

## Local electrochemical impedance spectroscopy: correlation with global impedance measurements

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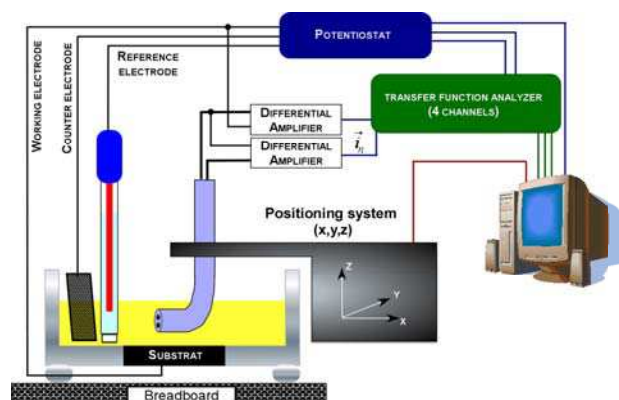


Fig. 1: Sketch of the LEIS setup.

Electrochemical techniques such as cyclic voltammetry or electrochemical impedance spectroscopy (EIS) are widely used for investigating the kinetics of heterogeneous electron-transfer reactions, coupled chemical reactions, or adsorption processes. In such conventional electrochemical experiments, the electrode response to a perturbation signal corresponds to a surface-averaged measurement, whereas the electrochemical systems rarely exhibits such an ideal behavior, and this can lead to difficulties with data interpretation. Among the various local techniques devised for investigating electrochemical processes on a local scale, local electrochemical impedance spectroscopy (LEIS) [1, 2] is very promising since it combines the advantage of a transient analysis with the use of potentiometric probes.

In a recent series of papers [3-5], our group revisited the basis of the LEIS technique. A key contribution was the definition of three local impedances. The local interfacial impedance ( $z_0$ ) was defined to involve both a local current density and the local potential drop across the diffuse double layer. The local Ohmic impedance ( $z_e$ ) was defined to involve a local current density and potential drop from the outer region of the diffuse double layer to the distant reference electrode. The local impedance ( $z$ ) was thus the sum of the local interfacial impedance and the local Ohmic impedance. All these measurements can be performed simultaneously with the experimental setup depicted in Fig. 1.

The objective of this presentation is to provide guidelines for implementation of LEIS and to outline on the main difficulties that are usually encountered with such experiments. A specific attention will be paid for data interpretation in the high frequency domain since it was shown that the cell geometry can contribute to the impedance response as shown in Fig. 2 which clearly evidences a HF contribution on the impedance response depending on the probe position. The spatial resolution will also be discussed as a function of the probe dimension and the probe positioning.

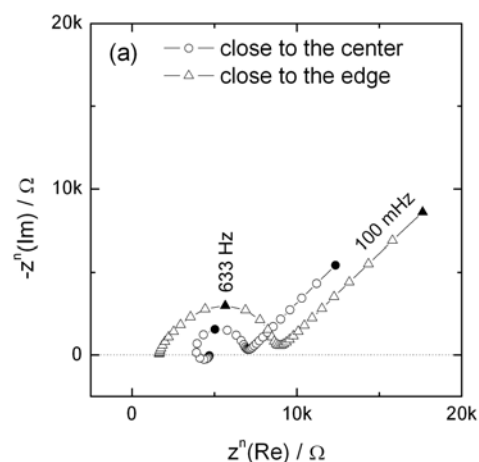


Fig. 2: LEIS responses at the center and close to the edge of a disk substrate for a faradaic system involving a simple electron transfer reaction and diffusion.

## References

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