



Article

Pre-Corroded ER Sensors as Realistic Mock-Ups for Evaluating Conservation Strategies

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Abstract

Electrical resistance (ER) sensors are established tools for monitoring atmospheric corrosion in real time, yet their application to cultural heritage requires adaptation to the complex stratigraphy of patinated surfaces. In this work, customised ER sensors were optimised to allow the sensors to be pre-patinated, enabling a more realistic simulation of corroded heritage metals. Different geometries and artificial patinas were applied to assess sensitivity, robustness, and representativeness under variable environmental conditions. The study confirms the decisive role of corrosion layers in shaping sensor response and highlights the potentialities of pre-patinated ER sensors as realistic mock-ups for testing conservation strategies and evaluating environmental corrosivity under conditions relevant to cultural heritage preservation.

Keywords: electrical resistance sensors; pre-patinated sensors; atmospheric corrosion; artificial patinas; copper alloy; environmental corrosivity monitoring; mock-ups for treatment testing; metal conservation



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1. Introduction

Corrosion is a major factor in the degradation of metallic cultural heritage objects. Monitoring its progression is essential for preventive conservation and informed decision-making [1]. On-site, non-destructive monitoring techniques allow the acquisition of valuable information about the conservation state of artworks without the need for sampling, damaging, or moving the objects. In the case of metallic surfaces exposed to the atmosphere, electrochemical techniques enable in situ, non-destructive or micro-invasive, real-time measurements of corrosion rates [2–11], thus also providing insights into the effectiveness of conservation treatments [12–23]. A major advantage of these methodologies lies in the possibility of performing measurements directly on the surface of the artefacts. Electrochemical methods such as Linear Polarisation Resistance (LPR) and Electrochemical Impedance Spectroscopy (EIS) provide valuable data but are discontinuous and, in case of atmospheric corrosion monitoring, they require electrolyte application [1].

In addition to in situ non-invasive or micro-invasive electrochemical techniques, it is also common practice to expose probes or specimens made of the same materials as the artefacts to the same environmental conditions. This allows the investigation of

degradation patterns on the specimens, enabling more invasive and destructive analyses without compromising the integrity of the original artworks [11,24–37]. However, it must be considered that using an alloy with the same composition is not always sufficient to accurately reproduce the real surface conditions of the artefacts, as corrosion layers can significantly influence their corrosion behaviour. Moreover, most of these methodologies do not allow for real-time and continuous monitoring. This limitation has driven the development of low-cost, real-time monitoring systems [1,38] such as atmospheric corrosion monitoring (ACM) sensors [1,38–47]. Like traditional coupons, ACM sensors are fabricated from materials that replicate those of the studied objects. However, unlike coupons—that only provide information after a defined exposure period—ACM sensors enable real-time monitoring of both corrosion processes and environmental corrosivity. Over the years, numerous sensor designs have been developed for use in sectors such as transportation, infrastructure, and various industrial applications [1,38,40,47–53]. Among the most widely adopted approaches [1], there are sensors based on electrical resistance [39,41,42,45,50,53–63], electrochemical impedance [47,57,60] and galvanic corrosion cells [64–73].

In particular, in the field of reinforced concrete structures, various types of embedded sensors have been developed for corrosion monitoring, including reference electrodes, polarisation resistance probes, and galvanic cells [69,74–76].

Galvanic sensors are appreciated for their robustness, but their use in long-term monitoring is limited [1,38]. The galvanic coupling between different metals, which is essential for their operation, can unintentionally accelerate corrosion, reducing the lifespan of the sensors. Moreover, in complex or aggressive environments, the interpretation of the data they produce can be challenging, making them less attractive for low-cost, field-deployable monitoring systems [1].

Another approach involves sensors based on piezoelectric quartz crystals [44,46,77]. In this case, corrosion is assessed by monitoring changes in their resonance frequency, which depends on its mass and, consequently, it reflects mass variations in the metallic layer as corrosion progresses.

Recently, passive RFID (Radio Frequency Identification) technology has been applied to develop corrosion sensors that can be queried without physical contact; several sensing principles and architectures have been adopted. For example, it is possible to exploit the different wave propagation in thin plates subject to corrosion [78,79], or changes in the antenna impedance due to the properties of corrosion products [80]. Alternatively, if the RFID tag is coated with resin containing steel powder, corrosion can be detected as changes in the reading rate, due to the higher magnetic permeability of the corrosion product and the resulting shielding effect [81]. Thanks to their simplicity and very low cost, RFID-based sensors are suitable for large-scale applications. On the other hand, they generally exhibit significant sensitivity to temperature and to the mutual position between tag and reader. In the cultural heritage field, these sensors have mainly been used to assess indoor air corrosivity according to ISO 11844 classes (IC1–IC3) [82], rather than to monitor corrosion kinetics on artefacts, and they are not intended for highly aggressive environments. Like electrical resistance (ER) sensors, RFID tags require extremely thin metallic layers to achieve good sensitivity; in fact, they often need even thinner films (10–30 nm) [78,79] compared to ER sensors (tens to hundreds of nm) to detect the very low corrosion rates typical of museum environments [41–43,45,58]. It is important to underline that most RFID architectures do not provide continuous monitoring: they must be read periodically and generally exhibit lower sensitivity than ER sensors [79].

Table 1 summarises the main strengths and limitations of the most commonly used corrosion monitoring techniques, based on the previously cited literature and, in particular, on the review by Popova et al. [38] and by Komary et al. [1].

Table 1. Comparative summary of corrosion monitoring techniques.

Technique	Strengths	Limitations
LPR	Accurate corrosion rate; direct measurement	Requires electrolyte; discontinuous; sensitive to setup
EIS	Detailed coating evaluation; non-destructive	Complex data interpretation; electrolyte needed
Galvanic Sensors	Robust; suitable for outdoor use	May accelerate corrosion; limited sensor lifespan; data interpretation issues
Coupons	Standardised; easy to analyse	No real-time data; long exposure times required
Electrochemical Noise (EN)	Detects localised corrosion; in situ	Complex interpretation; sensitive to noise
Passive RFID	Low-cost, contactless, flexibility	Sensitive to temperature and reading position
ER Sensors	Real-time; non-invasive; sensitive; low-cost; easy to interpret	Temperature-dependent; less effective for non-uniform corrosion

In this study, electrical resistance (ER) sensors are considered as an interesting option for monitoring the atmospheric corrosion of copper alloys in a cultural heritage context. ER sensors stand out among available techniques because they provide continuous, real-time measurement of metal loss, without the need for applying electrolytes or maintaining a continuous electrolyte layer on the surface. This makes them particularly effective in environments characterised by fluctuating humidity and discontinuous patinas, where electrochemical methods often fail to deliver reliable data. Moreover, ER sensors combine high sensitivity and low corrosion rates with a relatively simple measurement principle, ensuring robustness, reproducibility, and compatibility with long-term outdoor exposure. These advantages make ER sensors a promising tool not only to monitor environmental corrosivity, as in conventional applications, but also to develop more realistic mock-ups for assessing the corrosion behaviour of heritage surfaces and the performance of conservation strategies. In this perspective, particular emphasis is placed on their use as replicas of original artefacts, since conservation methods must be tested on surrogate samples rather than on the unique and irreplaceable objects of historical and artistic value.

ER-based sensors have been successfully employed in many application fields since the late 1950s. Besides atmospheric corrosion phenomena, ER-based monitoring devices have also been successfully applied to corrosion in concrete, soils, chemical plants, and oil and gas industries [1,50,83]. Often referred to as electronic coupons or ER-probes, these sensors are widely adopted thanks to their relatively simple operation, limited maintenance requirements, straightforward data interpretation, and reliability. For these reasons, several commercial solutions are already available [1,83]. The working principle relies on the correlation between electrical resistance and the geometry of the metallic probe. Assuming a constant, rectangular cross-sectional area A along the length l , resistance results are as follows:

$$R = \frac{\rho \cdot l}{A} = \frac{\rho \cdot l}{w \cdot h} \quad (1)$$

where ρ is the resistivity of the material, w is the width, and h is the thickness of the corroding element. An increase in resistance can thus be attributed to a reduction in the cross-sectional area due to corrosion, providing information analogous to that obtained from mass loss measurements. Since the first attempts at monitoring atmospheric corrosivity with ER-based sensors [37,45], the comparability of ER data with weight-loss results has been clearly demonstrated.

Assuming $h \ll w$, namely that thickness is much smaller than width, the decrease in A can be fully attributed to thickness reduction due to corrosion. Under these conditions, it

is important to assess the relative sensitivity S of the resistance with respect to corrosion (i.e., to the thickness reduction). From a mathematical point of view, it is the derivative of the resistance R with respect to $-h$ divided by R , namely

$$S = -\frac{1}{R} \frac{dR}{dh} = \frac{1}{h} \quad (2)$$

Therefore, sensitivity is enhanced by reducing thickness. In the cultural heritage field, promising results have been obtained with ER sensors developed within the MUSECORR and CORRLOG projects [41–45,58,83]. These sensors, typically consisting of metallic tracks of varying thicknesses, allowed corrosion monitoring of different metals under both mild and aggressive environments. Thin tracks (25–800 nm) proved effective for detecting very low corrosion rates in indoor environments on copper [41,42,84], silver [41,42], lead [42], iron [42] and bronze [58], whereas thicker tracks (5–250 μm) were applied for outdoor or more aggressive conditions on copper, silver, lead, iron, zinc, aluminium, tin, bronze, and brass [53]. Customisation of track thickness according to exposure conditions enabled reliable and sensitive monitoring, with detection limits as low as 1 nm/h when relative humidity exceeded 50% [42,85].

Resistivity of conductors is sensitive to temperature, which has to be properly considered for corrosion monitoring. This can be addressed by designing sensors with paired tracks: one exposed to the environment and one protected as a reference, but subject to virtually the same temperature. By simultaneously measuring the resistance of both tracks, temperature-induced variations could be compensated, allowing a more accurate estimation of thickness loss Δh and corrosion rate. A first mathematical relation was proposed by Sjögren and Le Bozec [44]:

$$\Delta h = h_0 \left(1 - \frac{R_r}{R_c} \cdot \frac{R_{r,0}}{R_{c,0}} \right) \quad (3)$$

where R_r and R_c are the electrical resistances of the reference and corroded tracks at the generic time instant, $R_{r,0}$ and $R_{c,0}$ their initial values, and h_0 , the initial thickness, are assumed to be identical for both the reference and corroded track. However, this last assumption is rather weak in practical implementations, in particular when adopting a very small thickness for increasing sensitivity. To overcome this limitation, a modified expression has then been proposed (Equation (4) [58]):

$$\Delta h = h_{r,0} \left(\frac{R_{r,0}}{R_{c,0}} - \frac{R_r}{R_c} \right) \quad (4)$$

where $h_{r,0}$ is the thickness of the reference track, which is assumed to be constant and, in general, it could be different from the initial thickness of the corroded track. This refinement improves the reliability of the calculated values and facilitates practical implementation.

