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Application Note

In this application note it is explained how to use the iR compensation module of the PalmSens4 and EmStat4X. We start by explaining the terminology and what issue is resolved by the iR compensation module. Then we show possibilities to determine the uncompensated resistance.

1 What are iR drop and uncompensated Resistance?

When using a potentiostat it is often assumed that the applied potential is only applied across the working electrode's solid-liquid interface. This is not true. The potentiostat controls the potential between the reference electrode (RE) and the working electrode (WE). Between the WE's interface and the RE is the solution, which acts as an Ohmic resistor. This resistance leads according to Ohm's law to a potential drop of current times resistance or i*R. The resulting potential drop is also called Ohmic drop.

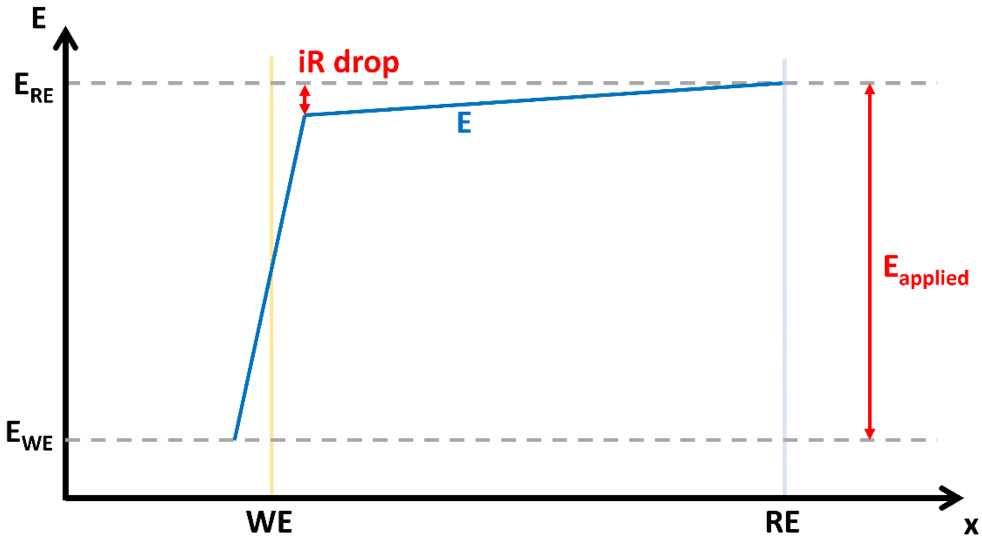

Figure 1 Scheme of a potential profile between RE and WE with highlighted IR drop

As a result, the driving force for the electrochemical reaction at the WE's interface is the $E_{applied}$ – iR. Due to the way a potentiostat works, the resistance between the counter electrode (CE) and the WE is not relevant. That resistance is compensated by the potentiostat circuit. The resistance between the RE and WE is not compensated in this way, it is called uncompensated resistance R_u.

For many experiments, the impact of the iR drop on measurements is minimal, primarily due to low currents (i) and/or a low resistance (R_u) between the working electrode (WE) and reference electrode (RE). For instance, with an R_u of 10 Ohms and a current of 100 µA, the resulting drop is just 1 mV. In most cases, such a 1 mV potential shift is not operationally relevant. However, experiments involving higher currents or solutions with low support electrolyte concentrations and, consequently, low conductivity can experience significant iR drops, necessitating compensation for accurate results. A commonly used threshold for deciding whether compensation is needed is 1 mV. According to the iR Ohm's law equation, this value becomes substantial when high currents and/or high resistances are introduced into the system. The impact of the iR-drop on a high-current measurement is illustrated in Error! Reference source not found..

