



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 in situ to follow blistering on a model epoxy-coated hot-dip galvanized steel without any initial artificial defects during alternating open circuit potential (OCP)/cathodic polarization cycles. Zones with high admittance were evident from the early stages of degradation, when no blisters were visible. Some of the zones (type I) could be distinguished on the admittance maps obtained at both open circuit and applied cathodic potentials. Other zones (type II) were not detectable by LEIM at OCP but were visible on the maps obtained under cathodic polarization. Blisters developed on both types of zones. Comparing the LEIS responses of the 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 is a flexible tool able to differentiate in situ between the development of anodic and cathodic zones on immersed polymer-coated metallic substrates on application of different DC biases or AC frequencies.

1. Introduction

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

The first application of local electrochemical impedance mapping (LEIM) 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 the steel surface, thus defining the blister formation, which was visible in the admittance maps. During the early stages the blister was unruptured and the local impedance response of the interface was entirely dominated by the dielectric properties of the film, while at later stages the rupture of the blister resulted in the domination of the LEIS response by the steel/electrolyte interface beneath the polymer. Later systematic studies confirmed the ability of LEIM to detect early blistering initiated by underfilm salt

deposits, adsorbed oil, subsurface bubbles, pinholes and directional underfilm corrosion [9]. LEIM imaging of an intact AA2024-T3 interface with vinyl- and polyurethane-based coatings revealed blistering, demonstrated by higher local admittance values after 1–2 days of exposure to Cl⁻ and SO₄²⁻ environments [10,11]. Supplementary capillary electrophoresis, local pH and open circuit potential (OCP) measurements showed an acidified pH, a large amount of soluble Al³⁺, Cu²⁺ and Mg²⁺ and less noble OCP in one type of blister called “red” or “clear”, compared with another type called “black”, where an alkaline pH and traces of Mg²⁺ were detected. These differences could indicate whether the dominating reactions in the various types of blisters were anodic or cathodic, which however could not be distinguished by in situ LEIS in [10,11].

The type of reactivity in blisters strongly influences the chemical stability of the metal/polymer interface because of the different susceptibility of the metal/polymer interface to anodic and cathodic disbondment [12,13]. For instance, organic coating disbondment on a MgZn₂/lacquer interface is possible only via an anodic undermining mechanism [12], while for Fe/- or Zn/epoxy interfaces the mechanism is mainly cathodic delamination [14,15]. This means that the formation of anodic or cathodic blisters can be detrimental to the service life of the assembly. From this point of view, an in situ methodology able to detect the early stages of the formation of blisters and distinguish the

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anodic or cathodic reactivity inside each one would be of great practical value and fundamental interest.

In the case of atmospheric corrosion or for ex situ characterization, a scanning Kelvin probe (SKP) is excellent in distinguishing between anodic and cathodic zones and in surveying the kinetics of degradation [16,17]. However, this technique cannot be applied in situ to immersed polymer-coated materials. The scanning vibrating electrode technique (SVET) is able to clearly distinguish in situ between anodic and cathodic reactivity for immersed metallic surfaces. However, the application of SVET to polymer-coated surfaces is limited to scratched metal/polymer interfaces [4]. The ability of LEIS to detect the electrochemical reactions of immersed polymer-coated metal is unique. However, interpretation of the absolute values of the admittance obtained using LEIS/LEIM is convoluted since the results do not indicate directly if the blistering process is associated with an anodic or a cathodic process without supplementary analysis [18].

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

2. Experimental

2.1. Materials

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

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

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

2.2. Experimental set-up for LEIS and LEIM measurement

The experimental set-up for performing local electrochemical impedance measurements consisted of a 5-electrode configuration described in detail elsewhere [19]. The local bi-probe consisted of two Ag wires $200 \mu\text{m}$ in diameter, which were sealed in two attached

capillaries with a diameter of $500 \mu\text{m}$. The distance between the Zn surface and the center of the closest WE probe was approximately $200 \mu\text{m}$. To ensure the highest quality maps under given conditions, all scans were measured with steps of $100 \mu\text{m}$ in the y direction and with a continuous scan rate of $100 \mu\text{m/s}$ in the x direction. All experiments were performed under continuous microscopic observation (time-lapse imaging using IP67 digital camera) to compare the visual observations and LEIM results. A detailed description of local impedance measurements can be found in [19] and in the Supplementary Information (SI).

