Admiral Instruments
Test the potential™

IR Drop Compensation in Squidstats

Written by Alexis Gray, PhD | alexis@admiralinstruments.com

Understanding and correcting the IR drop due to uncompensated ohmic resistance reduces errors in measurements

When a voltage is applied to the Working Electrode (WE), current flows between the WE and the Reference Electrode (RE) through the electrolyte, which has a resistance equal to R_s. This resistance causes a voltage drop, (also referred to as an ohmic or IR drop) equal to iR_s which is not seen by the WE. In systems with large electrodes, high current, or high resistance electrolytes, iR_s can significantly alter electrochemical data. A three-electrode system can be employed to minimize the voltage drop and largely negate the impact of R_s. The bulk of the current is passed between the WE and a Counter Electrode (CE), and the potential of the WE is measured against the RE, which experiences minimal current. However, even in three-electrode systems there is still a resistance between the WE and the RE, R_u, which causes a voltage drop that cannot be compensated for by a CE. **Figure 1** shows the resistance compensated for by the CE (R_A) and the uncompensated resistance R_u.

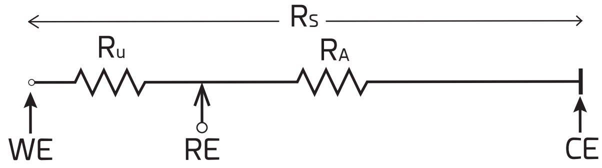


Figure 1. Uncompensated resistance in a 3-electrode cell

Thus, the potential experienced by the WE is equal to the potential applied by the potentiostat (E_{Appl}) minus the voltage drop (iR_u):

$$E_{WE} = E_{Appl} - iR_u$$

Ohmic drop influences the measured potential and the shape of a curve. For example, in cyclic voltammetry, the IR drop can result in larger peak current separation. There are many ways to minimize R_u:

1) Put the RE as close to WE as possible. This is traditionally done using a Luggin-Haber capillary in a three-electrode configuration.
2) Reduce the surface area of the WE. Current depends on surface area and reducing the current will reduce the impact of R_u.
3) Increase the conductivity of the electrolyte. Conductivity and resistance have an inverse relationship, therefore increasing the conductivity of the electrolyte decreases R_u such that the voltage drop becomes negligible.
4) Lower the current. This can be accomplished is by lowering the scan rate in DC Voltammetry experiments or reducing the applied voltage to the WE.

Most modern potentiostats, including the Squidstat, have a positive feedback compensation circuit to partially offset the impact of R_u. This method requires knowledge of R_u, which can be measured by EIS, current interrupt, potential step, and positive feedback. The representation of the circuit between the WE and the RE in **Figure 2** will be used as a model for the following explanations: R_u (100 Ω) is in series with the interface between the electrolyte and WE, which consists of the charge transfer resistance R_c (10 kΩ) in parallel with the double-layer capacitance C (1 μF).

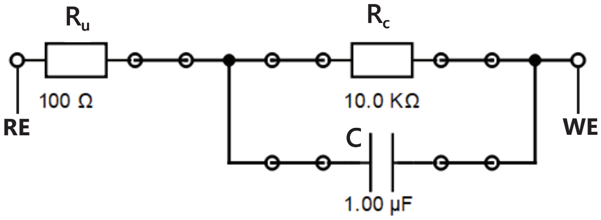


Figure 2. Circuit representation of the uncompensated resistance (R_u) and the electrolyte/WE interface (R_cC) between the RE and the WE in an electrochemical system.

Measuring R_u by EIS

The easiest way to measure R_u is by Electrochemical Impedance Spectroscopy (EIS), an AC technique which applies a sinusoidal potential or current to the device under test (DUT) and measures the current or potential response, respectively. EIS is a non-invasive method which does not alter the system or DUT.

When current is passed through the circuit, it must go through R_u, however it can travel through either R_c or C. At high frequencies the capacitor acts as a short circuit, and all current passes through C, bypassing R_c. Thus, R_u can be determined from the Nyquist plot generated by high frequency EIS experiments. Real impedance (Z′) is plotted on the x-axis as a function of the negative imaginary impedance (-Z″), and R_u is equal to the x-intercept. **Figure 3** shows a Nyquist plot of potentiostatic EIS on the circuit in **Figure 2**. The x-intercept, R_u, is equal to 100 Ω, which is the expected value from the circuit.

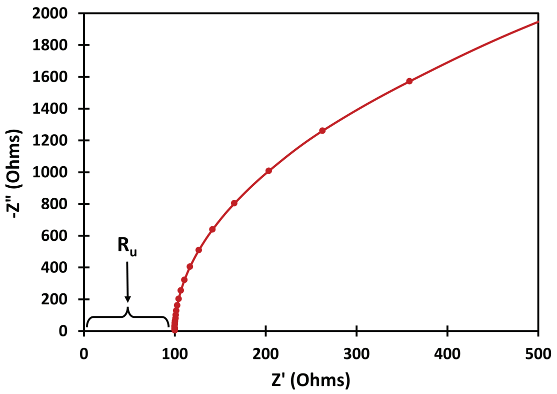


Figure 3. Nyquist plot generated by potentiostatic EIS of the circuit in **Figure 2** at high frequencies. The uncompensated resistance R_u is equal to the x-intercept.

