

The role of reference and counter electrodes in  
electrochemical impedance measurement

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The operating principle of a potentiostat is to maintain a constant potential difference between two measuring points. In the three-electrode setup this is usually between the (cable connected to a) working electrode and the reference electrode. In a four-point setup the measured and maintained potential is between two sensing (or reference) inputs. This result is affected by counter electrodes, which apply sufficient excess potential (and drive the needed current), so that the potential between the sensing points is at the desired value.

In a three-electrode system used for voltammetric studies, the counter electrode passes the same current as the working electrode (albeit with an opposite sign) and therefore any electrochemical process on the working electrode will be accompanied by an opposite electrochemical process on the counter electrode. This is of course well known fact, though often tacitly ignored by customarily placing counter electrodes away from the working electrode, often even in a separate compartment, to avoid the electrolytic product generated on the counter electrode to enter vicinity of the working electrode.

Impedance work takes often advantage of a four-electrode potentiostatic setup, with two reference electrodes, which sense the potential, and the two current supplying electrodes; the current is measured as it flows through either of these two electrodes. It should be noted that this is not a circuit identical to the four-point probe measurement, where current is supplied between two outside points and the potential is measured on the points between the two current supplying points. In the four-point probe the system is passive, without feedback. On the other hand the four-electrode potentiostat imposes potential on the two middle probes. This is not a trivial operating difference. The feedback of the potentiostat may impose relatively large currents to maintain the desired potential on the sensing electrodes. This current, as it has to pass through an electrolyte solution, will cause electrolysis on the counter electrodes. We have demonstrated, that the electrolysis on counter electrodes may become periodic, alternating between cathodic and anodic processes (Fig. 1). This can occur in systems, which lack natural redox couples and consequently, can rely only of reduction and oxidation of water in the aqueous environment.

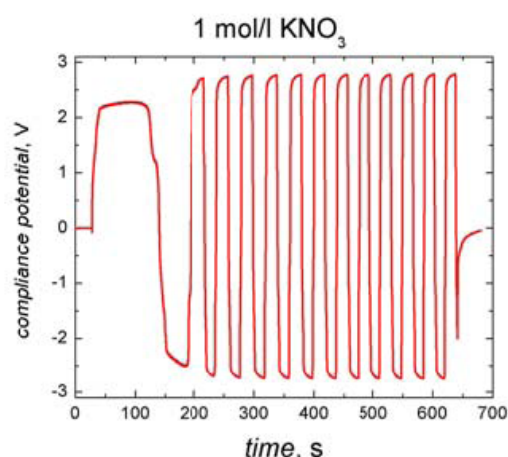
Thus, for a system with some appreciable resistance, the potential on the counter electrodes will cause gas evolution and local change in pH. If the counter electrode placement is close to the sensing electrodes, that the danger of containing the studied solution becomes prominent.

However, and perhaps somewhat surprisingly, it was found that the electrical effect of the counter electrode potential excursions had very little influence on the consistency of the collected AC impedance data. Although there are some changes in the data as the potential swings occur, they are merely a noise, as the absolute changes are minimal.

We will also demonstrate, that placement of the electrodes has an effect on these fluctuation and can either eliminate them or, at an opposite extreme, can cause them to become more prominent. However, counter and reference electrode placement, although thought in an ideal situation to be unimportant to the obtained impedance data, can cause large effects. We will demonstrate how electrode placement can lead to generation of impedance artifacts.

#### Acknowledgement

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**Figure 1** Switching of potential over period of time observed between a pair of counter electrodes in a 4-electrode system. The polarization potential, as dialed on the oscilloscope, was at 0.00 V vs. open circuit potential.