2.3. Modified AC-DC-AC procedure

After 2 h of immersion in 10 mM NaCl solution (necessary for OCP stabilization at -0.9 V vs Ag/AgCl), alternating cycles were applied. DC cycles consisted of 15 min of cathodic polarization at -1.5 V vs Ag/AgCl followed by 30 min of immersion under the OCP, during which LEIS/LEIM measurements were made. The cycles were repeated four times. This procedure, chosen to accelerate interface degradation by cathodic disbondment mechanisms [21,23], is more gentle than industrial procedures because of the relative thinness of the epoxy polymer used in this work.

3. Results

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

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

In Fig. 1b, the LEIS spectra over Cu and Zn look completely different at the OCP, although it is difficult to distinguish the characteristic features from the spectra and thus provide unambiguous fitting of the experimental data. The LEIS shapes were assigned to known electrochemical processes: the oxygen reduction reaction (ORR) over Cu and Zn dissolution over Zn at the OCP, and the hydrogen evolution reaction (HER) at both electrodes under cathodic polarization.

LEIS spectra recorded on the non-polarized Zn/Cu electrode (Fig. 1b) show a nearly straight line with a 45° slope over a Cu disk at $f > 10 \text{ Hz}$ in Nyquist coordinates. The impedance in this case may be dominated by the diffusion-limited ORR expected to occur on Cu (Eq. (1)). LEIS over Zn shows a semicircle associated with the anodic dissolution of Zn according to Eq. (2):



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

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

When the system is cathodically polarized at -1.5 V vs Ag/AgCl, the response over both Zn and Cu is clearly visible at 500 Hz and 10 Hz (Fig. 1c right). At this potential water reduction Eq. (3) is expected to occur on both Zn and Cu electrodes, which is reflected by two similar

