Ohmic drop: 1. Basic principles

A typical electrochemical experiment is performed using 3 electrodes: working electrode (WE), counter or auxiliary electrode (CE) and reference electrode (RE). The currents flow between the working electrode and the counter electrode and the potential at the working electrode is measured with respect to a nonpolarizable reference electrode.

When current is flowing in an electrochemical cell, there is potential drop between the reference electrode and the working electrode. This voltage drop is caused by the electrolyte conductivity, the distance between the two electrodes and the magnitude of the current.

Using Ohms law the voltage drop can be calculated to be equal to the product of the current (*I*) and the resistance (R_W),

$$\Delta E_{ohmic} = IR_{\Omega}$$

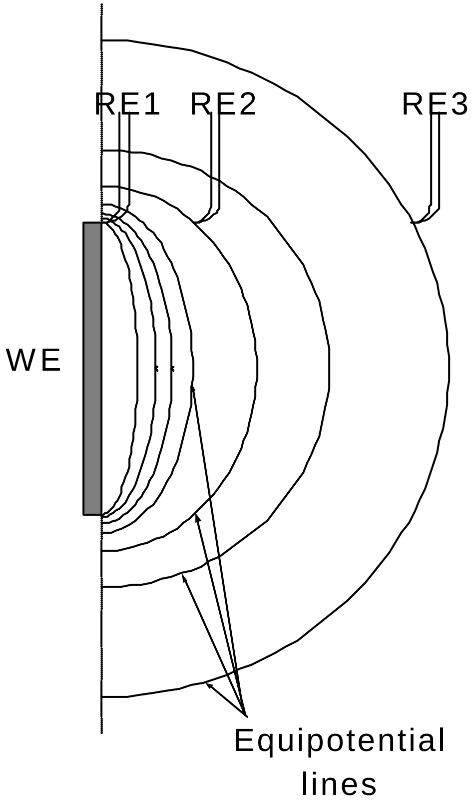
where DE_{ohmic} is the ohmic drop or *IR* drop, and R_W is the ohmic resistance[1]. Assuming that the passage of current does not affect the potential of the reference electrode (ideally nonpolarizable), the actual potential of the working electrode is given by the equation

$$E_{actual} = E_{applied} - \Delta E_{ohmic}$$

or

$$E_{actual} = E_{applied} - IR_{\Omega}$$

Factors affecting ohmic drop



Consider the potential profile in the solution between working electrode (WE) and counter electrode shown in the figure above. The counter electrode is assumed to be placed far and is assumed not to influence the current and potential distribution. RE1, RE2 and RE3 are the various positions where the reference electrode RE can be placed to measure the potential. One can see that the ohmic drop or the *IR* drop value depends on the following factors:

- *The current and potential distribution in the electrolyte.* The current and potential distribution in turn depends on the geometry of the experimental cell e.g. changing the size or shape of the working electrode will change the shape of the equipotential lines.
- *The position of the reference electrode with respect to the working electrode.* If the reference electrode is placed exactly at the electrode surface then the ohmic drop is zero (position RE1). As the reference electrode is moved away from the working electrode (positions RE2 and RE3) the ohmic resistance and therefore the ohmic drop between the working electrode and the reference electrode increases.
- *The conductivity of the electrolyte solution*. Lower the conductivity of the electrolyte higher the ohmic resistance and therefore higher the ohmic drop.

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[1] In the literature Ohmic resistance and Ohmic drop are sometime used interchangeably. This can be quite confusing. Ohmic resistance, as the name suggests, is a resistance and has units of ohms. It is an intrinsic property of the electrochemical setup and depends on the cell geometry, electrolyte conductivity etc. On the other hand, Ohmic drop is the voltage drop that occurs only when current is flowing in a cell with ohmic resistance and has the units of volts.

Impact of ohmic drop on measurements

The impact of ohmic drop in experiments that are fast or require long-term passage of currents (e.g. electrolysis) or are performed in low conductivity media (e.g. concrete, organic electrolyte) can be significant. Whenever currents are passed, there is always a potential control error due to the uncompensated ohmic resistance. If a cathodic current flows, the true working electrode potential will be less negative than the nominal value by that amount. The opposite holds for anodic values i.e. the potential will be more negative.

For large currents even small ohmic resistance values can cause large errors. For example if the ohmic resistance is 1 Ω and the current is 1A, the error due to ohmic drop is 1V. This is one of the reasons why, for example, very large-scale electro-synthesis is done galvanostatically.

For low conductivity media such as organic electrolyte or concrete, the resistance can be very high in the order of several kΩ and 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 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 true potential lags the applied potential according to the following equation:

$$E_{true} = E_{applied}\,(1 - e^{-\frac{t}{R_\Omega C_d}})$$

where, R_W is the ohmic resistance, C_d is the double layer capacitance and t is the time at which the measurement is taken. For fast scan rates (short t) $e^{-\frac{t}{R_\Omega C_d}}$ approaches 1 and therefore can lead to significant errors in E_{true} with respect to $E_{applied}$. For slow scan rates (long t) $e^{-\frac{t}{R_\Omega C_d}}$ approaches 0 and the errors can be negligible.

Cell design and electrode placement

From the equation in the previous section one can see that for fast experiments, the time constant $R_W C_d$ 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_W or C_d. This can be achieved as follows:

1) Increasing the conductivity of the solution by using a supporting electrolyte.
2) Decreasing the size of the working electrode to decrease C proportionally
3) Moving the reference electrode as close to the working electrode as possible to reduce the ohmic drop. This is often done by using a very fine capillary tip called Luggin-Haber or Luggin capillary[2] along with the reference electrode.

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[2] Care must be taken when using a Luggin capillary because it can cause shielding errors. Shielding is the blocking the working electrode surface by the reference electrode if it is too close. This can cause non-uniform current densities at the electrode surface. If a Luggin capillary with a tip diameter *d* is used, the closest distance it can be placed is *2d* from the working electrode without causing appreciable shielding error. Therefore, even when the tip of the reference electrode is designed for very close placement to the working electrode with a Luggin capillary, some uncompensated potential drop usually remains.

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