



Influence of probe size for local electrochemical impedance measurements



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ABSTRACT

Local electrochemical impedance spectroscopy (LEIS) is a promising technique for the characterization of heterogeneous surface reactivity. Significant development of LEIS relies on the improvement of the spatial resolution for reaching the micrometer scale. This work presents the influence of the probe size, especially in the high frequency domain where an inductive-like response ascribed to the stray dielectric capacitance between the two electrodes of the probe used for performing the local current measurement can be observed. A detailed analysis of the whole set-up (electrode geometry and measuring device) allows an analytical expression of the impedance for the whole system to be obtained. Based on the analysis of this expression and on experimental results, two different strategies have been proposed to cancel the HF time constant: a post treatment of the results via a preliminary electrical characterization of the local probe or the minimization of the electrolyte resistance by measuring the local potential in the close vicinity of the substrate. Both approaches were shown to be efficient.

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1. Introduction

The characterization of the local reactivity of an electrified interface is usually performed with the use of local probes with an adequate size depending on the spatial resolution required, but also on the technique used. The scanning electrochemical microscopy (SECM) is by far the most widely used local technique in electrochemistry [1–3], but only few works have been performed in the frequency domain. For instance, the use of a single frequency measurements at an ultra-microelectrode (UME) allows to map the surface heterogeneity [4–7], whereas the use of the ac-SECM in substrate generation–tip collection mode allows a complex collection efficiency to be obtained, and thus to study the formation and the relaxation of reaction intermediates involved in complex mechanisms such as proton reduction [8,9] or iron oxidation [10]. On the other hand, local current-density can be measured using the scanning vibrating electrode technique (SVET) [11–13] without the requirement of adding any redox mediator in solution. This technique then gives rise to the local electrochemical

impedance spectroscopy (LEIS) as an alternative route for the local investigation of an electrochemical reaction, which has been developed in the 90's with the pioneering works of Isaacs *et al.* [14,15]. It consists in using two reference electrodes (*e.g.* a bi-microelectrode) that are positioned close to the interface of interest for measuring the local current density in solution from the potential difference between the two micro-reference electrodes immersed in the electrolyte. The current is thus measured as the ohmic drop between the two sensing electrodes in solution, and depends on both the electrode distance and the electrolyte conductivity. Thus, the local impedance can be calculated similarly to a usual (*i.e.* global) electrochemical impedance using a frequency response analyzer, that is as the ratio of the potential to the local current density for each frequency [14]. This technique was successfully used for the investigation of coating degradation [16–18], pitting corrosion of iron chromium alloy [19,20], magnesium alloy corrosion [21], or time-constant distribution of a passive film formed on a stainless steel sample [22]. However, one of the key-points for the technique is the spatial resolution that is governed by the probe size and the probe-to-sample distance. Indeed, for many applications such as coating degradation [16,18], a spatial resolution in the millimeter range is usually sufficient, but

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for other applications such as the mapping of surface reactivity that depends on the grain size [21] or for the characterization of a single pit [19], a spatial resolution of few tens of micrometers is required. This can be obtained by diminishing both the size of each wire used for sensing the local potential in solution and the distance between these two wires. In this work, a specific attention has been paid to the response of local probes of few tens micrometers, since in the high frequency domain, a capacitive coupling may exist between two adjacent micro-wires, whereas in the low frequency domain, the potential difference to be measured between these two probes can be very small. A detailed analysis of experimental results was thus provided for a model system involving redox mediators studied at a metallic electrode, thus allowing the separation of the electrochemical contribution from the stray contribution of the measurement setup.

2. Experimental

All the electrochemical measurements were performed using a home-made setup previously described [21,23] and presented in Fig. 1. It consisted in a potentiostat with which the global impedance was measured allowing the surface averaged value of the electrode response to be recorded, whereas simultaneously, the local potential and the local current density were probed in solution with a bi-microelectrode [14,24,25]. Data acquisitions were performed using a 4-channel frequency response analyzer (1254–Solartron) allowing multiple transfer functions to be measured simultaneously. The probe positioning was achieved with stepper motors (UTM25, Newport) driven by a motion encoder (MM4005, Newport) allowing a spatial resolution of 0.2 μm in the three directions. A homemade DC-offset coupled with a variable gain differential amplifier was used for the measurement of the local potential difference in solution (*vide infra*). With such a configuration, it was possible to measure a potential difference of ca 1 μV between the two probes in the low frequency domain ($f < 100$ mHz). Interestingly, this limit can be lowered by adapting the amplification stages before and after the DC-offset as a function of the local impedance to be measured. The distance between the probe and the substrate was controlled by slowly bringing the probe in contact with the substrate and then by withdrawing it to the desired distance. This allowed a vertical positioning with a resolution of ± 5 μm , which was estimated with an independent set of experiments.

