Metrohm Autolab

Application Area: Fundamental

Ohmic Drop
Part 2 – Measurement

Keywords

Uncompensated resistance; Ohmic drop determination; Ohmic drop compensation

Summary

In a previous application note, the concepts of ohmic drop (or uncompensated resistance) and ohmic resistance were explained and some strategies for reducing the errors due to the ohmic drop were mentioned. These errors can be reduced but cannot be totally eliminated. However, the ohmic drop can be measured and partially compensated.

Estimating the ohmic drop

In a potentiostat connected to a three-electrode cell setup, the potential between the working electrode (WE) and a reference electrode (RE) is controlled with the help of a control loop. The desired potential difference between the RE and WE is maintained by adjusting the current flow between the counter (CE) and the working electrodes. The ohmic resistance, R_u, also known as uncompensated resistance, causes a potential control error, called ohmic drop, iR_u, which can be corrected by adding to the input of the potentiostat a correction voltage proportional to the current flow. Unfortunately, it is not possible to use a correction potential exactly equal to iR_u and fully compensate the ohmic drop, because the system will go into oscillation.

The ohmic drop depends on the ohmic resistance R_u, which is a function of the cell geometry and the conductivity of the electrolyte. For a planar electrode with uniform current density across its surface, the ohmic resistance is given by:

$$R_\mathrm{u} = \frac{X}{\kappa A} \qquad 1$$

Where, $X\ (cm)$ is the distance of the RE from the WE, $\kappa\ (S\ cm^{-1})$ is the solution conductivity, and $A\ (cm^2)$ is the WE surface area.

For a spherical electrode (DME, HDME) of radius r_0 the ohmic resistance is given by:

$$R_\mathrm{u} = \frac{1}{4\pi\kappa r_0}\left(\frac{X}{X + r_0}\right) \qquad 2$$

For a rotating disc electrode (RDE) of radius r, when the RE is placed far from the working electrode (typically for RDE measurements), the ohmic resistance is given by:

$$R_\mathrm{u} = \frac{1}{4\kappa r} \qquad 3$$

Measuring the ohmic drop

In most cases, the geometries are more complicated and therefore the ohmic drop must be measured experimentally. The three most common methods for measuring the ohmic drop are:

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

The electrical equivalent circuit shown in Figure 1 is used to illustrate the three methods. This circuit corresponds to dummy cell circuit (c) of the Autolab Dummy Cell 2.

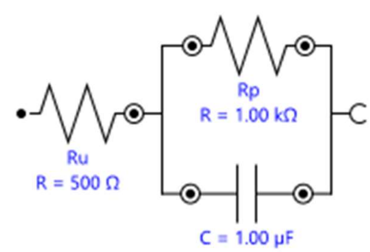


Figure 1 - The equivalent circuit used in this application note

Current interrupt

The measurement of ohmic drop using the current interrupt technique is based on the simple application of Ohm's law. When a current i flows through the circuit mentioned above, the voltage drop across the resistor R_u is iR_u, and the voltage drop across $(R_\mathrm{p}C)$ is iR_p. If the current is interrupted, then i will become 0 and the voltage across R_u drops almost instantaneously, while the voltage across $(R_\mathrm{p}C)$ drops with an exponential decay proportional to $EXP(-t/R_pC)$, due to the presence of the capacitor C.

If the voltage is measured just before and immediately after the current has been interrupted, the difference in the measured voltages is the ohmic drop ΔE_{ohmic}. The ratio between the ohmic drop and the current before the interruption is the ohmic resistance R_u. The measurement of the ohmic drop for the dummy cell circuit (c), (equivalent circuit in shown in Figure 1) using a PGSTAT302N with an ADC10M fast sampling module, is illustrated in Figure 2.

