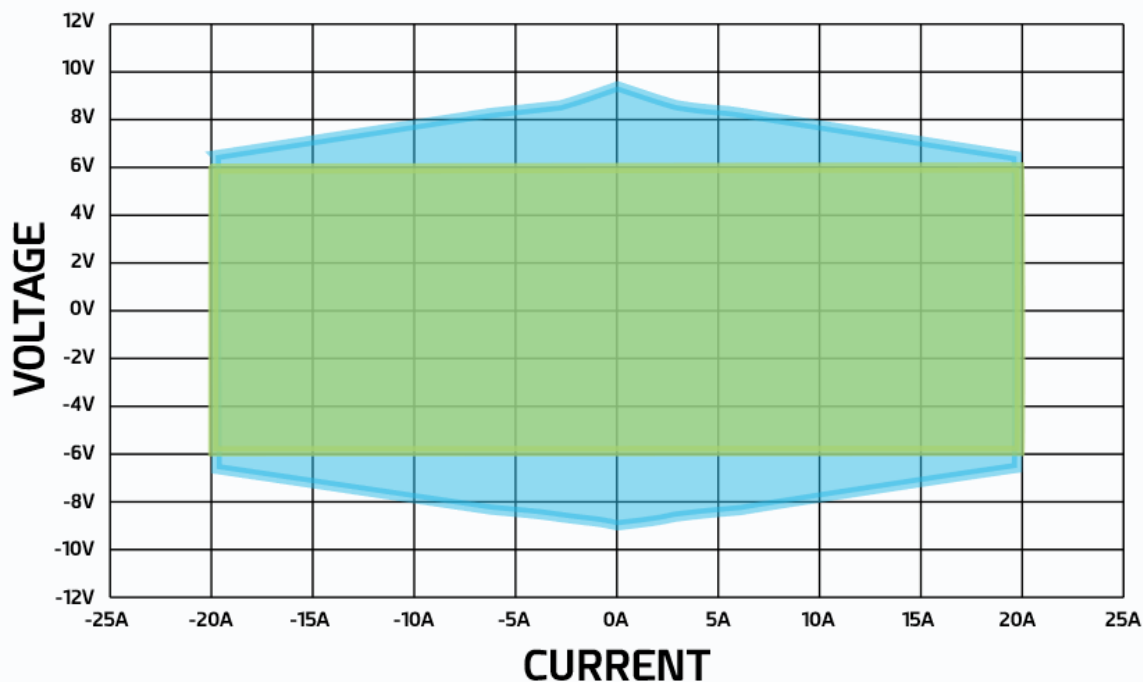


Understanding Compliance Voltage in Potentiostats



Abstract

Compliance voltage plays a critical role in determining the operating limits of potentiostats during electrochemical measurements. It represents the maximum voltage the instrument can supply to drive current through the electrochemical cell while maintaining the desired potential control at the working electrode. This application note explains the main sources of voltage loss within an electrochemical cell and how these contributions affect the overall compliance voltage requirement in both two- and three-electrode configurations. By understanding the origins and implications of compliance voltage, users can better interpret instrument limitations, diagnose possible measurement issues, and design electrochemical experiments that operate reliably within the potentiostat's capabilities.

What is Compliance Voltage

Compliance voltage is a critical hardware specification for potentiostats. It is defined as the maximum voltage the potentiostat's control amplifier can generate at the Counter Electrode (CE) to maintain the desired potential between the Working Electrode (WE) and Reference Electrode (RE). In addition to compliance voltage, manufacturers also list the voltage scan range. Unlike compliance voltage, the scan range is defined as the range of potential that the potentiostat can apply and control between the WE and RE.

Therefore, in a three-electrode setup, the compliance voltage is typically slightly higher than the voltage scan range because the controlled potential is applied between the WE and RE, while the cell voltage is

measured between the CE and WE. In contrast, in a two-electrode setup, the compliance voltage is equal to the voltage scan range because the applied potential is between the WE and the combined RE/CE electrode.