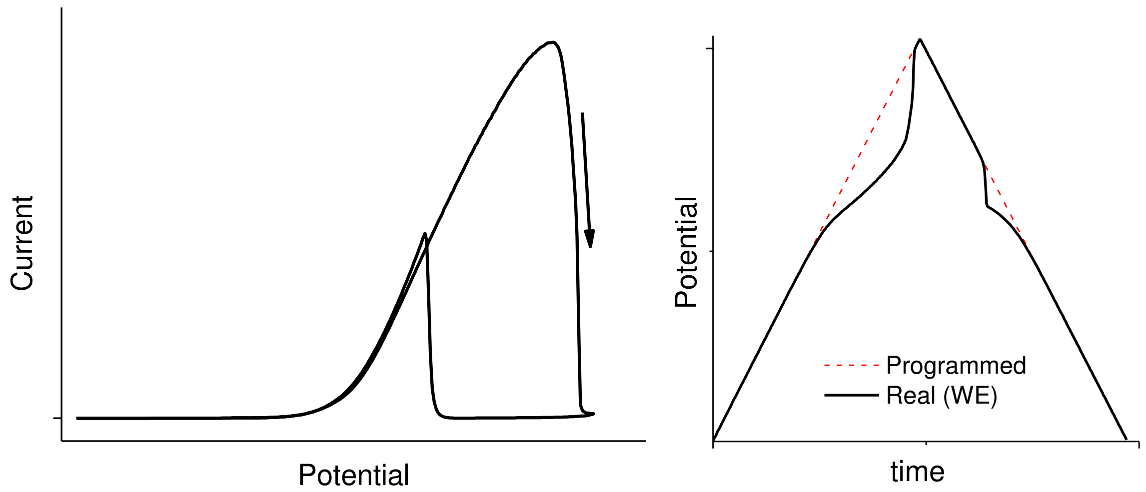

Figure 2 CV of a Au electrode in alkaline solution with glycerol. Left side: example of a high-current Cyclic Voltammogram without iR drop correction. Right: potential curve showing the difference between the programmed potential and the actual potential reached at the WE surface.

2 Post-Measurement Correction

While post-measurement mathematical correction can be considered as an approach to address the iR drop, it's important to recognize that the potential lost during the measurement inherently impacts the procedure itself. This impact cannot be removed through post-treatment corrections. Figure 3 shows the difference between post-measurement corrections and real-time compensation for the measurement performed in Figure 2. This emphasizes the need for real time compensation if the true electrochemical behavior of the system wants to be observed.

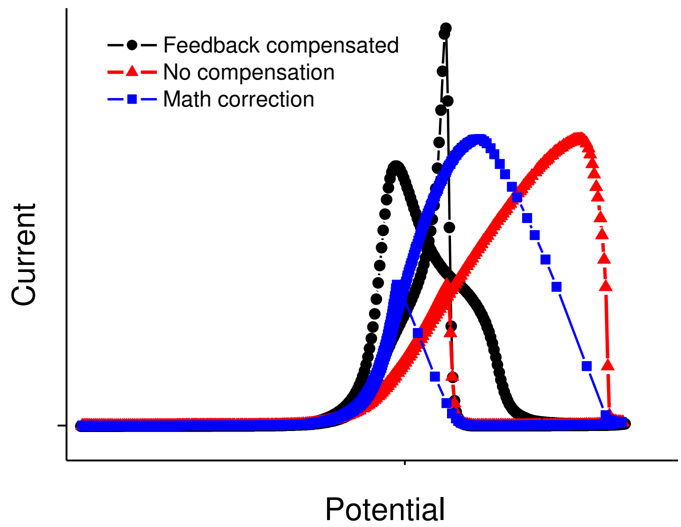

Figure 3 High-current Cyclic Voltammograms with and without iR compensation. These curves were obtained with a gold electrode on alkaline solution with glycerol.

3 iR Drop Compensation Module

For compensating the iR drop in real time, special hardware is required that can correct the applied potential dynamically during the measurement.
iR Compensation for PalmSens4 is available as an in-factory add-on module, and as standard included for EmStat4X. The module provides positive feedback to compensate for the iR drop between the reference electrode and the outside of the double layer of the electrochemical cell.

3.1 Positive Feedback

The iR Compensation module works by means of positive feedback. In a positive feedback loop an entered stimulus will produce a result that increases the stimulus. In this case the feedback loop dynamically adds more potential to the entered potential to compensate for the iR drop.

This is achieved with a 16-bit multiplying digital-to-analog converter (MDAC) in the module which scales the output of the current follower operational amplifier to provide a positive feedback voltage which is proportional to the current through the cell. The compensation voltage is added into the summing point before the control amplifier and thus increases the applied potential to counteract the iR drop.