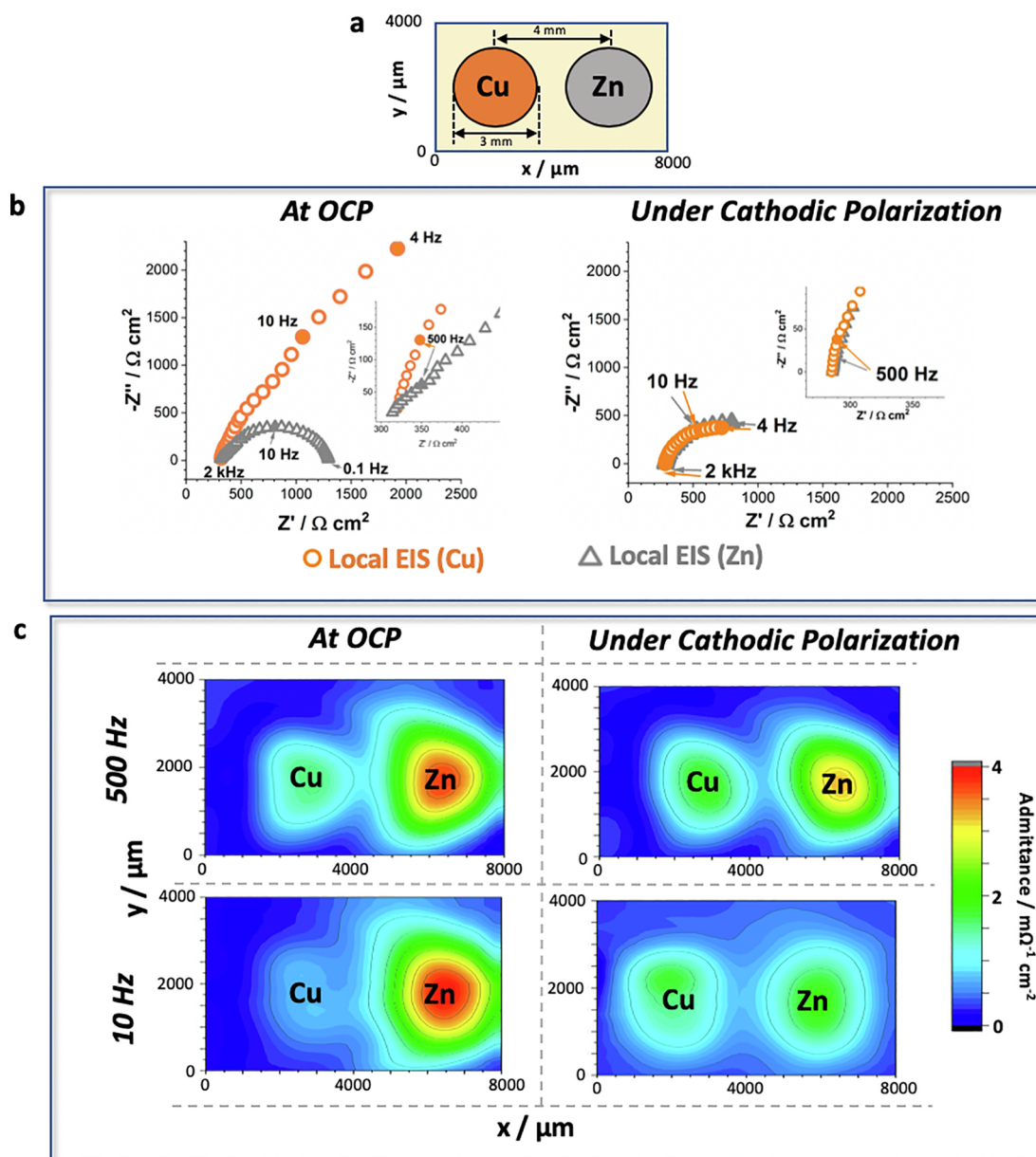


Fig. 1. (a) Schematic of the sample used to investigate LEIS response of the galvanic Zn/Cu couple. Electrodes were electrically connected from the bottom. (b) Local impedance spectra as a Nyquist plot at OCP and at cathodic polarization recorded under Cu and Zn. (c) Admittance maps recorded at 500 Hz and 10 Hz at -0.9 V vs Ag/AgCl (OCP) and -1.5 V vs Ag/AgCl (cathodic polarization). Maps were recorded with $100 \mu\text{m}$ step in x and y directions.

LEIS spectra for Zn and Cu, showing a single well-defined semicircle.



3.2. Local impedance spectroscopy as an efficient tool for a blister detection and characterization

Figs. 2–4 show LEIM, LEIS and optical observations of the Zn/epoxy interface exposed in 10 mM NaCl solution at different stages of blister evolution during AC-DC-AC accelerated tests. Maps were recorded at just one frequency (500 Hz) for sufficiently fast data acquisition, which is important for dynamically evolving systems. After 2 h of immersion and before application of cathodic polarization cycles, the admittance maps in Fig. 2a reveal two active zones, henceforth called blisters of type I (point I) and blisters of type II (point II), respectively. The remaining surface shows lower values of admittance (and hence larger values of impedance) corresponding to the intact polymer (e.g. point III). Local impedance spectra obtained over these three distinct zones

are presented in Fig. 3a and mainly show a capacitive response ascribed to the polymer coating. It should also be mentioned that the amplitude of the LEIS response is two orders of magnitude larger than the response obtained over the naked metal electrodes (Fig. 1). Spectra over the active zones tends towards a finite value of the polarization resistance (low frequency limit of the impedance diagram), ascribed to a contribution from a faradaic reaction at the Zn/coating interface. However, the macroscopic surface observation presented in Fig. 4a does not show any evidence of electrochemical activity at the interface at this stage.

Application of AC-DC-AC cycles causes an increase in admittance (and thus an increase in the local current density) over the blister of type I and the disappearance of the blister of type II, as shown in Fig. 2b–e. Dissimilar LEIS spectra over the blisters of type I and II at OCP in Fig. 3b indicate different reactivities inside the blisters. All around the active zones, the values of the admittance gradually increase, which can be assigned to the electrolyte uptake of the epoxy polymer, the initiation of electrochemical processes at the Zn/epoxy

