Application Note AN-EC-036

Ohmic iR drop

Part 3 – Measurement with EIS

SUMMARY

In the first Application Note of this series (AN-EC-003), the concepts of ohmic drop and ohmic resistance (or uncompensated resistance) were explained and some strategies for reducing the errors due to the ohmic drop were mentioned. By employing some of these strategies, the ohmic iR drop can be reduced, but cannot be totally eliminated.

The second part of this series (AN-EC-004) introduced the methods of current interrupt and positive feedback as tools for dealing with the ohmic drop. This Application Note introduces the third and final tool that is available to researchers—electrochemical impedance spectroscopy (EIS).

MEASURING THE OHMIC DROP

As mentioned in Part 2, although it is technically possible to estimate the ohmic drop, most of the time real systems are more complicated. As a consequence, the ohmic drop must be determined experimentally. There are three main experimental techniques for determining the iR drop:

1. Current interrupt
2. Positive feedback
3. Electrochemical impedance spectroscopy (EIS)

Within the Metrohm Autolab range of products, all modular and compact instruments equipped with a FRA32M module, as well as VIONIC powered by INTELLO, are able to perform EIS measurements across a wide frequency range. Of the three experimental techniques listed above, EIS is considered the most accurate method, making it the recommended choice. It is important to exercise caution when using the other two methods, as their incorrect usage can sometimes result in data misinterpretation or even damage to the setup. Therefore, in the subsequent discussion, we will primarily focus on measuring the iR drop through EIS.

More information regarding the current interrupt and positive feedback methods can be found in Application Notes AN-EC-003 and AN-EC-004.

EXPERIMENTAL

A three-electrode cell was used consisting of a Pt disc WE (3 mm), Pt sheet counter electrode, and an Ag/AgCl reference electrode. The cell was charged with 0.05 mol/L of $K_4[Fe(CN)_6]$, and in order to artificially increase the ohmic resistance, no additional supporting electrolyte was used.

MANUAL IR COMPENSATION – NOVA AND INTELLO

In NOVA and in INTELLO, it is possible to manually calculate the uncompensated resistance using EIS and then introduce this value in the appropriate section of the Apply Settings (INTELLO) or Autolab Control commands (NOVA).

The EIS measurement was conducted at 0 V vs OCP (open circuit potential), with an amplitude of 5 mV (V_{TOP}). A frequency range of 100 kHz to 100 Hz was used.

Usually, the uncompensated resistance can be obtained from both the Nyquist and Bode plots. In the former, it is the intersection of the data with the x-axis at the high frequency end, while in the latter, it is the plateau at the high frequency end in the |Z| vs log *f* plot. In Figure 1, the annotated Nyquist plot is shown with the high frequency end highlighted.

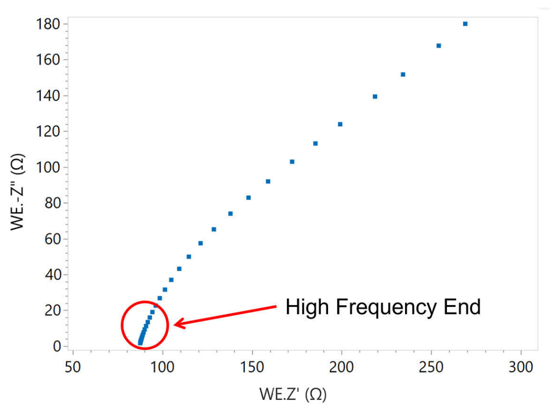

Figure 1. Annotated Nyquist plot indicating the high frequency end where the uncompensated resistance can be found at the point where the data crosses the x-axis (-Z″ = 0).

This returns an uncompensated resistance of 87 Ω. If for any reason it is not possible to read off the value from the plots, then the value can also be obtained from the Fit and Simulation tool in NOVA (Figure 2).

