Application Note AN-EC-003

Ohmic iR drop

Part 1 – Basic principles

When current flows through an electrochemical cell, a potential drop occurs between the reference electrode (RE) and the working electrode (WE). This voltage drop (termed ohmic resistance or ohmic iR drop) is influenced by the electrolyte conductivity, the distance between the reference and the working electrodes, and the magnitude of the current.

This Application Note provides an overview of the basic principles of ohmic iR drop in relation to electrochemical systems and its implications for accurate potential measurements. Explanations are given for the phenomenon of ohmic resistance and the resulting voltage drop that occurs when current passes through an electrolyte solution or conducting electrode. The causes and consequences of iR drop in electrochemical measurements are discussed, along with strategies to minimize its effects.

By understanding and managing ohmic iR drop, researchers and practitioners can ensure reliable and precise measurements in electrochemical experiments. Another Application Note (AN-EC-004) covers the tools that researchers using Metrohm Autolab products have at their disposal in order to measure and then correct (or compensate) for ohmic iR drop.

BACKGROUND

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 reliably measure the potential, the reference electrode should ideally be non-polarizable.

When current flows 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 E_{ohmic} can be calculated to be equal to the product of the current i and the ohmic or uncompensated resistance R_{u}:

$$\Delta E_{ohmic} = iR_{\text{u}}$$

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:

$$E_{measured} = E_{applied} - \Delta E_{ohmic} = E_{applied} - iR_{\text{u}}$$

FACTORS AFFECTING THE OHMIC DROP

Consider the potential profile in **Figure 1** at the working electrode-electrolyte interface.

The CE is placed relatively far away, and it is therefore assumed not to influence the current and potential distribution. RE1, RE2, and RE3 are examples of the various positions where the reference electrode 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 stays constant.

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

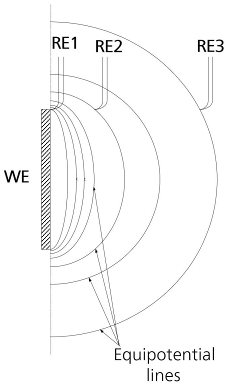

Figure 1. Equipotential lines shown at close proximity to the working electrode. RE1, RE2, and RE3 indicate possible positions of the RE at different distances from the WE surface.

The ohmic drop can have a significant impact on fast experiments, experiments with high currents, or those that require long-term passage of currents (e.g., 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. Therefore, depending on the sign of the current, the measured potential will be either less negative or less positive than the potential compared to 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 (i.e., 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 significant 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 is 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 kΩ. For this reason, even small currents can lead to large errors in potential. For example if the ohmic resistance is 10 kΩ and the current is 100 µA, the error is 1 V.

In a fast experiment (e.g., cyclic voltammetry with a fast scan), there is a current transient due to the charging and discharging of the double layer. In such cases, when the potential is scanned the measured potential lags the applied potential according to the following equation:

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

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 larger than $R_u C_{dl}$, the exponential approaches 0 and the errors can be negligible.

CELL DESIGN AND ELECTRODE PLACEMENT

From the previous equation, 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 the RE as close as possible to the 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 the RE. It must be noted that it is not possible to place the 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 the WE is blocked by the 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 2*d* 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. Therefore, 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.

CONCLUSION

Understanding and managing ohmic iR drop is crucial for obtaining accurate and reliable electrochemical measurements. By considering the factors influencing iR drop and implementing appropriate strategies, researchers and practitioners can minimize measurement errors and ensure precise interpretation of electrochemical processes. Methods for measuring and compensating for the iR drop are discussed in AN-EC-004.

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CONFIGURATION

1 L corrosion cell

The Autolab 1 L corrosion cell is suitable for corrosion measurements according to ASTM standards. The cell has a thermostatic jacket for temperature control and a series of openings for counter electrodes, pH sensor, thermometer, Luggin-Haber capillary and gas purging.

The 1 ll corrosion cell has been designed to measure the corrosion properties samples with a diameter ranging from 14.7 mm to 16 mm and a thickness from 0.5 mm up to 4 mm. The exposed surface is 1 cm^2 and the seals are made out of natural rubber.