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Influence of normal and radial contributions of local current density on local electrochemical impedance spectroscopy

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ABSTRACT

A new tri-electrode probe is presented and applied to local electrochemical impedance spectroscopy (LEIS) measurements. As opposed to two-probe systems, the three-probe one allows measurement not only of normal, but also of radial contributions of local current densities to the local impedance values. The results concerning the cases of the blocking electrode and the electrode with faradaic reaction are discussed from the theoretical point of view for a disk electrode. Numerical simulations and experimental results are compared for the case of the ferri/ferrocyanide electrode reaction at the Pt working electrode disk. At the centre of the disk, the impedance taking into account both normal and radial contributions was in good agreement with the local impedance measured in terms of only the normal contribution. At the periphery of the electrode, the impedance taking into account both normal and radial contributions differed significantly from the local impedance measured in terms of only the normal contribution. The radial impedance results at the periphery of the electrode are in good agreement with the usual explanation that the associated larger current density is attributed to the geometry of the electrode, which exhibits a greater accessibility at the electrode edge.

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1. Introduction

Local electrochemical techniques such as scanning electrochemical microscopy (SECM), scanning vibrating electrode technique (SVET) or local electrochemical impedance spectroscopy (LEIS) are now widely used for the characterization of surface reactivity [1–6], the determination of electron transfer kinetics [7–9], as well as studying complex electrochemical reactions [10–12]. Among these techniques, local electrochemical impedance spectroscopy (LEIS), pioneered by Isaacs et al. [13,14], takes advantage of electrochemical impedance spectroscopy to probe the local electrochemical reactivity of an interface [15–17]. From this seminal work, different approaches have been envisioned for measuring LEIS. The most widespread procedure employs a bi-electrode to sense simultaneously the local potential at two locations above the substrate [18,19]. This can be achieved using a large bi-electrode (Pt electrodes in the millimetre range with an inter-electrode distance of few millimetres are commercially available) [20–23] or smaller probes that consist of two micro-electrodes embedded in a glass capillary [14,19,24,25]. In the latter case, Ag/AgCl micro-reference electrodes can be used [19]. The local current density is thus calculated from this local potential difference and the Ohm's law for the electrolyte.

An adaptation of SVET to AC polarization was also devised and took advantage of the use of a single probe that is vibrated, allowing a fine and easy control of the inter-electrode distance by controlling the amplitude of the vibration [26,27]. This technique, however, suffers from local convection induced by the probe vibration and from the contribution of the redox potential at a metallic electrode [26]. Since the deposit of Ag/AgCl at the apex of the vibrating tip results in a fragile probe, no significant improvement in the measurement of the local potential can be reached.

A common feature of the above configurations is that only the normal component of the AC-current in solution is monitored, i.e., curvature of equipotential surfaces in solution is not taken into account. Therefore the resulting estimate for local current density is valid only when the sensing probe is located above the centre of the domain of interest; otherwise the local current in solution is the vector sum of both the normal and the radial components. In addition, in spite of the capability of SVET to measure simultaneously the normal and radial dc-current components [28–32], to the best

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of our knowledge, only the normal component of the current has been considered for the measurement of LEIS.

More recently, some developments of the microcell technique have been reported [33,34], where only a small area of an electrode is isolated by a glass capillary and placed in direct contact with the electrolyte for performing LEIS measurements. It should be noted that using a microcapillary, equipotential surfaces are constrained by the capillary geometry, thus equipotential surfaces are parallel to the electrode surface along the cylinder between the working electrode and the counter electrode. With such a device, local measurement can be performed, but the electrochemical response does not account for the surrounding environment of the local domain analyzed.

The objective of the present work is to report on the use of a tri-electrode system which is used for the first time to perform LEIS measurements. A theoretical framework is developed for a classical blocking electrode and for an electrode with faradaic reaction, allowing a direct comparison with previous works [24,25,35–37]. Then, experimental investigation for a model system (ferri/ferrocyanide redox couple at Pt electrode) was performed to illustrate the relevance of the simultaneous measurement of both normal and radial current components.

2. Experimental

The instrumentation, the new tri-electrode current sensor, and chemicals used in the experimental work are described below.