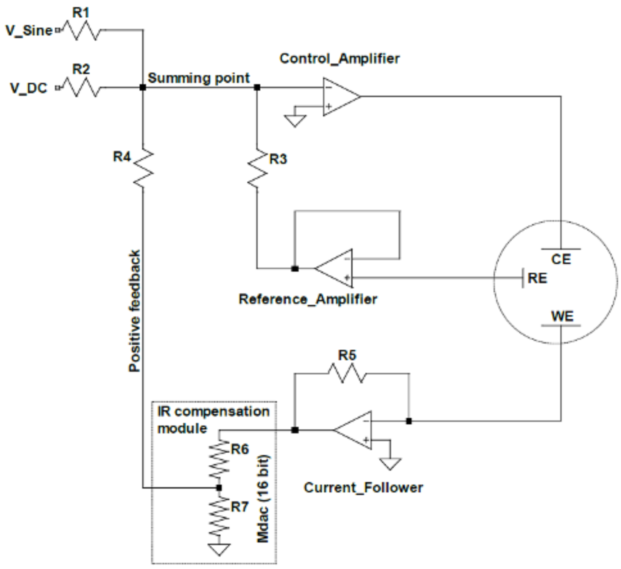

Figure 4 Scheme of the IR compensation module's circuit in a potentiostat

Positive feedback allows for fast scan rates up to 10 V/s, depending on the characteristics of the cell. If the potential error to be compensated becomes close to the value set for $E_{applied}$, the system might become unstable. Using iR compensation limits the measurement bandwidth to 10 kHz.

As mentioned, the potential is increased proportional to the measured current. The proportionality factor is the uncompensated resistance R_u. This compensation method uses one R_u value during the whole measurement. The value of R_u must be entered manually into the software, which means that the value of R_u must be determined before the measurement, which will be discussed in Chapter 5. This also implies that a constant R_u for the whole measurement is assumed.

3.2 Current Interrupt Modules

A very common, different method is the current interrupt method. This method is not used by the PalmSens iR Compensation Module. It is not common to describe what you do not have, but due to the widespread use of this method we would like to clarify that it is not the method used by our module.
The current interrupt method performs between two points of a measurement another small measurement. The current is interrupted for a moment, normally in the range of a few milliseconds. If the Randles circuit (see Figure 7) represents the cell, we have a parallel resistor and capacitor RC and a series resistor R. The latter is R_u. When the current is interrupted the potential across R_u immediately drops to 0, while the capacitor in the RC slowly decays. The drop of the potential is measured, and R_u calculated. These processes are very fast and usually require different hardware.
The Current Interrupt Method stands out for its ability to provide precise current control without the need for resistance determination, simplifying experimental setups. Its main drawback lies in its consequence of introducing perturbations to the electrochemical system, limiting its applicability primarily to lower-frequency measurements.

4 How to operate the iR compensation

When a potentiostat with iR drop compensation module is connected, you can find in the Method Editor of PSTrace a field to enter the resistance you want to compensate for after pressing the …-button. The Method Editor is the field on the left side of the PSTrace window, where all the measurement parameters are entered.

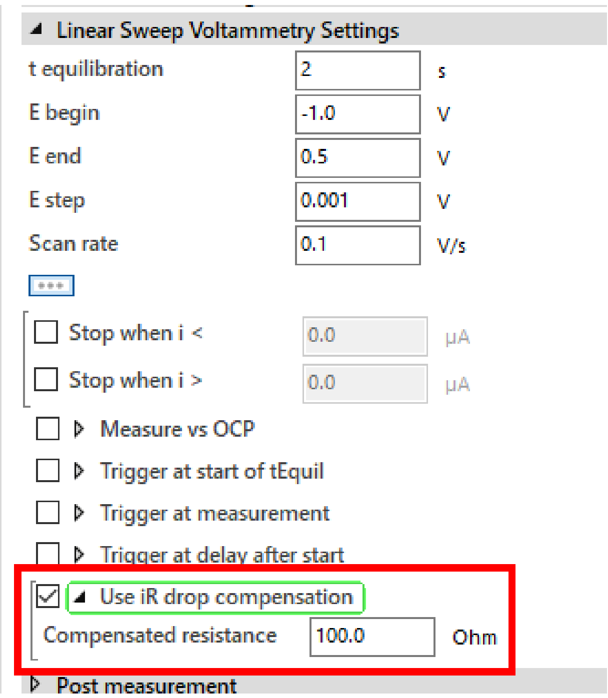

Figure 5 Activate IR drop compensation and define the resistance to compensate in PSTrace

Depending on the entered resistance some current ranges might not be available. If this is the case, you will get a message from PSTrace, as show in the Figure 6.