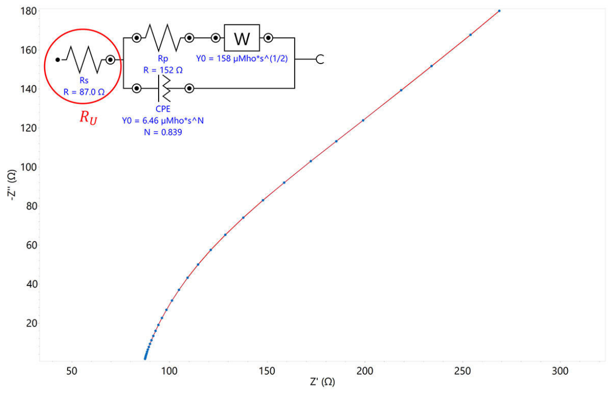

Figure 2. Nyquist plot and the associated equivalent circuit. The uncompensated resistance can also be determined by fitting the data to an equivalent circuit.

Once measured, R_u (the uncompensated resistance) should be introduced in the Apply Settings command in INTELLO (Figure 3). It is recommended to apply a maximum of between 80% and 90% of the total value in order to avoid having the system go into oscillation. In INTELLO, the desired percentage can be entered alongside the measured value, and the compensated resistance to be applied (R_c) will be automatically calculated.

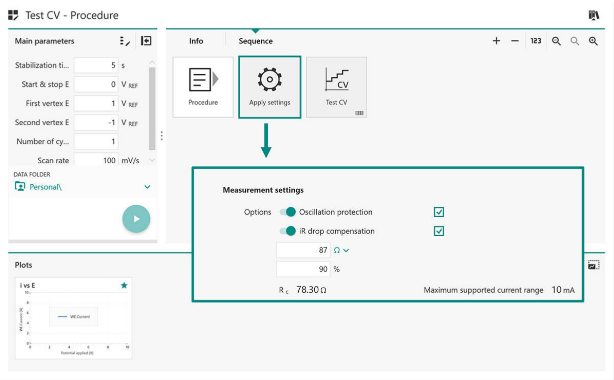

Figure 3. Screenshot of INTELLO. The calculated iR drop should be input in the Apply Settings command.

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AUTOMATIC IR COMPENSATION – INTELLO

A new command is available in INTELLO called «Measure iR Drop» (**Figure 4**). This command automatically measures and then compensates for the iR drop at the start of the measurement, assuming that the iR compensation option is activated in a subsequent Apply Settings command.

In order to obtain the uncompensated resistance (R_u), the command executes a single-frequency EIS measurement. The frequency is user-defined, though the default is 30 kHz. It is important to ensure that the chosen frequency is appropriate for the system by first performing a complete EIS measurement. For this measurement, it is recommended to set the DC potential to a value near the OCP and allow enough stabilization time (no superimposed sine) at this potential for the most accurate measurement. In order to avoid overcompensation and therefore oscillations of VIONIC, it is possible to set an acceptable range of values (safety limits) for R_u. Maximum and minimum values can be input. It is recommended to provide at least a maximum value for the uncompensated resistance (usually an estimated value plus 10%). If the measured value of R_u is not between the specified values, a warning message will appear. It is possible to stop the procedure or continue with the maximum input value. If the measured value of R_u is within the specified range, either no message will appear and the procedure will continue, or the acceptance window will appear for validation depending on the user's preference and settings.

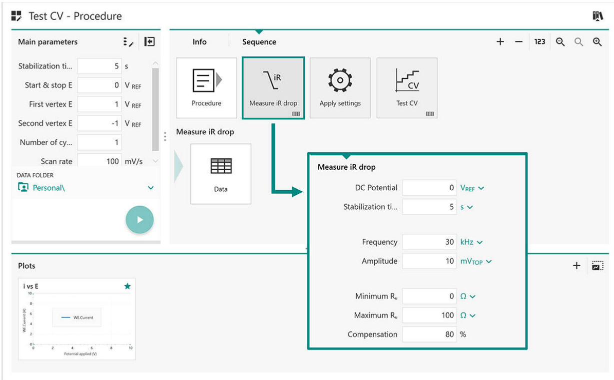

Figure 4. The Measure iR Drop command is a new feature in INTELLO. The software can automatically calculate and then compensate for the iR drop as shown in this example screenshot.