Figure 1 shows example compliance voltage graphs for **(A)** a three-electrode setup and **(B)** a two-electrode setup.

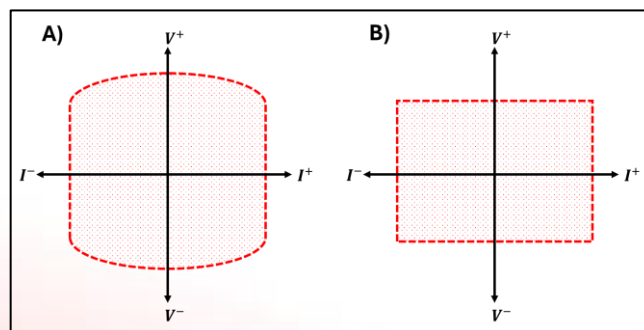


Figure 1. Compliance voltage graph A) for a three-Electrode Setup: The potentiostat adjusts the CE voltage sometimes to very high levels to ensure the WE stays at the exact setpoint relative to the RE. B) for a two-Electrode Setup: The compliance voltage is simply the maximum voltage applied between the WE and the CE/RE combined.

1. Components of the Compliance Voltage

Although, using a typical three-electrode electrochemical cell, potentiostats should offer enough compliance voltage at the CE to overcome all voltage drops in the circuit while maintaining the desired potential between WE and RE. For a two-electrode setup the Reference (RE) and Counter (CE) leads are shorted together, so the potentiostat no longer distinguishes between the potential of the counter electrode and the reference point. **Figure 2** illustrates the compliance voltage components for A) three -electrode setup and B) two-electrode setup.

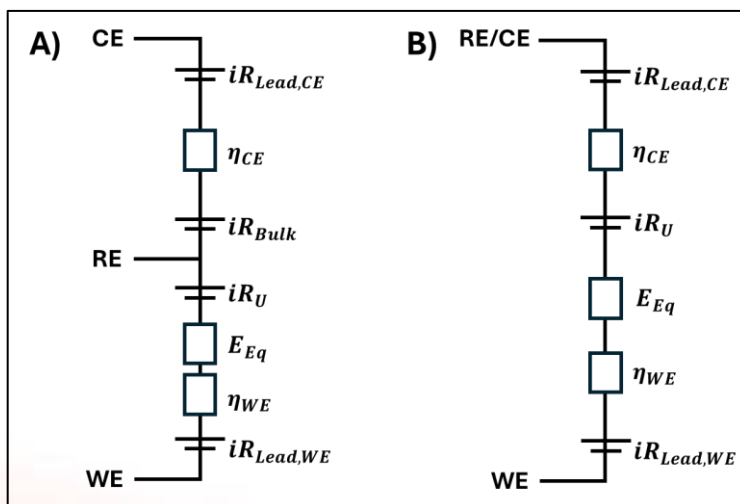


Figure 2. Compliance voltage components for A) three-electrode setup and B) two-electrode setup.

To maintain control of the electrochemical system, the potentiostat must overcome several cumulative voltage drops within the cell. The total voltage required at the CE can be expressed as:

$$V_{Compliance} = V_{Applied} + \Sigma V_{Drops}$$

Voltage drops occur due to the natural chemistry and physics of the cell. Some components cause higher voltage drops while the others have minimal contribution.

Some components contribute significantly to the total voltage requirement, while others have only a minor effect. The impact of several of these components can be minimized through good experimental practices, which will be discussed in the following sections.