The working electrode was a platinum rod of 0.5 cm in diameter laterally insulated by a cataphoretic paint (200 V/2 minutes, then cured for 1 hour at 80 °C) and an epoxy-resin (Radiospire), thus

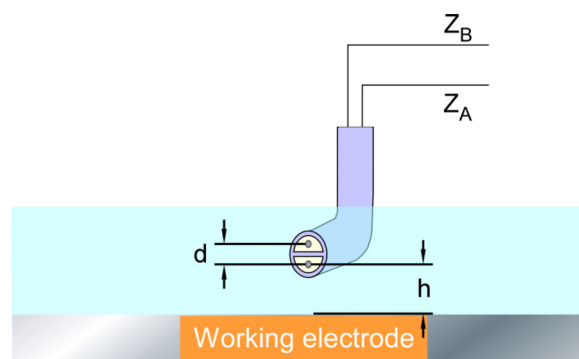


Fig. 2. Sketch of local probe with the relevant parameters investigated in this work.

exposing a disk of 0.2 cm^2 surface area to the electrolyte. No specific activation of the electrode has been performed before the experiments. The counter electrode was a platinum gauze of large surface area surrounding the whole electrochemical cell in order to minimize the frequency dispersion due to the geometry of the system, and the reference electrode was a saturated calomel electrode ($E/\text{SCE} = E/\text{NHE} - 0.244$ V, where NHE is the normal hydrogen electrode).

The local probe used for performing local impedance measurements consisted in a bi-microelectrode prepared with silver microwires laterally insulated with a cataphoretic paint (200 V/1 minute, then cured for 1 hour at 80 °C) and sealed with an epoxy-resin in a capillary. The apex of the probe was polished and each of the wires was anodized in a chloride containing solution to obtain an Ag/AgCl reference electrode. This procedure is in marked contrast to the use of platinum probes since it allows to minimize the contribution of the Nernst potential due to redox species in solution [26].

The spatial resolution that can be reached with such a probe depends on the size of the microwires, the distance between the two microwire centers (d), and the distance between the probe and the substrate (h) as sketched in Fig. 2. In addition, even if nanoelectrodes are available, the use of probe smaller than 1 mm is still challenging with respect to the potential measurement to be performed [27]. In this work, local impedance measurements were performed either by measuring the local current with the local probe and the global potential, or by measuring the local current with the local probe and the local potential with the closest probe to the electrode surface, similarly to the definition of Bayet *et al.* [28], emphasized later on by Huang *et al.* [27]. It is interesting to mention that the former experiment corresponds to the local impedance that can be usually measured with commercial equipment and will be labelled as local impedance in the following, whereas for the second definition, a home-made equipment is required and will be labelled local interfacial impedance [27].

Some electrical impedance measurements were performed with a dielectric interface (Solartron 1296A) coupled to a frequency response analyzer (Solartron 1255) for the characterization of the probes.

All electrolytic solutions (10 mM ferri/ferrocyanide + 0.5 M KCl) were prepared with analytical grade chemicals in twice distilled water.

3. Results and discussion

Fig. 3a shows the global impedance diagram in a Nyquist representation obtained with a 5 mm in diameter platinum electrode for the ferri/ferrocyanide redox couple (10 mM) in 0.5 M KCl electrolytic solution. The EIS response is typical of a redox system in solution. It shows the electrolyte resistance as the high

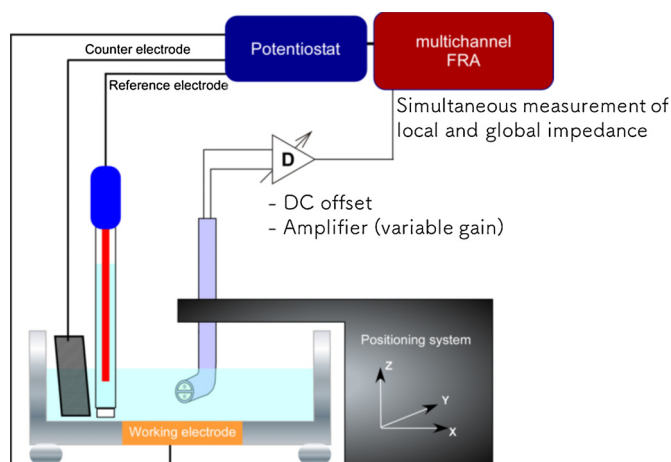


Fig. 1. Sketch of the experimental setup.

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