Despite these technological advancements, most ER sensors developed so far for cultural heritage applications rely on uncorroded metals. Such surfaces do not adequately reproduce the real conditions of historical artefacts, which are almost invariably covered by natural or artificial patinas and stratified corrosion layers. Considering these layers, whose chemical composition and morphology strongly influence corrosion behaviour [64,86–88], is essential when designing representative monitoring systems [39] or mock-ups.

For this reason, there is a need to design ER sensors that can be pre-patinated or pre-corroded, in order to better simulate the behaviour of heritage surfaces. However, introducing an artificial patina generally requires a higher initial track thickness, which inevitably reduces the relative sensitivity S , as from Equation (2). This trade-off highlights the importance of optimising sensor design to balance representativeness and sensitivity.

Building on previous work, the present study proposes the development of customised ER sensors that can act as realistic mock-ups of corroded heritage surfaces. Such pre-patinated sensors not only enable more representative corrosion monitoring, but they also provide a safe platform to test conservation treatments and evaluate their long-term performance under real or simulated conditions. This approach is particularly relevant in the cultural heritage field, where testing on original artefacts is not acceptable due to their uniqueness and irreplaceable historical and artistic value.

2. Design of Customised ER Sensors

2.1. Design Rationale: Geometry, Materials, and Fabrication Methods

To develop realistic mock-ups for corrosion monitoring and for the study of new conservation methods for patinated copper alloy objects, customised ER sensors were designed with geometries and materials tailored to simulate the surface conditions of heritage metals. Two fabrication approaches were adopted: printed circuit board (PCB) technology and lift-off (LO) lithographic processes. PCB sensors were realised on polymeric substrates with copper tracks of 17 μm thickness, while LO sensors were fabricated on glass wafers with copper tracks of 5 μm and 0.25 μm thickness. The choice of substrate and track thickness was guided by the need to balance sensitivity, durability, and compatibility with artificial patination procedures.

The sensor geometry was optimised to ensure sufficient sensitivity to detect low corrosion rates, while maintaining mechanical and chemical stability during long-term exposure. Thinner tracks (e.g., 0.25 μm) offer higher sensitivity but reduced lifespan, whereas thicker tracks (e.g., 17 μm) allow for pre-corrosion treatments, but they require more accurate resistance measurements for detecting a given corrosion level.

2.2. Challenges Related to Pre-Patination, Thickness and Sensor Lifespan

A patinated sensor, which is an ER sensor subject to a pre-corroding process to mimic real artefact surfaces, introduced challenges in terms of track thickness loss. Masking techniques were applied during patination to avoid the deposition of corrosion products in between the copper tracks. The monitoring was temporarily suspended during the corrosion layer formation. The patination process itself caused significant thickness reduction, which was carefully quantified and considered in the corrosion rate calculations.

2.3. Goal: Realistic Yet Functional and Adaptable Sensors

The ultimate goal was to produce ER sensors that could serve both as tools for monitoring atmospheric corrosivity and as representative mock-ups of heritage surfaces. By integrating artificial patinas and temperature compensation strategies, the sensors were adapted to various environmental conditions and corrosion scenarios, enabling reliable and reproducible measurements.

3. Materials and Methods

3.1. Sensor Fabrication Processes (PCB and LO Technologies)

Two types of customised ER sensors were fabricated to simulate the corrosion behaviour of heritage copper alloys (Figure 1). The first type was produced using printed circuit board (PCB) technology on polymeric substrates, with copper tracks having 17 μm thickness and 2 mm width. These sensors were double-faced, with tracks on both sides of the support. One face was exposed to corrosion, while the other served as a reference for temperature compensation. Electrical resistance was measured using the four-wire method, with current applied between inner terminals A and B and voltage drop measured between outer terminals C and D.

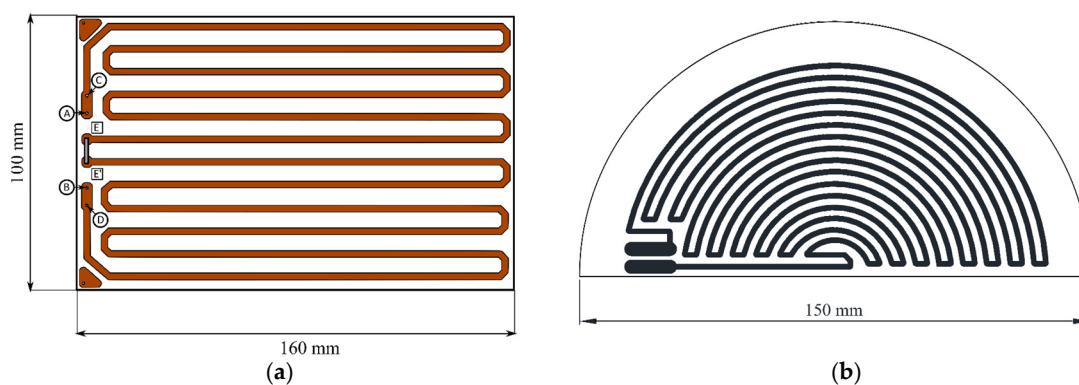


Figure 1. (a) Design of sensors produced by printed circuit board technology (PCB); (b) design of sensors produced by lift-off methodology (LO).

The second type was fabricated using a lift-off (LO) lithographic process on glass wafers. Copper tracks of 5 μm and 0.25 μm thickness were deposited via e-beam evaporation over a chromium adhesion layer. Photolithography was performed using AZ5214E (reversal mode) for the 0.25 μm sensors and AZnLOF2070 for the 5 μm sensors. LO sensors included one reference track and multiple corroding tracks, with the same measurement protocol adopted for PCB sensors. For PCB sensors, the reference track (R_r) was identical in design to the corroding track (R_c), but was located on the opposite side of the substrate; Figure 1a shows only the R_c face. The R_r track was supplied with a polymeric protective layer, applied during PCB fabrication. For LO sensors, a single track of the same design as in Figure 1b served as reference for multiple corroding tracks; it was protected with a double layer of Incralac[®] (INCRA, New York, NY, USA) and was not subjected to the patination process. The protective layer applied to R_r of PCB sensors successfully resisted the patination conditions, while for LO sensors this was not an issue, since the reference track was on a separate substrate. The choice of substrate and fabrication method was guided by the need to ensure compatibility with artificial patination procedures and long-term stability under varying environmental conditions.

3.2. Artificial Patination Procedures

Three artificial patinas were applied to copper specimens and selected ER sensors to replicate corrosion layers typically found on heritage surfaces. The procedures were adapted from both the literature and previous studies and further optimised in a previous work [89]. For each patination condition, at least two sensors were fabricated to ensure reproducibility; however, not all patinas were applied to both sensor types. Cuprite patina with the “boiling solution” recipe and the chloride- and sulphate-rich patina produced by the “applied paste” method were realised both on PCB and LO sensors. Brochantite-based patina was instead realised only on LO sensors. The recipes are briefly summarised below:

- **Cuprite (boiling solution):** Immersion in a boiling solution of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ (6.25 g/L), $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$ (1.25 g/L), NaCl (2 g/L), and KNO_3 (1.25 g/L) (Sigma-Aldrich, St. Louis, MO, USA), followed by rinsing and drying and applied on PCB and LO (5 μm) sensors [90]. This procedure was selected for its capability to produce a homogeneous and adherent reddish cuprite layer, representative of the initial stages of atmospheric corrosion [89].
- **“Applied paste” with chlorides and sulphates:** Mixture of CuCl , $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, and $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ (3:1:4) (Sigma-Aldrich, St. Louis, MO, USA), ground and mixed with water (1:2), applied by brush, and applied on PCB and LO (5 μm) sensors. This procedure was adapted from [90,91]. This patina was designed to simulate highly aggressive and

unstable corrosion layers, typical of polluted and chloride-rich environments, and to represent a worst-case scenario for conservation testing [89].

- **Brochantite patina:** Immersion in a 5.4 g/L boiling solution of CuSO_4 (Sigma-Aldrich, St. Louis, MO, USA) for 1 h, followed by 10 wet/dry cycles in 8 g/L CuSO_4 solution (2 days immersion, 2 days drying) and applied on LO (5 μm) sensors. This procedure was adapted from [92]. This method was chosen to reproduce a very common and stable sulphate-based corrosion product typically found on outdoor bronze surfaces in urban environments [89]. Surfaces were degreased with ethanol, and, during patination, masking was used to prevent conductive bridges between adjacent tracks. Monitoring was suspended during patina formation. This patina was not applied to PCB sensors due to the limited number of available monitoring channels. Given the higher sensitivity of LO sensor tracks compared to PCB sensors while considering the literature data indicating that brochantite is a relatively stable corrosion product, it was assumed reasonable to apply this patina only to the LO sensors.

Selected photographs of representative pre-patinated ER sensors are shown in Figure 2 to illustrate the appearance of the different artificial patinas applied. Examples include PCB and LO sensors treated with the procedures described above: (a) PCB sensor with cuprite patina obtained by immersion in the “boiling solution”; (b) LO sensor with brochantite patina; (c) PCB sensor and (d) LO sensor with atacamite patina produced by the “applied paste” method.

