

Autolab Application Note EC04

Ohmic Drop Part 2 – Measurement

Keywords

Uncompensated resistance; Ohmic drop determination; Ohmic drop compensation

Summary

In the previous application note the concept of ohmic drop and ohmic resistance was explained and some strategies for reducing the errors due to ohmic drop were mentioned. As explained earlier, these errors can be reduced but cannot be totally eliminated. In such cases it is important to measure and compensate for the ohmic drop.

Estimating ohmic drop

Ohmic drop depends on ohmic resistance, which is a function of the cell geometry and the conductivity of the electrolyte. If the conductivity of the electrolyte is known then for simple geometries analytical equations for the calculation of the ohmic drop are available. For a planar electrode with uniform current density across its surface the ohmic resistance is given by:

$$R_{\Omega} = \frac{X}{\kappa A}$$

where, *X* is the distance of the reference electrode from the working electrode κ is the solution conductivity and *A* is the working electrode area.

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

$$R_{\Omega} = \frac{1}{4\pi\kappa r_0} \left(\frac{X}{X + r_0} \right)$$

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

 $R_{\Omega} = \frac{1}{4\kappa r}$

Measuring 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 ohmic drop are:

- 1. Current interrupt
- 2. Positive feedback
- 3. AC Impedance

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



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 current, i, flows through the above circuit then the voltage drop across the resistor R_{Ω} is iR_{Ω} . And the voltage drop across the resistor $R_{\rm p}$ is $iR_{\rm p}$. If the flow of this current is stopped suddenly or interrupted then *i* becomes 0 and the voltage across $R_{\rm p}$ drops very quickly but the voltage across $R_{\rm p}$ drops slowly due to the presence of the capacitor, Cd.

If the voltage is measured immediately before and immediately after the current has been interrupted using a fast A/D converter, then the difference in the measured voltages is the ohmic drop ΔE_{ohmic} . The ohmic drop divided by the known current, i, before the interrupt gives the ohmic resistance, R_{Ω} . The measurement of the ohmic drop for the above equivalent circuit using PGSTAT302N with ADC10M, a fast A/D converter, is illustrated in Figure 2.





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

When no fast A/D converter is available, the method can still be used; but less data points are recorded, resulting in a less accurate measurement (see Figure 3).

The measured values are fitted using a linear and an exponential regression and the calculated R Ω are displayed in the Autolab display (see Figure 4).



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

Positive feedback

In a potentiostat, the potential between the working electrode and a reference electrode is maintained with the help of a control loop where the desired potential difference is maintained by adjusting the current flow. When ohmic resistance causes a potential control error equal to iR_{Ω} then it can be corrected by adding into the input of the potentiostat a correction voltage proportional to the current flow. When the compensation is too much then the potentiostat shows oscillation.

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Figure 4 – The resistance values obtained from the fitting of the data are reported in the Autolab display

One can adjust this proportionality factor until one reaches the R_{Ω} , the correct ohmic resistance and the measured current response shows damped oscillation as illustrated in Figure 5.



Figure 5 – Positive feedback measurements obtained with 95 Ω (top) and 101 Ω (bottom)

Electrochemical impedance spectroscopy (EIS)

Ohmic resistance can be determined very accurately by electrochemical impedance spectroscopy. In Figure 6 the results of an EIS measurement done with PGSTAT302N with a FRA2 on the above equivalent circuit is shown. In the Nyquist plot, the intersection of the impedance data with the



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real part of the axis at the high frequency end gives the ohmic resistance. For details on how to perform EIS measurements please refer to the application notes on EIS.



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

Fitting the data with the equivalent circuit shown in Figure 1 allows accurate determination of the ohmic resistance (see Figure 7).

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Element	Parameter	Value	Estimated Error (%)
R1	R	100.38	0.055
C1	С	1.0122E-06	0.055
R2	R	996.67	0.031
	χ²	0.00011208	

Figure 7 – Fitting the data allows for an accurate determination of the ohmic resistance

Date

1 July 2011