Compliance Voltage – How Much is Enough?

Introduction

The compliance voltage of a potentiostat is the maximum voltage that the potentiostat can apply to the counter electrode in order to control the desired voltage in the electrochemical cell. It is generally measured as the difference between the counter electrode and the working electrode. Most potentiostat manufacturers include the compliance voltage as one of the significant specifications in their data sheet.

Compliance voltage is also one specification that users consider when purchasing a potentiostat. Although it is tempting to think “the higher the better,” a high compliance voltage is not without its price. The higher the compliance voltage, the higher the power requirements are within the potentiostat. Higher power means more complexity, more weight, and generally higher cost. The frugal electrochemist asks “How much compliance voltage do I really need?”

The response of a potentiostat depends upon the nature of the electrochemical cell to which it is connected. This is true for compliance voltage as well. The manufacturer’s data sheet should also tell you the conditions under which the compliance voltage was measured. For example, the Gamry Series G™ 750 Potentiostat specifications give the compliance voltage as >15V @ 15 mA and >12V @ 500 mA, while the Reference™ 600 specifications give the compliance as >22V @~110 mA.

A Simple Cartoon of Your Cell

There are several components to the compliance voltage and we can evaluate them by looking at the schematic in Figure 1. Some of the components depend upon the nature of the electrodes and the electrolyte, while some depend upon the geometry of your cell.

![Figure 1. The Distribution of Voltage Drops Across an Electrochemical Cell.](image)

Overloads – Control Overload

For the potentiostat to properly control the cell, the voltage difference between the counter electrode and the working electrode must be less than the manufacturer’s stated compliance voltage. This is true for galvanostatic as well as potentiostatic experiments. If your experiment demands a voltage higher than the compliance voltage limit then the potentiostat or your software should give you an indication of an “overload.” This overload might be called a “control amp overload”, “CA overload”, or a “control overload.”

This is not the only type of overload that is possible. Another common overload condition is a “current overload.” In the case of a “current overload”, the current may simply be too large for the current range that has been selected. Often the answer is to simply choose a less sensitive current range, or to allow the potentiostat to autorange and select the proper current measuring scale automatically.

The Components of Compliance Voltage

If you can estimate the size of each of the four components shown in Figure 1, you can determine the
The compliance voltage that will be needed for your application, without triggering a “control amp overload.” The easiest to estimate is shown as $V_{e,w}$. It is the voltage drop across the uncompensated resistance, the resistance between the tip of the reference electrode or Luggin tip and the working electrode. This obviously depends upon the geometry of your cell, but also depends upon the conductivity of the electrolyte and the current. In spite of these unknowns, we are safe in assuming that the iR drop, $V_{iR}$, is about 1V or less. The rationale for this assumption is that we are actually trying to make a meaningful electrochemical measurement.

Remember that this voltage drop depends upon the current! A ten per cent change in current will change this voltage drop by as much as 100 mV. If you are performing a cyclic voltammetric experiment or a potentiodynamic scan, peaks or transitions might change by as much as 100 mV for this small change in current. Interpretation of the results will be obscured by the effects of the iR voltage drop. If you attempt to correct for the effects of this voltage drop, either by post-run correction or by real-time correction using the positive feedback or current interrupt technique, a few per cent error in the Ru value for post-run or positive feedback correction, or a few percent error in the iR drop using current interrupt, can give oscillations, noise, and unusual apparent current-voltage curves. Recognizing this, most manufacturers limit the automatic correction circuitry to a volt or two of iR correction.

The second voltage drop in our cartoon in Figure 1 is $V_{iR_BULK}$. This is equivalent to the iR drop across the uncompensated resistance, the resistance between the tip of the reference electrode or Luggin tip and the working electrode. This obviously depends upon the geometry of your cell, but also depends upon the conductivity of the electrolyte and the current. In aqueous electrolytes this is generally within the limits -2 < $V_{iR_BULK}$ < +2. Even in aprotic non-aqueous (organic) solvents, it is unusual for it to exceed ±3V.

In the absence of a large bulk solution resistance, we can sum the components and expect a voltage magnitude of about 5V (= 2+1+2) between working and counter electrodes in the most extreme case.

The Bulk Resistance of Your Cell

The one component of the compliance voltage that has the widest variability is the iR drop across the bulk resistance of your cell, $V_{iR_{BULK}}$. The size of this voltage drop depends upon the current passed, but it also depends upon the electrolyte, its concentration, and the design of your cell. We will give a few examples to establish some guidelines.

