



# Feasibility study and cell design for performing local electrochemical impedance spectroscopy measurements using an atomic force microscopy set-up



Thibault Muselle<sup>a,\*</sup>, Hans Simillion<sup>a</sup>, Dries Van Laethem<sup>a</sup>, Johan Deconinck<sup>a,b</sup>, Annick Hubin<sup>a</sup>

<sup>a</sup> Vrije Universiteit Brussel, SURF department, Pleinlaan 2, 1050 Brussels

<sup>b</sup> Vrije Universiteit Brussel, ETEC department, Pleinlaan 2, 1050 Brussels

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## ABSTRACT

This paper studies the feasibility of performing Local Electrochemical Impedance Spectroscopy (LEIS) and Atomic Force Microscopy (AFM) within a single set-up, using a hybrid probe. The geometry of the set-up along with the extremely small size of the probe used is expected to result in distorted impedances and very low potentials, respectively. Numerical simulations using a multi-ion transport and reaction model (MITReM), show that the distortions can be mathematically corrected for and that our electronic equipment is capable of measuring the minute potentials.

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## 1. Introduction

When performing global electrochemical impedance measurements on heterogeneous surfaces, such as metal surfaces containing precipitates or a metal covered with a damaged coating, localised information is lost. As this information is valuable for the characterization of such samples, local electrochemical impedance spectroscopy was considered [1].

Often, topographic information is also indispensable when characterizing surfaces, e.g. dealing with self-healing coatings during the closure of a scratch where the topographic data shows the mechanical healing and the local impedance assesses the resulting recovery of the corrosion protection offered by the coating.

This interest in both topographic and impedance data has led to the concept of combined atomic force microscopy and local electrochemical impedance spectroscopy (AFM-LEIS). Moreover, using a hybrid probe and an adapted set-up, both techniques can be executed simultaneously and in-situ, thus providing a clear

correlation between the topographic and the impedance mappings.

### 1.1. Local electrochemical impedance spectroscopy

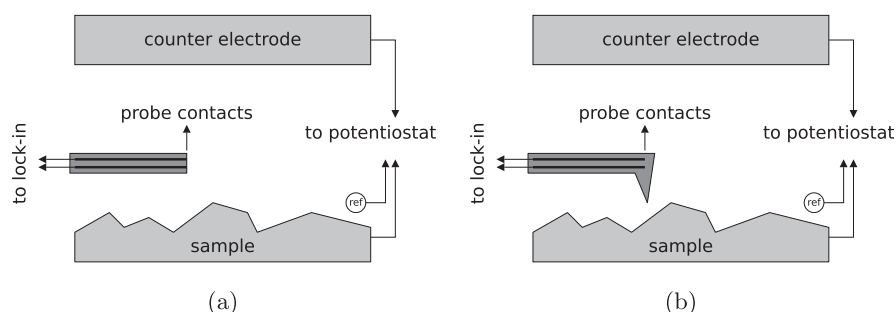
Local electrochemical impedance spectroscopy was first introduced by Lillard, Moran, and Isaacs in 1992 [1]. Using a small bi-electrode probe, the local current density was estimated, based on the potential difference between the probe's contacts. Combining this local current density with the global excitation potential produces the specific local electrochemical impedance (Eq. (1)).

$$Z_{local} = \frac{\Delta U_{local}}{i_{local}} \quad (1)$$

This type of set-up is schematically represented in Fig. 1a. The sample is configured in a three-electrode set-up, where the three macroscopic electrodes are connected to a potentiostat. This allows an excitation potential to be applied across the sample and the reference electrode. The probe is scanned on top of the sample and the potential difference measured between its two contacts, allowing the local current density to be determined. This potential difference can be acquired by connecting the two probe contacts to a lock-in amplifier. This also provides a mapping of the local electrochemical impedance, but cannot provide any topographical information about the surface.

\* Corresponding author.

