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Carbon steel corrosion monitoring: Why opting for an electroanalytical approach

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ABSTRACT

Corrosion of carbon steel is a critical area of interdisciplinary research, bridging materials science, chemistry, physics, and engineering disciplines. Traditional corrosion monitoring techniques, while practical, often lack the precision and real-time data acquisition capabilities required for effective corrosion management. In contrast, electroanalytical approaches, such as Voltammetry, Electrochemical Impedance Spectroscopy and Electrochemical Noise analysis, offer the possibility to achieve superior sensitivity, precision, and detailed insights into corrosion mechanisms, with analysis that can be directly performed on-site. This review explores the pivotal role of these methods in advancing the in-situ monitoring of corrosion processes of this material. Additionally, it discusses the application of these techniques to study the effectiveness of corrosion inhibitors and of protective coatings in enhancing corrosion resistance. Many applicative examples are here discussed to highlight how these methods should be applied in the industrial field, aligning with sustainable development goals and enhancing the safety and durability of infrastructure worldwide. This work is intended to serve as a valuable resource for corrosion scientists and other professionals in related fields, offering a perspective on the intersection of surface science and corrosion studies.

1. Introduction

Carbon steel is commonly used as a fundamental material in infrastructures, particularly in reinforced concrete and pipelines, due to its favorable mechanical properties. Nevertheless, its susceptibility to corrosion, particularly in environments rich in chloride ions, poses great challenges to the longevity of infrastructure. The corrosion of carbon steel involves complex electrochemical processes, culminating in the formation of rust, which progressively undermines structural integrity. This phenomenon has been extensively studied in [1–3].

As many other metals and alloys, the thermodynamic susceptibility of carbon steel to undergo corrosion can be predicted by the potential-pH diagrams, commonly known as Pourbaix diagrams [4]. These diagrams delineate the stability domains of various redox species in aqueous media, mapping conditions under which a metal tends to remain in its native state (immunity), to form passive layers (passivation) or to dissolve as ions (corrosion). From a thermodynamic point of view, corrosion, i.e. continuous dissolution of the metal due to the spontaneous oxidation (Fig. 1a), is not expected either in the immunity region nor when the oxidation leads to a compact and stable passive layer. The Pourbaix diagram of iron underlines the high tendency of this material to undergo spontaneous oxidation to ionic species (e.g., $Fe \rightleftarrows Fe^{2+} + 2e^-$) even in moderately acid conditions which are common in the natural environment. The driving force of this reaction is the presence of natural oxidizing species, like protons ($2H^+ + 2e^- \rightleftarrows H_2$) and dissolved oxygen ($O_2 + 4H^+ + 4e^- \rightleftarrows 2H_2O$).

Despite being extremely useful, Pourbaix diagrams only represent equilibrium conditions and do not provide information on the corrosion rate. This is directly proportional to the current intensity flowing between anodic and cathodic sites (i_{corr}) at the spontaneous corrosion potential (E_{corr}); thus, i_{corr} is a quantifiable parameter of the kinetics of these interfacial reactions. Therefore, both thermodynamic and kinetic aspects must be considered to effectively monitor and control corrosion processes.

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The environmental repercussions of corroded carbon steel are profound, even including the potential dissemination of heavy metals into the surrounding ecosystem; this is particularly acute in marine environments, where it can induce ecological disruptions and threaten aquatic biodiversity [5,6]. Moreover, the socio-economic ramifications are significant, requiring substantial financial investments in maintenance and repair to sustain infrastructure functionality [7]. Addressing these challenges demands a comprehensive understanding of corrosion mechanisms and the implementation of effective prevention strategies [8,9]. Various factors influencing corrosion behavior of carbon steel, including the influence of CO_2 concentration, pH, temperature, and the addition of reinforcing materials like carbon fiber reinforced polymer composites have been explored [1,9,10].

The drawbacks implied in corrosion processes underscore the urgency of proactive measures to assess an early identification of corrosive processes, which are mainly summarized in Fig. 1. The development and use of effective corrosion monitoring and prevention techniques is crucial for economic viability.

Analytical methods offer a promising avenue for corrosion monitoring due to their sensitivity, real-time capabilities, and non-destructive nature, providing invaluable insights into metal behavior. Researchers and engineers apply these techniques to assess corrosion rates, to identify potential failure points, to devise mitigation strategies, and to evaluate corrosion protection methods, such as inhibitors [11–13]. Significant advancements in corrosion monitoring techniques have emerged, driven by a growing need for more accurate, timely, and cost-effective corrosion assessment methods [14–20].