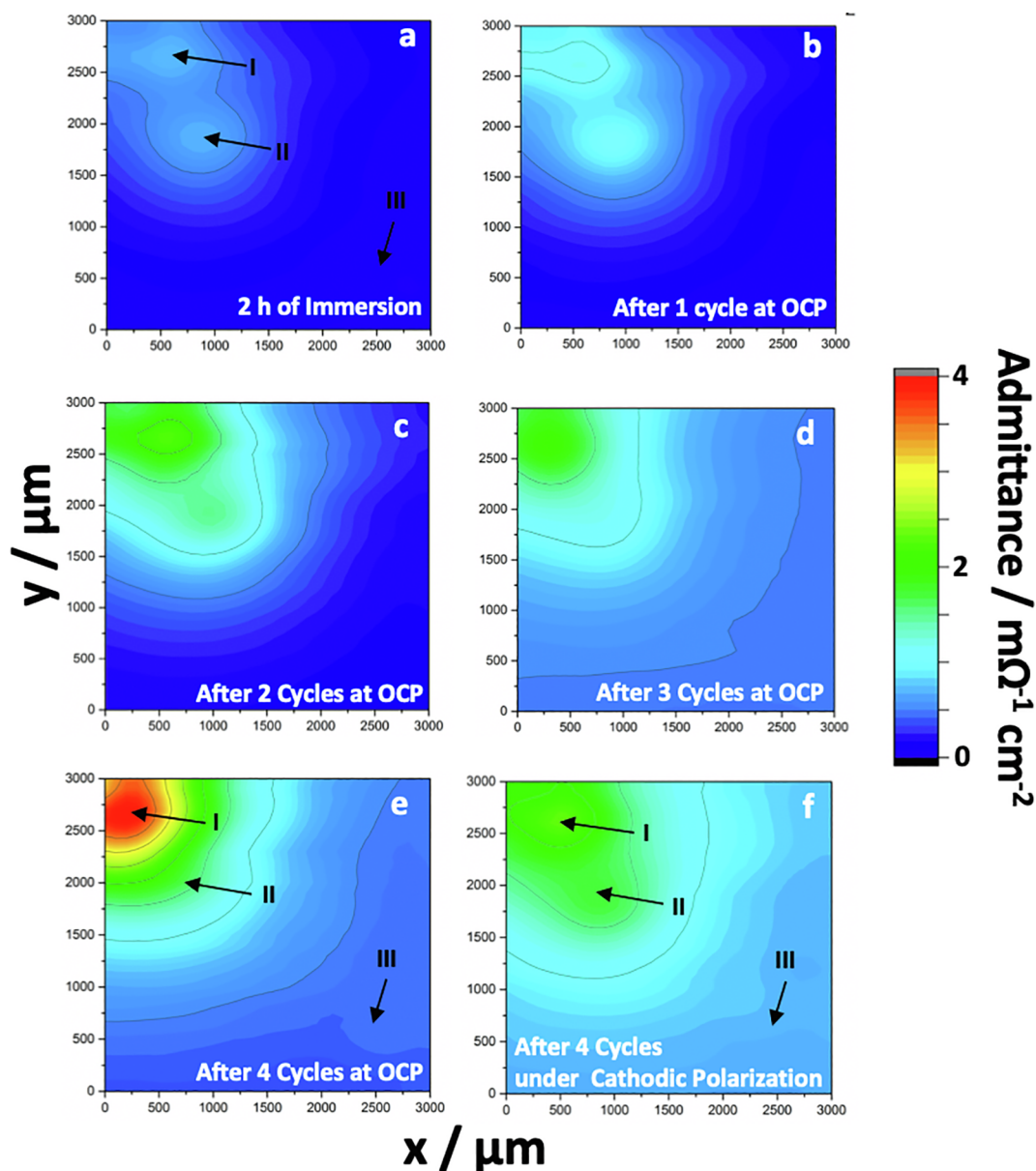


Fig. 2. Admittance maps at 500 Hz at OCP (a) after 2 h of immersion in a 10 mM NaCl and after application of (b) 1, (c) 2, (d) 3 and (e) 4 cycles at cathodic polarization at -1.5 V vs Ag/AgCl. (f) LEIM under cathodic polarization at -1.5 V vs Ag/AgCl after the 4 polarization cycles. LEIS were recorded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

interface in these areas and/or disbonding of the coating. LEIS spectra over the blister of type II and over the non-blistered zones (e.g. point III) look similar after 4 polarization cycles, as shown in Fig. 3b.