Three-Electrode Setup

In a typical three-electrode cell, the main voltage drop components are the uncompensated resistance, bulk solution resistance, electrode overpotentials, and connection resistances:

$$V_{Compliance} = V_{Applied} + V_U + V_{Bulk} + V_{CE} + V_{Leads}$$

Two-Electrode Setup

In a typical two-electrode configuration, the voltage drop components are usually the uncompensated resistance, electrode overpotentials, and connection resistances:

$$V_{Compliance} = V_{Applied} + V_U + V_{CE} + V_{Leads}$$

1.1 Voltage Applied by the Potentiostats

$V_{Applied}$ is the voltage set between the WE and RE by the potentiostat. It represents the thermodynamic and kinetic driving force required for the electrochemical reaction.

$$V_{Applied} = E_{WE} - E_{RE}$$

This is the "intentional" voltage applied during the experiment. Although it is not a physical loss, it contributes directly to the total compliance voltage that the CE must supply. The $V_{Applied}$ can be further expressed as:

$$E_{WE} - E_{RE} = E_{Eq} + V_{WE}$$

Where E_{eq} is the equilibrium potential, and V_{WE} is the working electrode overpotential.

In a typical aqueous electrochemical experiment, this is often between 0 and 2 V vs reference. In non-aqueous systems or water splitting experiments it might reach 3–5 V. Substituting this relationship into the compliance voltage expression gives:

Three-Electrode Setup

$$V_{\text{Compliance}} = E_{\text{Eq}} + V_{\text{WE}} + V_U + V_{\text{Bulk}} + V_{\text{CE}} + V_{\text{Leads}}$$

Two-Electrode Setup

$$V_{\text{Compliance}} = E_{\text{Eq}} + V_{\text{WE}} + V_U + V_{\text{CE}} + V_{\text{Leads}}$$

1.2 Working Electrode Overpotential

V_{WE} accounts for the kinetic loss at the working electrode interface, required to drive the desired Faradaic reaction (Nernst Equation):

$$V_{\text{WE}} = \eta_{\text{WE}}(i_F) = \frac{RT}{\alpha_{\text{WE}} n_{\text{WE}} F} \ln \left(\frac{i_F}{i_{0,\text{WE}}} \right)$$

Where $\eta_{\text{WE}}(i_F)$ is the overpotential needed to drive the Faradaic current (i_F) at the WE, R = gas constant, T = temperature, F = faraday constant, n = number of electrons transferred, α = charge transfer coefficient, i_0 = exchange current density

This term represents the additional voltage required beyond the equilibrium potential to drive electrons across the electrode–electrolyte interface and overcome activation barriers. Capacitive current (i_C) does not contribute to this overpotential because it does not involve charge transfer.

For moderate reactions with decent exchange current density, overpotentials are typically 50–300 mV at low current densities. For reactions such as oxygen evolution or hydrogen evolution, this can reach 300–600 mV, and at very high current densities even 1 V or more.

Faradaic Current i_F

Faradaic current results from charge-transfer reactions occurring at the electrode surface and is governed by electrode kinetics. For a simple redox reaction, the Butler–Volmer equation describes this behavior:

$$i_F = i_0 \left[e^{\frac{\alpha n F \eta}{RT}} - e^{-\frac{(1-\alpha) n F \eta}{RT}} \right]$$

Capacitive current, i_C

Capacitive current arises from charging the electrical double layer at the electrode surface:

$$i_C = C_{dl} \frac{dE}{dt}$$

Where C_{dl} = double layer capacitance, dE = interfacial potential (true electrode surface potential)

1.3 Uncompensated Voltage Drop

V_U represents the ohmic loss across the specific portion of the electrolyte located between the WE surface and the tip of the RE. Both Faradaic (i_F) and capacitive (i_C) current contribute to this drop:

$$V_U = (i_F + i_C) R_U = (i_{\text{total}}) R_U$$

$i_{\text{total}} R_u$ is the uncompensated voltage drop where R_u is the solution resistance between the WE and RE.

In a well-conducting aqueous electrolyte such as 0.1 M KCl, the solution resistance might be 5–20 Ω . At 10 mA, this causes only 0.05–0.2 V of loss which is relatively small. However, in dilute electrolytes, nonaqueous solvents, or poorly spaced electrodes, resistance can easily reach 100–1000 Ω . At 50 mA with 200 Ω , the drop becomes 10 V. At this point, bulk resistance dominates the compliance requirement. In most practical laboratory three-electrode systems, uncompensated resistance can be one of the major contributions to the required voltage.