Analytical methods for the monitoring of carbon steel corrosion can be broadly categorized into material loss methods, sensing methods, and electroanalytical methods (Table 1). The former ones, implying the use of corrosion coupons and electrical resistance probes, are known as conventional techniques, since they are widely employed for field corrosion monitoring; they offer direct measures of corrosion extent, but lack real-time monitoring capabilities [21,22]. Sensing methods, including ultrasonic and optical sensors, are also conventionally used to provide non-destructive assessments of corrosion processes; however, they may require surface preparation and specialized equipment [23–28]. Electroanalytical methods, such as Voltammetric techniques, Electrochemical Impedance Spectroscopy (EIS) and Electrochemical Noise (EN), offer real-time data, high sensitivity, and versatility for various materials and environments [29,30]. In this field of application, they offer several advantages over the former categories, including real-time data availability, high sensitivity for early detection, non-destructive nature, and cost-effectiveness in the long run. This notwithstanding, they can be still considered non-conventional techniques for the monitoring of corrosion processes occurring in real environments.

These methods play a pivotal role in developing proactive maintenance strategies and enhancing infrastructure durability. In particular, they can play a major role in the monitoring of internal corrosion, which still remains a challenge to ensure the integrity of metal structures. Monitoring techniques to achieve an early detection of this drawback can be applied to different structures, such as industrial equipment (condensers, heat exchangers, boilers, etc.) or pipelines.

Classic corrosion protection methods—including corrosion inhibitors, cathodic protection, and coatings—are widely used for internal corrosion protection. The choice of approach to use depends on the specific structure and operational conditions. In the case of inhibitors, their performance must be monitored continuously, so that implantable analytical devices can be fundamental. In particular, shifts in E_{corr} and reductions in the I_{corr}, which can be measured by electroanalytical techniques, provide key indicators of inhibitor performance, while changes in polarization resistance (R_p) offer complementary insights. These outputs allow an accurate and dynamic assessment of inhibitor behavior, especially under variable field conditions, although a deep comprehension of the chemical effects induced by the application of the corrosion inhibitor is mandatory and is behind the information provided by electrochemical parameters.

The application of cathodic protection must be well-dimensioned and distributed appropriately to achieve the protection criterion. In the case of internal coatings, organic or metallic, their natural degradation is expected to occur. Therefore, whatever protection technique is defined to be used, it is necessary to ensure the efficiency of the protection. In this sense, applying techniques that can be used in industrial units is necessary.

