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Development of anodic and cathodic blisters at a model Zn / Epoxy interface studied using local electrochemical impedance

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Abstract

Local Electrochemical Impedance Spectroscopy (LEIS) and Mapping (LEIM) were used to *in situ* follow blistering on a model epoxy coated hot dip galvanized steel without any initial artificial defect during alternating Open Circuit Potential (OCP) / cathodic polarization cycles. Zones with high admittance were evidenced from the early stages of degradation, when no visible blisters have yet occurred. Some of the zones (type I) were distinguishable on the admittance maps obtained at both, open circuit and applied cathodic potentials. Other zones (type II) became non-detectable by LEIM at OCP but stayed visible on the maps obtained under cathodic polarization. Blisters developed on both types of zones. Comparing the LEIS responses of blistered zones with the responses of a model Zn/Cu galvanic couple, the observed behavior was attributed to the formation of a galvanic couple between the blisters, and consequently a gradual increase of anodic and cathodic activities in blisters of types I and II. LEIM can be a flexible tool able to differentiate *in situ* the development of anodic and cathodic zones on immersed polymer coated metallic substrates by application of different DC bias or AC frequency.

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Keywords: Local electrochemical impedance spectroscopy; Coating; Galvanic coupling; Material degradation

1. Introduction

Local electrochemical methods have become attractive tools in the investigation of metal/polymer interfaces degradation [1]. Operated in mapping mode, they can identify *in situ* and *in real time* the location of local galvanic cells at metal interface due to the measurement of local corrosion potentials [2,3] or local ionic currents [4], topography during swelling and blister formation [5], concentration gradients above polymers [6,7], etc. In this work, a novel application of Local Electrochemical Impedance Spectroscopy (LEIS) is proposed to expand the analytical capabilities of existing methodologies.

The first Local Electrochemical Impedance Mapping (LEIM) application to polymer coated metals was performed for a carbon steel coated with a 60 μm epoxy resin [8]. Prior to epoxy application a drop of 0.1 M NaCl solution was deposited on steel surface thus defining the blister formation, visible in admittance maps. At the early stages the blister was unruptured and local impedance response of the interface was entirely dominated by the dielectric properties of the film while on later stages the blister rupture resulted in the domination of LEIS response from a steel/electrolyte interface beneath the polymer. Later systematic studies confirmed the LEIM capability to detect early blistering initiated by underfilm salt deposits, adsorbed oil, subsurface bubbles, pinholes and directional underfilm corrosion [9]. LEIM imaging of intact AA2024-T3 interface coated with vinyl- and polyurethane based coatings revealed blistering, evidenced from higher local admittance values after 1-2 days of exposure to Cl^- and SO_4^{2-} environments [10,11]. Supplementary capillary electrophoresis, local pH and Open Circuit Potential (OCP) measurements showed acidified pH, high amount of soluble Al^{3+} , Cu^{2+} and Mg^{2+} and less noble OCP in one type of blisters called “red” and “clear” in reference to another type called “black” where alkaline pH and only traces of Mg^{2+} were detected. These differences could indicate the dominating anodic or cathodic reactions in different types of blisters, which however were not distinguished by *in situ* LEIS in [10,11].

The type of reactivity in blisters, however, strongly influences the chemical stability of the metal/polymer interface because of a different susceptibility of the metal/polymer interface to anodic and cathodic disbondment [12,13]. For instance, organic coating disbondment on MgZn_2 /lacquer interface is possible only via anodic undermining mechanism [12] while for Fe/- or Zn/epoxy interfaces it is mainly cathodic delamination [14,15]. This means that the formation of anodic or cathodic blisters can be detrimental for the service life of the assembly. From this point of view, a methodology able to detect the early stages of the formation of blisters and distinguish *in situ* the anodic or cathodic reactivity inside these blisters has high applied and fundamental interests.

In the case of atmospheric corrosion or for *ex situ* characterization, Scanning Kelvin Probe (SKP) can be an excellent tool to distinguish anodic and cathodic zones and to survey the kinetics of degradation [16,17]. However, it cannot be applied *in situ* to immersed polymer coated materials. Scanning vibrating

1 electrode technique (SVET) is able to clearly distinguish anodic and cathodic reactivity *in situ* for
2 immersed metallic surfaces. However, the SVET application for polymer coated surfaces is limited to
3 scratched metal/polymer interfaces [4]. LEIS capability to sense electrochemical reactions of immersed
4 polymer coated metal is unique. The interpretation of the absolute values of the admittance obtained in
5 LEIS/LEIM is convoluted since it does not indicate directly if the blistering process is associated with an
6 anodic or a cathodic process without supplementary analysis [18].