1.4 Voltage Drop Across the Bulk Electrolyte

In a three-electrode system, V_{Bulk} refers specifically ohmic loss due to ions moving through the electrolyte between the RE and the CE. Both i_F and i_C contribute because both generate ionic motion:

$$V_{Bulk} = (i_F + i_C)R_{Bulk}$$

Unlike R_U , the bulk resistance does not affect the accuracy of the potential measured at the WE. Instead, it acts as a load on the potentiostat's power supply. Simply, this voltage drop does not affect the $V_{Applied}$, but the potentiostat must overcome it to push current through the cell. If the solution is non-aqueous or the RE and CE are far apart, this term can be massive (10–50 V), leading to "Compliance Voltage" errors where the instrument hits its limit.

1.5 Counter Electrode Overpotential

V_{CE} is the voltage the counter electrode must supply to carry the entire cell current as the CE must pass the total current ($i_F + i_C$) to balance the WE.

$$V_{CE} = \eta_{CE}(i_{total}) = \frac{RT}{\alpha_{CE}n_{CE}F} \ln \left(\frac{i_{total}}{i_{0,CE}} \right)$$

The CE must pass all the total current (faradaic + capacitive). If the CE is large and highly catalytic the overpotential at the CE can be small (10–100 mV). However, if the CE is small, poorly catalytic or generating gas, the overpotential can rise dramatically (0.1–2 V).

1.6 Voltage Drop in Wiring and Contacts

All physical wires, connectors, and clips carry current and therefore introduce a small ohmic drop:

$$V_{Leads} = i_{total}R_{Leads}$$

$$V_{Leads} = i_{total}(R_{Lead,WE} + R_{Lead,CE})$$

The resistance of the reference electrode lead does not significantly affect the measurement because the RE circuit has "infinite" input impedance meaning almost zero current flows through it. Similarly, the WE lead resistance usually does affect the potential control if a proper 4-electrode setup is used. So most lead-related compliance demand comes from the CE side, where entire cell current flows. In most laboratory setups using the default cabling would be a wise decision as the typical resistance of default cables is very small (0.01–0.2 Ω). At 10 mA, the voltage loss is essentially negligible (less than 2 mV). Even at 100 mA, it may only be 10–20 mV. However, in battery testing, fuel cells, or high-current experiments where currents reach amperes or tens of amperes, this term can become significant if additional cabling is used to increase the length of default cabling (0.2–0.5 Ω). For example, 1 A flowing through 0.5 Ω gives 0.5 V drop. At 10 A, that becomes 5 V. Despite this, wiring losses are typically the smallest contribution when default cabling is used.

2. Total Compliance Voltage

Three-Electrode Setup

The compliance voltage for a three-electrode setup is the sum of the contributions listed under section 1:

$$V_{Compliance} = [E_{eq} + \eta_{WE}] + [i_{total}R_U + i_{total}R_{Bulk} + \eta_{CE} + i_{total}R_{Leads}]$$

Two-Electrode Setup

Similarly, for a two-electrode setup:

$$V_{Compliance} = [E_{eq} + \eta_{WE}] + [i_{total}R_U + \eta_{CE} + i_{total}R_{Leads}]$$

In simpler terms for both electrode configurations the Compliance Voltage can be expressed as:

$$V_{Compliance} = V_{Applied} + V_{Load}$$

3. Do You Really Need High Compliance Voltage?

In most well-designed electrochemical setups, these losses are relatively small. Conductive electrolytes, reasonable electrode spacing, and proper reference electrode placement all help minimize resistance in the system. As a result, the potentiostat only needs a small amount of additional voltage to maintain control of the working electrode potential. Very high compliance voltages become important primarily in high-current or highly resistive systems such as battery testing, electrolysis, fuel cells, or experiments with poorly conductive electrolytes. These cases represent a small fraction of typical electrochemical measurements.