Measuring R_u by Current Interrupt

The current interrupt method is a DC technique based on Ohms law. When a constant current is flowing across the circuit in **Figure 2**, the voltage drop across the uncompensated resistance is $-iR_u$ and the voltage drop across the electrolyte interface is $-iR_c$. If the current is interrupted, the potential across R_u will immediately go to zero while the potential across R_cC and will decay exponentially due to the presence of the capacitor. The decay is exponential because the capacitor is slowly discharging according to the time constant of the circuit, τ, equal to R_cC. If the potential is measured immediately before and after the current is interrupted (the linear region in **Figure 4**), the difference between those voltages is equal to iR_u.

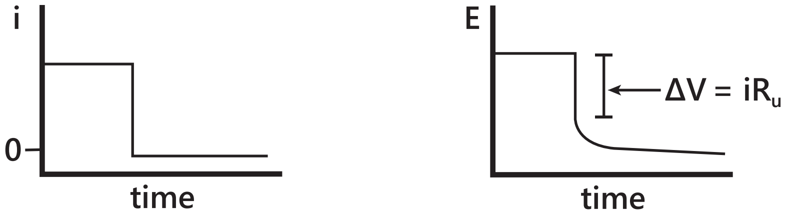


Figure 4. The applied current waveform (right) and voltage profile (left) of current interrupt. The voltage change in the linear region is equal to iR_u.

Since all electrochemical systems are capacitive in nature, R_u can be calculated using this method. Advantages of the current interrupt method are:

1) R_u can be determined quickly
2) No prior knowledge of R_u is needed
3) The potentiostat does not need AC capabilities

Limitations of the technique include:

1) The double-layer capacitance C must be large. If C is small, the capacitor will discharge quickly, so a small sampling interval is required to determine iR_u. The smallest sampling interval in Squidstats is 200 µs, hence it is better if the time-constant of the system is 1000 µs or more. This means if R_u is 10 Ω, the capacitance of the system should be 100 µF, which is very high for a regular electrochemical system.
2) The capacitance of the cable is non-zero, and forms an RC circuit with R_u which has a different time constant. This means the potential across R_u does not immediately go to zero. Fortunately, if the double-layer capacitance is sufficiently large, the capacitance in the cable will fully discharge before the voltage decay becomes non-linear.

Measuring R_u by a Potential Step

At the open circuit potential, there is no voltage across the circuit and the double-layer capacitance is fully discharged. If a potential step is applied to the WE, the discharged capacitor initially acts as a short circuit. Similar to high frequency EIS, the current preferentially travels across the shorted capacitor, bypassing R_c. Thus, the only resistor in the circuit at time t=0 is R_u, which can be calculated from the initial current spike using Ohms law.

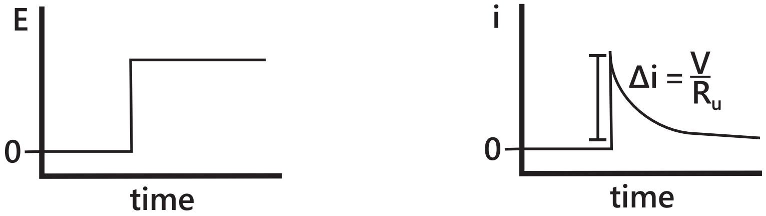


Figure 5. The applied potential waveform (right) and current profile (left) of potential step. The initial current spike is equal to $\frac{V}{R_u}$