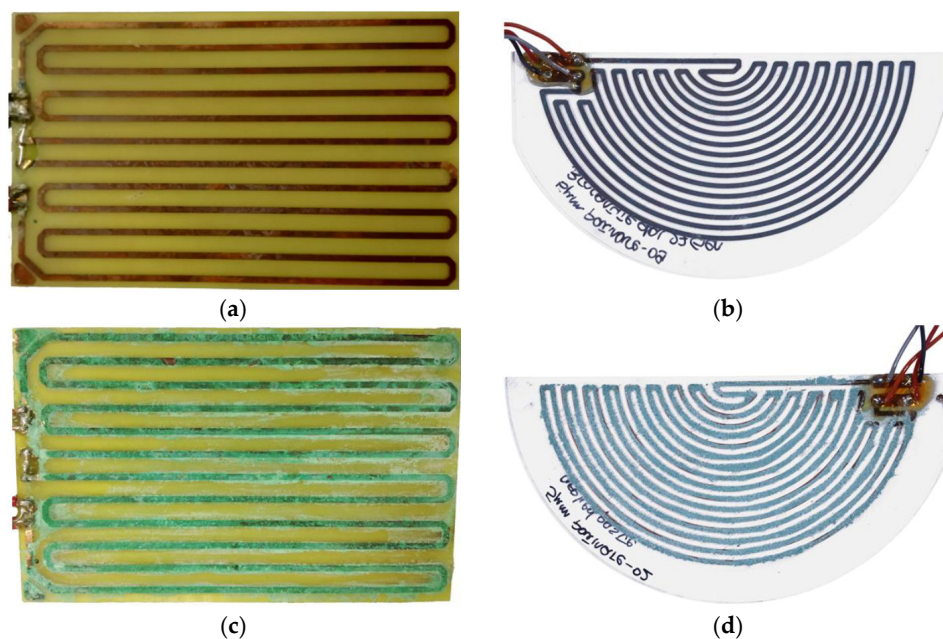


Figure 2. Selected examples of pre-patinated ER sensors: (a) PCB ER-based sensor with cuprite patina by immersion in “boiling solution”; (b) LO ER-based sensor with brochantite patina; (c) PCB and (d) LO ER-based sensors with atacamite patina produced by “applied paste method”.

3.3. Experimental Setup

Sensors were exposed to variable environmental conditions in a climatic chamber. Relative humidity (RH) ranged from 20% to 90%, and temperature was maintained close to 25 °C. It should be noted that the climatic chamber used in this study was a custom, home-made device. The RH level in the test chamber is controlled by an RH control group MCG4 via two ventilation pipes, whose activity is regulated by an internal humidity sensor. Both temperature and relative humidity have been monitored with dedicated sensors. In particular, Testo 175 H and Testo Comfort Software Basics 5.0. (Testo SE & Co.,

Titisee-Neustadt, Germany) were used for RH monitoring, while a PT100 resistor with a 316 L stainless steel tip having a 6 mm diameter, directly connected with the Keithley 3706 multimeter (Keithley Instruments, Solon, OH, USA), was adopted to measure its resistance and thus temperature. Due to limitations of the climatic chamber, relative humidity and temperature could not always be precisely controlled, which represents a significant limitation of this study. This lack of control affected the ability to establish a clear correlation between RH fluctuations and corrosion rate, making data interpretation more challenging. PCB sensors were monitored for up to 300 days, while LO sensors were monitored for up to 120 days. Thickness loss due to corrosion was calculated from electrical resistance variations, using temperature compensation via reference tracks.

Although it is always useful and interesting to compare the results obtained with ER sensors to weight-loss measurements, such measurements were not performed in this study. This decision was due to the difficulty of separating the mass loss caused by the patination process from that resulting from subsequent exposure to controlled humidity and temperature. This challenge is further compounded by the extremely small thickness variations involved, which would require extremely long-term monitoring to obtain reliable gravimetric data. It is important to note that the good correlation between ER sensor measurements and weight-loss coupons has already been demonstrated in previous works and, in particular, in a recent work [93]. ER-probes showed good agreement with weight-loss measurements across different environments, with differences generally below 30% and never exceeding 45%. Overall, ER-probes proved a reliable alternative to gravimetric methods for long-term monitoring. Moreover, the only real interpretative limitation of ER sensors relates to possible localised corrosion phenomena—a challenge that also affects weight-loss methods, leading to underestimation. For these reasons, ER sensors were considered a robust and validated approach for the scope of this study.

3.4. ER Measurement Protocol and Temperature Compensation Strategy

Electrical resistance was measured periodically using the four-wire method with a Keithley 3706 high-resolution multimeter equipped with 3721 multiplexer cards. The time interval between each ER measurement was 15 min. Temperature effects were compensated by monitoring the resistances of both exposed and reference tracks. The expression proposed by Kouril et al. [42] was used to calculate thickness loss. In LO sensors, reference tracks were placed on separate substrates, which introduced challenges in temperature compensation, especially when patina thickness differed significantly from the copper track.

4. Results

4.1. Sensor Not Subject to Pre-Corrosion

As expected, the PCB sensor geometry did not provide sufficient sensitivity to detect atmospheric corrosion on non-pre-corroded sensors. Even under high relative humidity conditions (above 80%), no significant resistance variation, and thus thickness loss, was observed (Figure 3). The minor fluctuations recorded on one of the sensors (Figure 3, yellow line) between days 200 and 300 are attributed to disturbances rather than actual corrosion. This is consistent with the known detection limit of the measurement system, which is unable to reliably detect thickness variations below 3 nm [94]. The investigation shows that the most significant uncertainty contribution is not introduced by the adopted instrumentation, but instead it comes from a non-ideal temperature compensation, due to the (small) temperature gradient between the exposed and reference track. In fact, using (4) for evaluating thickness reduction implicitly assumes that the corroded and reference track have the same temperature. In this respect, it is possible to derive a simple

approximated expression quantifying the impact δh_T on the measured thickness reduction due to the temperature difference ΔT between the corroded and reference track. Using (4), considering the temperature coefficient α of copper and linearizing the expression results in the following:

$$\delta h_T \approx h_{r,0} \alpha \Delta T \quad (5)$$

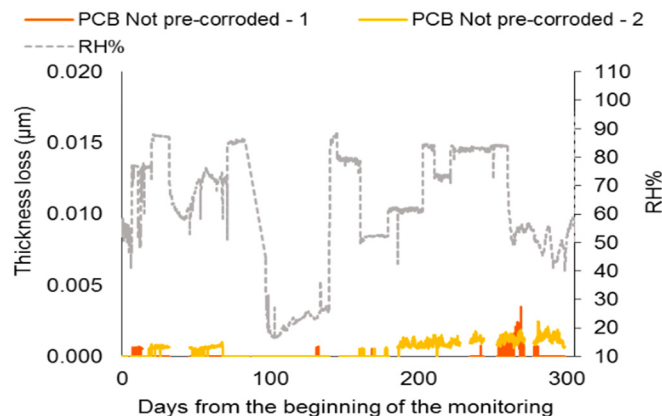


Figure 3. Thickness loss of not pre-corroded PCB sensors during the entire monitoring period.

Therefore, $\alpha \approx 3.9 \times 10^{-3} \text{ } ^\circ\text{C}^{-1}$ represents the apparent relative thickness variation for every degree of temperature difference between reference and corroded trace. Thus, a 3 nm peak-to-peak ripple of the evaluated thickness is produced by a $0.03 \text{ } ^\circ\text{C}$ temperature oscillation between traces. From a different point of view, measuring a given thickness reduction adopting thicker traces makes it more sensitive to temperature gradients.

A similar limitation was observed for LO sensors with $5 \text{ } \mu\text{m}$ thick tracks (Figure 4a). In this case, the signal was highly disturbed and did not allow for the identification of any significant thickness loss. It should be noted, however, that relative humidity exceeded 60%—a commonly reported threshold for copper corrosion initiation only for a few days during the monitoring period. Additionally, the reference track used for temperature compensation was not located on the same substrate as the exposed track, although it was positioned nearby within the same climatic chamber. This configuration may have introduced additional uncertainty due to imperfect thermal matching between the two supports, which, as previously discussed, represents a major uncertainty source. If we consider a $0.03 \text{ } ^\circ\text{C}$ oscillation between the temperature of the corroded and reference track, this effect alone results in a variation in the measured thickness reduction of about 0.5 nm.

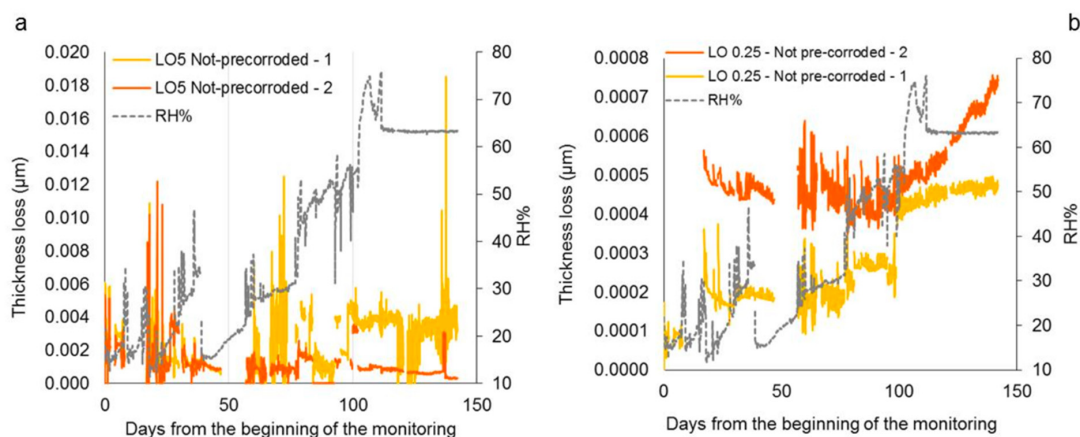


Figure 4. Thickness loss of not pre-corroded LO sensors during the entire monitoring period. (a) Sensors with $5 \text{ } \mu\text{m}$ track; (b) sensors with $0.25 \text{ } \mu\text{m}$ track.

In contrast, the LO sensors with 0.25 μm thick tracks showed a measurable response when RH exceeded 60% (Figure 4b). After day 100, a thickness reduction of approximately 0.1 nm for sensor 1 and of 0.4 nm for sensor 2 was observed. As it can be observed, these two LO sensors exhibited slightly different responses. This variability anticipates what is discussed later in this work: in general, LO sensors showed lower reproducibility compared to PCB sensors, likely due to the reference track being located on a separate substrate, which may have affected temperature compensation, and possibly also due to microstructural differences related to the fabrication method. These sensors were specifically designed to enhance sensitivity compared to the PCB configuration, thanks to reduced thickness. Based on the slope of the thickness loss curve, a corrosion rate of approximately 0.003 $\mu\text{m}/\text{year}$ was calculated for the most responsive sensor (sensor 2, Figure 5). This value aligns well with the literature data: Prosek et al. [58] reported detectable corrosion on 0.5 μm copper sensors exposed to RH above 50%, with a corrosion rate of 0.025 $\mu\text{m}/\text{year}$ under constant 85% RH over 30 days. The measured thickness loss exhibits oscillations of about 0.05 nm, corresponding to 0.05 $^{\circ}\text{C}$ temperature deviation between exposed and corroded trace.