In the upcoming sections, we will delve deeper into the

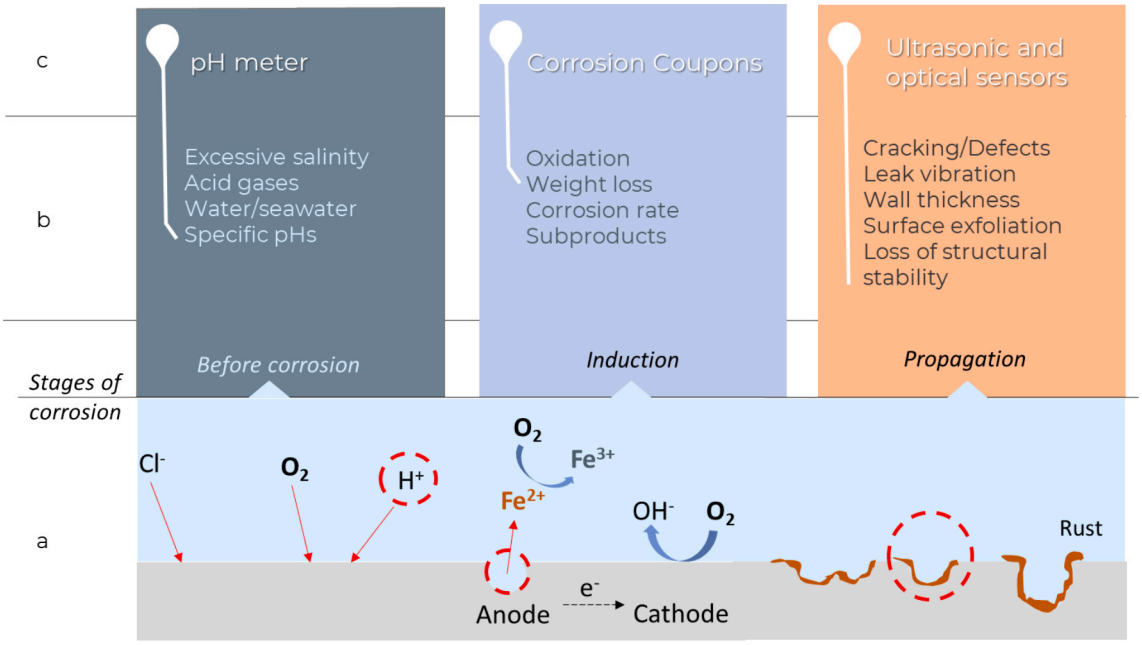

Fig. 1. **a)** Schematic representation of a corrosion process; **b)** specific chemical/physical conditions/transformations occurring as a consequence of these process; **c)** diagnostic techniques principally used at each stage: pH meters for the early detection of aggressive conditions, corrosion coupons to monitor the weight loss due to metal corrosion; ultrasonic and optical sensors to identify damage progression such as cracks, thinning, and structural instability.

Table 1
Summary of different analytical methods applicable for the in-situ monitoring of carbon steel corrosion; pros and cons of each conventional and unconventional technique are also indicated [30].

	Type	Method	Real-time	Local	Advantages	Disadvantages
Conventional	Weight loss	Corrosion coupon	No	Local probe	Standard method (precise), inexpensive, easy to operate	Time-consuming, long exposure
		Electrical resistance probe	Yes	Local sensor	Measurement in environments with different conditions, direct response	Salts and oxides forms can give wrong results, time-consuming, measure only uniform corrosion
	Sensing	Ultrasonic sensor	Yes	Local sensor, PIG	Non-destructive, precise	Surface preparation, less effective on rough surface
		Optical sensor	Yes	Distributed in line	Monitoring long distance	High implementation cost
Unconventional	Electroanalytical	Electrochemical Impedance Spectroscopy	Yes	Local sensor	Corrosion mechanisms, high sensitivity	Complex data interpretation
		Potentiodynamic Polarization	Yes	Local sensor	Precise corrosion rates	Invasive method
		Linear Polarization Resistance	Yes	Local sensor	Short response time, industrial applications	Sensible to variations on the surface
		Electrochemical Noise	Yes	Local sensor	Measurement of localized corrosion	Non-quantitative

electroanalytical methods, comparing their efficacy and applicability for carbon steel corrosion monitoring. The large-scale application of these methods will be possible after encompassing issues such as matrix effects, interferences, long-term monitoring and durability, quantitative correlation to corrosion rates, standardization, data analysis and interpretation, in-situ monitoring, and multi-phase systems, all of which require attention [23,24]. In addition, the integration of digital technologies, including the Internet of T Things (IoT), machine learning, and artificial intelligence (AI), into corrosion monitoring systems has gained significant interest [31–36] to overcome the limits previously listed to the use of electroanalytical techniques. These data treatment approaches make data-driven decision-making, predictive maintenance, and optimization of corrosion control strategies, thereby offering a comprehensive approach to corrosion management [37–42].

It is worth to note that, despite limiting the discussion to carbon steel for the reasons previously underlined, these same electrochemical techniques can be broadly applied to a wide range of metallic materials, such as stainless steels [43] copper alloys [44], and aluminum [45]. This review aims to provide researchers, engineers, and industry professionals with a thorough overview of the current state of the field and to outline promising directions for future research and innovation in contrasting carbon steel corrosion.

2. Electroanalytical approaches

2.1. Voltammetric techniques

Voltammetric techniques play a crucial role in corrosion monitoring of carbon steel, offering valuable insights into the electrochemical behavior of metallic materials and their surfaces. Techniques such as Potentiodynamic Polarization (PDP) and Linear Polarization Resistance (LPR) have become increasingly used to analyze corrosion processes and to measure parameters like corrosion rate, passivation potential, and corrosion current. Voltammetric techniques are essential in evaluating and characterizing corrosion mechanisms, protective coatings, and developing advanced corrosion mitigation strategies [28–30,46].

