*How To Guide*

**Subject: Measuring the Compliance Voltage Used During an Electrochemical Experiment**

## Introduction

A potentiostat controls the requested voltage between the working (WE) and reference electrode (RE) by supplying power from the control amplifier, also referred to as power amplifier, to the counter electrode (CE). The total available power from this control amplifier is specified as the compliance voltage. The amount of compliance voltage used in a given experiment is not always known to the user; and projecting how much compliance voltage is required for a given experiment is difficult. This document describes how to measure and record the compliance voltage used during an experiment with real-world examples of classic electrochemical applications.

The compliance voltage is a sum of voltages throughout the cell as shown in Figure 1. Where $V_{WE}$ is the voltage at the WE vs the reference electrode (RE), $V_{iRs,1}$ is the voltage drop due to uncompensated resistance, commonly referred to as $V_{iRu}$ , $V_{iRs,2}$ is the voltage drop due to current flowing through the bulk solution and $V_{CE}$ is the voltage drop due to the balancing reaction at the counter electrode.

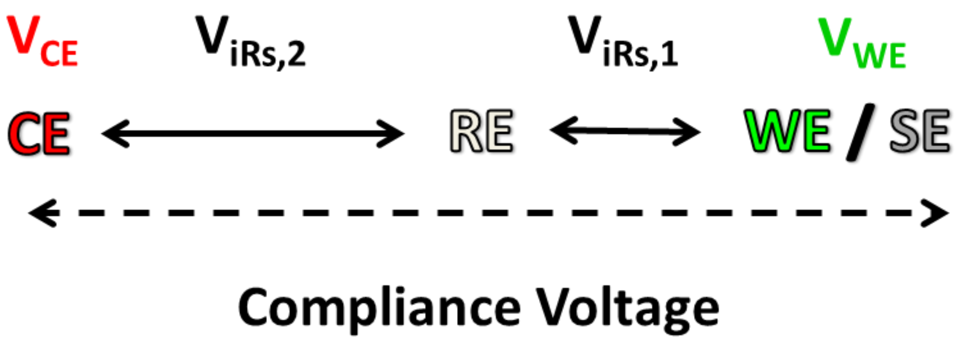


**Figure 1: Diagram illustrating the various components that constitute the compliance voltage of an electrochemical cell.**

As is suggested by the figure above, the compliance voltage will increase as $V_{iRs,1}$ and $V_{iRs,2}$ increase. The magnitude of these two voltage drops depends on the current, the cell geometry and the solution resistance ($R_s$). The solution resistance can become significant when using a low concentration aqueous electrolyte, non-aqueous electrolyte or other low conductivity electrolytes such as concrete or soil, as is common in the study of corrosion. Another factor that can increase $R_{s,2}$ is the use of a frit at the CE to separate the byproducts produced by the balancing reaction from the bulk solution. Large currents, which must also be considered, are common in electroplating, bulk electrolysis and battery applications. If the compliance voltage is not sufficient, the potentiostat will be unable to properly control the voltage of the working electrode. In these scenarios, the compliance voltage defines the useable limits of the potentiostat; therefore, measuring its value can be valuable for optimization of cell and experiment design. All VersaStudio compatible instruments are capable of measuring the compliance voltage, though the procedure differs with the instrument model.

## Procedure

The PARSTAT 4000 and VersaSTAT 3 / 4 / 3F all have a SYNC ADC Input as a BNC connection on the rear panel of the instrument designed to connect to a coaxial cable. The PARSTAT MC (PMC) potentiostats have these available as a pin on the 9-pin Analog connection (pinout in the manual; optional cable as PMC ALG01). The compliance voltage can be measured by connecting the positive terminal of a coaxial BNC cable to the counter electrode during an experiment. Figure 2 demonstrates this connection using a BNC to double banana adapter, where the alligator clip would be connected to the counter electrode.