The data presented here was obtained using a Gamry EuroCell™ Kit and a Reference 600 Potentiostat. The Reference 600 Potentiostat was selected because it has the capability to easily record the voltage output of its control amplifier. This voltage is nominally the same as the counter electrode voltage. The two voltages are separated only by the voltage drops across the cell switch and counter electrode cable. For the data shown, both of these voltage drops are not significant. The control amplifier voltage is internally divided by a factor of ten so that it may be read on the ±3.276 V full scale A/D converter. For other Gamry Potentiostats, an external voltage divider is required to read the counter electrode voltage.

Figure 2 shows the current voltage curves obtained for 430 Stainless Steel in 0.1M H2SO4. The counter electrode voltage is also shown on this plot. The blue curves show the data obtained using the standard graphite rod counter electrode that is standard for the EuroCell Kit. About 3 cm of this 6 mm diameter rod were immersed in the electrolyte (about 6 cm2). The working electrode was a cylindrical sample of 430 stainless steel, fabricated according to ASTM standard dimensions (5/8” diameter, ¼” long). The exposed area of the working electrode was about 5 cm2. The red curves were recorded using the same cell and 430 SS sample, but using the isolated counter electrode accessory, 990-194. This accessory consists of a platinum wire counter electrode and a glass tube with a coarse sintered glass frit at the end (See Fig 3). The isolation tube is placed into the cell so that the
electrolyte fills the inside of the tubing (through the sintered glass frit) to a depth of a few centimeters. The platinum counter electrode is placed inside the isolation tube, immersed in the electrolyte.

Figure 2. The Current Voltage Curves for 430 Stainless Steel in 0.1M H$_2$SO$_4$. The darker curves are the current voltage data. The lighter curves are the control amplifier output recorded at the same time. Blue: graphite counter electrode. Red: isolated Pt counter electrode.

For the curve recorded with the graphite rod counter electrode (blue) the counter electrode voltage (light blue) reaches a maximum of about 5V at the start of the experiment where the current is the largest, about 200 mA. The counter electrode voltage was plotted against the measured current and the slope of the line (dVoltage/dCurrent) was about 9 ohms. This represents the total resistance between counter and working electrodes. If we assume that the other three voltage drops in Figure 1 are constant or small, then the resistance of the solution between the working and counter electrodes is 9 ohms or less.

Figure 3. The Counter Electrode Isolation Tube.

Using this estimate of the bulk resistance of this electrolyte, we can estimate the compliance needed to overcome the bulk solution resistance for any given current. In particular, we can do this calculation assuming that the current has reached the potentiostat’s maximum value given in the manufacturer’s data sheet.

For example, the Reference 600 data sheet gives the maximum current output as 600 mA. For our cell configuration, the maximum voltage drop across the bulk electrolyte resistance of the cell is estimated to be 5.6 V (= 600 mA x 9 ohms). Our previous worst-case estimate of 5 V for the remaining voltage drops in the cell must be added to the bulk iR drop. The result is 10.6 V. This represents the maximum compliance voltage needed to perform an experiment in this cell with this electrolyte.

The experiment was repeated, but this time using the isolated counter electrode kit shown in Figure 3. The data is shown in Figure 4, and is also shown as the red curves in Figure 2. From Figure 2, we see that the familiar current-voltage curves are essentially independent of the counter electrode used, even though the counter electrode voltage (light blue and light red curves in Fig. 2) may be dramatically different. This is expected. The same sample and solution were used for both experiments. The slight potential shifts between the two curves arose because the sample was not re-polished between the experiments, and insufficient time was allowed for the open circuit potential to stabilize between the experiments. The two curves were ‘normalized’ by plotting the potential vs. the open circuit voltage.

The data from Figure 2 for the isolated platinum counter electrode is repeated in Figure 4. In this case, the compliance voltage limit for the Reference 600 was exceeded briefly at the start of the experiment. Control Amp Overloads were observed at the points highlighted in red in the figure. Considerably higher voltages are required for the isolated counter electrode compared to the graphite rod immersed directly in the test solution.