Designing instruments to support extremely high compliance voltages requires more power and more complex circuitry, which increases system complexity and cost. For the majority of electrochemical experiments, the voltage required to compensate for cell resistance is relatively small, making very high

compliance voltage unnecessary in practice. Instead of relying on large voltage reserves, good electrochemical practice focuses on minimizing resistance within the cell through appropriate electrolyte choice, electrode geometry, and cell design.

4. How To Test the Compliance Voltage

Typically, voltages higher than the instrument's voltage scan range are not required for most experiments when a proper electrochemical setup is used. However, understanding the actual limits of your instrument is important for fully utilizing the capabilities of your potentiostat. This section describes the procedure for generating a compliance voltage graph for a single instrument, using the Squidstat Venta potentiostat as an example. **Figure 3** shows an example compliance voltage graph (blue) and voltage scan range (green) generated for a Squidstat Venta potentiostat (Item#: VE-2X-M2).

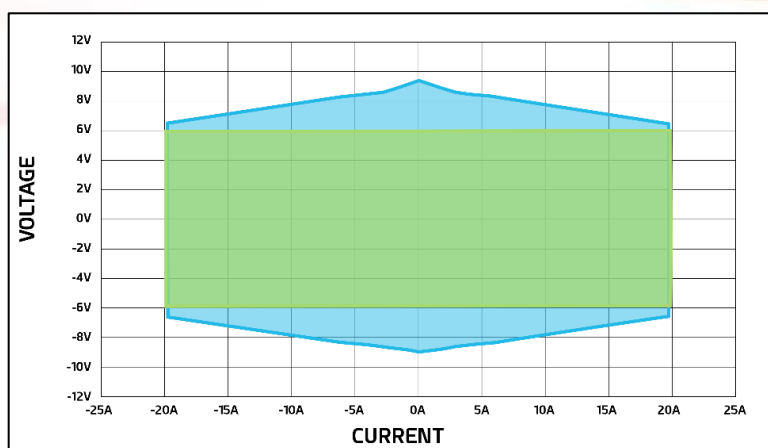


Figure 3. Example device-specific compliance voltage and voltage scan range for a Squidstat Venta unit.

4.1 Cabling, Resistors and Setup

Compliance voltage depends on the experimental setup. To minimize the effect of unnecessary voltage drop components, the standard 1m cable supplied with the instrument should be used. Using different cables

may alter the results because additional compliance voltage components can be introduced. If cables are swapped or replaced, it is recommended to run the cable calibration function in the Squidstat Support Utility before performing further experiments.

In addition to the cables, generating a compliance voltage graph requires several materials. Specifically, three stable and reliable resistors with different resistance values are needed, each capable of handling the Squidstat's current and voltage limits. For this application note, 0.33 Ω , 1.33 Ω , and 3 Ω precision resistors, along with an open-lead configuration (infinite resistance), were used to generate the compliance voltage graph for the Squidstat Venta potentiostat. For compliance characterization of other Squidstat potentiostat models, please contact us directly.

4.2 Data Collection

Effective utilization of compliance voltage requires a structured approach to data collection. In this section, the procedures for collecting and post-processing the DC data are outlined.

4.2.1 Parameters

As an initial step, create an experiment sequence with two constant current tiles arranged consecutively using the "Build an Experiment" tab in the Squidstat User Interface (SUI). The duration for both constant current tiles should not exceed 3 seconds to prevent overheating and potential damage to the resistors. The sampling interval can be set to 0.2 seconds (5 data points per second).

For the first Constant Current tile, the "Current" parameter value should be set to the maximum positive current that the instrument can apply. In this case (Squidstat Venta), the maximum current value should be set to +20 A.

For the second Constant Current tile, the "Current" parameter value should be set to the maximum

negative current that the instrument can apply. In this case, the maximum negative current value should be set to -20 A.

After configuring the parameters, save the sequence using a preferred name. The experiment can then be accessed from the "Run an Experiment" tab. **Table 1** summarizes the parameters used for each tile for testing the Compliance Voltage of a Squidstat Venta.