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

Macroscopic surface observations after the AC-DC-AC experiments shown in Fig. 4a show blister formation at the location identified from the first LEIM scan in Fig. 2a. The color change of the blisters to black can be attributed to the partial reduction of Zn oxides during cathodic polarization at -1.5 V vs Ag/AgCl [29]. The high resolution optical images presented in Fig. 4b show detachment of the polymer at the blister of type I. This can change the local ionic environment inside the blisters, causing a significant difference in the LEIS response. Complementary Raman surface characterization, provided in the Supporting

Information, showed the presence of $\text{Zn}(\text{OH})_2$ and ZnO as the main corrosion products of the corroding Zn/polymer interface. Similar observations have been reported previously in [30].

4. Discussion

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

In this configuration LEIM resembles SVET, with the difference lying

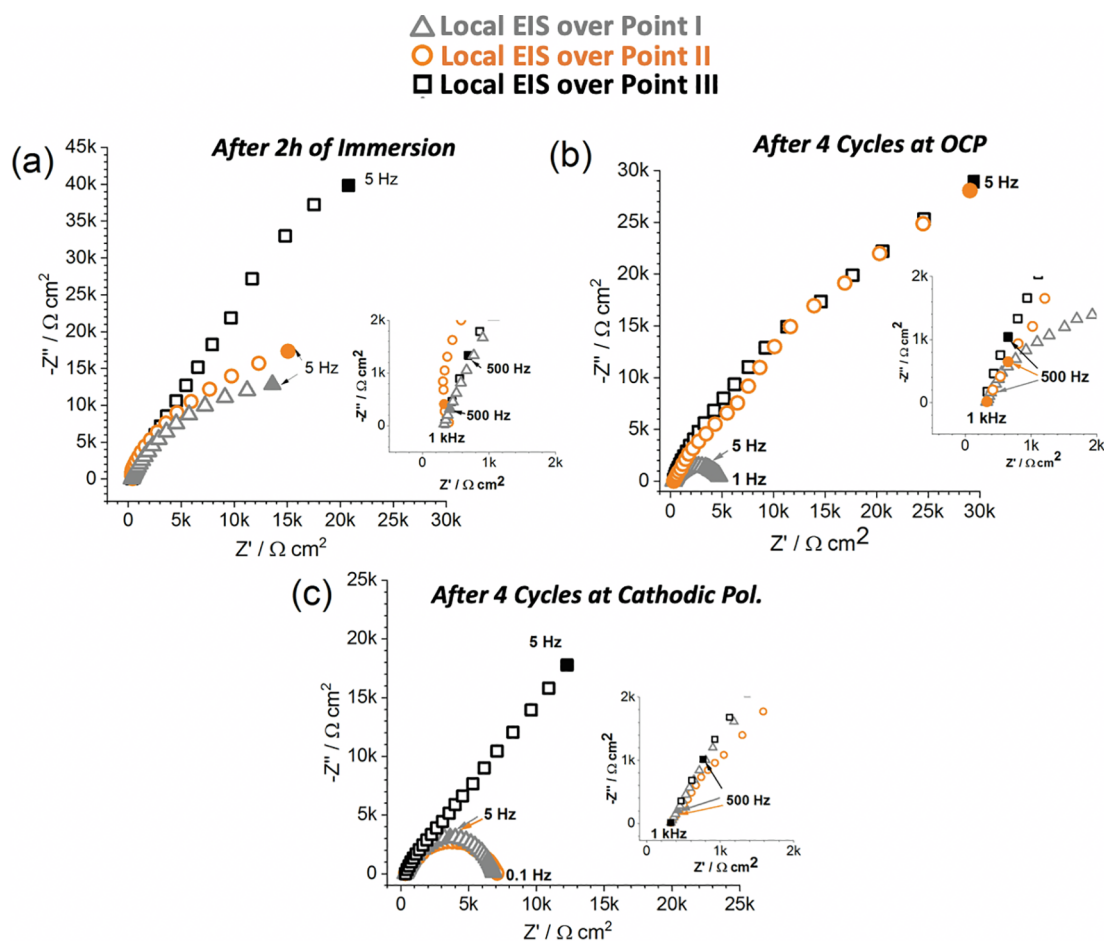


Fig. 3. LEIS in Nyquist coordinates recorded over points I, II, and III (over the intact polymer) defined in Fig. 2 after (a) 2 h of immersion in 10 mM NaCl, (b) after 4 polarization cycles at OCP and (c) after 4 polarization cycles under cathodic polarization of -1.5 V vs Ag/AgCl.

