Extraneous Components in Impedance Equivalent Circuits Arising from Sample Geometry and the Real Properties of the Equipment

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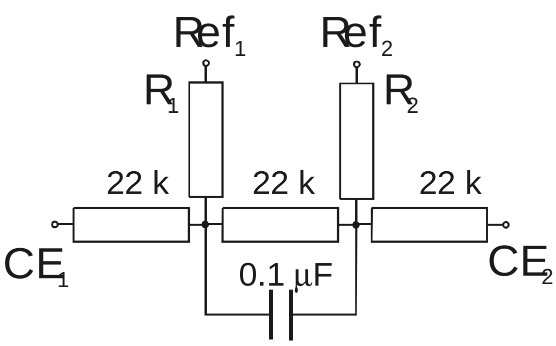
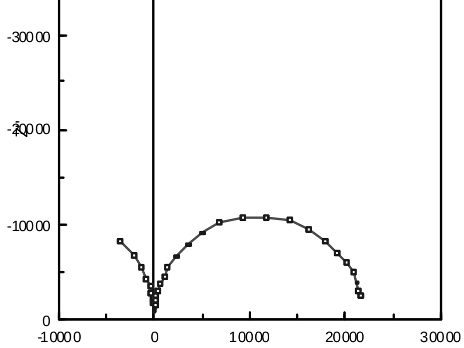
Impedance of reference electrodes and the instrument inputs introduces a phase shift in addition to any phase shift caused by the sample itself. The total retrieved signal is interpreted as that of the sample and judgment must be made to decide which response is germane to the studied system.

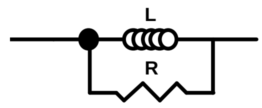
The artifact of the measurement is caused by the fact that the typical 4-probe instrument, such as the Solartron Interface, has its own capacitance and resistance (i.e., time constant) on its inputs. When these inputs are not evenly loaded, additional phase shift to the system is introduced.



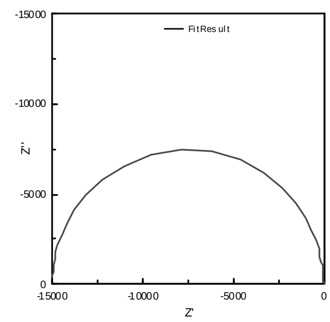
In the above figure the resistors R_1 and R_2 represent the resistance of the reference electrodes leading to the instrument. The two side resistors, 22 kΩ represent the resistance of the bulk material between the voltage-sensing and current-sending electrodes and in an ideal potentiostat system would be invisible just like the R_1 and R_2 resistors. Therefore, the impedance response of such a system should be just a simple semi-circle on the Nyquist plot, stemming from the parallel resistor of 22 kΩ and the capacitor of 0.1 µF. However, for the case of an uneven resistance of the reference electrodes (here 0 Ω on Ref1 and 20 kΩ on Ref2) the Nyquist plot will show, besides the expected semicircle an additional feature, as shown in the next figure:



Such a feature left of the origin is troublesome in interpretation. It calls for adding a parallel RL circuit



added in a series with the existing parallel RC circuit. However, in this particular case both R and L will have negative values.



We will present a catalog of non-ideal behaviors one can expect from various values and ratios of input resistances of reference electrodes.

An asymmetry of the input electrodes causes in particular complications. We demonstrated how asymmetric resistance in reference electrodes causes the well-fitting equivalent circuit to contain additional inductor and resistor in series. In some cases, the inductor, the resistor, or both may formally require negative values. Fortunately, such negative values will not stem from real systems and can be easily spotted and readily subtracted. Likewise, inductance, with the exception of nucleation and adsorption, is usually absent in electrochemical systems and can be discounted.

The measurement artifacts can be subtracted from the response if their contribution is constant. However, one needs to be extremely careful in situations, e.g., in sensors, where the contact resistance of the potential sensing electrodes in the 4-probe setup is changing, perhaps even with the change of the analyte concentration.

Finally, we have also studied the effect of sample geometry on impedance response. It is possible to find rather bizarre impedance behavior when electrodes ale placed onto the sample without a careful forethought. For example a “bulk” system modeled from a two-dimensional matrix of parallel RC circuits can produce a Nyquist plot of the type shown in the next figure: