

Ohmic drop: 2. Measurement

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:

$$R_{\Omega} = \frac{x}{kA}$$

where, x is the distance of the reference electrode from the working electrode k 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

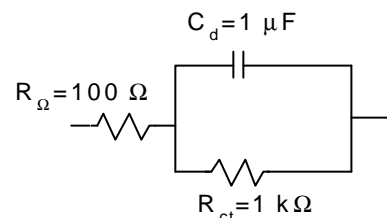
$$R_{\Omega} = \frac{1}{4pk r_0} \left(\frac{x}{x + r_0} \right)$$

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

$$R_{\Omega} = \frac{1}{4kr}$$

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 and 3) AC Impedance. The following electrical circuit is used to illustrate the three methods.



Current interrupt

The measurement of ohmic drop using the current interrupt technique is based on the simple application of ohms law. When current, I , flows through the above circuit then the voltage drop across the resistor R_W is IR_W . And the voltage drop across the resistor R_{ct} is IR_{ct} . If the flow of this current is stopped suddenly or interrupted then I becomes 0 and the voltage across R_W drops very quickly but the voltage across R_{ct} drops slowly due to the presence of the capacitor, C_d .

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 DE_{ohmic} . The ohmic drop divided by the known current, I , before the interrupt gives the

ohmic resistance, R_W . The measurement of the ohmic drop for the above equivalent circuit using PGSTAT30 with ADC750, a fast A/D converter, is illustrated in Figure 1.

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_W then we can correct it 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. One can adjust this proportionality factor until one reaches the R_W , the correct ohmic resistance and the measured current response shows damped oscillation as illustrated in Figure 2.

Electrochemical Impedance Spectroscopy (EIS)

Ohmic resistance can be determined very accurately by electrochemical impedance spectroscopy. In Figure 3 the results of an EIS measurement done with PGSTAT30 with FRA2 on the above equivalent circuit is shown. In the Nyquist plot, the intersection of the impedance data with the 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 1: Measurement of ohmic resistance with current interrupt using PGSTAT30 with ADC750.

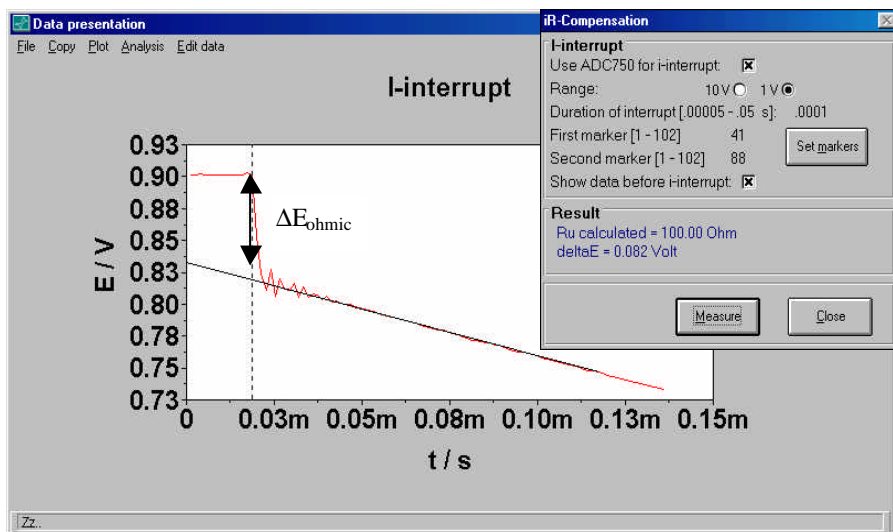


Figure 2: Measurement of ohmic resistance with dynamic IR compensation.

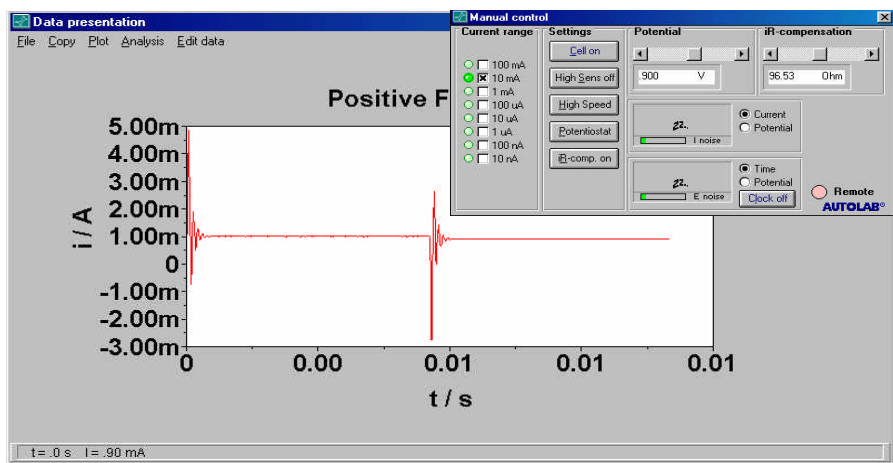


Figure 3: Measurement of ohmic resistance with EIS using PGSTAT30 with FRA2.