7 In a recent work [19] we have demonstrated the capability of LEIM/LEIS in a 5-electrode
8 configuration [20] to follow the kinetics of metal/polymer disbonding starting from an artificial defect
9 under immersion. The present work follows up on adapting LEIM for investigation of the metal/polymer
10 interface degradation without initial defect in the polymer coating with a particular attention on the
11 discrimination of cathodic and anodic underpaint reactivity. The main objective of the present work is to
12 propose an experimental LEIM/LEIS procedure able to distinguish and to survey *in situ* the formation of
13 anodic and cathodic blisters at initially intact Zn interface with a model unruptured epoxy polymer. This
14 differs our work since only blistering on pre-corroded interfaces has been reported in the literature with
15 no differentiation of electrode kinetics inside blisters [8–11]. To accelerate blistering, an alternating
16 current-direct current-alternating current (AC-DC-AC) procedure was adopted known to give a good
17 ranking for the stability of industrial coated systems [21]. The results obtained for blisters formed in
18 Zn/polymer system were compared with LEIS and LEIM results obtained on the model Zn/Cu galvanic
19 couple.

20 **2. Experimental**

21 **2.1. Materials**

22 The 3.5 x 3.5 cm² coupons of hot dip galvanized steel (HDG) (type: HDG/5 with an average
23 thickness of Zn layer of approximately 20 μm supplied by “Chemetall”) were used as a substrate. Prior to
24 the application of epoxy coating, the coupons were cleaned with ethanol and water, dried under nitrogen
25 and pre-treated in 1 M NaOH solution at 50° C for 30 s, then rinsed with water and dried under nitrogen
26 flow (see Ref. [22] for the detailed surface characterization). The samples were coated by a 10 ± 2 μm
27 thick transparent epoxy coating (Sader®) deposited by a spin-coating procedure (3000 rpm) and cured at
28 50° C for 12 h.

29 A model Zn/Cu galvanic couple was prepared using a 0.5 mm thick Cu foil applied on hot-dip
30 galvanized steel (HDG) coupons. Then, the sample was covered with a hydrophilic and impermeable
31 electroplating tape (3M 470, 0.18 mm thick - Gamry) with two circular holes (hole diameter: 3 mm,
32 distance between the holes: 1 mm) exposing Zn and Cu surfaces.

1 Measurements were performed in 10 mM NaCl aqueous solution prepared using analytical grade
2 NaCl and deionized water (Millipore®, 18 MΩ cm).

3 **2.2. Experimental set up for LEIS and LEIM measurement**

4 The experimental set-up for performing Local Electrochemical Impedance measurements consisted of
5 a 5-electrode configuration described in detail elsewhere [19]. Local bi-probe consisted of two Ag wires
6 of 200 μm in diameter, which were sealed in two attached capillaries with a diameter of 500 μm. The
7 distance between a Zn surface and the center of the closest to WE probe was approximately 200 μm. To
8 reassure best quality maps under given conditions, all scans were measured with steps of 100 μm in the *y*
9 direction and with a continuous scan rate of 100 μm/s in the *x* direction. All experiments were made under
10 continuous microscopic observation (time-lapse imaging using IP67 Digital camera) to compare visual
11 observations and LEIM results. Detailed description of local impedance measurements can be found in
12 [19] and in Supplementary Information (SI).

13 **2.3. Modified AC-DC-AC procedure.**

14 After 2 hours of immersion in 10 mM NaCl solution necessary for OCP stabilization at -0.9 V vs
15 Ag/AgCl, alternating cycles were applied. DC cycles consisted in 15 minutes of cathodic polarization at
16 -1.5 V vs Ag/AgCl followed by 30 minutes of immersion under the OCP during which LEIS/LEIM
17 measurement were made. The cycles were repeated 4 times. This procedure, chosen to accelerate interface
18 degradation by cathodic disbondment mechanisms [21,23], is more gentle compared to industrial
19 procedures because of the small thickness of the epoxy polymer used in this work.

20 **3. Results**

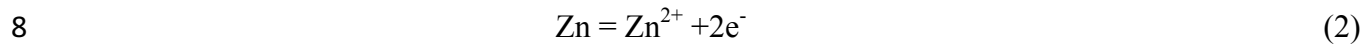
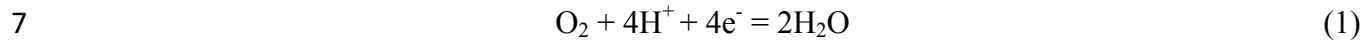
21 **3.1. Proof of concept via LEIS/LEIM study of a model Zn/Cu galvanic couple**

22 In order to show that LEIS/LEIM can clearly distinguish anodic and cathodic behavior in two
23 galvanically coupled blisters, LEIS and LEIM signals were measured on a model Zn/Cu electrode in
24 which Cu acts as a cathode and Zn acts as an anode. The WE (Fig. 1a) was prepared as described in section
25 2.1 and its specific geometry was chosen in order to rationalize the local EIS spectra in case of
26 inhomogeneous current distribution, typical for galvanic coupling [24,25]. In this work, the LEIS
27 measurement considers only the normal component of the local current density, disregarding the radial
28 contribution as usually reported in the literature. This can affect the LEIS spectra in the case of uneven
29 current distribution [26–28], specifically in the case of galvanic couples [24,25].