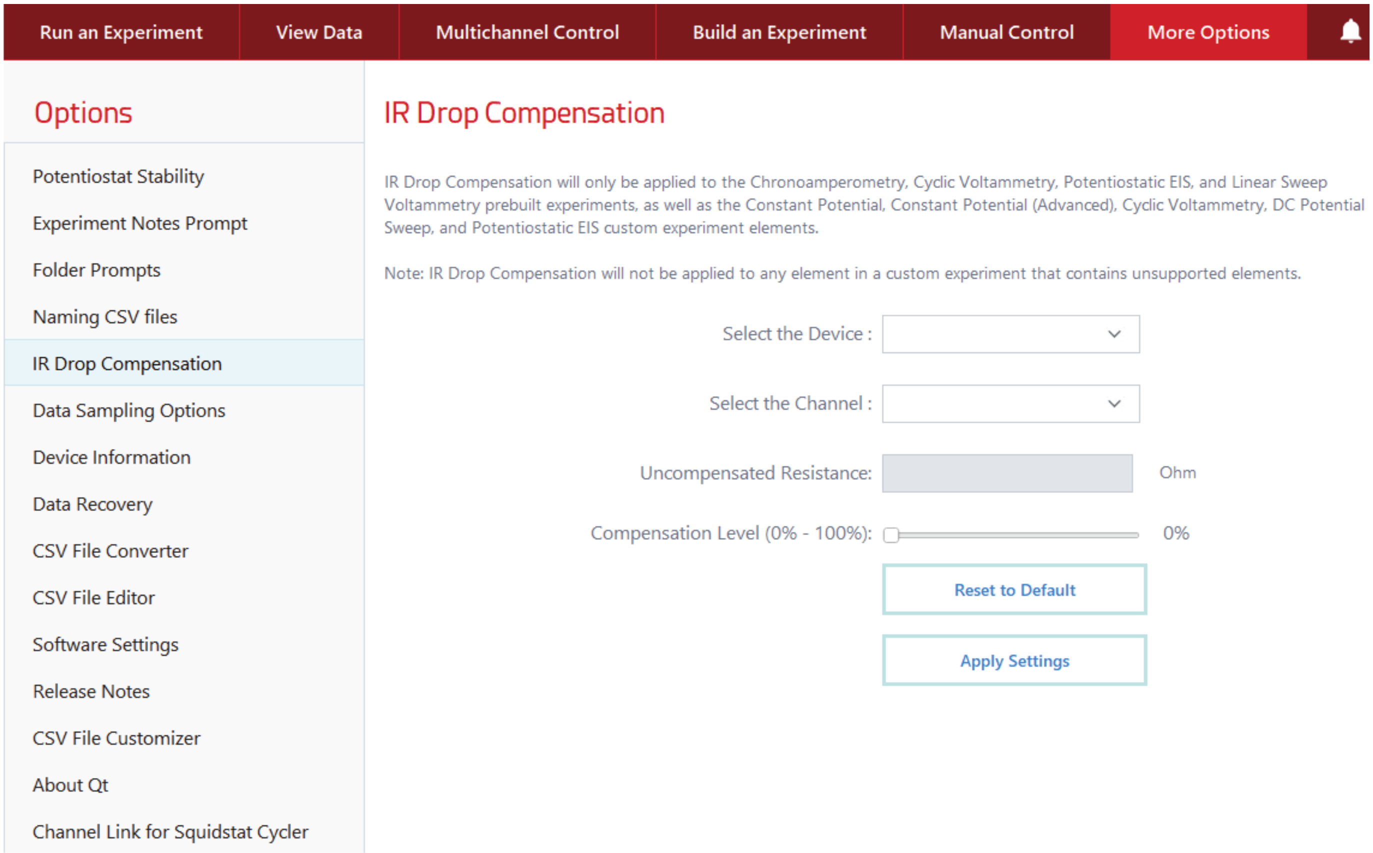
The advantages of the potential step method are much the same as the current interrupt method, however potential step is preferred for systems which are sensitive to large currents, as the amount of current passed is small. Additionally, when the linear region from the current interrupt method is not clear, potential step can be used to find R_u instead.

Compensating for R_u by Positive Feedback

Most potentiostats can be programmed to accomodate for the IR drop using a positive feedback loop. This method requires prior knowledge of R_u, which can be obtained from the previously outlined methods. Since the voltage drop is equal to $-iR_u$, the potentiostat can correct for this by applying a compensating voltage close to iR_u. The potentiostat will adjust the applied voltage in real-time based on current input to the feedback loop. Positive feedback can continuously compensate for R_u, even with fast scan rates.

There are three primary disadvantages to this method. Overcompensation can induce potentiostat instability and oscillations, therefore the optimal value for R_u must be determined by trial and error, which can be tedious. Potential steps under IR compensation over a range of R_u values will show the highest R_u with minimal potential oscillations. Additional adjustments can be made by changing the level of compensation. Second, 100% compensation is still not possible due to hardware and stability limitations and time lags between the application of correction and sensing the correction. Third, the system is not dynamic and cannot accomodate changes in R_u.

The Squidstat offers IR drop compensation in the “More Options” tab of the Squidstat User Interface shown below. Here, the user can enter the value of the predetermined uncompensated resistance R_u as well as the compensation level (0% = no compensation, 100% = full compensation). If there are signs of potentiostat instability such as oscillations, lower R_u or the compensation level.



IR Drop Compensation

IR Drop Compensation will only be applied to the Chronoamperometry, Cyclic Voltammetry, Potentiostatic EIS, and Linear Sweep Voltammetry prebuilt experiments, as well as the Constant Potential, Constant Potential (Advanced), Cyclic Voltammetry, DC Potential Sweep, and Potentiostatic EIS custom experiment elements.

Note: IR Drop Compensation will not be applied to any element in a custom experiment that contains unsupported elements.

Select the Device :
Select the Channel :
Uncompensated Resistance: Ohm
Compensation Level (0% - 100%): 0%

The raw data in the CSV file will contain both the uncompensated (E_{WE}) and compensated (E_{Appl}) potential, labeled respectively as “Working Electrode (V)” and “IR Compensated WE (V).” **Figure 6** shows the profile of these two potentials and the current response recorded during a chronoamperometry experiment with IR compensation. While the profile of the WE potential is linear, the profile of the compensated applied potential mimics the exponential profile of the current, demonstrating the positive feedback loop inside the Squidstat.