**Figure 2: Image showing how to connect between the SYNC ADC and the counter electrode using a coaxial BNC cable and BNC to double banana adapter with a single alligator clip.**

Data from the SYNC ADC is recorded with every data point in every experiment within VersaStudio. Cyclic voltammetry using a typical physical electrochemistry setup (K0264 Micro-cell kit with a Au milli electrode P/N G0227) was collected, as seen in Figure 3, to demonstrate how the compliance voltage can be measured during the experiment. Figure 4 plots the compliance voltage, cell potential, referred to as Polarization Voltage, and current as a function of time. The blue data was obtained using a non-fritted Pt wire counter electrode, while the red data used the same counter electrode with the addition of a frit (P/N

K0266). Note that the compliance voltage always exceeds the cell potential ($V_{WE}$), as expected based on the diagram in Figure 1. It is clear that the frit increases the compliance voltage required to maintain the same potential at the working electrode (red vs. blue). When the compliance voltage is overlaid with the current measured at the working electrode, it can be seen that the changes in compliance required when using a fritted counter electrode closely match the changes in current. This suggests that the frit increases the contribution of $V_{iRs,1}$ to the compliance voltage as compared to when a frit was not used.

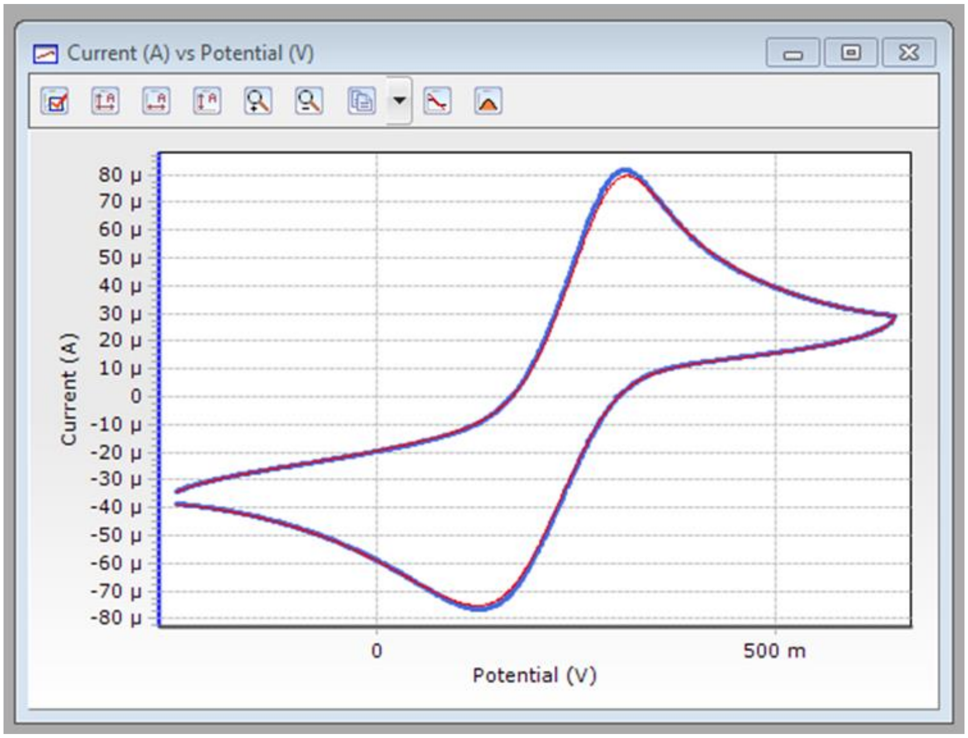


**Figure 3: Cyclic voltammetry of a Au electrode ((2 mm ± 0.2mm diameter) in 1 mM $K_3[Fe(CN)_6]$ in 0.1 M KCl using a Pt counter electrode with (red) and without (blue) a frit. Scan rate = 200 mV/s.**