30 LEIS spectra over Cu and Zn look completely different in Fig. 1b at OCP, even though it is difficult
31 to distinguish the characteristic features from spectra and thus, provide unambiguous fitting of
32 experimental data. Shapes of LEIS were assigned to known electrochemical processes, oxygen reduction

1 reaction (ORR) over Cu and Zn dissolution over Zn at OCP and hydrogen evolution reaction (HER) at
2 both electrodes at cathodic polarization.

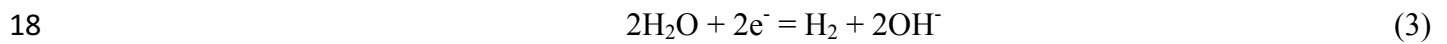
3 LEIS spectra recorded on the non-polarized Zn/Cu electrode (Fig. 1b) reflect a nearly straight line
4 with a 45° slope over Cu disk at $f > 10$ Hz in Nyquist coordinates. The impedance in this case can be
5 dominated by the diffusion-limited ORR expected to occur on Cu (Eq. (1)). LEIS over Zn shows a semi-
6 circle associated with the anodic Zn dissolution of Zn according to Eq. (2):



9 The high value of electrolyte resistance observed on LEIS diagrams can be ascribed to the distance
10 between the probe and the WE.

11 The admittance maps (Fig. 1c left) obtained for the Zn/Cu electrode display distinctly the Zn
12 electrode at both 10 Hz and 500 Hz at the OCP (-0.9 V vs Ag/AgCl). For Cu the admittance is significantly
13 lower than for Zn and decreases from 500 Hz to 10 Hz.

14 When the system is cathodically polarized at -1.5 V vs Ag/AgCl, the response over both Zn and
15 Cu is clearly visible at 500 Hz and 10 Hz (Fig. 1c right). At this potential water reduction Eq. (3) is
16 expected to occur on both Zn and Cu electrodes, which is reflected by two similar LEIS spectra for Zn
17 and Cu, showing a single well-defined semi-circle.



19 **3.2. Local Impedance Spectroscopy as an efficient tool for a blister detection and** 20 **characterization**

21 Figs. 2, 3 and 4 show LEIM, LEIS and optical observations of Zn/epoxy interface exposed in 10 mM
22 NaCl solution at different stages of blisters evolution during AC-DC-AC accelerated tests. Maps at only
23 one frequency of 500 Hz were recorded for a sufficiently fast data acquisition, which is important for
24 dynamically evolving systems. After 2h of immersion and before application of cathodic polarization
25 cycles, admittance maps in Fig. 2a reveal two active zones further called blister of type I (point I) and
26 blister of type II (point II), respectively. The remaining surface shows lower values of admittance (thus
27 larger values of impedance) corresponding to the intact polymer (example of point III). Local impedance
28 spectra over these 3 distinct zones presented in Fig. 3a show mainly a capacitive response ascribed to the
29 polymer coating. It should also be mentioned that the amplitude of the LEIS response is two orders of
30 magnitude larger than the response obtained over the naked metal electrodes (Fig. 1). Spectra over the
31 active zones tends towards a finite value of the polarization resistance (low frequency limit of the
32 impedance diagram) ascribed to a contribution of a faradaic reaction at Zn / coating interface. However,

1 a macroscopic surface observation presented in Fig. 4a does not show any evidence of electrochemical
2 activity this interface at this stage.

3 Application of AC-DC-AC cycles causes an increase of admittance (thus an increase of the local
4 current density) over the blister of type I and the disappearance of the blister of type II as shown in Fig.
5 2b-c-d-e. Dissimilar LEIS spectra over the blisters of type I and II at OCP in Fig. 3b indicate different
6 reactivities inside blisters. All around the active zones, the values of the admittance gradually increase
7 which can be assigned to the electrolyte uptake of the epoxy polymer, the initiation of electrochemical
8 processes at Zn/epoxy interface in these areas or/and disbonding of the coating. LEIS spectra over the
9 blister of type II and over the non-blistered zones (example of point III) look similar after 4 polarization
10 cycles as shown in Fig. 3b.

11 Similarly, to Zn/Cu galvanic couple, the admittance map under cathodic polarization reveals different
12 response, both blisters being clearly distinguishable as shown in Fig. 2f. The LEIS response above the
13 blisters of type I and II look similar showing a well-defined capacitive response as presented in Fig. 3c,
14 whereas the LEIS response over the polymer (above the point III) still exhibits a capacitive behavior.

