

Application Area: Fundamental

Ohmic Drop

Part 1 – Basic Principles

Keywords

Uncompensated resistance; Ohmic drop determination; Ohmic drop compensation

Summary

A typical electrochemical experiment is performed using a three electrode setup; a working electrode (WE), a counter or auxiliary electrode (CE), and a reference electrode (RE). In addition, a sense (S) lead is connected to the WE. Therefore, the potential applied to the cell is controlled by applying current between the CE and WE, and measuring the potential between the RE and S. In order to have reliable measurements of the potential, the reference electrode should ideally be non-polarizable.

When current is flowing through an electrochemical cell, a potential drop between the RE and the WE will occur. This voltage drop is influenced by the electrolyte conductivity, the distance between the reference and the working electrodes, and the magnitude of the current.

Using Ohm's law, the ohmic (voltage) drop ΔE_{ohmic} can be calculated to be equal to the product of the current i and the ohmic or uncompensated resistance R_u :

$$\Delta E_{ohmic} = iR_u \quad 1$$

Assuming that the passage of current does not affect the potential of the reference electrode (ideally non-polarizable), the measured potential of the working electrode is given by the equation:

$$E_{measured} = E_{applied} - \Delta E_{ohmic} = E_{applied} - iR_u \quad 2$$

Factors affecting the ohmic drop

Consider the potential profile in Figure 1, at the working electrode – electrolyte interface.

The CE is placed relatively far and it is assumed not to influence the current and potential distribution. RE1, RE2 and RE3 are examples of the various positions where the reference electrode RE can be placed to measure the potential vs. the WE. The geometry of the WE surface and

the composition of the electrolyte give rise to the equipotential lines, i.e., regions of the electrode-electrolyte interface where the potential between RE and WE has the same value.

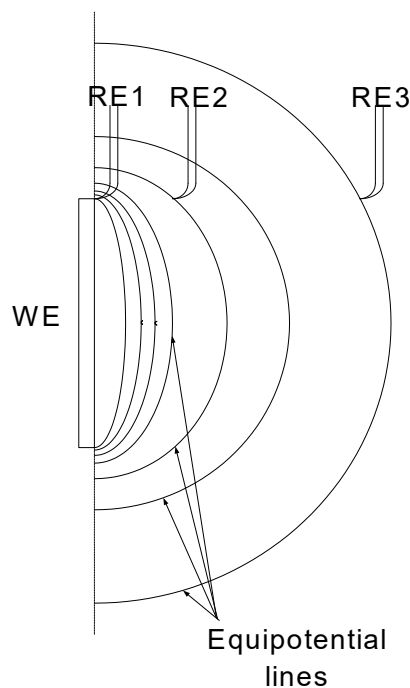


Figure 1 – Equipotential lines shown at close proximity to the working electrode.

Consequently, the ohmic drop value depends on the following factors:

1. The current and potential distribution in the electrolyte, which in turn depends on the geometry of the experimental cell. Therefore, changing the size or shape of the WE will change the shape of the equipotential lines.
2. The position of the RE with respect to the WE. If the RE is placed exactly at the electrode surface, then the ohmic drop is zero (RE1). As the RE is moved away from the WE (RE2 and RE3), the ohmic resistance, and therefore the ohmic drop between WE and RE increases.
3. The conductivity of the electrolyte solution. The lower the conductivity of the electrolyte, the higher the ohmic

resistance and therefore the ohmic drop. Conductivity is in turn affected by other experimental factors, such as the temperature of the system.

Impact of the ohmic drop on measurements

The ohmic drop can have significant impact in fast experiments, experiments with high currents, or those that require long-term passage of currents, like during electrolysis. Also experiments carried out in low conductivity media, such as in concrete or organic electrolyte, can be strongly affected by the ohmic drop.

Under potentiostatic control, there is always a potential drop due to the ohmic resistance Equation 2. Therefore, depending on the sign of the current, the measured potential will be less negative or more positive than the potential if there would be no iR_u drop, called nominal potential. If cathodic (negative) currents flow, the measured potential will be less negative than the nominal potential. If anodic, therefore positive currents flow, the measured potential will be less positive than the nominal potential.

When large currents are employed, even small ohmic resistance values can cause large errors. For example, if the ohmic resistance is 1 Ω and the current is 1 A, the error due to ohmic drop is 1 V. This is one of the reasons why industrial electrosynthesis are usually carried out under galvanostatic control, where the potential between RE and WE is only measured, but not controlled, therefore no iR_u drop is present.

For low-conductivity media such as electrolytes with low salt concentration organic electrolytes, or concrete, the ohmic resistance can be very high, on the order of several k Ω . Therefore, even small currents can lead to large errors in potential. For example if the ohmic resistance is 10 k Ω and the current is 100 μ A, the error is 1V.

In a fast experiment (cyclic voltammetry with a fast scan) there is a current transient due to the charging and discharging of the double layer.

Therefore, when the potential is scanned the measured potential lags the applied potential according to the following equation:

$$E_{measured} = E_{applied} \left(1 - e^{-\frac{t}{R_u C_{dl}}} \right) \quad 3$$

Where R_u is the ohmic resistance, C_{dl} is the double layer capacitance and t is the time at which the measurement is taken. For fast scan rates, i.e., when t is much smaller than $R_u C_{dl}$, the exponential approaches 1 and significant errors in $E_{measured}$ with respect to $E_{applied}$ can arise. For slow

scan rates, i.e., when t is much bigger than $R_u C_{dl}$, the exponential approaches 0 and the errors can be negligible.

Cell design and electrode placement

From Equation 3, it can be seen that for fast experiments, the time constant $R_u C_{dl}$ has a significant influence on the errors in the true potential at the electrode surface. Even for slow experiments, high ohmic resistance can lead to incorrect or misleading results.

These errors can be minimized by reducing either R_u or C_{dl} . This can be achieved by

1. Increasing the conductivity of the solution by using a supporting electrolyte. The conductivity is inversely proportional to the resistivity and therefore to R_u .
2. Decreasing the size of the working electrode, to decrease C_{dl} . The area of a capacitor is directly proportional to its capacitance.
3. Moving RE as close as possible to WE, in order to reduce R_u . This is often done by using a very fine capillary tip, called Luggin-Haber or Luggin capillary, along with RE. It must be remarked that it is not possible to place RE in contact with the WE surface, since the measured potential would be zero!

Note: care must be taken when using a Luggin capillary because it can cause shielding errors. Shielding can appear when the surface of WE is blocked by RE, which can occur if they are too close to each other. This can cause non-uniform current distribution at the electrode surface. If a Luggin capillary with a tip diameter d is used, the closest distance it can be placed without causing appreciable shielding error is $2d$ from the WE. Therefore, even when the tip of the RE is designed for very close placement to the WE, with a Luggin capillary, some uncompensated potential drop usually remains.

At distances very close to the WE, the equipotential lines are close together and small variations in the position of the RE can lead to large variations in the ohmic drop. In some cases, it is preferable not to use a Luggin capillary but to place the reference electrode far from the working electrode and measure and compensate for the ohmic drop, as explained in a separate application note.

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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.