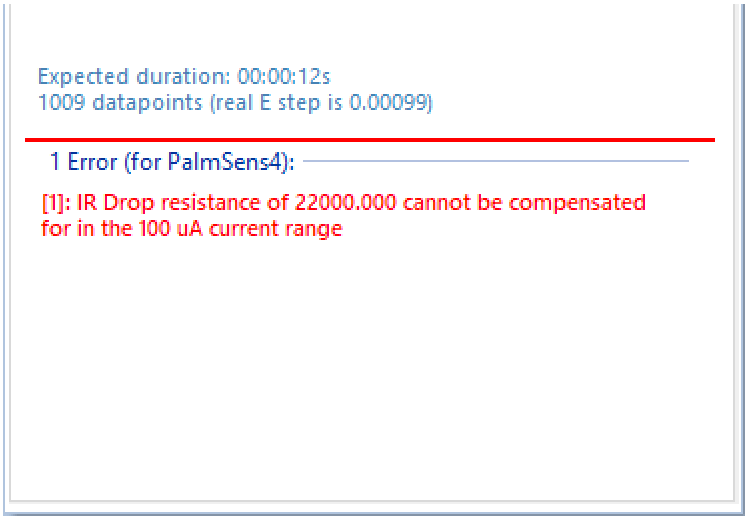

Figure 6 Error in PSTrace when a selected current range is not suitable for the entered resistance to compensate

5 Determining the Uncompensated Resistance R_u

Knowing the uncompensated resistance R_u of your cell allows you to use the IR compensation module to reduce the iR drop to a negligible level. There are multiple ways to determine the uncompensated resistance R_u in your cell. Most of these techniques use the Randles circuit as a basis for their approach. We are looking here at very fast processes, so the Warburg element can be ignored and the simplified Randles circuit with the double layer capacitiance C_{dl}, the charge transfer resistance R_{ct} and the solution resistance R_{sol} is used. For the sake of clarity, we will replace the R_{sol} with the R_u.

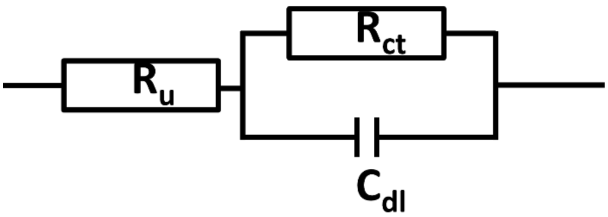

Figure 7 Randles Circuit

5.1 Electrochemical Impedance Spectroscopy

Most likely the quickest and most convenient way to determine the uncompensated resistance is impedance spectroscopy. Electrochemical Impedance Spectroscopy (EIS) is an ac technique, i.e., the applied and measured potentials or currents are sine waves.
EIS is a complex topic, and we already have multiple articles and videos about this topic and if you would like to dive deeper into this technique, we recommend the following articles:
https://www.palmsens.com/knowledgebase-article/electrochemical-impedance-spectroscopy-eis/
https://www.palmsens.com/knowledgebase-article/impedance-analyzer/
https://www.palmsens.com/knowledgebase-article/bode-and-nyquist-plot/
https://www.palmsens.com/knowledgebase-article/pstrace-tutorial-14-eis-parameters/

When an ac voltage is applied across the circuit in Figure 7 it will show an impedance that depends on the frequency of the ac voltage. We are only interested in the R_u, which is frequency independent. The other resistor R_{ct} has a frequency independent impedance too, but the capacitor C_{dl}'s impedance depends on the frequency. The higher the frequency, the lower the impedance of C_{dl}. At sufficiently high frequencies all current will flow through R_u and C_{dl}, but C_{dl} contribution is negligible, so you only see R_u in the spectrum.
Even in more complex cells, in aqueous solutions, the electrolyte resistance still remains the only relevant factor for the total impedance at the highest frequencies. This is because all other elements will be in parallel with some capacitor-like element.
As higher frequencies have the possibility that stray capacitance i.e., unwanted capacitance from cables or other metal surfaces, becomes significant it is advisable to measure a full spectrum and acquire the R_u by equivalent circuit fitting. How to perform equivalent circuit fitting is explained in the following video tutorial:
https://www.palmsens.com/knowledgebase-article/pstrace-tutorial-10-equivalent-circuit-fitting/

In an ideal Randle's circuit, the resistance R_u remains independent of the applied E dc parameter during Electrochemical Impedance Spectroscopy (EIS), allowing for sampling at multiple E dc values. The Positive Feedback technique typically assumes a constant R_u value corresponding to the E dc as well. Most variation of R_u with E dc is usually insignificant.
It is possible that real systems show a significant change of R_u for different values of E dc. EIS can be employed to assess the potential variation of R_u with E dc. Should you observe any variation, it is typically practical to compensate for the smaller resistance deviation, to avoid the overcompensation (see next chapter).