2.2. Potentiodynamic polarization and related methods

PDP remains a cornerstone for evaluating the corrosion rate (i_{corr}) and potential (E_{corr}) of carbon steel. This method is effective in achieving a frequent monitoring of the corrosion extent and of the influence of inhibitors. However, it is an invasive technique that can alter the corrosion process during measurement, and it requires a controlled laboratory environment [22]. This notwithstanding, the improvements in instrumentation and data analysis software have increased the precision of corrosion rate measurements [47] and demonstrated the applicability of this method in the evaluation of corrosion protection strategies [28,48–51].

In PDP methods, the carbon steel specimen as such is used as a working electrode, and the current flowing in the system is recorded while it is polarized at a potential variable in the time around the open circuit potential, which represents the equilibrium potential of the system. This technique involves sweeping the potential either linearly or cyclically and reporting the measured current in a logarithmic scale versus the applied potential. The resulting Tafel plot, allowed the extrapolation of the most important thermodynamic and kinetic parameters previously described, namely E_{corr}, i_{corr}, as well as of the corrosion rate from the slope of the Tafel plot in the anodic and in the cathodic region. The data obtained helps in plotting polarization curves, which are crucial for understanding the electrochemical behavior of the metal [52]. Subbiah et al. reported the fabrication of a corrosion monitoring device containing the counter and the reference electrode (Fig. 2a), highlighting its precision in predicting the corrosion status of carbon steels contained in concrete (acting as the working electrode) [53]. Its advantage lies in reducing the internal resistance drop due to its proximity to the carbon steel bar, thereby enhancing measurement accuracy. However, the performance is affected by the concrete's humidity conditions. In a subsequent study, the same authors emphasized the long-term stability of the device in-situ applications conducted over 24 months, providing clear distinctions between active and passive corrosion states, regardless of humidity conditions [54].

Ramón et al. introduced an innovative approach called Potentiostatic Step Voltammetry-Tafel extrapolation (PSV-TE), an adaptation of PDP, for measuring the corrosion rate of reinforcements in concrete [55]. This method, based on TE, offers significant advantages over traditional approaches. Unlike traditional TE, which requires lengthy and potentially damaging potentiodynamic scans, PSV-TE achieves Tafel slope determination more rapidly and reduces the risk of irreversible polarization of the rebars, making it a non-destructive method. The approach employs a series of potentiostatic pulses to gather data (colored points in Fig. 2b), which are then fit to a theoretical model to obtain essential corrosion parameters. The method demonstrates high accuracy, with a slight tendency to overestimate the corrosion rate compared to traditional TE but within acceptable margins. However, the method's effectiveness depends on the pulse duration and amplitude, with optimal settings identified to balance speed and accuracy. In a subsequent work, the same group refined the approach, adjusting the instrumental setup for different steel-mortar systems, especially those with significant ohmic drops [58]. This refinement ensured the reliability of Tafel line