In Figure 5, the acceptance window is shown. This window shows the real part of the impedance (WE.Z'), the imaginary impedance (WE.-Z") and the total impedance (WE.|Z|). The real part of the impedance is analogous to the uncompensated resistance, R_u. The percentage of this value to be compensated is also shown. Finally, R_c, the value which will be compensated, is shown here. If these values are acceptable to the user, the measurement can continue by pressing the Accept button. Note that the values should be considered acceptable if WE.Z' and WE.|Z| are very close to each other, indicating that most of the impedance is purely resistive. This can also be observed in the phase (WE.-Phase), which should be close to 0.

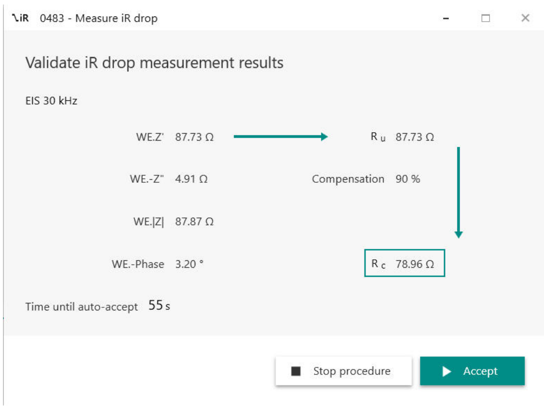

Figure 5. Acceptance window for the Measure iR Drop command.

The effect of iR drop compensation is illustrated in Figure 6 with the CV of $K_4[Fe(CN)_6]$ in ultrapure water. In blue, the iR drop is not compensated for, resulting in an increase in the peak-to-peak separation and a lower peak current. In extreme cases, without iR drop compensation it may be wrongly assumed that a redox process is irreversible, when in fact it is reversible. Shown in orange is the iR-drop corrected cyclic voltammogram, where the peak-to-peak separation is consistent with a one-electron reversible process.

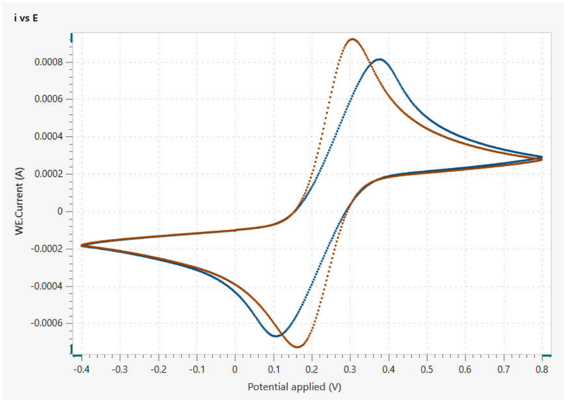

Figure 6. Cyclic voltammogram of potassium ferrocyanide (0.05 mol/L) in water: compensated (orange) and non compensated (blue).

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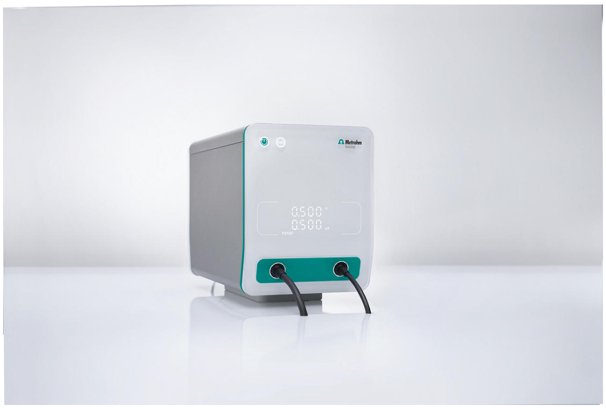
CONFIGURATION



VIONIC

VIONIC is our new-generation potentiostat/galvanostat that is powered by Autolab's new **INTELLO** software.

VIONIC offers the **most versatile combined specifications of any single instrument** currently on the market.

- Compliance voltage: ± 50 V
- Standard current ± 6 A
- EIS frequency: up to 10 MHz
- Sampling interval: down to 1 µs

Also included in **VIONIC's** price are features that would usually carry an additional cost with most other instruments such as:

- Electrochemical Impedance Spectroscopy (EIS)
- Selectable Floating
- Second Sense (S2)
- Analog Scan