Table 1. Constant Current Parameters Used to Generate Compliance Voltage Graph for Squidstat Venta

Tile #	Current (A)	Duration (s)	Sampling Interval (s)
1	+20	3	0.2
2	-20	3	0.2

4.2.2 Experimental Setup

After setting up the experiment, begin by connecting the Squidstat leads to the lowest resistor in your set using a 4-point Kelvin connection. Next, select the experiment you created under the "Run an Experiment" tab and start the measurement.

Once the experiment is complete, open the generated .csv data file. At this stage, a simple calculation is required. First, calculate the average of the "Current (A)" column separately for positive current values and negative current values. Then, calculate the average of the "Voltage (V)" column separately for positive voltage values and negative voltage values. After measuring the first resistor, repeat the same procedure for each of the remaining resistors in the set. **Table 2** shows an example dataset generated using the Squidstat Venta potentiostat with 0.33 Ω , 1.33 Ω , and 3 Ω precision resistors measured in an open-lead configuration.

Table 2. Compliance Voltage Test Results for Squidstat Venta

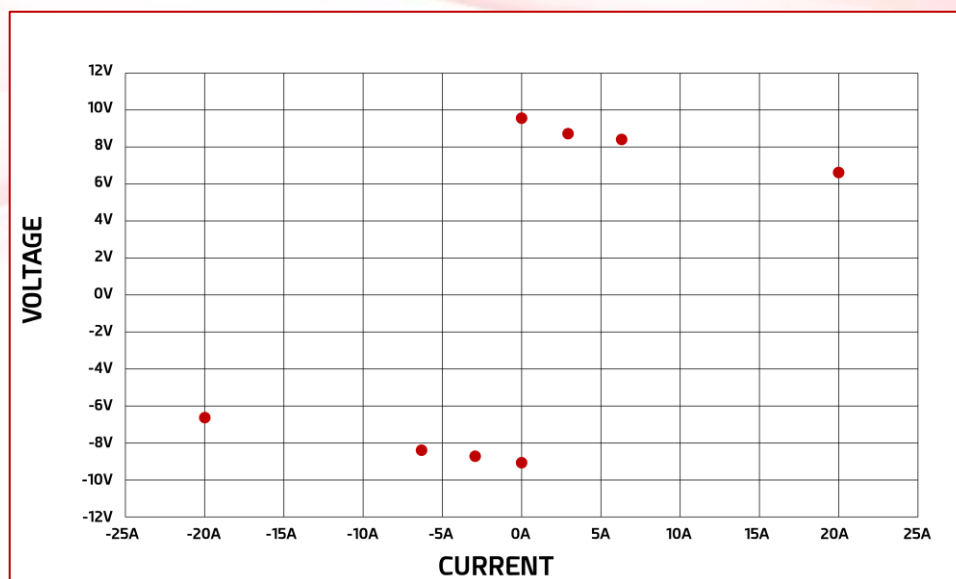
R_{used} (Ohm)	$I_{applied}$ (A)	$I_{measured}$ (A)	$V_{measured}$ (V)
0.33	+20	19.99	6.63
0.33	-20	-19.98	-6.63
1.33	+20	6.31	8.41
1.33	-20	-6.32	-8.40
3	+20	2.92	8.73
3	-20	-2.93	-8.71
Open-Leads	+20	0.00	9.56
Open-Leads	-20	0.00	-9.06

4.3 Graph Generation

Once the data collection is completed the resulting graph will look like **Figure 4**. Because resistors are used in the measurement, the system follows Ohm's law, meaning the voltage response is directly proportional to the applied current. As a result, when a positive current is applied, a positive voltage is

measured, and when a negative current is applied, the voltage is also negative.

To complete the graph, the data can be mirrored. This is done by multiplying the measured current values ($I_{measured}$) with -1 plotting these mirrored current values against the corresponding measured voltages ($V_{measured}$).

**Figure 4.** Plot illustrating the raw data collected, as shown in Table 2.

After mirroring the data, an additional dataset is created that complements the originally measured values. This mirrored dataset is then added to the graph to complete the symmetric response expected for a purely resistive system. The calculated mirrored values and their corresponding voltage points are summarized in **Table 3**.

