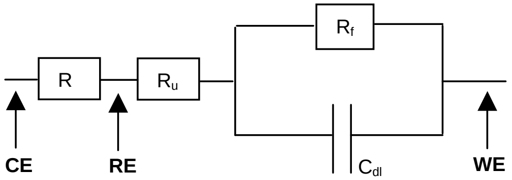
Measuring uncompensated resistance on micro-electrodes using positive feedback.

Introduction

In a standard three electrode electrochemical cell, there will always be a non-zero solution resistance (R_u) that may affect the potential applied to the WE. A schematic description of that situation is given below, where R_f is the charge transfer resistance and C_{dl} is the double layer capacitance.



In cases where an aqueous solution is used in the electrochemical cell, the solution resistance is usually low and therefore negligible. For example, a solution resistance of R_u= 50 Ohm at a current of I =10 µA, will give a voltage drop between RE and WE of $V=I*R_u$= 0.5 mV, a value that can be neglected. However, in cases where the currents increase, or non-aqueous solvents are used (with solution resistances up to 50 kOhm or more), the voltage drop may go up to hundreds of millivolts, causing a severe distortion of the measurement.

There are a number of ways to reduce the ohmic drop between RE and WE:

1. Adjusting the cell geometry in such a way that the distance between RE and WE becomes as small as possible, thus reducing the resistance between them.
2. Increasing the concentration of supporting electrolyte, thus reducing the solution resistance.
3. Measuring the solution resistance and compensating for it electronically, for example by using the so-called positive feedback method.
4. The use of micro-electrodes. Due to their small surface area, typically a factor of 100,000 or more smaller then a conventional electrode, the currents on micro-electrodes tend to be small, in the nA range or lower. This makes the voltage drop due to uncompensated resistances very small. However, with measurements at higher scan rates, the current increases and the voltage drop becomes considerable. Compensating for this voltage drop needs to be done with great care, as will be shown below.

Measurement of solution resistance

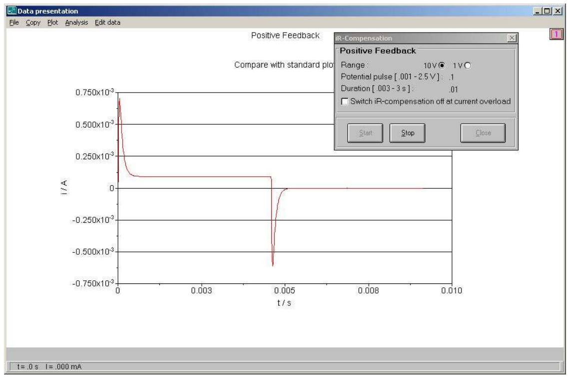
Three main methods to measure the solution resistance can be distinguished:

1. Positive feedback
2. Current Interrupt
3. Impedance measurement at high frequencies.

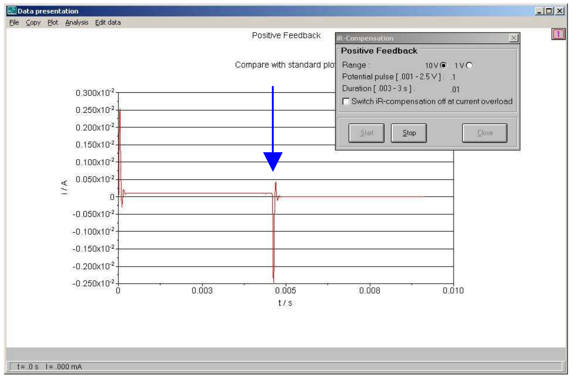
This application note describes the principle of positive feedback, the current interrupt method is not suitable for micro-electrodes, impedance measurements are described in separate notes.

Positive feedback

A potential pulse is applied to the cell, and the current response is measured, this is done continuously (see the figure below).
Slowly the resistance that is compensated for, is increased until one sees the onset of oscillation in the current response (indicated by the blue arrow in the figure below).