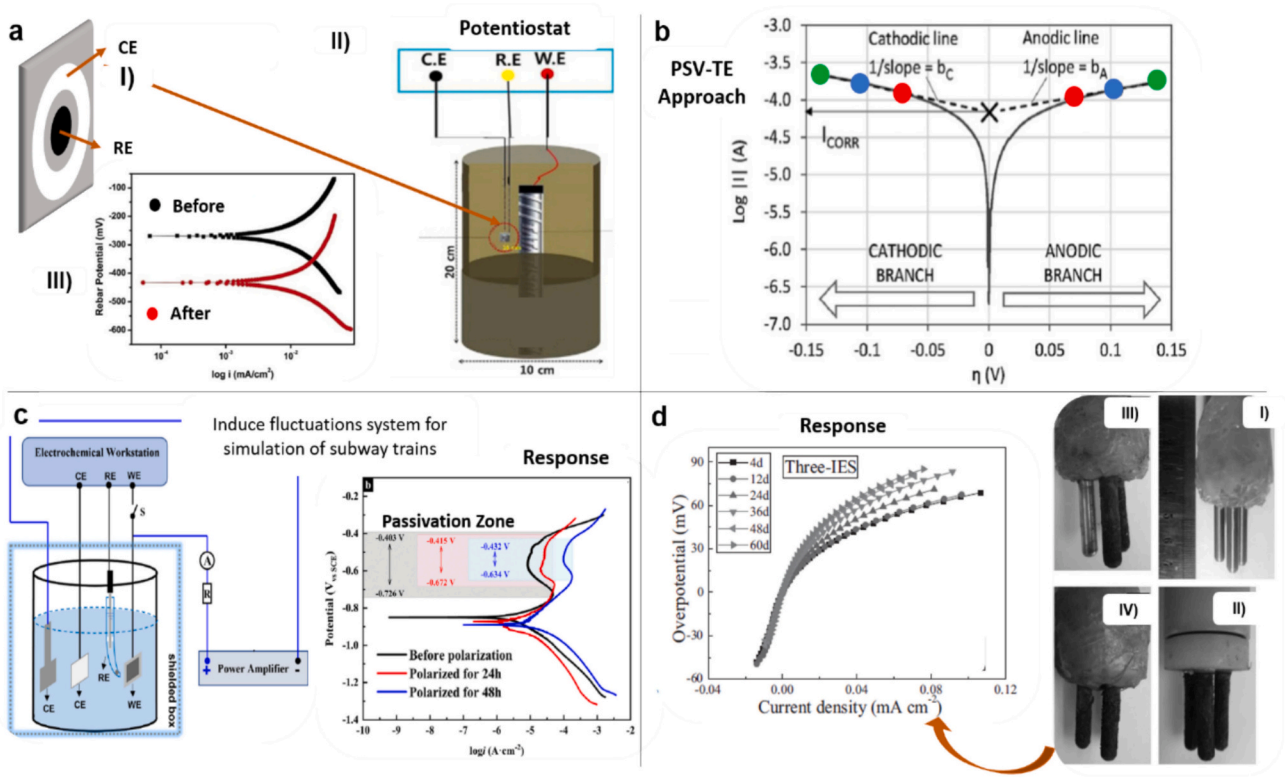

Fig. 2. **a)** I) Representation of an embeddable corrosion rate monitoring sensor, II) the placement in concrete slab and III) response before and after embedding the sensor, adapted from [53,54]. **b)** Principles of the proposed PSV-TE approach, adapted from [55] **c)** Schematic diagram of the self-made experimental system used to monitor pitting corrosion behavior and the Tafel plot before polarization and after 24- and 48-h polarization, adapted from [56]. **d)** Surface morphologies of electrode systems tested by weak polarization as manufactured three identical electrode systems (I) before and (II) after test; (III) three identical electrode systems with stainless steel as a reference electrode after test; (IV) two identical electrode systems after test and the response of the shift of weak polarization curves over 60 days, adapted from [57].

determination by adjusting PSV pulse amplitudes to the specific system under assessment.

Another frequent application for PDP is in assessing the passivation films of stainless steel. As an example, Villegas-Tovar et al. investigated the electrochemical behavior of various precipitation-hardening stainless steels, employing this technique [59]. The study delved into how factors like passivation temperature and immersion time influence the corrosion kinetics of these steels. Through PDP, they unveiled distinct electrochemical processes underscoring passivation occurring during the anodic reaction and variable pitting potential. The parameter of pitting potential is among the most scrutinized in stainless steel studies using PDP, given that even minor surface alteration is the starting point for a most severe corrosion. In a related vein, Yu et al. probed the pitting corrosion of X70 steel in soil solution subjected to dynamic direct current interference (Fig. 2c) — a prevalent issue where stray currents from subway trains induce fluctuations in pipe-to-soil potential — culminating in significant corrosion [56].

The use of the PDP technique has been frequently applied in research activities directed to assessing corrosion inhibition. Indeed, this method has shown to be an excellent tool to help identify the type of inhibitor and the action mechanisms. As an example, El-Hashemy et al. leveraged this method to delineate the efficacy of *Calendula officinalis* flower heads extract as a corrosion inhibitor [60]. The study reveals that this extract can offer a remarkable 94.88 % protection against corrosion. Using the same conventional PDP technique, Semedo et al. demonstrated that the exploration of electrodeposited coatings reveals the superior corrosion resistance of Zn—Mn coatings, attributed to negative potential shifts and the formation of protective corrosion products [61]. However, a typical problem using PDP can emerge for this type of application, since this method involves the application of external potential to the carbon steel surface, which may affect naturally formed protective inhibitor layers, leading to alterations in the actual surface conditions and potentially affecting the accuracy of the inhibition efficiency evaluation. To overcome this limitation, Wu et al. proposed a novel approach which involves the use of a very weak polarization (Fig. 2d) to mitigate electrode surface disturbance, pinpointing a cathodically dominated corrosion process [57]. This methodological variance underscores a pivotal divergence from the conventional PDP technique, advocating for tailored electrode systems based on specific environmental exigencies.