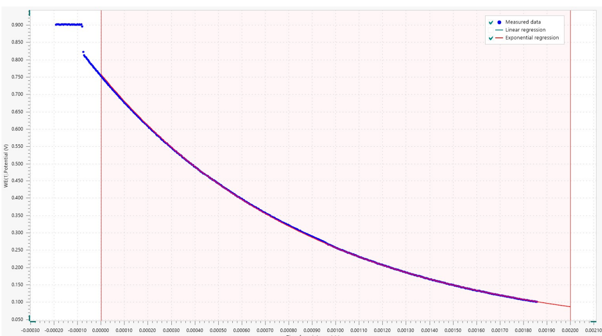


Figure 2 - Measurement of ohmic resistance with current interrupt using a PGSTAT302N with the ADC10M

When an ADC10M module is not available, the method can still be used. However, less data points will be recorded, resulting in a less accurate measurement (see Figure 3).

Figure 3 – Measurement of the ohmic resistance with current interrupt using the PGSTAT302N

The measured values are fitted using a linear and an exponential regression and the calculated R_u are displayed in the tab of the instrument (see Figure 4).

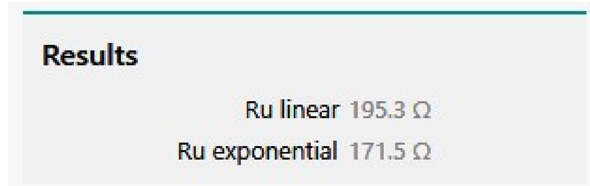


Figure 4 – The resistance values obtained from the linear and exponential fitting of the data

The calculated values strongly depend on the specified start and stop positions for the linear and exponential regression. If these positions are not adjusted properly, the calculated values can be significantly different from the real uncompensated resistance.

Positive feedback

Another way to measure the ohmic drop is the so-called positive feedback. Since the ohmic drop iR_u is proportional to the ohmic resistance R_u, it might be possible to compensate the ohmic drop by measuring the current i, multiplying it by the ohmic resistance R_u and feeding back the resulting ohmic drop to the control loop. In this case, the following need to be considered: the ohmic resistance is unknown at this stage, and a complete compensation of the ohmic drop would led the system into oscillation, losing the control of the potentiostat.

In the positive feedback measurement, a voltage iR_x, is fed back into the control loop, during a short potential step measurement. The goal is to find the value of R_x, called iR compensation value, close enough to the ohmic resistance R_u. This is accomplished by trial and error, therefore repeating the procedure with different values of the iR compensation resistance and looking at the resulting plot. An acceptable iR compensation will result in damped oscillations of the signal, like shown in Figure 5.

Figure 5 – A positive feedback measurements of the circuit in Figure 1, dummy cell (c), with an acceptable iR compensation value, 101 Ω.

This method should be used with care. A system that oscillates is a system with more potential, thus more energy, than necessary. Therefore, undesired side reactions could be triggered, affecting or damaging the electrolyte and the working electrode.

The positive feedback can be directly measured in the Nova software.

Electrochemical impedance spectroscopy (EIS)

Ohmic resistance can be determined very accurately by electrochemical impedance spectroscopy (EIS). In Figure 6, the Nyquist plot of an EIS measurement performed with PGSTAT302N with a FRA32M on the same dummy cell circuit (c) is shown.

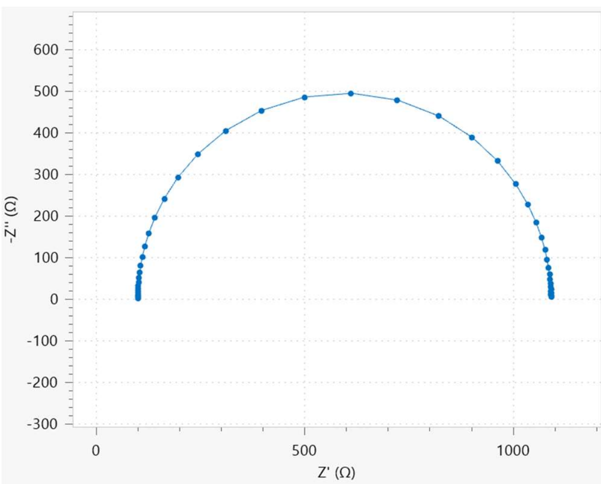
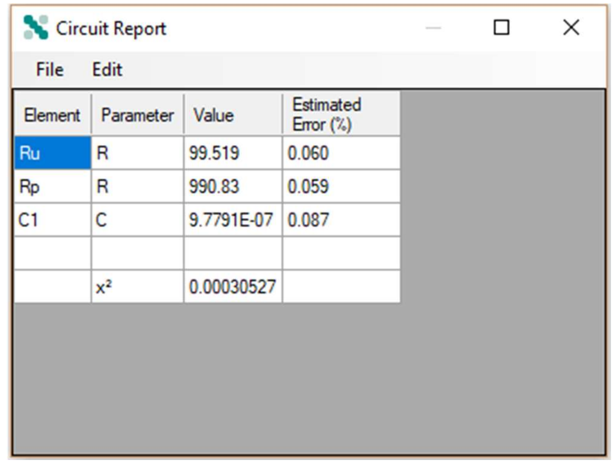