in the application of small AC perturbations at different frequencies making it possible to focus on a specific step of the degradation mechanism. Previously, LEIS spectra were reported to reflect electrode kinetics in the case of ruptured blisters and polymer dielectric properties in the case of unruptured blisters [8]. Our data did not show any visible polymer damage in the type II blisters and the electrode kinetics still seem to be dominated by the response from the underlying Zn electrode. In the case of series of Zn/(electrolyte in blister)/polymer/(bulk electrolyte) interfaces, a response from the interface with the highest resistance should dominate the measured local impedance values. It appears that the selected model polymer possesses low electrical resistance, probably due to the presence of mesopores. This allowed us to use LEIM/LEIS to survey the evolution of cathodic and anodic activities under this polymer during an accelerated AC-DC-AC test.

Based on the obtained results, some conclusions can be drawn concerning the blistering mechanism at Zn/epoxy interfaces. Common mechanisms of blister generation and growth include the formation of local electrochemical cells at the metal/polymer interface with both anodic and cathodic reactions established in a single blister [31–34]. Our data showed that the formation of adjacent net cathodic and anodic blisters is possible, probably due to an ionic connection between them via the conductive electrolyte which accumulates in the pores of the polymer. Cathodic blisters can be formed from anodic blisters as the test progresses. The reason for this transformation may be related to the presence of defects in the polymer. If initially the central zone of all blisters is considered to promote anodic dissolution, the local chemical environment evolves differently in the non-damaged (“sealed”) and perforated blisters [14,35], creating a difference in electrochemical potential and the formation of a galvanic couple. This process has rarely

been reported in the literature and may be the focus of further LEIM research.

5. Conclusions

- 1) LEIM and LEIS of a model Cu/Zn galvanic couple demonstrated that closely displaced anodic and cathodic active zones can be distinguished by their characteristic LEIS/LEIM responses, even when only the normal component of the local current is included in the measurement.
- 2) Application of LEIM/LEIS to modified accelerated AC-DC-AC ageing of an undamaged macroscopically homogenous Zn/epoxy interface was able to identify the positions of early blisters before they could be observed visually, and survey the evolution of their reactivity.
- 3) Two types of blisters can be formed at Zn/epoxy interface during AC-DC-AC cycling. Type I blisters with a net anodic reactivity were detectable by LEIM/LEIS at both OCP and cathodic polarization. The blisters of type II behaved similarly to the blisters of type I under cathodic polarization, but were passivated after several cathodic polarization cycles and demonstrated cathodic reactivity. These blisters disappeared from the admittance maps collected at OCP but can be observed using the LEIM/LEIS under cathodic polarization.
- 4) The findings suggest that local galvanic cells are formed at a Zn/epoxy interface due to the interconnection between segregated blisters with a net anode (type I) and net cathode (type II) activities. This phenomenon has rarely been reported in the literature and may be the focus of further LEIM investigations.