Table 3. Compliance Voltage Calculation Results for Squidstat Venta

R_{used} (Ω m)	$I_{applied}$ (A)	$I_{measured}$ (A)	$V_{measured}$ (V)	$-I_{measured}$ (A)
0.33	+20	19.99	6.63	-19.99
0.33	-20	-19.98	-6.63	19.98
1.33	+20	6.31	8.41	-6.31
1.33	-20	-6.32	-8.40	6.32
3	+20	2.92	8.73	-2.92
3	-20	-2.93	-8.71	2.93
Open-Leads	+20	0.00	9.56	0.00
Open-Leads	-20	0.00	-9.06	0.00

Then the raw measured values and the calculated mirrored values are plotted together on the same graph. The resulting plot (**Figure 5**) presents the full dataset and provides a more complete visualization of the measurement.

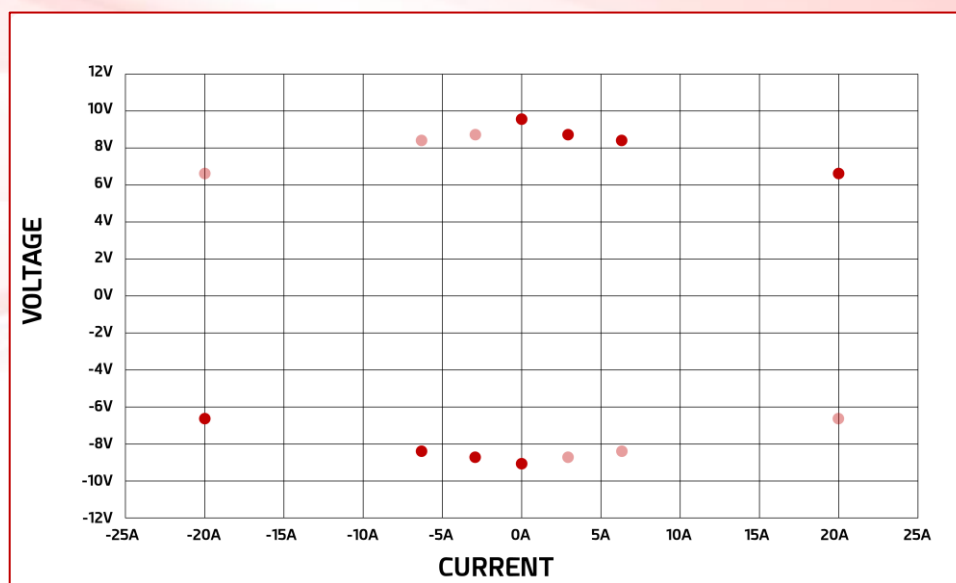


Figure 5. Plot illustrating the mirrored data used to achieve a complete visualization of the measurement.

As a final step to improve visualization, the area defined by the plotted data points is highlighted in blue and labeled as the compliance voltage range (**Figure 6**). Additionally, to provide a clear comparison, the voltage scan range is also highlighted on the graph where the voltage scan range is ± 6 V and the current range is ± 20 A for the Squidstat Venta, allowing the compliance voltage range to be viewed in the context of the instrument's full operating limits.