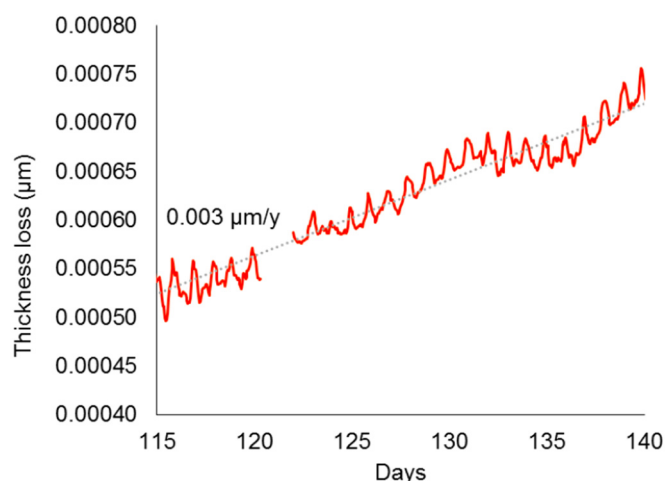


Figure 5. Thickness loss of not pre-corroded sensor (LO—not pre-corroded—2) in controlled environment with constant relative humidity ($\approx 60\%$), with indication of the estimated corrosion rate. The solid red line represents the measured thickness loss, while the dashed line corresponds to the linear regression.

4.2. Thickness Loss Induced by Artificial Patination

Figure 6 illustrates the thickness loss experienced by all sensors throughout the monitoring period. For clarity, Table 2 summarises the timeline of each patination process and the beginning of the post-stabilisation monitoring (t_0) for all sensor types. This includes patination duration and the day when post-patination monitoring started, to help interpret the thickness loss trends shown in the figures. Patinas were considered stabilised when the thickness loss curve displayed a linear trend under constant relative humidity, indicating the attainment of a stationary condition, where the corrosion rate remains approximately constant. A sharp and immediate reduction in track thickness is clearly visible for both PCB and LO sensors, corresponding to the artificial patination. Results indicate that the patination process itself accounts for most of the total thickness loss observed on the copper tracks.

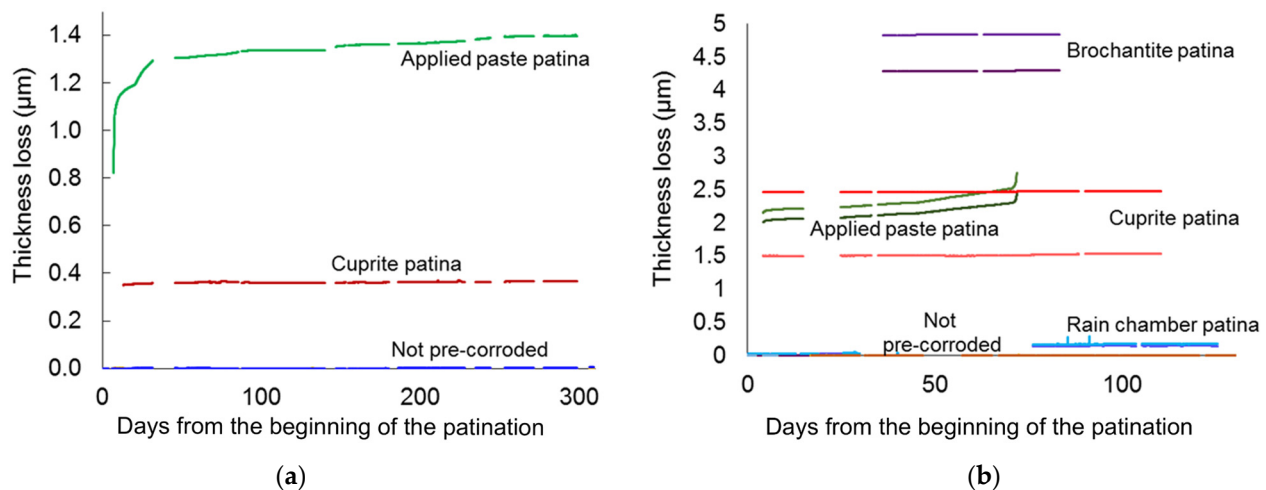


Figure 6. Thickness loss during the entire monitoring period, including the sharp initial increase due to patination and subsequent stabilisation: (a) PCB sensors; (b) 5 μm LO sensors. For clarity, details of the timeline for each patina and type of sensor, including patination duration and beginning of monitoring (t_0), are reported in Table 2.

Table 2. Timeline of each patination process and the start of post-stabilisation monitoring (t_0) for all sensor types *.

Patina	Sensor Type	Patination Details	t_0 —Start of Post-Stabilisation Monitoring
Cuprite (boiling)	PCB	Day 0–1 (single immersion in boiling solution)	Day 14
Cuprite (boiling)	LO	Day 0–1	Day 5
Applied paste	PCB	First layer: Day 0; Second layer: Day 20	Day 45
Applied paste	LO	First layer: Day 0; Second layer: Day 20	Day 5
Brochantite	LO	Day 0 (immersion in boiling solution + wet/dry cycles)	Day 35

* A technical interruption occurred between day 30 and day 45 for all sensors. Other short monitoring interruptions occurred at different times during the entire monitoring period.

In the case of PCB sensors, the cuprite patina produced via the boiling solution patination started on day 0 and ended on day 1 (single immersion in boiling solution). Monitoring resumed after approximately two weeks (day 14), following patina stabilisation. The thickness loss measured at the beginning of the monitoring period corresponds to the patination process and its subsequent stabilisation. Figures showing corrosion trends after t_0 refer exclusively to the post-patination period. This patination process resulted in a relatively moderate thickness reduction—significantly lower than that caused by the “applied paste” method used to generate a chloride- and sulphate-rich patina. For the latter, patination started on day 0 with the first layer and continued on day 20 with the second layer, applied without interrupting the monitoring. Stabilisation was considered complete when the slope of the thickness loss curve became linear. It is not possible to provide a precise stabilisation time because a technical interruption occurred for all sensors between day 30 and day 45. The thickness loss measured at the beginning of monitoring reflects the patination process and its subsequent stabilisation. The two distinct sudden increases in thickness loss visible in Figure 6a correspond to the two application layers.

LO sensors, in general, exhibited greater thickness losses than their PCB counterparts. For example, the “applied paste” patina caused a reduction of about 1.3 μm on PCB sensors,

compared to over 2 μm on LO sensors. Similarly, the cuprite boiling solution patina led to a loss of less than 0.4 μm on PCB sensors, while LO sensors showed reductions of 1.5 μm and 2.5 μm , respectively, immediately after patination, as seen in Figure 6b. The consistently higher thickness losses observed on LO sensors suggest that the fabrication method itself may influence the interaction between patina and substrate. This hypothesis deserves further investigation.

The brochantite patination procedure, applied only to LO sensors, proved unexpectedly aggressive, leading to the near-complete consumption of the LO copper tracks (Figure 6b). Patination started on day 0, and monitoring could only begin on day 35 (t_0), when the patina had likely been stabilised for some time. The thickness loss measured at the beginning of monitoring therefore reflects both the patination process and its subsequent stabilisation. As mentioned in the materials and methods section, this patina was not applied to PCB sensors due to the limited number of available monitoring channels. Such a significant thickness loss was not expected and highlights the need for further optimisation of the patination process. Additionally, the two LO sensors suffered significantly different thickness losses.

The significantly faster thickness loss observed in LO sensors compared to PCB sensors strongly suggests that the fabrication methodology plays a decisive role in their corrosion behaviour. Copper films produced by e-beam evaporation and patterned via lift-off are known to grow in a Volmer–Weber (island) mode, often resulting in a columnar microstructure with considerable defect density, vacancies, or voids [95,96]. This porous and less-dense morphology increases the electrochemically active surface area, thereby accelerating the metal dissolution. Conversely, electroplated copper typically exhibits larger grain structures, self-annealing behaviour at room temperature, and overall denser microstructure with fewer defects [97–99]. It is therefore reasonable to attribute the rapid thickness loss of LO copper tracks to their microstructural characteristics—namely, higher porosity and less compact microstructure—stemming from deposition via e-beam evaporation and lift-off patterning. This aspect warrants further investigation to fully elucidate the influence of fabrication-induced microstructural features on corrosion dynamics.

To better isolate the effects of atmospheric corrosion from those due to the patination process, the moment of patina stabilisation was defined as time zero (t_0) for all subsequent analyses. From this point onward, all graphs report only the thickness loss occurring after patina stabilisation, allowing a clearer assessment of how each artificial corrosion layer influences corrosion rates under varying environmental conditions. The monitoring data presented in the following sections, therefore, focus exclusively on the post-patination period, allowing for a clearer assessment of how each artificial corrosion layer influences the corrosion rate under varying relative humidity conditions.

4.3. Pre-Corroded Sensors with Cuprite Patina Produced by “Boiling Solution”

The cuprite patina produced by “boiling solution” was monitored on one PCB sensor and two LO sensors with 5 μm thickness. As previously discussed, even if the same recipe has been followed for the production of the patinas, it caused different thickness loss on the different sensors (Figure 6).

During the post-stabilisation monitoring period, thickness losses due to atmospheric corrosion were clearly detectable on both PCB and LO sensors. As illustrated in Figures 7 and 8, variations in the slope of the thickness loss curves generally correspond to changes in relative humidity (RH). For instance, between day 200 and 220 on the PCB sensor (Figure 7) and between day 65 and 80 on the LO sensors (Figure 8a), an increase in RH led to a steeper slope, indicating accelerated corrosion. Conversely, when RH decreased, the slope of the curve also diminished. It should be noted that, due to the limitations of the

experimental setup and the technical issues encountered, achieving systematic and periodic control of relative humidity (RH) was not feasible. For this reason, establishing a precise correlation between RH and corrosion rate is not among the primary objectives of this study. The focus is instead on comparing PCB and LO sensor performance, demonstrating the feasibility of producing pre-corroded ER sensors, and highlighting how sensor response varies depending on the corrosion layers present, particularly in chloride-rich patinas. Although a clear correlation could not be established, the graphs still show a consistent trend: the slope of the thickness loss curve (and thus the corrosion rate) increases when RH rises and decreases when RH falls, providing qualitative insight into the influence of RH.

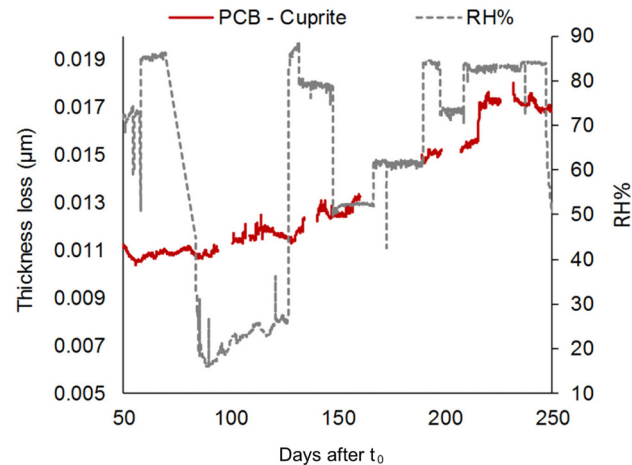


Figure 7. Thickness loss of PCB sensor with cuprite patina, after patina stabilisation.