5.2 Oscillation due to Overcompensation

If your potentiostat is not very fast and does not have EIS, a simple way of determining the right uncompensated resistance R_u is checking at which resistance you are overcompensating.
Using positive feedback can lead to instabilities in your systems. When you are compensating with more resistance than your R_u the compensation will trigger the feedback loop of your potentiostat, and you will observe overshoots and ringing. This means the potential will rise beyond the set value and then will go back to the set value. In the case of ringing there is a small decaying sine wave. These are harbingers of oscillation, a state where the feedback loop of the potentiostat is permanently overcompensating, leading to a signal that looks like noise.
You can exploit this effect by performing a series of measurements with increasing compensated resistances. When the system starts to oscillate the compensated resistance is too high. A ringing effect is still acceptable. Choosing around 90 % of the value where your potentiostat starts to show strong ringing or oscillation is usually close enough to R_u without triggering the oscillation.

5.2.1 How to perform this

We want to perform fast potential steps and observe how the potential reacts to this. These steps are not our real experiment, we just use them to determine R_u, so small potential steps are preferred to keep the impact on the system low. The potential before and after the step should not trigger Faraday currents.
For your convenience you can download here a script that performs multiple measurements with varying Ru. It can be easily adjusted to your requirements, but we recommend reading the following steps to understand what the script does.

1. Connect your cell and the potentiostat as usual.
2. Choose *MultiStep Amperometry* as Technique.
3. Set a current range according to the expected current. We want to perform a fast measurement, so only a single current range can be active to prevent auto-ranging.
4. Set a *t equilibration* of 5 s.
5. Set a *t interval* of 0.0004 s, which is the lowest limit for the t interval.

6. Set the *Cycles* to 1 and the *Levels* to 3, because we want to make one step forward and one step backwards. No repetition is required.
7. Set the *E level 1* to the potential before the step. And *t 1* to 0.02 s. We can keep each level short, to make the measurement fast.
8. Set *E level 2* to 50 mV higher or lower than *E level 1*. We want a potential step big enough to see a clear step, but small to keep changes to our system small. The duration *t 2* is also 0.02 s.
9. *E level 3* and *t 3* are the same as level 1.
10. Check in the segment *Record additional data* the box *Record WE potential*.
11. You can first perform a measurement with no iR compensation.
12. Then perform multiple measurements with increasing resistances to compensate.
13. Look at the plots of E vs t. The R_u should be close to the resistance where the ringing begins. Just choose a resistance slightly beneath it (90 %).

It is helpful if you know roughly the R_u. If you don't know R_u approximately, choose a wider range for your compensation and choose big increments for the resistance to compensate. For example, perform measurements from 0 to 800 Ohm with 100 Ohm steps. Should you see an oscillation at 800 Ohm, perform measurements with smaller steps between 600 and 800 Ohm to see where ringing begins.

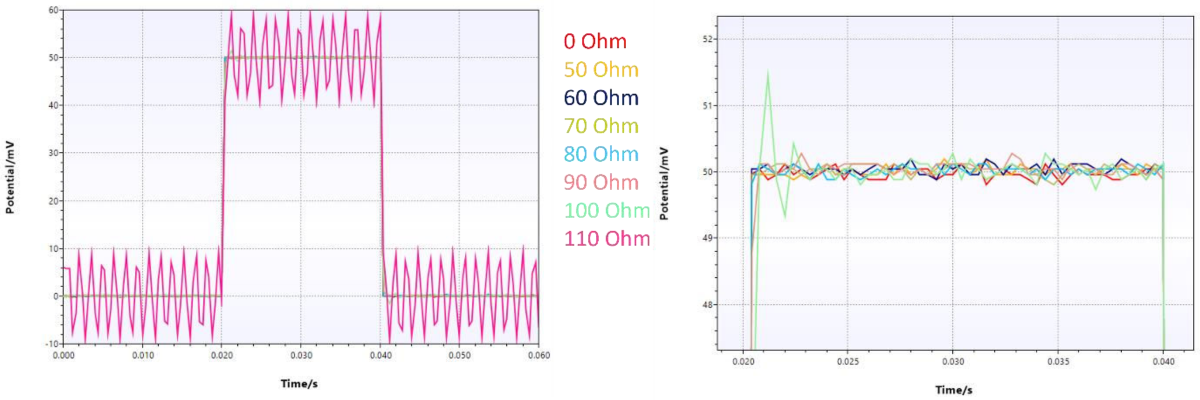

Figure 8 Measured potential of the WE during a MultiStep Amperometry with varying compensated resistances (left) and a zoom in (right)