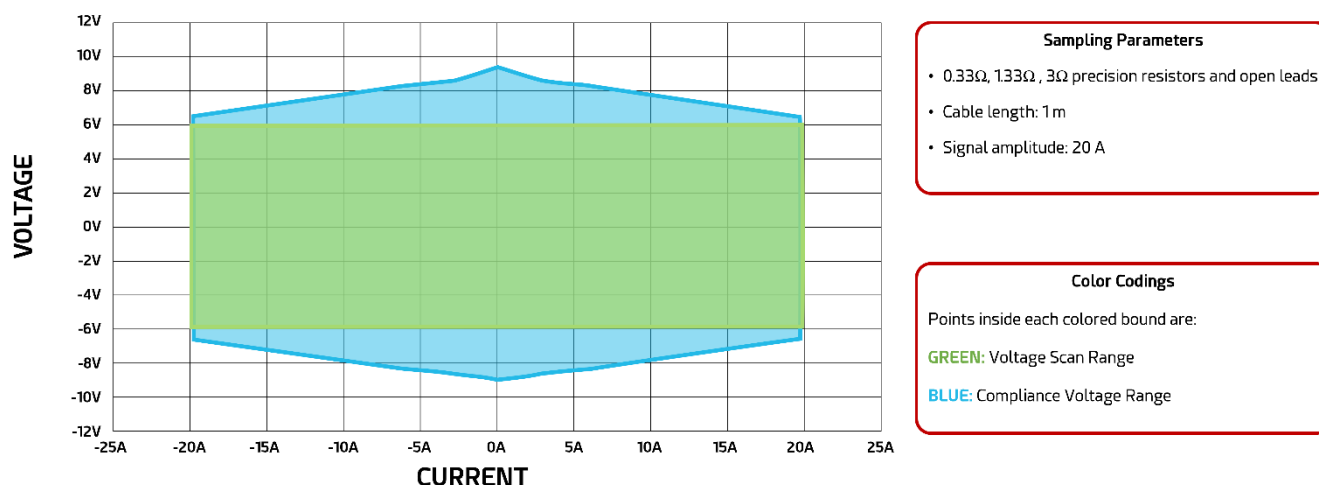


Figure 6. Device-specific compliance voltage (blue) and voltage scan range (green) for a Squidstat Venta unit.

This is why compliance voltage is important; it can help you get more out of your instrument than you might initially expect. If your desired measurement is just beyond the instrument's specified voltage scan range, the compliance voltage graphs can show whether performing measurements in that region are still possible.

For example, with the Squidstat Venta, at a current of 15 A the voltage reaches approximately 7.3 V, which is above the nominal voltage scan range, and at 5 A the voltage reaches around 8.5 V. By examining the compliance voltage range, you can determine whether these measurements can still be performed safely and effectively.

5. How to Check Compliance Voltage Issues

A compliance voltage issue arises when the potentiostat cannot supply enough voltage to achieve the target potential at the working electrode. Detecting this issue early can save time and prevent

misinterpreting experimental data. Here are some ways to spot it:

Differences between applied voltage versus target voltage / applied current versus target current

Compare the applied voltage or current to the values you set. If the applied voltage or current never reaches the target, this may indicate the potentiostat has hit its voltage limit.

For example, setting a constant voltage of ± 5 V in a three-electrode setup may result in the voltage plateauing at a lower level. Similarly, applying a constant current of ± 5 A may plateau below the target.

Discrepancies between expected and measured current

In many electrochemical measurements, current should scale predictably with applied voltage. If the current stops increasing or behaves inconsistently despite changes in the applied voltage, the potentiostat may be unable to drive enough current to reach the desired potential.

Monitoring the CE voltage:

Squidstat potentiostats record the voltage at both the WE and the CE. The sum of these two voltages reflects the total voltage applied across the cell and should remain below the compliance voltage limit for the current being passed. Monitoring CE voltage alongside WE voltage provides a more complete picture of how close the system is to reaching the instrument's compliance limit and can help identify potential issues before they affect the experiment.

Software notifications:

Many modern potentiostats provide notifications when the compliance voltage is exceeded. Monitoring for these alerts can help identify potential issues before they affect data.

6. Best Practices to Minimize Issues

Check electrode and cell design:

High solution resistance or CE with a small surface area can increase the voltage required to achieve a given current. Check the distance between electrodes, electrolyte conductivity, and CE size. Adjusting these factors can reduce the likelihood of hitting the compliance voltage.

Use mirrored or test scans:

Performing a small, controlled test scan on a resistor while monitoring the current and voltage can reveal whether the system operates fully within the potentiostat's limits. This helps confirm if any unexpected limitations are due to the cell rather than the measurement parameters.