Contents lists available at ScienceDirect

Electrochimica Acta

Development of quantitative Local Electrochemical Impedance Mapping: an efficient tool for the evaluation of delamination kinetics

V. Shkirskiy [a,b,*], P. Volovitch [b], V. Vivier [a]

[a] Sorbonne Universités, UPMC Univ Paris 06, CNRS, Laboratoire Interfaces et Systèmes Electrochimiques, 4 place Jussieu, F-75005, Paris, France
[b] Chimie ParisTech, PSL Research University, CNRS, Institut de Recherche de Chimie Paris (IRCP), F-75005 Paris, France

A B S T R A C T

Local Electrochemical Impedance Mapping (LEIM) methodology was adopted to quantify the propagation of electrochemically active regions with a micrometric precision. The method consisted in the use of the gradient modulus of the admittance map as a parameter for the spatial quantification. Numerical simulations were used to optimize the experimental conditions, namely the AC frequency, the distance between the local bi-probe and the working electrode, and the distances between the probes for the local bi-probe used for the local current mapping. This analysis was reinforced by experimental verifications on coated electrodes. The quantitative LEIM methodology was successfully applied to follow the delamination kinetics on Zn coated with the polyvinyl butyral polymer in NaCl solutions. At 1 kHz, the LEIM response only reflected the position of the anodic front beneath the polymer because oxygen reduction reaction was diffusion limited and hence, independent of the applied potential. This novel LEIM methodology completes the set of usual tools used to investigate the delamination mechanisms on metal substrates.

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1. Introduction

Recently, local electrochemical scanning techniques have attracted a lot of attention due to their ability to resolve macroscopic electrochemical phenomena on nano- and micrometer scales [1–3]. The key parameters of these techniques are (1) the spatial resolution and (2) the spatial quantification *i.e.* the ability to define the precise geometry and the size of electrochemical regions.

Scanning ElectroChemical Microscopy (SECM) [4–6] and Local Electrochemical Impedance Mapping (LEIM) [7–9] are among the leading techniques competing on these criteria. In the pioneering work, Bard et al. [10] envisioned a possible nanometeric error for the spatial quantification in SECM (*i.e.* in DC amperometric mode). The compulsory presence of a redox mediator in the solution was required for such a purpose, but recent advances in Alternative-Current Scanning Electrochemical Microscopy (AC-SECM) allowed to eliminate this restriction [1,2,11]. The minimal experimental error of the spatial quantification in AC-SECM was in the order of several micrometers achieved on the oriented hematite single crystal surfaces [1]. Conversely, the limits of the spatial quantification of the alternative LEIM methodology have not been well explored.

Several works [12–14] focused on the improvement of the spatial resolution of LEIM technique reporting the spatial resolution of about 30 to 40 μm [12]. The main parameters limiting the spatial resolution were (1) the diameter of microelectrode in the bi-probe (D), (2) the distance between the bi-probe and the working electrode (WE) (h), and (3) the distance between the two microelectrodes (d). In ref. [12] these parameters were $D = 10\ \mu$m, $h = 25\ \mu$m and $d = 80\ \mu$m. Numerical simulations of the primary potential distribution for a disk electrode embedded in an isolator were in a good agreement with experimental results. In the more recent work [13], a spatial resolution of 35 μm was obtained with $D = 125\ \mu$m, $d = 250\ \mu$m and $h = 200\ \mu$m.

Even though the spatial resolution in the micrometer range can be reached, the precise size of electrochemically active zones did not match their actual size on the admittance maps in LEIM [15,7,16–18]. Moreover, this size was shown to depend on the applied frequency of the AC perturbation [15]. For instance, the apparent size obtained from the admittance maps for a Mo wire of 1.27 mm in diameter embedded in an Al matrix was about 3.0 mm at 4.7 Hz [15]. This value decreased to approximately 1.88 mm at 4.7 kHz. The size of admittance maps is influenced by the AC frequency because the potential distribution depends on this parameter in the case of nonuniform potential distribution induced by the cell geometry. This phenomenon was first predicted theoretically by Newman [19] for a disk electrode embedded in an isolating plane,
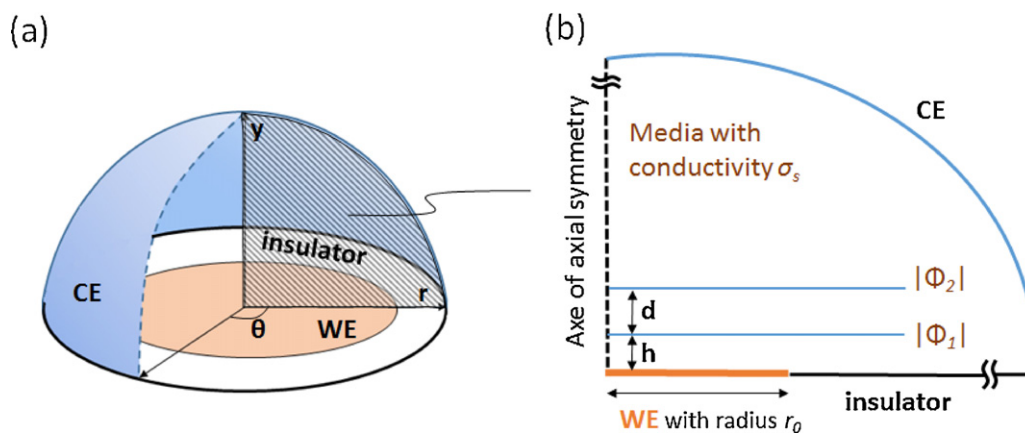
(a)