5.3 Interrupted Current

A capacitor reacts slowly to changes of potential or current compared to a resistor. As explained in chapter 5.1, very fast changes of potential or current lead to a negligible impedance of the capacitor. This is exploited in the interrupted current method. A constant current is applied to the system. Then the circuit is opened, which interrupts the current flow, leading to a current of 0. The uncompensated resistance will immediately react and the potential drop across it is 0.
After that the capacitor, or electrochemical double layer respectively, will discharge. A capacitor in parallel to a resistor, here the charge-transfer resistance, discharges exponential according to

$$E = E_0 e^{-\frac{t}{R_{ct}C_{dl}}}$$

Where E_0 is the initial potential and E the potential over time t. This means we need to measure the potential before the current is interrupted and right after the interruption that will be E_0 for the capacitor. For this you need a potentiostat that can very accurately measure the very fast potential drop. With that potential drop you can calculate R_u. Just divide the potential drop by the current value before the interrupt.
How fast this measurement must be is defined by time constant τ.

$$\tau = R_{ct}C_{dl}$$

T is the time in which around 63 % of the initial current is gone. For a successful measurement you need to measure at least 100 times faster.
Alas, at the moment our instruments don't offer the software and hardware properties that are required to perform this measurement.

5.4 Potential Step

Analog to the current interrupt described in chapter 5.3 you can also use a potential step to determine the uncompensated resistance R_u. For this technique Faraday currents need to be avoided. A potential step is applied between two potentials and both potentials should not lead to a Faraday current. This means the R_{ct} can be removed from Figure 7:

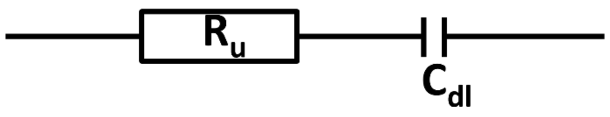

Figure 9 Circuit model for potential step

The potential step will change the amount of charge the capacitor can store and we are going to observe this change. For example, you could jump from 0.02 V to 0.03 V and observe the current flowing.
From electronics it is known that the current during a charging or discharging decays exponentially according to:

$$I = I_0 e^{-\frac{t}{R_u C_{dl}}}$$

Here I_0 is the initial current caused by the potential step. Please note that here the time constant τ is in this situation defined by R_u:

$$\tau = R_u C_{dl}$$

An instrument with fast data sampling and precise timing is required to measure the current.
Ideally, you could use the initial current step I_0 of the curve to calculate with the potential step ΔE the resistance R_u using Ohm's law, because during the potential step the capacitors impedance is negligible. This would require a very fast measurement but could be sufficient for a rough estimation.
A more accurate way is linearizing the curve, making a linear regression and use the intercept to determine I_0. The linear form of the equation for I is

$$\log I = \log I_0 - \frac{t}{R_u C_{dl}} \log e$$

5.4.1 How to perform this

When you want to perform this technique, you need to consider multiple parameters. You need to avoid a Faraday reaction current, otherwise you have an additional current pathway across R_{ct} (see Figure 7). A low time constant τ will lead to inaccuracies because the charging is happening too fast. You need software that allows you to perform linear regression.

Considering the amount of work and possible sources for inaccuracies, EIS (see chapter 5.1) and overcompensation (see chapter 5.2) are both preferrable to the potential step experiment.

1. Connect your cell and the potentiostat as usual.
2. Choose *Fast Amperometry* as Technique.
3. Set a current range according to the expected current. We want to perform a fast measurement, so only a single current range can be active to prevent auto-ranging.
4. Set a *t equilibration* of 10 s or long enough to have a stable current.
5. Set *E equilibration* to the potential before the step and *E dc* to the potential after the step.
6. A *t run* of 0.001 s should be sufficient.
7. Set a *t interval* of 0.00002 s, which is the lowest limit for the *t interval*.
8. Perform the measurement.
9. Export the data to the software where you want to perform the processing.
10. PalmSens4 has under the given settings a small delay before starting the recording. To compensate for that add 0.00016 s to the time. Plot the logarithm of the current lg I versus time t.
11. Perform a linear regression on the linear part of the curve to acquire the intercept.
12. The intercept is $\lg I_0$. Convert it to I_0 and calculate Ru with $\Delta E / I_0$.