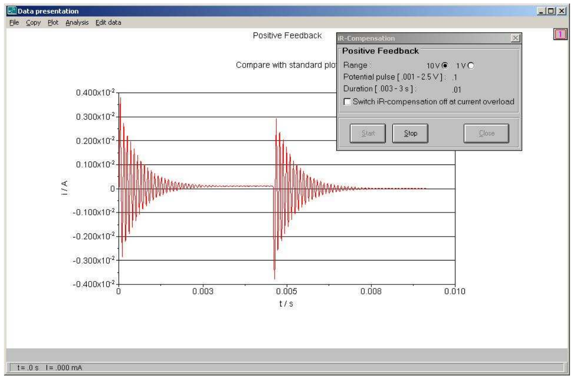


Range : 10 V ● 1 V ○
Potential pulse [.001 - 2.5 V] : .1
Duration [.003 - 3 s] : .01
☐ Switch iR-compensation off at current overload
t= .0 s I= .000 mA



Range : 10 V ● 1 V ○
Potential pulse [.001 - 2.5 V] : .1
Duration [.003 - 3 s] : .01
☐ Switch iR-compensation off at current overload
t= .0 s I= .000 mA

In case the resistance would be fully compensated for, the system goes into damped oscillation, as shown in the figure below.



Positive Feedback

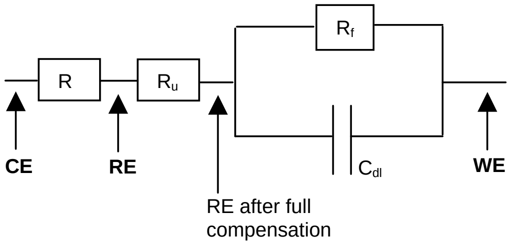
Range: 10 V ● 1 V ○

Potential pulse [.001 - 2.5 V]: .1

Duration [.003 - 3 s]: .01

☐ Switch iR-compensation off at current overload

The reason the system goes into oscillation, is that the position of the RE is virtually moved into such a position that a purely capacitive cell arises, as shown schematically below:



The impedance of such a capacitive cell is determined by the impedance of the capacitor itself since Z(C)= 1/2πfC, where f in this case is the bandwidth of the potentiostat control loop. For a standard electrochemical cell with a macro electrode, a reasonable value for C is 10µF/cm2. The bandwidth of the Autolab potentiostats in High Speed Mode is 125 kHz (the 1 MHz bandwidth of the instrument is normally only available for impedance measurements), giving an impedance of the capacitance of Z(C)= 0.08 Ohm, which is close to a short circuit situation and causes the instrument to go into oscillation.

When the instrument goes into oscillation, the WE in the cell is subject to high potentials, it is therefore wise to take only 80-90% of the resistance value at which onset of oscillation is seen. By activating the option “Switch iR-compensation off at current overload” damage to the cell is avoided.

Overcompensation

When used on micro-electrodes, this way of measuring the uncompensated resistance may cause problems. As the surface area of a micro-electrode is very small, the double layer capacitance value will be very low. For a micro-electrode with diameter 20 µm, the surface area will be 3*10^{-6} cm. An impedance measurement on such a micro-electrode in Acetonitril (0.05 M TBAH and 5 mM Ferrocene) gives a double layer capacitance of 3 pF. Resulting in an impedance of Z(C)= 424 kOhm at 125 kHz (the bandwidth of the potentiostat); due to this high impedance value, the instrument will still be able to control the potential and not go into oscillation. Thus the problem arises that one can overcompensate without realising it, as no oscillation will be seen.

The effect of overcompensation can be seen in cyclic voltammograms for example. For a reversible one electron transfer the theoretical peak separation is 59 mV. In the next figure, it can be seen that the peak separation becomes lower than this value in case of overcompensation. The blue curve is a cyclic voltammogram with 50 kOhm compensation (a value that was verified by using impedance measurements), whereas the red curve has 200 kOhm compensation. In the blue curve the peak separation is 70 mV, in close enough agreement with the theoretical value of 59, (it is usually very difficult to reach the theoretical value exactly) while the red curve has a peak separation of only 40 mV, which is impossible for a single (reversible) electron transfer at room temperature. This shows that although iR compensation can be used with micro-electrodes, measuring the uncompensated resistance with the positive feedback method must be done with extreme care.