We may estimate the resistance of coarse glass frit in this electrolyte (0.1M H$_2$SO$_4$) if we make a few assumptions. The counter electrode is a platinum wire. At pH 1 the voltage drop across the double layer at the platinum surface will certainly be less than 1V. Similarly, the voltage drop between the solution and the 430 sample is also less than 1 V. At the start of the experiment it is only 0.9 V since it is the voltage recorded on the X-axis of our plot! So, for a current of about 70 mA the
voltage drop across the bulk of solution and the coarse glass frit is about 20 V (22 V -1 V -1 V). The resistance can be calculated from:

\[
\frac{E}{I} = \frac{20 \text{ V}}{70 \text{ mA}} = 285 \text{ ohms.}
\]

This crude estimate was checked with an EIS experiment without moving the electrodes. Because the resistance from the reference electrode to the counter electrode was to be measured, the working and working sense electrode leads were connected to the isolated platinum electrode. The counter electrode lead was connected to the 430SS sample. The impedance spectrum was recorded at 0 V vs. Open Circuit and the high frequency data was fit to a simplified Randles cell model, but with the capacitor replaced with a constant phase element (CPE). The fit gave a “solution resistance” of 284±4 ohms. Because of the non-traditional connection to the potentiostat, this represents the solution resistance between the reference electrode and the isolated platinum electrode. The tortuous path through the sintered glass frit substantially raises the resistance across the frit, even in reasonably good conducting media.

**Poorly Conducting Media**

The change to alternative fuels will require examination of the corrosion properties of materials in these poorly conducting media. Alternative fuels based on ethanol and other alcohols will certainly have some water content (ca. 1%), and may contain acetic acid as well (10-100 ppm). To see the compliance requirements in these media we tested our 430 Stainless Steel sample in isopropanol (2-Propanol) to which 1% aqueous 0.1N Acetate Buffer had been added. This electrolyte contained 1% water and about 60 ppm acetate. The potentiodynamic scan recorded for the 430 stainless steel is shown in Figure 5. The currents are smaller than those observed in Figure 2, as we would expect.

The counter electrode voltage is also shown in Figure 5 (green line). Even though the currents are smaller, the counter electrode voltage is considerably higher. Since a graphite rod immersed directly in the test solution was used as the counter electrode, the higher counter electrode voltage is due to the low conductivity of this electrolyte. We can estimate the bulk resistance from the counter voltage (23.5 V) and current (1.3 mA) near the end of the scan. This yields about 18 kohm (= 23.5 V/1.3 mA) for the resistance.
Figure 6. Counter Electrode Voltages vs. Current.
The slope of the least squares fit gives the bulk resistance of the solution, 17.14 kΩ.

Plotting the counter electrode voltage against current (linear plot) also allows us to estimate the bulk resistance (Figure 6). From this plot, the resistance is estimated to be 17.1 kohm. EIS was also used to measure the bulk resistance, and the value was consistent with the 17-18 kohm values already calculated. However, the analysis of the data was complicated by artifacts introduced by the high impedance nature of this electrolyte. These artifacts and possible solutions will be the subject of a separate Application Note.

Factors Influencing $R_{\text{bulk}}$

The compliance requirements are strongly controlled by the resistance of the bulk of the solution. If we can minimize the bulk resistance, then we will minimize the compliance voltage required. The value of a resistor can be calculated from:

$$R = \frac{\rho l}{A}$$

Where,

$R$ = Resistance ($\Omega$)
$\rho$ = Resistivity of the Medium ($\Omega$-cm)
$l$ = Length of Resistor (cm)
$A$ = Cross-sectional Area of Resistor (cm$^2$)

Often we do not have control over the resistivity, $\rho$, such as in our last example. We cannot increase the ionic concentration without changing the electrolyte.

We can, though, change $l$ or $A$. If we place the counter electrode closer to the working electrode we will reduce the length, $l$, or our bulk resistance. This will reduce the bulk resistance. If we increase the area of our counter electrode, we will increase the cross-sectional area, $A$, of our “resistor”, and the bulk resistance will decrease. Increasing the size of the working electrode also increases the area of our “resistor”, but it will not help. It also increases the current! The iR product, and the compliance voltage requirements, will remain the same.

Summary

We hope that the three examples presented here will provide you with some feel for the compliance voltage requirements in some common applications, and have provided you with some ways to estimate the required compliance in your electrochemical cell.

For a non-isolated counter electrode, commonly employed electrolyte concentrations (0.1M or above) generally require compliance voltages of 10 V or less. Substantially lower Ionic concentrations (such as 0.002M) or non-aqueous media may require more than 10 V for currents in excess of 1 mA. For isolated counter electrodes, the frits commonly used for isolation can dramatically increase the bulk resistance, even in concentrated electrolytes.