15 Macroscopic surface observations after the AC-DC-AC experiments shown in Fig. 4a evidence the
16 blister formation at the identified location from the first LEIM scan presented in Fig. 2a. The color change
17 to black in the blisters can be attributed to the partial reduction of Zn oxides during the cathodic
18 polarization at -1.5 V vs Ag/AgCl [29]. High resolution optical images presented in Fig. 4b show a
19 detachment of the polymer at the blister of type I. This can change the local ionic environment inside the
20 blisters causing a significant difference in the LEIS response. Complementary Raman surface
21 characterization, provided in *Supporting information*, showed the presence of Zn(OH)₂ and ZnO as the
22 main corrosion products at corroding Zn/polymer interface. Similar observations were previously reported
23 in [30].

24

25 **4. Discussion**

26 Experiments on a model Zn/Cu galvanic couple with well-defined anodic and cathodic zones
27 showed that LEIM can distinguish these regions through variations of AC frequency and DC bias. After
28 4 polarization cycles, the LEIS and LEIM responses over the blisters of type I and II look similar to the
29 responses of Zn/Cu galvanic couple in Fig. 1. This can be an indication of identical electrochemical
30 process where blister of type I serves as a net anode while blister of the type II acts as a local cathode.
31 Such a coherence can be interpreted as a development of cathodic and anodic active zones at Zn/polymer
32 interface during cycling and show the Zn dissolution in type I blisters and the ORR in type II blisters (Fig.
33 5).

1 In this configuration LEIM resembles SVET with the only difference in the application of small
2 AC perturbations at different frequencies allowing to focus on a specific step of the degradation
3 mechanism. Previously, LEIS spectra were reported to reflect electrode kinetics in the case of ruptured
4 blisters and polymer dielectric properties in the case of unruptured blisters [8]. Our data did not show any
5 visible polymer damage in the type II blisters and the electrode kinetics seems to be still dominated by the
6 response from the underlying Zn electrode. In the case of series of Zn/(electrolyte in blister)/polymer/(bulk
7 electrolyte) interfaces, a response from the interface with the highest resistance should dominate the
8 measured local impedance values. Apparently, the selected model polymer possesses low electrical
9 resistance probably due to the presence of mesopores. This allowed us to apply LEIM /LEIS to survey the
10 evolution of cathodic and anodic activities under this polymer during accelerated AC-DC-AC test.

11 Based on the obtained results, some precisions can be made concerning a blistering mechanism at
12 Zn/epoxy interfaces. Common mechanisms of blister generation and growth include the formation of local
13 electrochemical cells at metal/polymer interface with both anodic and cathodic reactions establishing in a
14 single blister [31–34]. Our data showed that the formation of adjacent net cathodic and anodic blisters is
15 possible probably due to an ionic connection between them via the conductive electrolyte accumulated in
16 the pores of the polymer. The cathodic blisters can be formed from initially anodic blisters with
17 advancement of the test. The reason for this transformation can be related to the presence of defects in the
18 polymer. If initially the central zone of all blisters is considered to promote anodic dissolution, the local
19 chemical environment evolves differently in the non-damaged (“sealed”) and perforated blisters [35,36],
20 creating a difference in electrochemical potential and a formation of galvanic couple. This process has
21 been rarely reported in the literature and can aim to be the center of further LEIM investigations.

22 5. Conclusions

- 23 1) LEIM and LEIS of a model Cu/Zn galvanic couple demonstrated that closely displaced anodic
24 and cathodic active zones can be distinguished by the characteristic LEIS / LEIM responses
25 even when only the normal component of the local current is included in the measurement.
- 26 2) LEIM/LEIS application to a modified accelerated AC-DC-AC ageing of the undamaged
27 macroscopically homogenous Zn/epoxy interface was able to identify the positions of early
28 blisters before their visual appearance at and survey the evolution of their reactivity.
- 29 3) Two types of blisters can be formed at Zn/epoxy interface during AC-DC-AC cycling. Type I
30 blisters with a net anodic reactivity were detectable by LEIM/LEIS accumulated at both, OCP
31 and cathodic polarization. The blisters of type II behaved similar to the blisters of type I under
32 cathodic polarization but were passivated after several cathodic polarization cycles and
33 demonstrated a cathodic reactivity. These blisters disappeared from the admittance maps
34 collected at OCP but can be evidenced using the LEIM/LEIS under cathodic polarization.

1 4) The findings suggest that local galvanic cells at Zn/epoxy interface are formed due to the
2 interconnection between segregated blisters with a net anode (type I) and net cathode (type II)
3 activities. This phenomenon has been scarcely reported in the literature and can be a focus of
4 further LEIM investigations.

5

6 **Appendix A.** Supplementary data.