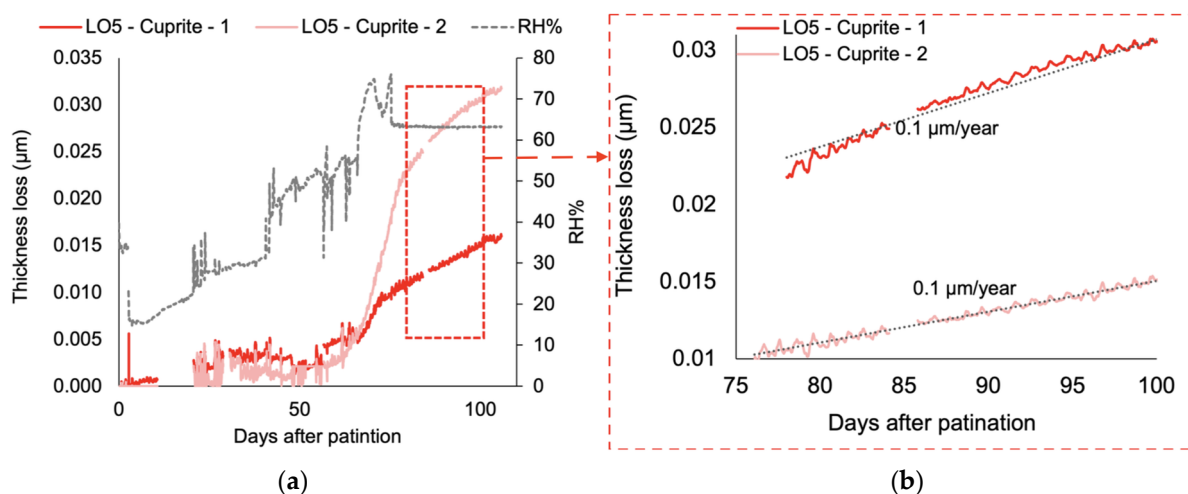


Figure 8. Thickness loss of LO sensors with cuprite patina after patina stabilisation. (a) Entire monitoring period, with variable RH levels; (b) with constant relative humidity ($\approx 60\%$), with indication of the estimated corrosion rate (here the dashed black lines correspond to the linear regressions).

Interestingly, the PCB sensor showed measurable thickness loss even at RH levels around 20–30%, while the LO sensors produced noisier data in the same range. This may be due to the fact that the reference track (R_r) in LO sensors was placed on a separate substrate, albeit within the same climatic chamber, thus reducing the effectiveness of temperature compensation. A clearer thickness reduction was observed on LO sensors when RH exceeded 50% (Figure 8a), with both sensors showing similar trends, although sensor 2 exhibited a more pronounced loss. This could be attributed to the thicker cuprite

layer formed during patination, as sensor 2 had experienced a greater initial thickness reduction (2.5 μm , Figure 6b).

The signals from PCB sensors appeared more disturbed, even at high RH, mostly because of their different geometry and higher initial track thickness (17 μm vs. 5 μm for LO). Nevertheless, both sensor types proved suitable for monitoring environmental corrosivity on copper surfaces with cuprite-based corrosion layers.

A corrosion rate evaluation was possible over a 25-day period in which RH was maintained at 60%. As shown in Figure 8b, the slope of the thickness loss curve remained nearly constant, allowing the calculation of a corrosion rate of 0.1 $\mu\text{m}/\text{year}$ for both LO sensors. During a period of increased RH (70%, day 66–78), higher corrosion rates were recorded—approximately 0.2 $\mu\text{m}/\text{year}$ for sensor 1 and 0.4 $\mu\text{m}/\text{year}$ for sensor 2. These results confirm the good reproducibility of LO sensors pre-corroded with the same procedure and highlight their effectiveness in capturing corrosion dynamics under varying environmental conditions.

A plausible explanation for the unexpected corrosion activity at such low RH is the presence of residual hygroscopic compounds within the cuprite layer formed by the boiling solution method. FTIR spectra confirmed the presence of cuprite only, but CuCl and NaCl—both strongly hygroscopic and, in the case of CuCl, highly aggressive—cannot be detected in the mid-infrared region and may have remained embedded in the patina in low amounts. This interpretation is consistent with electrochemical data: the cuprite obtained by boiling solution exhibited a very low R_p [89], whereas preliminary tests on cuprite patinas produced without chlorides showed R_p values almost one order of magnitude higher. These findings suggest that, despite its homogeneous reddish appearance, the “boiling” cuprite does not provide effective protection to the underlying copper substrate and may even accelerate corrosion: the boiling solution recipe used in this work may form a patina representative of cuprite formed in chloride-rich environments, which explains why corrosion rates remain measurable even at low RH. Another possible explanation for this behaviour is that the cuprite formed under boiling conditions may grow predominantly through precipitation from the solution rather than through electrochemical corrosion of the metal surface. While this hypothesis is not directly demonstrated in the literature, it is consistent with the observed differences in corrosion resistance and with the nature of the patination procedure, which involves immersion in a hot, reactive solution rather than exposure to atmospheric agents. This interpretation finds indirect support in the work of Thoury et al. (2016) [100], who showed that cuprite formed by eutectic solidification during casting (eu-Cu₂O) differs structurally and optoelectronically from corrosion-grown cuprite (co-Cu₂O). The former exhibits intense photoluminescence due to oxygen vacancies, while the latter does not, likely due to its slower growth and more ordered crystal structure. Similarly, Li et al. (2019) [101] observed distinct cuprite phases within corroded copper artefacts, suggesting that formation conditions may significantly influence cuprite properties.

Later in the paper, these electrochemical results (LPR/EIS) are compared with data obtained from ER sensors, allowing further insight into the reactivity and stability of the different patinas.

4.4. Pre-Corroded Sensors with Chloride- and Sulphate-Rich Patinas by “Applied Paste” Method

The chloride and sulphate-rich patina realised with the “applied paste” method was applied to one PCB and two LO sensors with an initial copper track thickness of 5 μm . The monitoring results following patina stabilisation are shown in Figures 9 and 10. For both sensor geometries, the corrosion-induced thickness losses were clearly detectable, confirming the effectiveness of the ER-based approach even in the presence of highly aggressive corrosion layers.

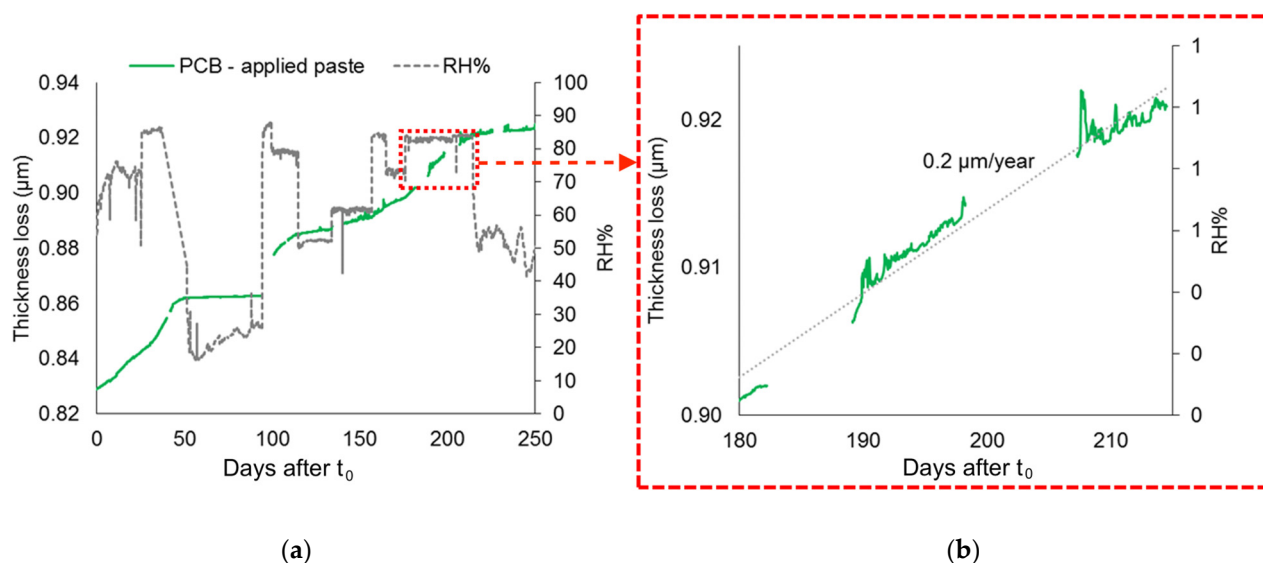


Figure 9. Thickness loss of PCB sensors with “applied paste” patina after the patina stabilisation. (a) Entire monitoring period, with variable RH levels; (b) with constant relative humidity ($\approx 80\%$), with indication of the estimated corrosion rate (here the dashed black lines correspond to the linear regressions).