E-mail addresses: [thibault.muselle@vub.ac.be](mailto:thibault.muselle@vub.ac.be) (T. Muselle), [hans.simillion@vub.ac.be](mailto:hans.simillion@vub.ac.be) (H. Simillion), [dvlaethe@vub.ac.be](mailto:dvlaethe@vub.ac.be) (D. Van Laethem), [johan.deconinck@vub.ac.be](mailto:johan.deconinck@vub.ac.be) (J. Deconinck), [annick.hubin@vub.ac.be](mailto:annick.hubin@vub.ac.be) (A. Hubin).



**Fig. 1.** A schematic representation of (a) a local electrochemical impedance spectroscopy set-up and (b) a combined atomic force microscopy - local electrochemical impedance spectroscopy set-up and the electrical connections. The three macroscopic electrodes (sample, counter electrode and reference electrode) are connected to a potentiostat and the two probe contacts are connected to a lock-in amplifier. The probe contacts, where the probe measures local potentials, are indicated. In (b), the cell needs to allow the laser beam from the AFM technique to come down to the probe and back up again.

Some alternative approaches for the estimation of the local impedance can also be found in literature. It can be assessed by isolating the area of interest in an electrochemical microcell ([2,3]) or a droplet cell ([4,5]). A drawback of this is that the effects of the surrounding areas remain neglected, as they are excluded from the cell.

Simultaneous sampling of multiple locations can be done using an array of tips ([6,7]). This is useful for mapping dynamic phenomena, as each location is measured at the same moment in time. An interesting alternative to the use of a bi-electrode probe for LEIS is the use of a SVET (scanning vibrating electrode technique) set-up ([8]). Just as with a classical SVET, local potentials are measured with a single vibrating electrode. Deducing local currents from the measurements and combining them with the globally applied potential should lead to the local electrochemical impedances, but the convection created by the vibrating electrode can be an added difficulty.

## 1.2. AFM-LEIS

A possibility of combining atomic force microscopy with local impedance spectroscopy has been described in literature ([9–14]). However, these publications deal with a totally different approach from the one used in this work. They describe the use of a single-electrode probe in contact with the surface, but in the absence of an electrolyte. The method thus estimates the electrical impedance and not the electrochemical impedance. This implementation also excludes the influence of the surrounding areas, along with the

added difficulty of dealing with the presence of a contact impedance, which is difficult to separate from the sample's impedance [13].

The configuration used in this work is illustrated in Fig. 1b. The difference with an LEIS set-up (cfr. Fig. 1a) is the use of an AFM probe that has two electrical contacts instead of a simple bi-electrode probe along with an adapted cell with characteristics prerequisite for both techniques. However, these requirements introduce constraints on such a set-up, resulting in non-ideal circumstances for local electrochemical impedance measurements.

Topographic data acquisition requires implementing this hybrid technique within an AFM set-up, thus strongly limiting the height of the cell, and given the position of the probe holder in AFM set-ups, the counter electrode cannot be positioned immediately above the measured area: indeed, the probe holder is just above the probe and thus also right on top of the sampled area. Additionally, space needs to be reserved to allow the AFM's laser beam to come down onto the probe and then back up again. This less than ideal positioning of the counter electrode is expected to cause a non-uniform current distribution, resulting in a distortion of the impedance data. Literature also mentions the effects of cell geometry and sample positioning/embedding on impedance data distortions ([15–17]). These effects can result in an apparent inductive and/or capacitive behavior, leading to invalid data if left untreated.

The hybrid probe proposed in this paper has a much smaller size compared to regular LEIS probes. The use of a modified nano

**Table 1**  
List of symbols.

symbol	meaning
$c$	molar concentration
$d$	distance between the two probe contacts
$D$	diffusivity
$\epsilon$	permittivity
$\vec{E}$	electric field
$\Delta U_{global}$	globally applied potential difference
$\Delta U_h$	potential difference between sample and probe contact at height $h$
$h$	distance between sample and the lower probe contact
$j_{local}$	local current density
$J_{global}$	global current
$\kappa$	conductivity
$q$	electric charge density
$Q$	electric charge
$U$	potential
$\omega$	angular frequency
$Z_i$	ionic charge of species $i$
$Z_{e,local,h}$	local specific electrolyte impedance (estimated at height $h$ )
$Z_{local}$	"total" local specific impedance
$Z_{local,h}$	local specific impedance between sample and probe (estimated at height $h$ )

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