7 Supplementary data to this article can be found online at ...

8

1

2 **References**

3

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14
15

1 **Figure captions**

2

3 **Fig. 1** (a) schematic of the sample used to investigate LEIS response of the galvanic Zn/Cu couple.
4 Electrodes were electrically connected from the bottom. (b) local impedance spectra in Nyquist plot at
5 OCP and at cathodic polarization recorded under Cu and Zn. (c) admittance maps recorded at 500 Hz and
6 10 Hz at -0.9 V vs Ag/AgCl (OCP) and -1.5 V vs Ag/AgCl (cathodic polarization). Maps were recorded
7 with 100 μm step in x and y directions.

8

9 **Fig. 2** Admittance maps at 500 Hz at OCP (a) after 2 h of immersion in a 10 mM NaCl and after application
10 of (b) 1, (c) 2, (d) 3 and (e) 4 cycles at cathodic polarization at -1.5 V vs Ag/AgCl. (f) LEIM under cathodic
11 polarization at -1.5 V vs Ag/AgCl after the 4 polarization cycles. LEIS were recorded over the points I, II
12 and III and are presented in Fig. 3.

13

14 **Fig. 3** LEIS in Nyquist coordinates recorded over points I, II, and III (over the intact polymer) defined in
15 Fig. 2 after (a) 2h of immersion in 10 mM NaCl, (b) after 4 polarization cycles at OCP and (c) after 4
16 polarization under cathodic polarization of -1.5 V vs Ag/AgCl.

17

18 **Fig. 4** (a) macroscopic observation of the Zn/epoxy surface after 2 h of the immersion in a 10 mM NaCl
19 and at the end of the experiment in Fig. 2 after the complete set of polarization cycles. The polymer coating
20 is transparent. (b) high magnification optical images of blisters of type I and type II. White spot in (b)
21 corresponds to a hole in the polymer that was systematically observed in blisters of type I.

22

23 **Fig. 5** Scheme of the proposed degradation mechanisms in blisters of type I and II: net cathodic reaction
24 in blisters of type II is galvanically coupled to the anodic Zn dissolution dominating blisters of type I.
25 LEIS signatures of corresponding reactions are the appearance of a diffusion-limited process for blisters
26 of type II with a slope of ca. 45° and semi-circle for blisters of type I in Nyquist coordinates at OCP and
27 semi-circle for both types of blisters under cathodic polarization.

28

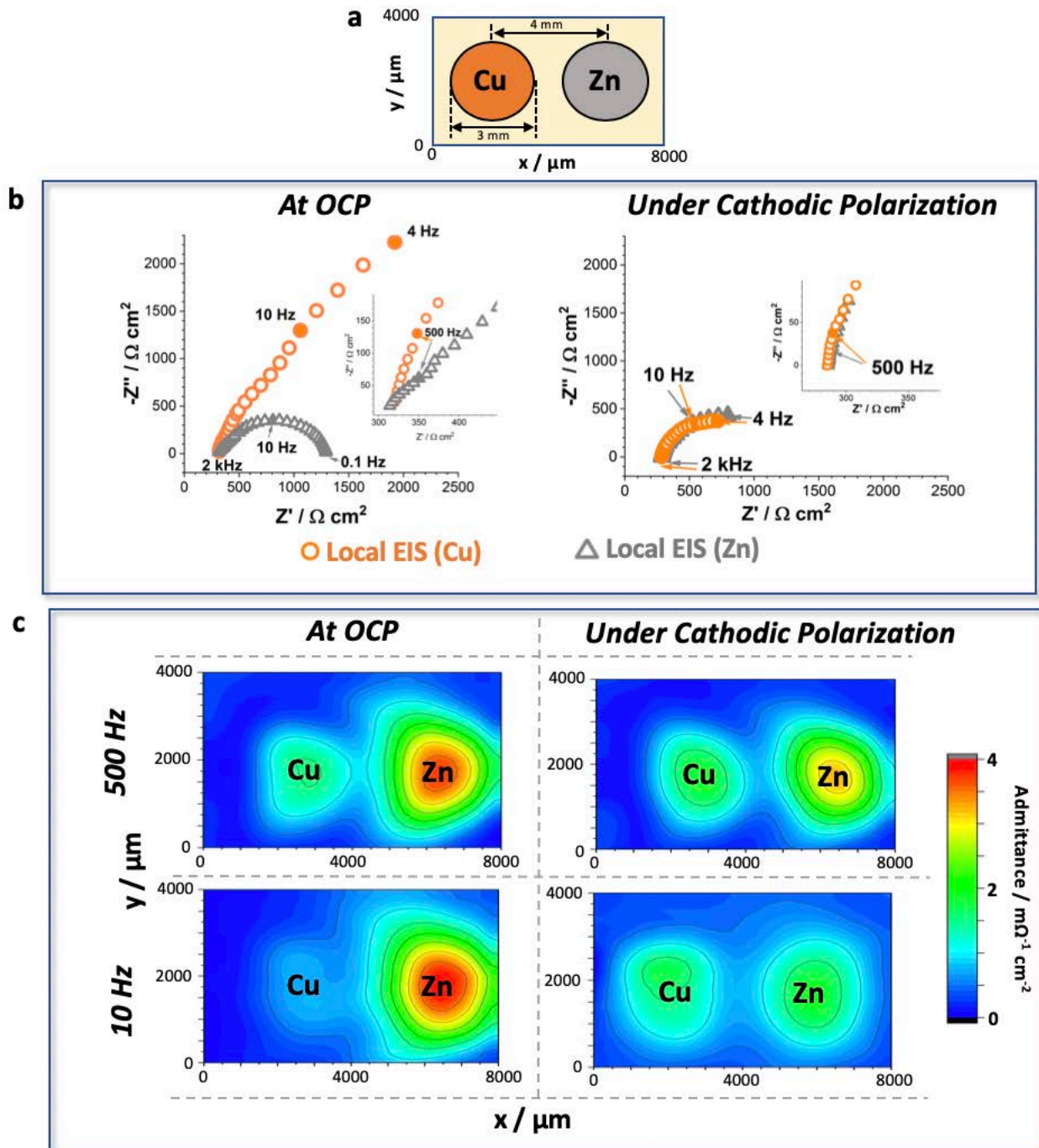
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1 **Figures**