(b)

Fig. 1. Schematic representation of (a) 3D and (b) cross section of the electrochemical cell used for the numerical simulations.

then expanded and explained in details for other systems in more recent works [20–25].

In several works, an attempt was made to define the propagation of electroactive zones beneath a polymer coating on metal substrates leading to the loss of adhesion (*i.e.* the position of delamination front) [7,16–18]. Larger apparent size of the delaminated area from the admittance maps in comparison with the optical observations was always reported in the literature: delamination on the steel/epoxy-vinyl interface scanned at 5 kHz [7], vinyl coating on steel and Al alloy 5182 scanned between 100 and 1 kHz [16], industrial coil coated galvanized steel scanned at 1 kHz [17], epoxy based polymers on Al alloy AA2024-T3 scanned at 700 Hz [18]. In several works, LEIM revealed the formation of blisters in polymer even before they were visible by an optical technique [16,18]. The early detection of the electrochemical activity on the metal beneath the organic polymers makes LEIM an appealing tool for the quantitative determination of delamination kinetics. However, to the best of our knowledge no attempt was made to quantitatively correlate the response from the admittance maps and the size of electrochemically active zones.

The aim of the present work is to improve the existent LEIM methodology in order to quantify the precise geometry and the size of electrochemically active regions on the surface of WE. Firstly, the numerical simulations were used to find a parameter for the spatial quantification and then optimize the experimental set-up for such purpose, namely the AC frequency, the distance between the WE and the local bi-probe, and the size of the bi-probe. In the second part of the paper, the novel quantitative LEIM methodology was verified by measuring the delamination kinetics of Zn covered with the model polyvinyl butyral (PVB) polymer.

2. Numerical model

The mathematical foundation for the simulation of the potential and current distributions was adapted from the works by Newman [26,19] originally developed for a planar disk electrode embedded in a coplanar insulator and successfully applied to other cell geometries in order to investigate the edge effect of the electrode on the impedance response [21,24,25]. This treatment accounts for both the potential drop due to the ohmic resistance of the media and the electrode polarization.

Fig. 1 shows the geometry of the system used for the simulations. The potential distribution between the WE and the counter electrode (CE) is governed by Laplace equation (see Table 1 for notation):

$$\triangledown^2 \Phi = 0 \tag{1}$$

where Φ is the potential in the electrochemical cell. In cylindrical coordinates (r, θ, y), Eq. (1) expresses as

$$\frac{1}{r}\frac{\partial}{\partial r}\left(r\frac{\partial \Phi}{\partial r}\right) + \frac{1}{r^2}\frac{\partial^2 \Phi}{\partial \theta^2} + \frac{\partial^2 \Phi}{\partial y^2} = 0 \tag{2}$$

where y is the axis normal to the electrode surface, r is the radial coordinate and θ is the azimuth (Fig. 1). The cylindrical symmetry

Table 1
Notation

WE	working electrode
CE	counter electrode
RE	reference electrode
R	electrical resistance
C	electrical capacitance
N^n	free ion N in solution with charge n
$N(n)$	species containing N with valence of n
i	electrical current
i_N	current density of the reduction/oxidation of N
i_{loc}	local current density
j	imaginary unit
t	time
t_0	time of the onset of the delamination
f	frequency of AC variation
w	angular frequency of AC variation $(2\pi f)$
K	dimensionless frequency defined in Eq. (11)
h	distance between the probe and the WE
d	distance between the centres of the microelectrodes in the bi-probe
D	diameter of the microelectrode in the bi-probe
σ_s	conductivity of the electrolyte
Φ	potential in the solution
Φ_{ref}	potential of the reference electrode
Φ_0	potential just outside of the double layer
Φ_1	potential at the distance h from the WE
Φ_2	potential at the distance d from h
V	electrode potential
V_{OC}	potential at open circuit
V_0	amplitude of the potential applied to the WE
r	radial distance in cylindrical coordinates
r'_0	radial distance of the WE defined as a position of extreme of $z^{-1}(r)$ defined in Fig. 2
r_0	radius of the round WE
r_d	position of the electrochemical front defined by LEIM
r_N	radius of circle N
θ	azimuth in cylindrical coordinates
y	normal to the WE axis in cylindrical coordinates
b	coefficient of the linear LEIM spatial calibration defined in Eq. (13)
z	local value of the impedance defined in Eq. (10)
z^{-1}	local value of the admittance defined as reciprocal of z
X_C	global impedance of the single C