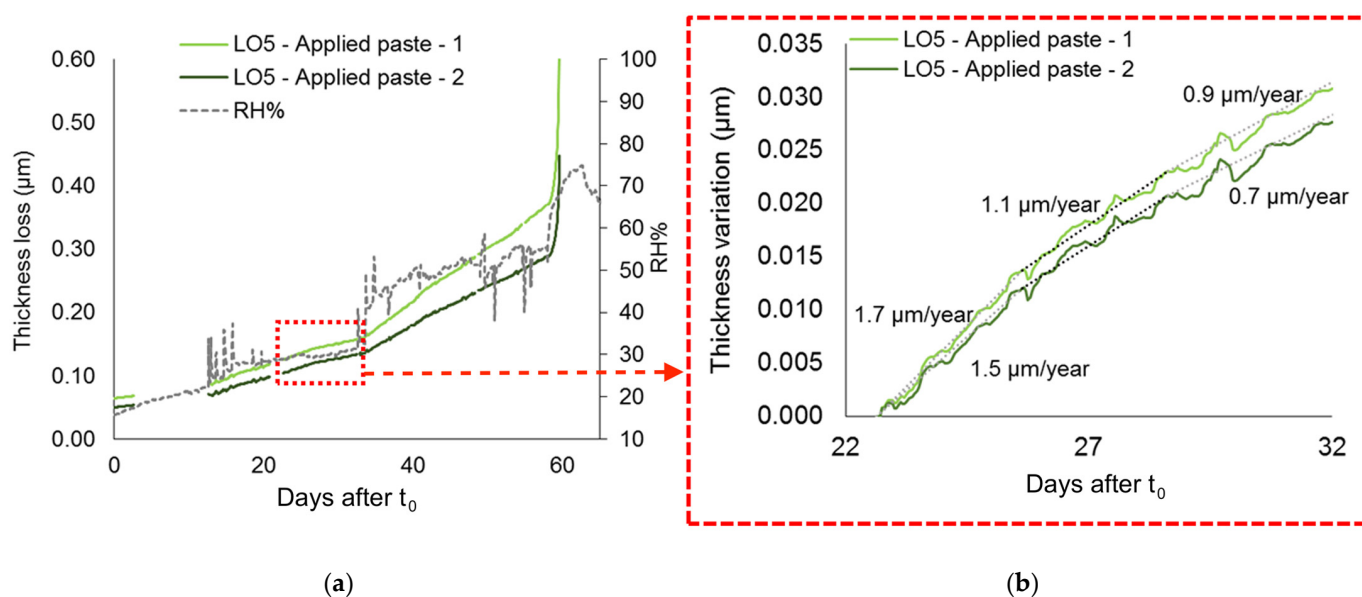


Figure 10. Thickness loss of LO sensor with “applied paste” patina after the patina stabilisation. (a) Entire monitoring period, with variable RH levels; (b) with constant relative humidity ($\approx 30\%$), with indication of the estimated corrosion rates (here the dashed black lines correspond to the linear regressions).

Sensors with the “applied paste” patina exhibited a higher sensitivity to changes in environmental relative humidity (RH) compared to those with cuprite patina. This is evident from the more pronounced variations in the slope of the thickness loss curves (Figures 9a and 10a). Notably, corrosion was measurable on both PCB and LO sensors when RH exceeded 20%, while no significant thickness variation was observed below this threshold—despite the high reactivity of the patina. This observation aligns well with the literature data, which suggests that atmospheric corrosion is negligible below 20% RH [47], even in the case of highly destabilising corrosion products [64,102]. This behaviour of these pre-corroded sensors was expected, as the applied paste patina was deliberately

formulated to reproduce highly critical conservation conditions, typical of chloride-rich layers containing CuCl—a compound known to be highly hygroscopic and destabilising, often associated with severe deterioration phenomena such as bronze disease. Its presence explains why corrosion activity persists even under nominally dry conditions, confirming the suitability of this patina for simulating worst-case conservation scenarios.

Unfortunately, the LO sensors could only be monitored for 60 days after patination. Around day 58, following three consecutive days at 70% RH, a sharp increase in thickness loss was recorded (Figure 10a). Monitoring was then interrupted due to a sudden increase in R_c . Although the total thickness loss (2.7 and 2.5 μm , respectively) remained below the initial track thickness (5 μm), the data suggest the onset of localised corrosion. This phenomenon is a known limitation of ER sensors: as mentioned in the Introduction, the underlying model assumes uniform thickness. On the other hand, a localised thickness reduction produces a significant increase in resistance, potentially leading to misinterpretation of data and premature sensor failure. In this case, localised corrosion may have been triggered by the presence of highly reactive corrosion products and the narrower track width and more defective microstructure of LO sensors compared to PCB ones. Moreover, thinner tracks, leading to higher sensitivity, are more prone to suffering from premature failures due to localised corrosion.

These results confirm that both sensor geometries are capable of monitoring environmental corrosivity on surfaces with aggressive corrosion layers. However, they also indicate that the PCB configuration may be more suitable in such scenarios, offering greater robustness and longer service life.

By analysing the slope of the thickness loss curves, it was possible to evaluate the variations in corrosion rate over time. During the initial monitoring period, particularly in the first 40 days after patination, the PCB sensor exhibited a very high corrosion rate of 10 $\mu\text{m}/\text{year}$ under RH levels between 70% and 80% (Figure 9a). Such a fast rate is primarily attributed to the fact that the patina had not yet reached a stationary condition after its application. The “applied paste” method produces a layer containing highly reactive compounds, including CuCl, which strongly promote corrosion when RH increases. These compounds gradually react over time, progressively transforming into less aggressive forms, reducing the initial aggressiveness of the patina; however, due to their hygroscopic and destabilising nature, this type of patina is unlikely to achieve true stabilisation, even after prolonged exposure. This interpretation is supported by the significant reduction in corrosion rate observed later: after a long period of exposure involving several RH cycles, between day 180 and 215 under constant RH of about 80%, the corrosion rate dropped to 0.2 $\mu\text{m}/\text{year}$. These findings suggest that the time required for the patina to approach a stationary condition can vary significantly, depending on the patination method. In the case of the “applied paste,” the initial reactivity is particularly high, and the process leading to a more stable behaviour may extend over several weeks. However, given the hygroscopic and destabilising nature of compounds such as CuCl, a true stabilisation is unlikely.

For the LO sensors, a corrosion rate of 2.2 $\mu\text{m}/\text{year}$ was recorded between day 35 and 55, when RH increased from 45% to 55% (Figure 10a). This rate corresponds to a highly corrosive atmosphere according to European standards [103]. Even under moderately low-RH conditions ($\approx 30\%$), corrosion remained active: during a 10-day period at this level, rates of 1.7 and 1.5 $\mu\text{m}/\text{year}$ were measured on the two LO sensors (Figure 10b). These values then decreased to 0.7 and 0.9 $\mu\text{m}/\text{year}$, respectively, indicating a gradual stabilisation of the corrosion layer, especially under lower humidity [64,102]. These results confirm that the “applied paste” patina remains highly reactive even at RH levels just above the 20% threshold, and that corrosion rates tend to decrease progressively as the

patina evolves toward a less reactive state. A true stabilisation is unlikely expected due to the presence of hygroscopic and destabilising compounds such as CuCl .

4.5. Pre-Corroded Sensors with Brochantite Patina

Brochantite patina was applied to two LO sensors with an initial copper track thickness of $5\text{ }\mu\text{m}$. As shown in Figure 6, this patination method caused the most significant thickness loss among all tested procedures that were considered suitable for pre-corroded sensor fabrication.

After the corrosion layer had stabilised (Figure 11), the sensors were exposed to environmental conditions with RH maintained between 50% and 80%. Under these conditions, the sensors successfully captured variations in corrosion rate as a result of RH fluctuations. For instance, between day 7 and day 17, when RH reached approximately 70%, corrosion rates of $0.15\text{ }\mu\text{m}/\text{year}$ and $0.11\text{ }\mu\text{m}/\text{year}$ were recorded for sensor 1 and sensor 2, respectively. In the subsequent period (day 17 to day 36), when RH stabilised above 60% (Figure 10b), corrosion rates decreased to $0.05\text{ }\mu\text{m}/\text{year}$ and $0.04\text{ }\mu\text{m}/\text{year}$, respectively. These results confirm the good reproducibility of LO sensors in monitoring corrosion dynamics under mildly humid conditions.

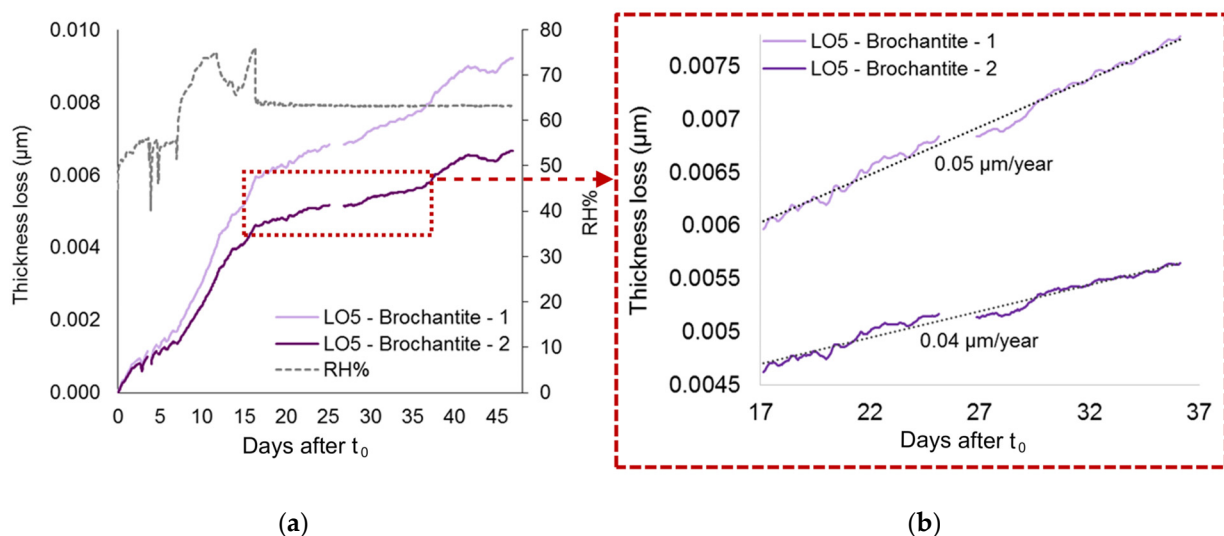


Figure 11. Thickness loss of LO sensors with $5\text{ }\mu\text{m}$ track, with brochantite patina after the patina stabilisation: (a) Entire monitoring period, with variable RH levels; (b) with constant relative humidity ($\approx 60\%$), with indication of the estimated corrosion rate (here the dashed black lines correspond to the linear regressions).

Temperature Compensation and Signal Artefacts

Despite the overall reliability, the thickness loss curves for brochantite sensors displayed some artefacts, particularly between day 2–7 and day 35–47.

These oscillations appear to be linked to suboptimal temperature compensation. As illustrated in Figure 12, the fluctuations in thickness loss are negatively correlated with temperature variations, suggesting a mismatch in thermal response between the corroded and reference tracks. This issue is likely exacerbated by the sensor design: in LO sensors, the reference track (R_r) is placed on a separate substrate, which may experience slightly different thermal conditions compared to the corroded track (R_c). Additionally, the brochantite patina is expected to be significantly thicker than the residual copper track, potentially altering the thermal behaviour of the sensor and further jeopardising the effectiveness of temperature compensation. These findings highlight the importance of co-locating R_r and R_c within the same substrate to ensure accurate temperature correction, which represents

the performance bottleneck. Moreover, the possibility of pre-corroding both tracks should be considered, so that they share similar thickness and thermal response characteristics.