2

3

4 **Fig. 1**

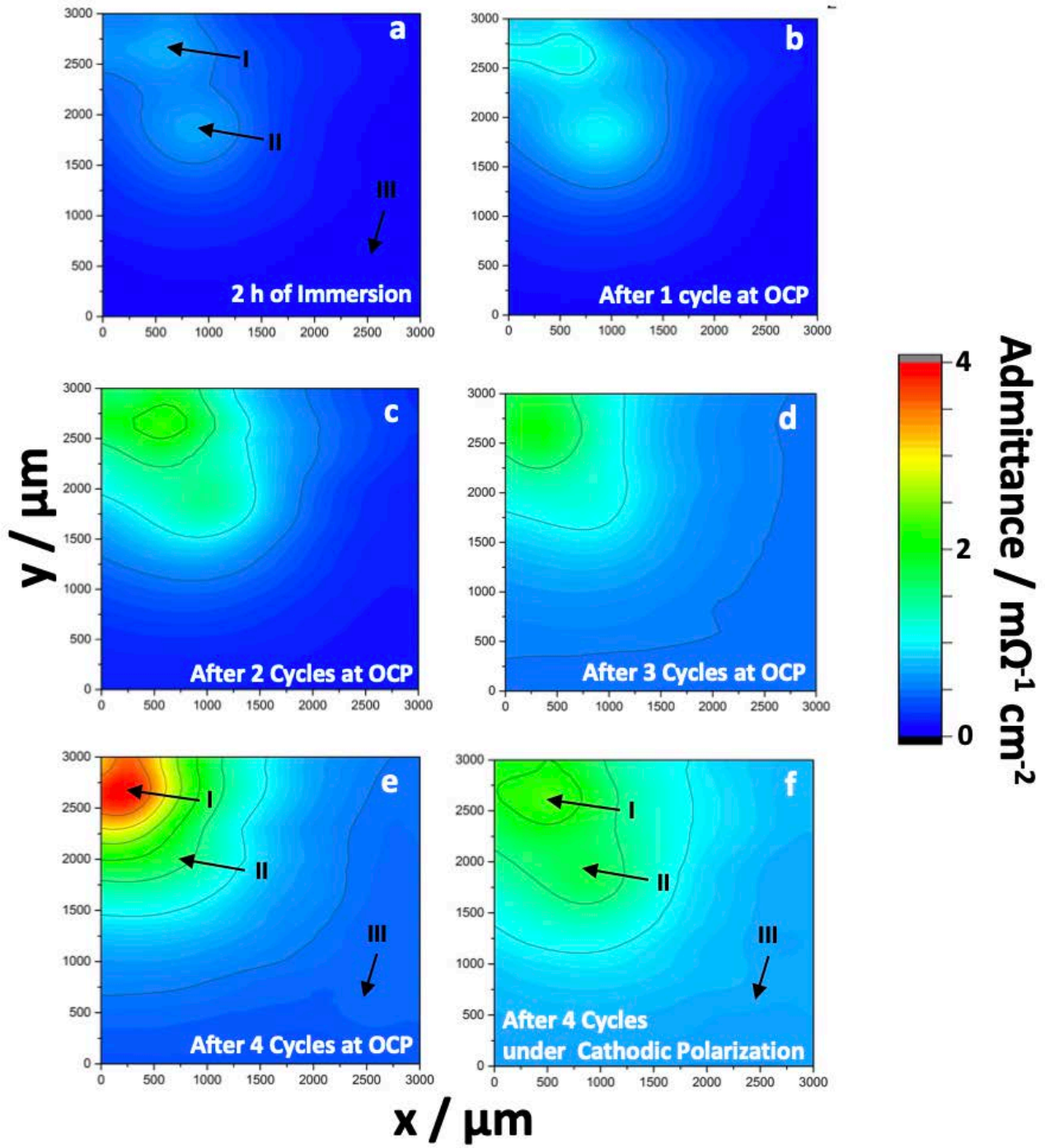


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1 Fig. 2

