Using iR compensation

Case study: how to use the iR compensation option in NOVA?

1 – What is the iR drop

Potentiostats are instruments that are designed to control the potential of the working electrode (WE) relative to an ideal non-polarizable reference electrode (RE). While this is the apparent operating principle of a potentiostat, in reality the potentiostat controls the potential of the counter electrode (CE) relative to the WE (which is at virtual ground). The potential of the CE is set to the required voltage within the compliance voltage limits in order to keep the potential difference between the RE and the WE equal to the user-defined value.

For the following basic electrochemical cell (see Figure 1):

![Figure 1 – An overview of an electrochemical cell (simplified)](image)

RΩ corresponds to the solution resistance and Rp is the polarization resistance (also known as the charge transfer resistance). In order to keep the potential of the WE at +1 V relative to the RE, the CE is set to -1.1 V relative to the WE.

Note

A complete description of the working principle of a potentiostat can be found in the *Electrochemical Methods – Fundamentals and Applications* handbook by L. Faulkner and A. Bard.

In practice, this means that the potentiostat will always compensate the solution resistance, within the limits of the compliance voltage.

Unfortunately, the electrochemical cell shown in Figure 1 does not correspond to a real electrochemical cell. In a real electrochemical cell, the reference electrode is always located at a distance relative to the working electrode. This means that an
additional resistance, the *uncompensated resistance, $R_u$,* can never be avoided completely (see Figure 2).

![Diagram of an electrochemical cell (complete)](image)

**Figure 2 – An overview of an electrochemical cell (complete)**

The uncompensated resistance leads to voltage change across the electrochemical interface, called the iR drop, given by:

$$V_{iR} = i \cdot R_u$$

Therefore, whenever a current is passed through the circuit described in Figure 2, there is always a potential control error due to the uncompensated resistance. If a cathodic current flows, the true potential difference across the electrochemical interface is *less negative* than the specified potential. The opposite holds in the case of an anodic current.

Even with a very low uncompensated resistance value, the voltage drop can become significant when the current is high\(^1\).

### 2 – How to minimize iR drop?

Although iR drop cannot be avoided, it is possible to minimize its value. The following strategies can be used:

1. Use a supporting electrolyte with high conductivity: this will reduce the total resistance of the solution (and therefore also the uncompensated resistance).
2. Reduce the size of the working electrode: the total current depends on the surface of the working electrode. Smaller currents decrease the iR drop.
3. Use a Luggin capillary: this can be used to reduce the distance between the reference electrode and the working electrode, therefore reducing the uncompensated resistance.

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\(^1\) A $R_u$ of 1 $\Omega$ with a current of 100 mA leads to a voltage drop of 100 mV.
2.1 – The iR compensation circuit

An additional strategy that can be used to reduce the effects of the uncompensated resistance is to use the so-called positive feedback built into the Autolab potentiostat in order to partially compensate the iR drop. The iR drop functionality is available in the Autolab PGSTAT series.

In the Autolab PGSTAT, the iR compensation circuit is fitted with a DAC that can be used to compensate the iR drop. The voltage range of the compensation circuit is $0 - 2\,\text{V}$ ($\text{DAC}(V)$). This means that the resistance range that can be compensated through this circuit is:

$$R_{\text{Comp}} = \frac{\text{DAC}(V)}{CR}$$

where $CR$ is the current range.

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2.2 – How to use iR compensation in NOVA?

It is possible to define the value of the resistance to compensate using the iR compensation circuit in the Autolab control interface. Using the Autolab control command, it is possible to switch the iR compensation circuit on and off and to specify the value of the resistance to compensate.

Import the procedure NOVA technical note 7 - iR compensation [NOVA 1.10].nox provided with this technical note. Expand the procedure and click the button next to the Autolab control command (see Figure 3).

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*The option is not available with the µAutolab.*
The Autolab control interface displays a list of hardware settings for the potentiostat/galvanostat. Using this interface, it is possible to set the initial current range, set the instrument mode and bandwidth and switch the iR compensation On or Off (as shown in Figure 4).

![Autolab control interface](image)

**Figure 4 – All the hardware settings are available in the Autolab control interface**

Using the procedure as provided with the technical note, connect dummy cell (c) and start the measurement. A single potential scan will be performed, without iR compensation. WE(1).Current and WE(1).Potential will be sampled during the experiment. The measured data should look like the data displayed in Figure 5.
The data measured with the original procedure has been used in Figure 5 to illustrate that the measured current does not quite reach 1 mA, although dummy cell (c) is fitted with a 1000 Ohm resistor. This is because of the extra 100 Ohm resistance located in series with the (RC) circuit of the dummy cell.

We will now modify the procedure in order to compensate the 100 Ohm resistance in the circuit. To switch iR compensation On and to define the resistance value, click the button next to the Autolab control command in the procedure setup in order to open the Autolab control interface.

Using the slider, set the iR compensation to On (see Figure 6).
Next, change the value of the iR compensation circuit, from 0 to 95. The value can be typed directly into the field, replacing the 0 value (see Figure 7).

**Figure 6 – Switching iR compensation on**

**Figure 7 – Defining the resistance value**
Click the OK button to confirm the settings and start the measurement again.

During the measurement, the iR-C indicator on the Autolab display (F10 key) will indicate that the iR-C circuit is in use (see Figure 8).

![Autolab display](image)

**Figure 8 – The status of the iR-C circuit is shown in the Autolab display**

The data measured with this modified procedure should be similar to the data displayed in Figure 9.

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**Note**

It is common practice to compensate about 90 to 95% of the uncompensated resistance. Remember that over-compensating the resistance can lead to oscillations in the potentiostat.
It is possible to change the value of the compensated resistance and repeat the experiment to see the effect of this value on the measured current. Figure 10 shows an overlay of three different values.
Figure 10 – Overlay (detail) showing three different resistance values used in the iR compensation circuit

How to determine the value of Ru?

Several methods can be used to determine the value of the uncompensated resistance, Ru:

- Current interrupt
- Positive feedback
- Impedance spectroscopy

More information on these methods is provided in the dedicated iR compensation tutorial available from the Help menu in NOVA. The reader is kindly invited to refer to this documentation for detailed information regarding these methods.