Figure 6 – Impedance measurement obtained on the circuit specified in Figure 1

In the Nyquist plot, the intersection of the measured impedance data with the x-axis (real part of the impedance) at high frequencies gives the ohmic resistance. For details on how to perform EIS measurements, please refer to the application notes on EIS.

Fitting the data with the equivalent circuit shown in Figure 1 allows accurate determination of the ohmic resistance, as shown the circuit report in Figure 7; low values for the estimated error and χ^2 are obtained.



Element	Parameter	Value	Estimated Error (%)
Ru	R	99.519	0.060
Rp	R	990.83	0.059
C1	C	9.7791E-07	0.087
	x²	0.00030527	

Figure 7 – The circuit report

EIS is a relatively fast and reliable method to determine precisely the ohmic resistance. Furthermore, the cell is kept around the equilibrium potential with a low-amplitude AC signal applied; therefore, the cell is not put at risk for side reactions or damage.

Practical compensation of the ohmic drop

Once the value of the ohmic resistance has been measured, it can be used in any desired NOVA procedure. In the properties of the Autolab control command, it is possible to toggle the “iR compensation” switch and insert the ohmic resistance value, like shown in Figure 8.

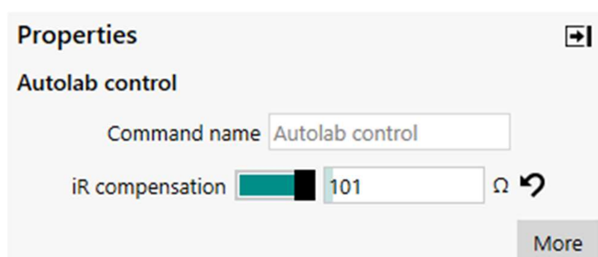


Figure 8 - The properties of the Autolab control command, with the iR compensation on.

The system will apply the iR compensation value similarly to the positive feedback method described above. Therefore, it is strongly recommended to use 80-90% of the ohmic resistance, to avoid oscillations and damage to the WE and electrolyte.

Another way to use the ohmic drop is to perform one of the three above-mentioned measurements, and then to use the value of the ohmic resistance to correct the experimental data mathematically.

The current i from the electrochemical experiment is multiplied by the ohmic resistance R_{u}, in order to find the ohmic drop $V_{drop} = iR_{\mathrm{u}}$. Then, V_{drop} is subtracted from the experimentally measured potential V_{exp}, resulting in the corrected potential $V_{corr} = V_{exp} - V_{drop}$. Finally, V_{corr} can be used in the plots and in further post-data treatments.

Conclusions

This application note describes three different measurement methods of the ohmic drop and the ohmic resistance presented. Current interrupt and positive feedback are fast methods, but care is necessary for their use in order to avoid data misinterpretation or damage to the setup. EIS, on the other way, is a more reliable method to determine the ohmic resistance, but requires the FRA32M module. The ohmic drop can be compensated by the potentiostat during the measurement, or a mathematical correction can be applied to the data.

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For more information

Additional information about this application note and the associated NOVA software procedure is available from your local **Metrohm distributor**. Additional instrument specification information can be found at **www.metrohm.com/en/products/electrochemistry**.