

## A Short Introduction to EIS (Electrical Impedance Spectroscopy)

Electrochemical impedance spectroscopy is a technique used to study kinetic behaviour of a battery system near the electrodes surface. Small amplitude oscillations in Voltage are used to induce an alternating current. This small amplitude results in a minimal perturbation of our system. Further, a potential can be chosen at which no Faradaic current is drawn (current that is generated by the reduction/oxidation of chemical species at the electrode), making it possible to focus on processes like the reorganization of the electrode double layer. If potentials that do generate a Faradaic current are chosen, processes like mass transport become important and can be studied as well. The small amplitude in potential oscillation however, results in irreversible changes to our system can be avoided.

If we, for example, hold our system at +0.2V, a current will flow that is constant to  $0.2V/R$  (DC resistance). If we now change the potential by 5mV, for a time there will be only non-Faradaic current flowing, due to the reorganization of our electrode double layer and the changes in electrode polarization that come with it. We can now oscillate this 5mV around our 0.2V (to create potentials of 0.205V-0.195V) with a high frequency, to generate a “lag time”. This “lag time” means that the ions in solution are too slow to reorganize as fast as the voltage changes. This results in the current response being negligible. The frequency can now be changed from high to low experimentally, which will result in an investigation of kinetic and mass transfer control of the system.

Practically we can now measure two components of impedance.  $Z'$  [ $\Omega$ ], which is the “real” part of the total impedance and is the contribution that emerges through **energy loss**. It is the “classical” resistance so to speak (as in a resistor). The second component  $Z''$  [ $\Omega$ ], is the “imaginary” part of the impedance, which arises from the electrostatic **energy being stored** in the electrode double layer (as in a capacitor).

If we now measure our impedance spectrum like in figure A ( $Z''$  being on the y-axis and  $Z'$  being on the x-axis), we get a semi-circle like course. The first intercept at the x-axis marks our solution resistance. Here  $Z''$  is zero because the frequency is too high for mass transfer to play a role. As the frequency drops, the capacitor properties of our electrode double layer start to play a role and  $Z''$  rises.

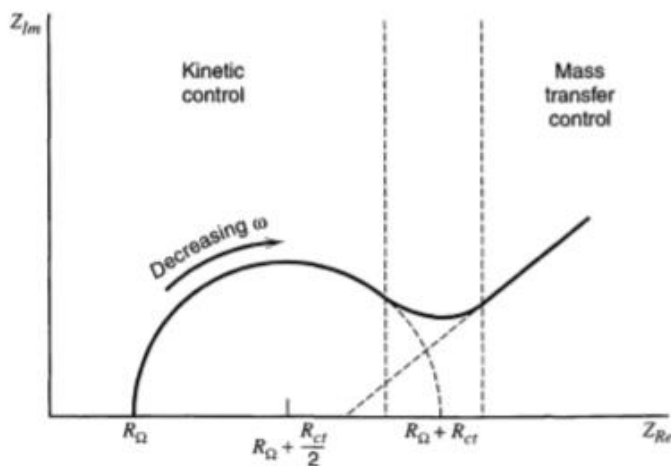


Figure A: Depiction of a typical impedance spectrum. Illustration taken from [1]

In most real battery systems,  $Z''$  will not intercept the x-axis again (which would result in the semi-circle, drawn by the dashed line), since the Warburg impedance (the impedance which arises from mass transport) will start to play a bigger role. We can however, neglect the influence by Warburg impedance, if we apply mathematical functions to “finish” the semi-circle and let it intercept the x-axis a second time. This intercept will now mark the resistance of solution resistance + charge transfer resistance. If we now take the diameter of our semi-circle, we get the charge transfer resistance at our electrode surface. Steric functionalisation of our electrodes surface will result in an increase of charge transfer resistance, thereby making EIS a suitable technique for our project.

[1] BARD, A. J., & FAULKNER, L. R. (2001). *Electrochemical methods: fundamentals and applications*. New York, Wiley.