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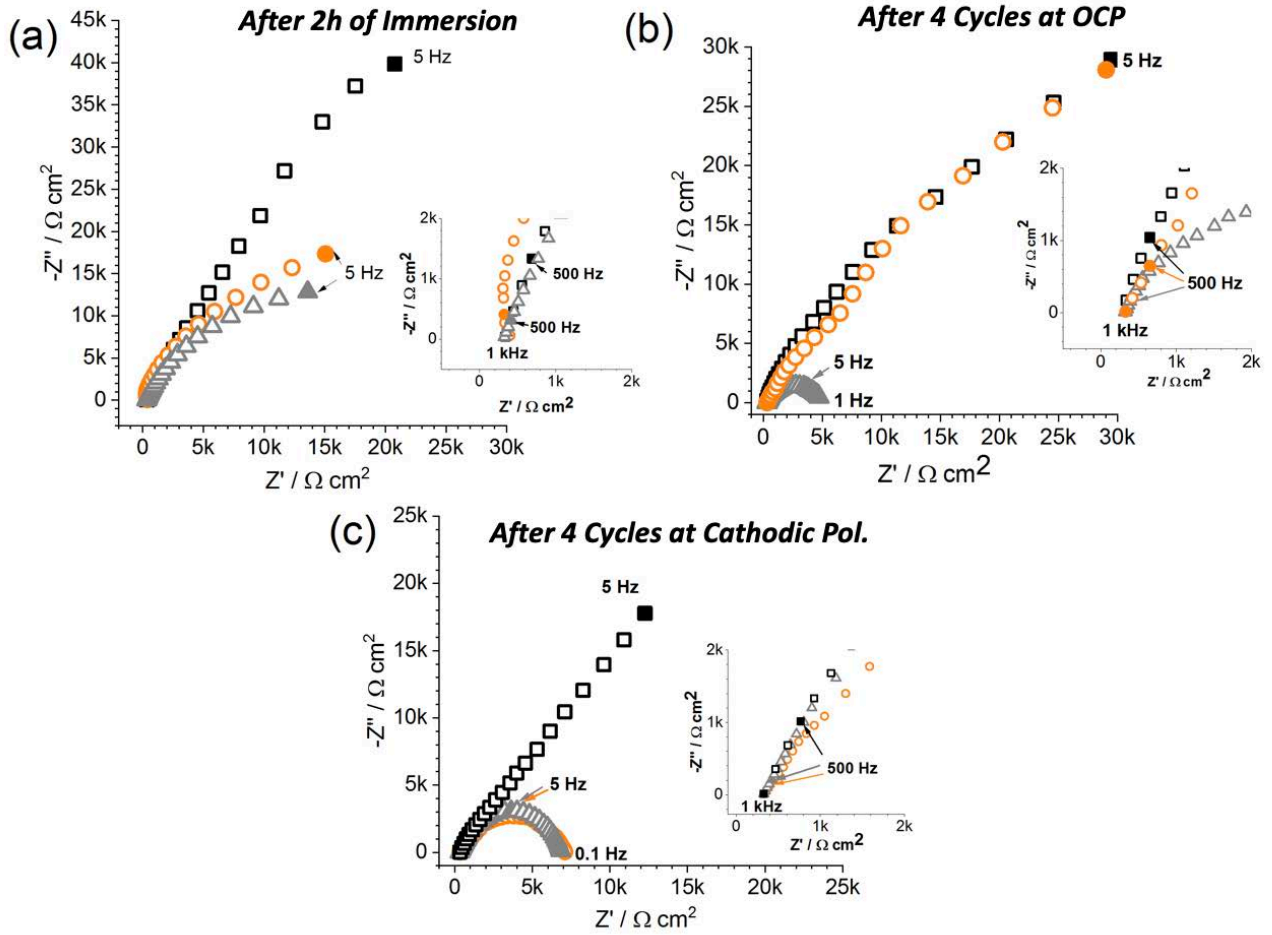
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1 **Fig. 3**