2.1. Instrumentation

The LEIS apparatus consisted of an in-house made device with a 3-axis positioning system (UTM25, Newport) driven by a motion encoder (MM4005, Newport) allowing a spatial resolution of 0.2 μm in the three directions. The potentials were controlled by a home-made potentiostat. The experimental setup was computer controlled by a single software developed under the Labview® environment. Use of a four-channel frequency response analyzer (Solartron – FRA 1254) allowed both global and local impedances to be recorded simultaneously [24,36,38]. Home-made low-noise analog differential amplifiers with both variable gain and high input impedance were developed for recording both the local potentials and current variations.

The LEIS experiments were performed using 50 mV peak-to-peak sine wave perturbation, 50 acquisition cycles over a frequency range of 65 kHz to 100 mHz with 7 points per decades.

2.2. Tri-electrode current sensor

The tri-electrode consisted of three silver microwires of 100 μm in diameter, each of them laterally insulated using a cataphoretic paint (few micrometers thick), and then sealed in a capillary glass with an epoxy resin. The electrode arrangement was optimized for the measurement of both normal and radial local current densities (Fig. 1). Such a setup is equivalent to the vibrating probe developed for SVET experiments, except that the use of a multi sensor avoided local forced convection. The apex of the electrode was polished with SiC emery paper up to 1200 grade, and an electrochemical deposit of AgCl was performed by potentiostatic oxidation of Ag in a KCl 0.5 M solution on each electrode. This set of reference microelectrodes allowed simultaneous measurement of three local potentials in the close vicinity of the substrate. It should be mentioned that, as previously demonstrated, the relevant parameters for the local measurements are the size of each probe, the distance between two probes, and the tip-to-sample distance [15].

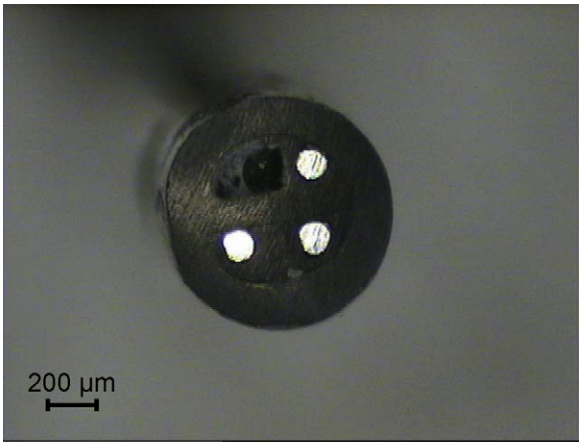

Fig. 1. Optical image of a silver tri-electrode used for LEIS measurement. Each wire is 100 μm in diameter.

2.3. Chemicals and samples

All the experiments were performed using analytical grade chemicals as received. Electrolytic solutions were prepared in twice-distilled water (18 MΩ cm). A 10 mM ferri/ferrocyanide solution was prepared in a 0.5 M KCl electrolyte. A Pt working electrode was laterally insulated with a cathaphoretic paint, heat treated for 1 h at 150 °C, and then molded into an epoxy resin (Buhler, Epoxycure™). This electrode was secured at the bottom of a Teflon cell with an O-ring larger than the nominal Pt diameter. The counterelectrode was a large platinum gauze surrounding all the electrochemical cell in order to minimize current and potential distributions due to the cell geometry. A saturated calomel electrode (SCE) was used as reference electrode. All potentials are reported with respect to this reference unless otherwise stated.

3. Mathematical models

The mathematical models developed for this work and the definitions employed in the description of the impedance response are presented below. First, the definitions employed in the description of the impedance response are presented. Then, simulations were developed for a blocking electrode and an electrode with Faradaic reaction. All simulations were performed using finite element method, implemented in Comsol Multiphysics on a PC.

3.1. Definitions

Previous works defined global, local, local interfacial, and local ohmic impedances using a bi-electrode for probing the solution potential and a multi-channel frequency response analyzer [35–37]. The local AC-current density $i_{loc}(\omega)$ was obtained through the Ohm's law using [13]:

$$i_{loc}(\omega) = \frac{\Delta V_{probe}(\omega)\kappa}{d} \tag{1}$$

where κ is the electrolyte conductivity, $\Delta V_{probe}(\omega)$ is the AC-potential difference between the two probes, and d is the distance between the two probes. As shown in Fig. 2, for the disk geometry, the local current density in solution is the vector sum of radial and normal contributions:

$$i^n(\omega) = \frac{\Delta V^n(\omega)\kappa}{d_n} \tag{2}$$

$$i^r(\omega) = \frac{\Delta V^r(\omega)\kappa}{d_r} \tag{3}$$

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