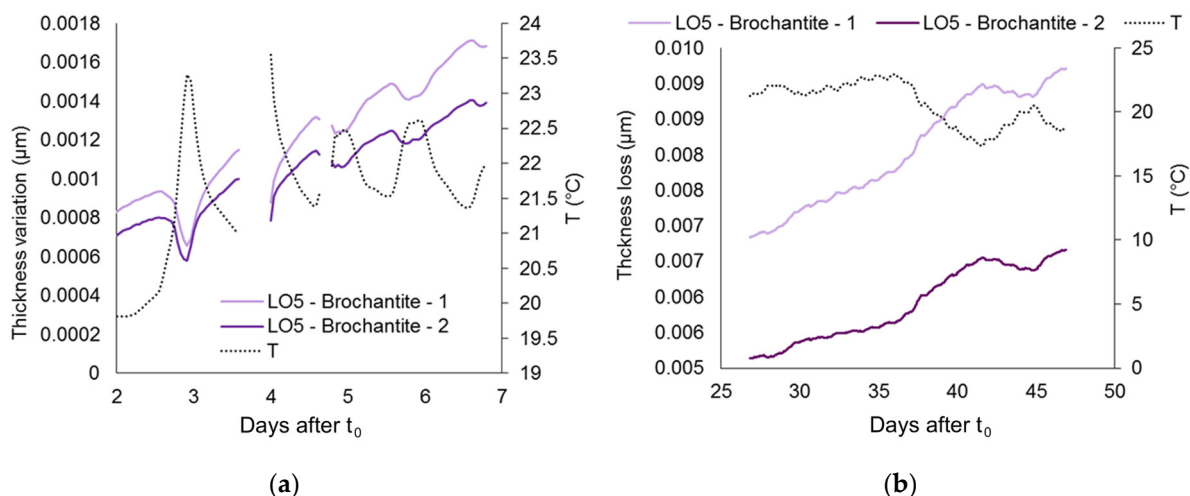


Figure 12. Thickness loss of LO sensor with Brochantite patina after the patina stabilisation and temperature values. (a) from day 2 to day 7 with RH relatively stable around 55%; (b) with constant relative humidity ($\approx 60\%$).

4.6. Corrosion Behaviour of Wet Surfaces: Simulation of Operating Conditions of In Situ LPR and EIS

As discussed in the introduction, in situ LPR and EIS measurements require the constant presence of an electrolyte on the analysed surface. In a previous study [89], electrochemical characterisation of artificial patinas was performed using a ContactProbe setup, where a long-tailed sponge soaked in oligomineral (i.e., low mineral content water) water ensured continuous wetting of the surface during measurements. To simulate these conditions and allow a direct comparison between ER and electrochemical data, the same sponge and electrolyte were applied to a set of PCB sensors for 41 days: one not pre-corroded, one with cuprite patina, and one with the “applied paste” patina.

As shown in Figure 13, the application of the wet sponge caused a sudden and significant increase in thickness loss across all sensors. Figure 14 reports the trends of thickness losses and of the corresponding corrosion rates calculated for each sensor from the slope of the thickness loss curve during the wetting period. For the sensor with the “applied paste” patina, a time-resolved evaluation of corrosion rate was possible. For the cuprite and non-pre-corroded sensors, broader time intervals were used to reduce the influence of disturbances.

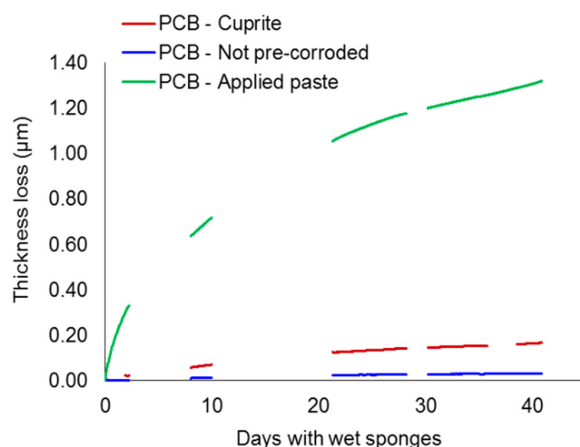


Figure 13. Thickness loss in PCB sensors during the period of application of the wet sponges.

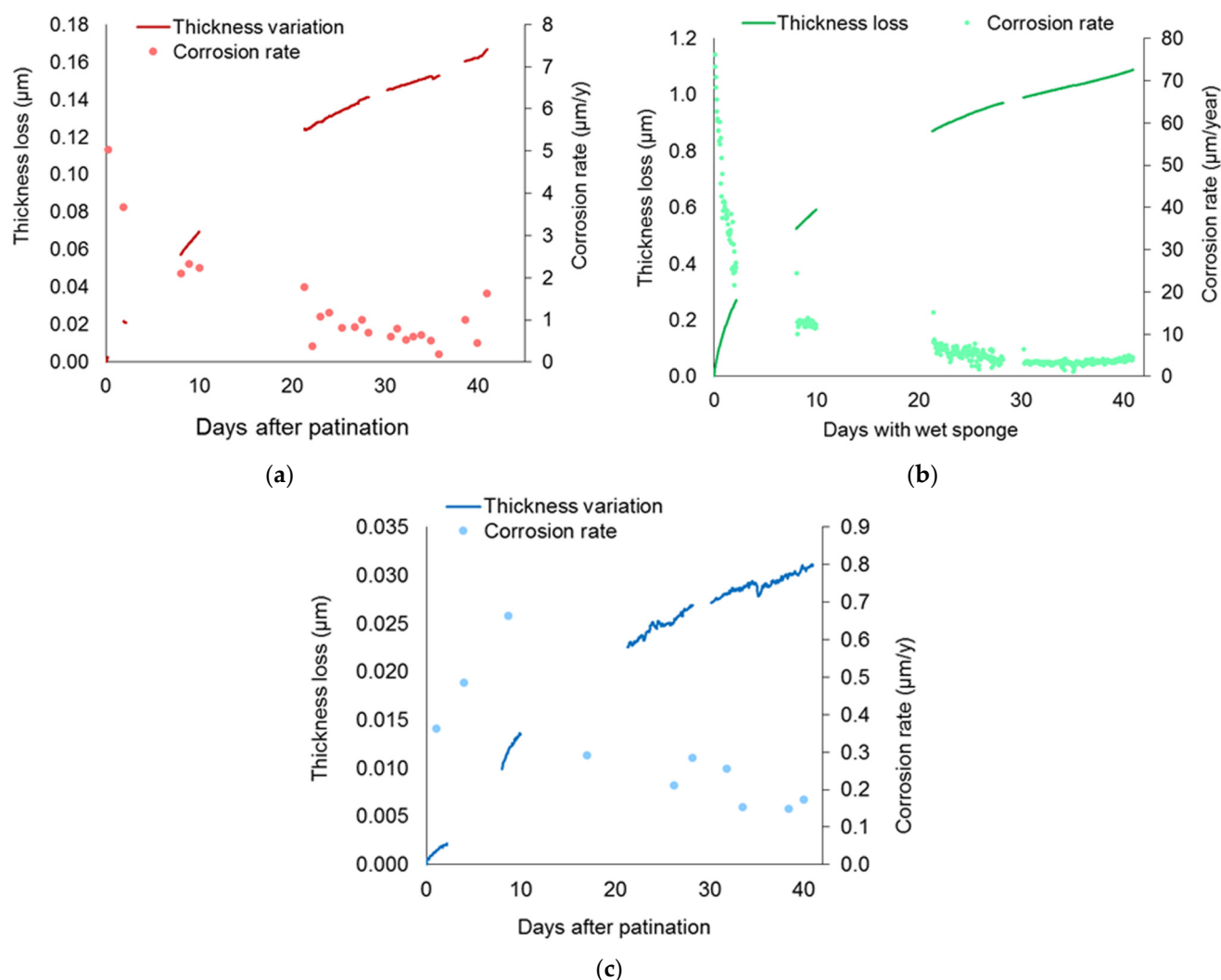


Figure 14. Thickness loss and corrosion rate calculated during the period of application of wet sponges on (a) PCB sensor with cuprite patina; (b) PCB sensor with applied paste patina; (c) not pre-corroded PCB sensor.

During the first two days of sponge application, the cuprite-patinated sensor exhibited a corrosion rate of approximately 5 $\mu\text{m}/\text{year}$ (Figure 14a), while the “applied paste” sensor showed a dramatic increase of up to 58 $\mu\text{m}/\text{year}$ (Figure 14b). The corrosion rate decreased over time, indicating a gradual stabilisation of the patina under wet conditions. In particular, for the cuprite sensor, the rate dropped from 3.7 $\mu\text{m}/\text{year}$ on day 3 to 1.2 $\mu\text{m}/\text{year}$ in the final days. Similarly, the “applied paste” sensor showed a reduction from 32 $\mu\text{m}/\text{year}$ on day 2 to 1 $\mu\text{m}/\text{year}$ by the end of the test.

The non-pre-corroded sensor displayed a slower initial response, with corrosion rates reaching 0.7 $\mu\text{m}/\text{year}$ in the first 10 days, followed by a gradual decrease to approximately 0.2 $\mu\text{m}/\text{year}$ (Figure 14c).

These results confirm that wetting the surface with a sponge significantly influences its corrosion behaviour, and consequently, the outcomes of LPR and EIS measurements. This is particularly relevant given that such measurements are typically performed within 10 to 30 min after sponge application—precisely when surface reactivity is at its peak.

Moreover, the amount of corrosion rate acceleration is strongly dependent on the composition of the corrosion layer. For example, the cuprite-patinated sensor showed a fourfold increase in corrosion rate compared to its behaviour under constant 60% RH without sponge (0.1 $\mu\text{m}/\text{year}$). The “applied paste” sensor, on the other hand, exhibited an

increase of nearly four orders of magnitude—from 0.2 $\mu\text{m}/\text{year}$ at 60% RH to 58 $\mu\text{m}/\text{year}$ under wet-sponge conditions.

These findings are consistent with the electrochemical results reported in a previous study [89], where the values of polarisation resistance (R_p) measured on the same patinas under wet conditions were significantly lower than those of unpatinated copper. In particular, the “applied paste” patina showed R_p values up to four orders of magnitude lower than bare copper, confirming its high reactivity and poor protective behaviour.

Therefore, when interpreting in situ LPR and EIS data from surfaces exposed to the atmosphere, it is essential to consider the influence of surface wetting and patina composition.