2

△ Local EIS over Point I
○ Local EIS over Point II
□ Local EIS over Point III

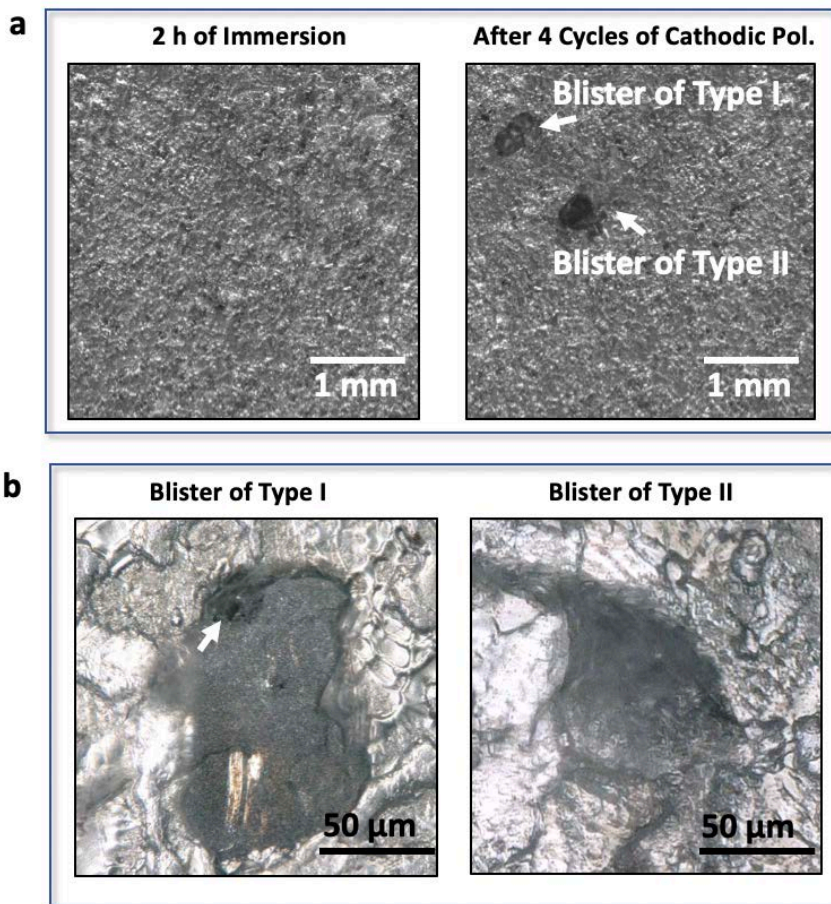


3

4

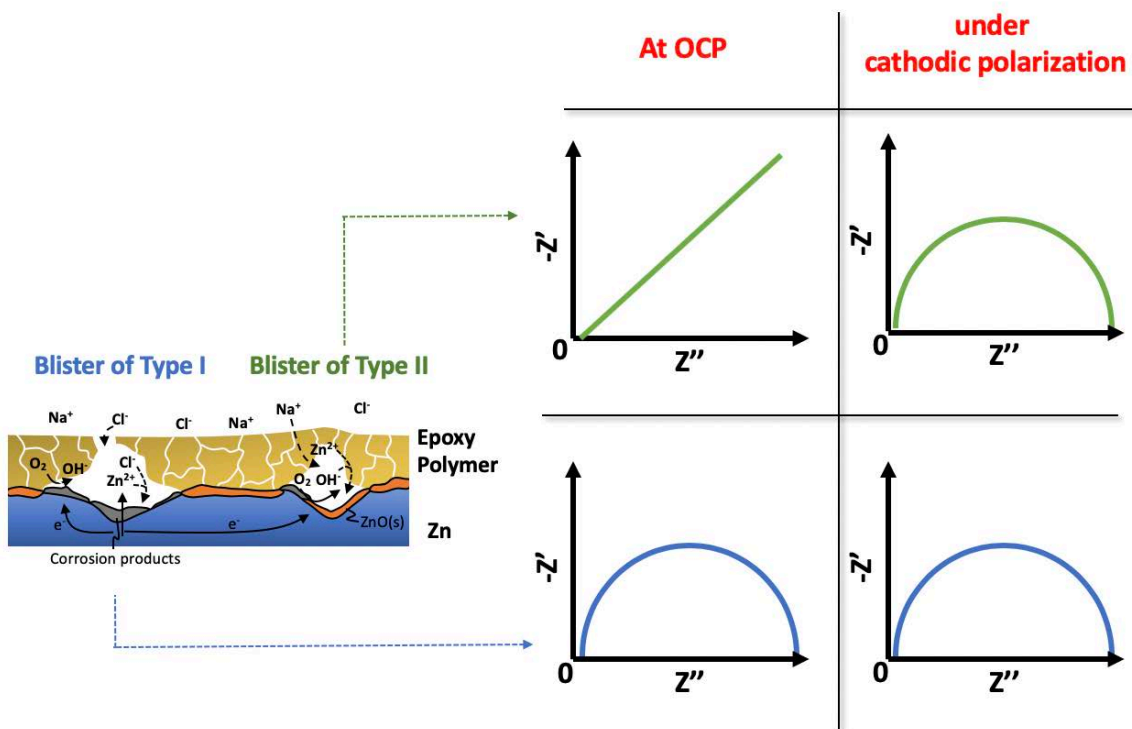
5

1 **Fig. 4**



2

3 **Fig. 5**



4