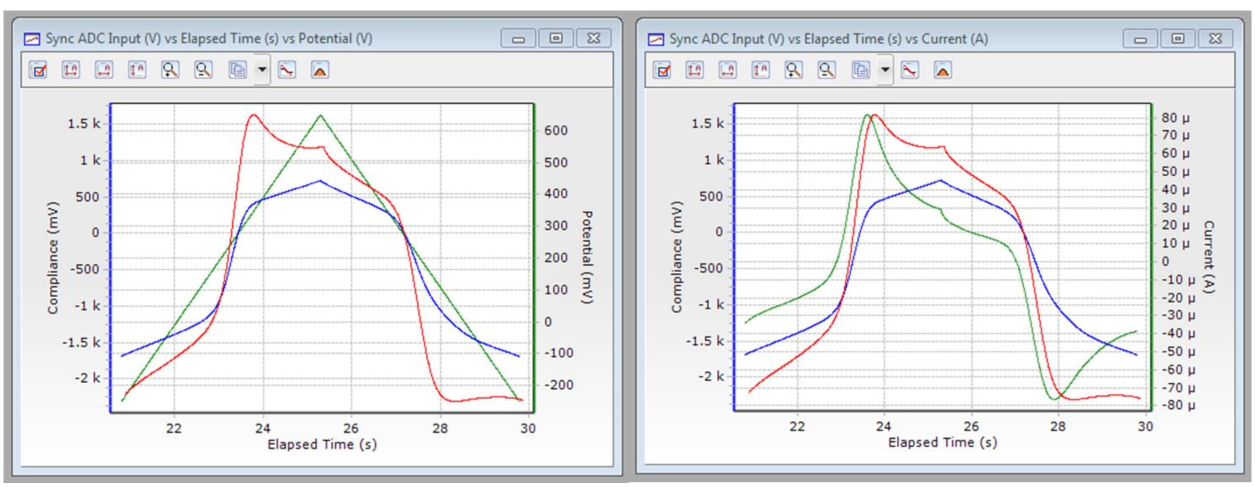


**Figure 4: Plots of the compliance and polarization potential as a function of time and the compliance and current as a function of time corresponding to the CVs in Figure 3 using a Pt counter electrode with (red) and without (blue) a frit.**

Similar studies comparing different electrolytes with varying conductivities and/or various sizes of working electrodes that generate different magnitudes of current could be conducted to determine how these factors impact compliance voltage.

*The graphs in Figure 4 were generated by plotting the SYNC ADC Input (V) on the y-axis, selecting Negate Values and naming this axis "Compliance (mV)". Data math (*1000) was used to convert the voltage from V to mV.*

The amount of compliance available depends on the potentiostat design. Princeton Applied Research offers potentiostat models that can accommodate a range of polarization and compliance needs, as shown in Table 1. While the VersaStat series and PMC-1000 / PMC-500 are suitable for many applications, the PARSTAT 2273 and 4000 offer substantially more compliance and are often preferred by corrosion researchers. Additionally, the PMC-2000 offers an increase in polarization and compliance voltage, two features that are advantages for many researchers in the energy storage field.

**Table 1:**

| Potentiostat Model | Polarization Voltage | Compliance Voltage |
|---|---|---|
| PARSTAT 2273 | +/- 10 V | +/- 100 V |
| PARSTAT 4000 | +/- 10 V | +/- 48 V |
| VersaSTAT 3 / 4 / 3F | +/- 10 V | +/- 12 V |
| PMC-1000, PMC-500 | +/- 10 V | +/- 12 V |
| PMC-2000 | +/- 30 V | +/- 30 V |

***Note** – the SYNC ADC has a +/- 10 V range; therefore, a voltage divider must be used to measure compliance voltages greater than 10 V. Please contact Technical Support at pari.info@ametek.com or http://www.princetonappliedresearch.com/support-center/contact-us/index.aspx for assistance.

## Conclusion

The compliance voltage is one of many important considerations when selecting a potentiostat and designing experiments. Its value throughout an experiment can be easily measured using the SYNC ADC Input on the PARSTAT 4000, VersaSTAT 3 / 4 / 3F and PARSTAT MC (PMC-2000, PMC-1000, and PMC-500) and VersaStudio software. If you have additional questions regarding the procedure or your particular instrument and experimental setup, please contact the Princeton Applied Research technical support staff at pari.info@ametek.com or http://www.princetonappliedresearch.com/support-center/contact-us/index.aspx.