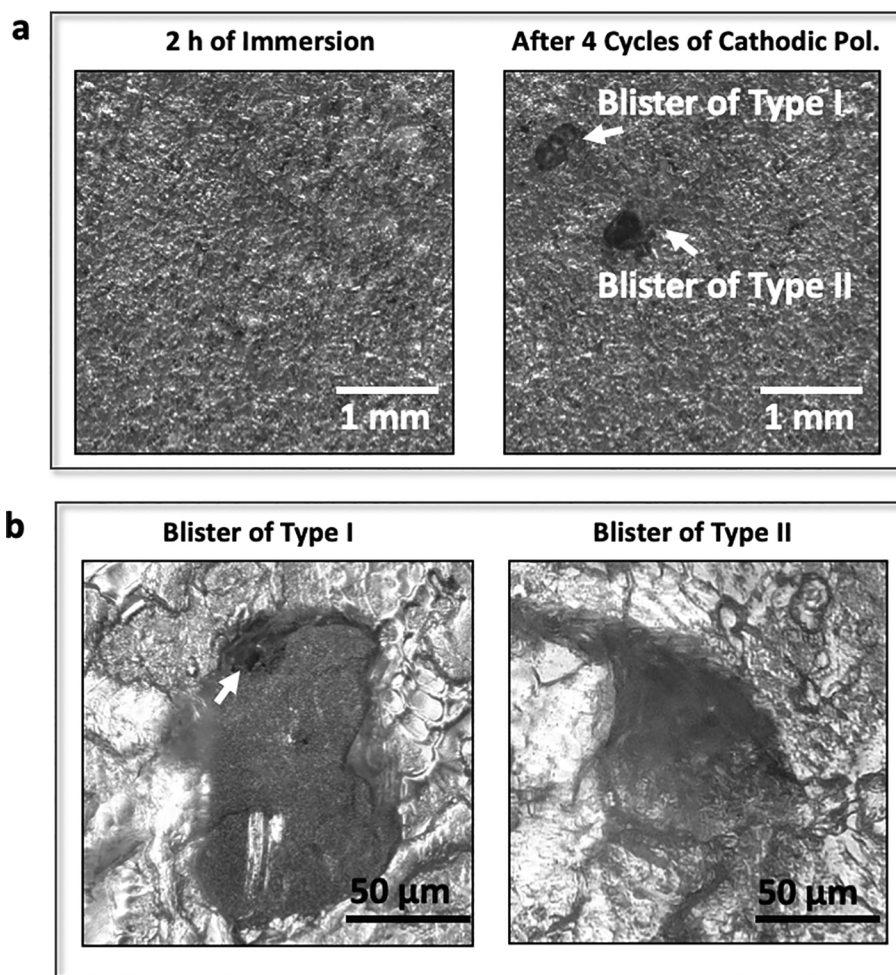


Fig. 4. (a) Macroscopic observation of the Zn/epoxy surface after 2 h of immersion in a 10 mM NaCl and at the end of the experiment shown in Fig. 2 after the complete set of polarization cycles. The polymer coating is transparent. (b) High magnification optical images of blisters of type I and type II.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

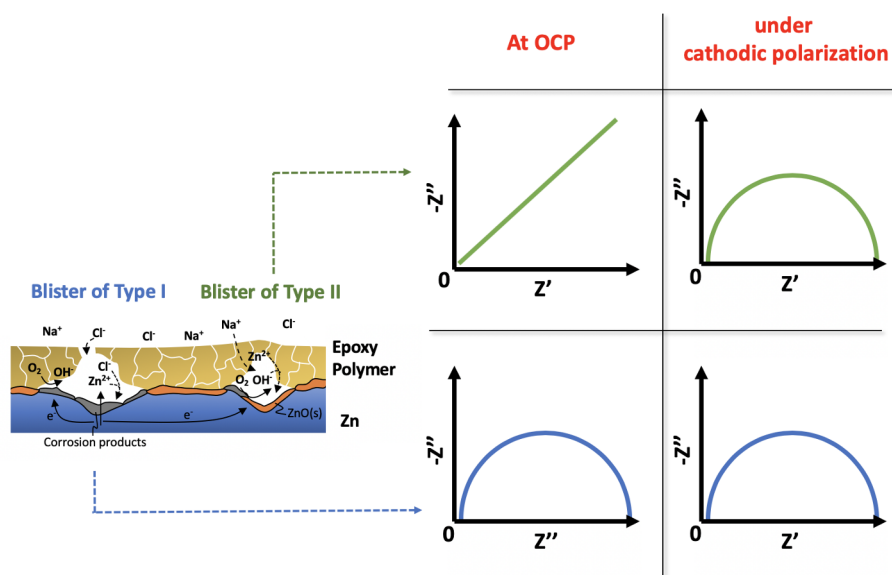


Fig. 5. Scheme showing the proposed degradation mechanisms in blisters of type I and II: the net cathodic reaction in blisters of type II is galvanically coupled to the anodic Zn dissolution dominating blisters of type I. LEIS signatures of corresponding reactions are the appearance of a diffusion-limited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

CRedit authorship contribution statement

V. Shkirskiy: Conceptualization, Methodology, Software, Data curation, Visualization, Supervision, Writing - original draft, Writing - review & editing. **A. Krasnova:** Investigation, Validation. **T. Sanchez:** Methodology, Resources, Writing - review & editing. **A. Amar:** Investigation, Validation. **V. Vivier:** Writing - review & editing. **P. Volovitch:** Conceptualization, Writing - review & editing, Supervision, Funding acquisition.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.elecom.2019.106633>.

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