4.7. Critical Analysis of Sensor Behaviour and Patina Effects

4.7.1. Relevance of Pre-Corroded Sensors for Conservation Applications

The results of this study confirm the importance of designing corrosion sensors that realistically replicate the surface conditions of heritage metals. Unlike polished or uncorroded probes, pre-corroded sensors allow for a more representative assessment of environmental corrosivity, especially in the presence of complex patina stratigraphies. This is particularly relevant for cultural heritage applications, where direct testing on original artefacts is not acceptable.

While the present work is focused on evaluating the corrosion behaviour of different artificial patinas under controlled conditions, the findings open up promising perspectives for future applications. In particular, pre-corroded ER sensors could be employed as realistic mock-ups for testing conservation treatments. Their capability to simulate the chemical and morphological characteristics of aged surfaces makes them ideal candidates for assessing the long-term performance and compatibility of protective strategies—without risking damage to original artworks.

This twofold application—both as monitoring tools and as experimental surrogates—makes pre-corroded ER sensors a valuable innovation in the field of conservation science, bridging the gap between laboratory research and real-world heritage preservation.

4.7.2. Sensor Response to Patinas in Light of Published Corrosion Rates

The corrosion behaviour observed on pre-corroded ER sensors was strongly influenced by the chemical composition of the applied patinas. Sensors with the chloride- and sulphate-rich “applied paste” patina exhibited the highest reactivity, followed by those with cuprite and brochantite layers. These differences were evident in the corrosion rates measured via thickness loss over time, with the “applied paste” sensors showing active corrosion even at relative humidity levels as low as 20%.

To contextualise these findings, corrosion rate data from the literature were considered. Studies on uncorroded copper and bronze surfaces exposed to various environments typically report corrosion rates in the same order of magnitude as those detected by ER sensors—generally ranging from 0.5 to 5 $\mu\text{m}/\text{year}$ depending on the exposure conditions [88,104–108]. However, the relative difference between the two alloys is usually rather small. Depending on the exposure environment, deviations in the order of tens of nm/y were observed between copper and bronze (about 50% of the total corrosion rate values measured). This is clearly illustrated in Figure 15, where corrosion rates of copper and bronze from the literature are compared across different exposure scenarios. The environment instead, as well-known, within the range of historical copper-based alloys, plays a more significant role than the alloy composition itself. For instance, in marine

environments, where corrosion rates are generally significantly higher than in rural or urban environments, the difference between copper and bronze remains limited.

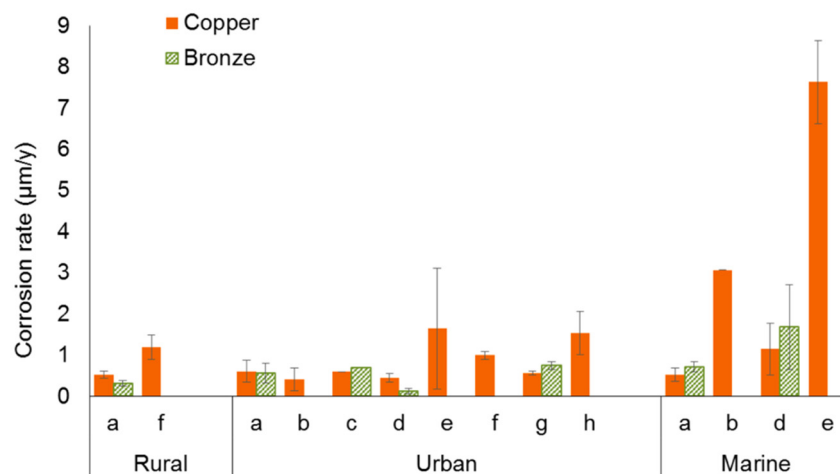


Figure 15. Corrosion rate of copper and copper alloys in different exposure environments: a [88]; b [108]; c [11]; d [105,106]; e [105]; f [109]; g [107]; h [104].

In contrast, the presence of specific corrosion products—particularly those rich in chlorides—can drastically amplify surface reactivity. The sensors with artificial patinas in this study showed corrosion rates that varied significantly depending on the patina type, confirming that the composition of the corrosion layer plays a more decisive role than the alloy itself.

Ideally, mock-ups for conservation research should replicate both the alloy and the corrosion layer of the original artefact. However, this is not always feasible, especially when dealing with historical alloys or complex stratigraphies. The results of this study suggest that, when a compromise is necessary, reproducing the correct stratigraphy and chemical composition of the corrosion layers may be more critical than precisely matching the alloy composition—at least when working within the range of traditional copper-based heritage materials. This consideration may not apply to modern alloys with passivating behaviour, which can exhibit significantly different corrosion dynamics compared to copper.

5. Discussion

This section discusses the main findings and limitations of the study in relation to sensor performance and environmental factors. It should be emphasised that the random RH variations during monitoring prevented a systematic correlation between RH and corrosion rate. Nevertheless, the analysis of the data still revealed important trends, confirming the responsiveness of pre-patinated ER sensors under fluctuating conditions and allowing a meaningful comparison between different sensor geometries and fabrication methods. Future work should implement controlled RH cycles to refine the interpretation of environmental effects.

5.1. Sensor Geometry and Microstructural Effects

The fabrication method strongly influenced sensor performance. LO sensors, produced via e-beam evaporation and lift-off, systematically exhibited higher corrosion rates than those measured with PCB sensors, likely due to their porous, columnar microstructure and higher defect density. This intrinsic difference in microstructure must be considered when interpreting corrosion data.

In addition to these differences in corrosion rate, LO sensors showed lower reproducibility compared to PCB sensors. These variations are likely related to the fact that the reference track was located on a separate substrate, which could have affected temperature compensation and measurement accuracy. Microstructural characteristics and their interaction with patination procedures should also be considered as contributing factors.

These microstructural differences must also be considered when selecting sensor geometries and fabrication methods for long-term monitoring, especially in aggressive environments. Additionally, the separation of reference and corroded tracks in LO sensors reduces the effectiveness of temperature compensation, confirming that co-location on the same substrate may highly improve accuracy. The possibility of pre-corroding both tracks should also be considered to ensure thermal and electrochemical compatibility.

5.2. Sensitivity and Detection Limits

Non-pre-corroded sensors with 17 μm (PCB) and 5 μm (LO) tracks did not show detectable thickness losses under any tested RH conditions, confirming their limited sensitivity; values are more affected by temperature differences between corroded and reference trace. Only the 0.25 μm LO sensors provided detectable responses at RH above 60. These results underline and confirm the importance of tailoring track thickness to the expected corrosion rate and environmental conditions.

Previous studies on PCB sensors showed that the main limiting factor was temperature compensation, which prevented the reliable detection of thickness variations below approximately 3 nm. As far as the 5 μm LO sensors, the thinner traces enable mitigating the aforementioned effect. More specifically, the peak-to-peak amplitude of the oscillations of the measured thickness is reduced to about 0.05 nm, which can be considered the detection limit.

5.3. Effect of Wetting and Electrolyte Application

To simulate the operating conditions of in situ LPR and EIS measurements, a wet sponge soaked in oligomineral (i.e., low mineral content water) water was applied to the sensor surfaces. This setup, consistent with the ContactProbe method used in previous electrochemical studies, caused a dramatic and immediate increase in corrosion rate across all sensors.

The extent of this increase was strongly dependent on the patina composition. For example, the “applied paste” sensor showed a corrosion rate of 58 $\mu\text{m}/\text{year}$ immediately after wetting, compared to 0.2 $\mu\text{m}/\text{year}$ at 60% RH. Cuprite and non-patinated sensors also exhibited significant increases, though less pronounced. These findings confirm that surface wetting significantly alters corrosion behaviour and must be considered when interpreting LPR and EIS data.

5.4. Design Recommendations and Future Improvements

The following recommendations can be suggested for future sensor design:

- Always locate reference and corroded tracks on the same substrate to improve temperature compensation. This is also well-aligned with the literature.
- Prioritising patina composition and morphology over alloy replication when designing mock-ups for conservation testing or ER sensors for environmental corrosivity monitoring.

Future research and improvements:

- Consider the pre-corrosion of reference tracks to match thermal and electrochemical behaviour. Further research is required for this aspect.
- Refine patination procedures to reduce initial thickness loss and improve layer stability.

Both proposed geometries—PCB and LO—proved effective for monitoring environmental corrosivity on pre-corroded surfaces when RH exceeded 50%. However, the PCB configuration offered greater robustness and longer service life, particularly in the presence of aggressive patinas.

6. Conclusions

This study demonstrates the feasibility of designing ER sensor geometries that can be pre-corroded, enabling the inclusion of corrosion layer effects during their use as environmental corrosivity sensors and as mock-ups for conservation testing. In this context, the characterisation of corrosion layers on heritage surfaces and the development of customised patination procedures are essential to ensure representativeness and reliability. The findings highlight several key aspects:

- Corrosion layers exert a decisive influence on corrosion rates, often outweighing the role of alloy composition.
- Pre-corroded ER sensors allow realistic and sensitive monitoring, revealing that corrosion can already be active at RH levels of 20–50% when corrosion layers contain hygroscopic and highly reactive compounds such as CuCl, as in the patina produced by the “applied paste” method. The presence of CuCl explains the persistence of corrosion even under nominally dry conditions and reflects the highly critical conservation scenarios that such stratigraphies can generate.
- Sensor design must be adapted to the intended application: PCB sensors provide robustness and longer service life, while LO sensors offer higher sensitivity but reduced stability.
- The fabrication methodology of the copper tracks plays a crucial role: LO sensors, produced by e-beam evaporation and lift-off, systematically exhibited higher corrosion rates due to their porous, defect-rich microstructure, whereas PCB sensors benefited from denser and more stable electrodeposited copper. Such microstructural effects must be considered when interpreting data from LO sensors; at the same time, a more porous structure may enhance sensitivity, even if this comes at the cost of reduced stability and increased uncertainty in corrosion rate calculations.
- Surface wetting, as applied in LPR/EIS protocols, causes an immediate and significant acceleration of corrosion, which must be taken into account when interpreting results.

Overall, pre-patinated ER sensors emerge as valuable mock-ups for heritage science, bridging the gap between laboratory experiments and real environmental conditions. Their development not only enhances the representativeness of corrosion monitoring, but it also opens new perspectives for testing conservation treatments under realistic scenarios, paving the way for more effective strategies in cultural heritage preservation.

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Abbreviations

The following abbreviations are used in this manuscript:

ER	Electrochemical Resistance
ACM	Atmospheric Corrosion Monitoring
LPR	Linear Polarisation Resistance
EIS	Electrochemical Impedance Spectroscopy
PCB	Printed Circuit Board
LO	Lift-Off
R_c	Electrical resistance of the corroded track
RFID	Radio Frequency Identification
R_r	Electrical resistance of the reference track

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