Other examples of application of PDP technique to investigate corrosion inhibition can be found in a paper from Tan et al. [62], which assesses the corrosive behavior of sodium dodecyl sulfonate and potassium iodide, while Kasim Sheit et al. [63] used this same technique to examine the effectiveness of a Schiff base inhibitor.

PDP was found to be essential in understanding the inhibition mechanism, showing how compounds act in the inhibitor process and allowing for an accurate quantification of the inhibition efficiency. Indeed, the use of PDP provides detailed insight into the electrochemical behavior of the inhibitors and the formation of protective films on the steel surface. Moreover, while PDP offers valuable insights into the inhibitors' effectiveness, it cannot fully unravel the molecular mechanisms at play. It points to the need for complementation with additional theoretical and experimental techniques, such as the molecular modeling conducted by Tan et al [62].

2.3. *Linear polarization resistance*

The LPR method operates by applying a minimal potential change to the metal sample and measuring the corresponding current variations. LPR is known for its simplicity and quick measurement capabilities,

which make it suitable for real-time monitoring in industrial applications [52]. Indeed, the technique enables a direct estimation of the corrosion rate through the calculated resistance value (by the Stearn-Geary equation), providing a quick and non-destructive means of evaluating the metal's susceptibility to corrosion [64]. This makes LPR particularly effective to assess the integrity of carbon steel components, which is vital for maintaining safety and operational efficiency [52], as well as for routine inspection and the evaluation of corrosion inhibitors [65]. As a main drawback, it provides less detailed information compared to EIS and may be less accurate in complex environments [66].

Despite its initial use dating back to around 1950, the LPR technique has undergone significant improvements in methodology to date, rendering it increasingly sensitive to specific usage characteristics. For example, Yahi et al. developed a method to monitor the corrosive effects of hygroscopic salts at low temperatures [67], by integrating LPR with the more traditional mass loss measurements to assess corrosion rates. The authors mapped how different water vapor concentrations and temperatures influence the corrosion process, providing insights into managing and mitigating corrosion in industrial applications. This real-time monitoring assists in the early detection of corrosion, which would not be feasible using traditional mass loss measurements alone.

As an additional example, Eškinja et al. conducted a separate polarization experiment to measure the corrosion of ferritic steel in specific oilfield conditions [68]. The corrosion rates measured by both LPR and total polarization methods fell within acceptable ranges as per industry standards. Through the former measurements, it was demonstrated that temperature significantly impacts the formation of protective layers on material surfaces, with higher temperatures fostering thicker layers. The total polarization analysis, on its hand, allowed correlating the characteristics of the protective layers with key-parameters, such as temperature and exposure time.

To support the innovation in the application of LPR to access carbon steel pipeline corrosion, two notable examples from different research teams have to be mentioned, providing comprehensive current advancements and challenges. Durrani et al. focused on conventional LPR probes alongside coupon methods in a simulated heating ventilation and air conditioning system (Fig. 3a), emphasizing the comparability of these techniques in determining corrosion rates, revealing only an 8.3 % discrepancy between the conventional technique and an electroanalytical approach, under varied conditions [69].

This minor variance underscores the reliability of LPR in effectively tracking general corrosion rates, especially when the electrochemical characteristics at anodic and cathodic sites are similar. Conversely, Liu et al. introduced a novel approach by incorporating a ring pair electrical resistance (RPER) device array with LPR to tackle the challenge of localized erosion-corrosion in carbon steel pipelines (Fig. 3b) [70]. This setup distinguishes between erosion and corrosion contributions to metal loss, crucial in environments with complex flow patterns that can mask the true extent of corrosion if using traditional LPR alone. The research highlights RPERS's capability in identifying localized corrosion with precision, offering a significant improvement over traditional methods that might underestimate the severity of corrosion due to erosion influences. The RPERS-LPR combination marks a significant innovation, providing an accurate assessment of the complex dynamics of erosion-corrosion interactions not achievable with traditional LPR systems.

In the pursuit of monitoring methods more applicable in practice, several authors have increasingly sought to simulate pipelines in the laboratory to carry out monitoring tests as closely as possible to real conditions. For example, due to the difficulties of in-situ monitoring for Corrosion Under Insulation (CUI) systems and the lack of literature,

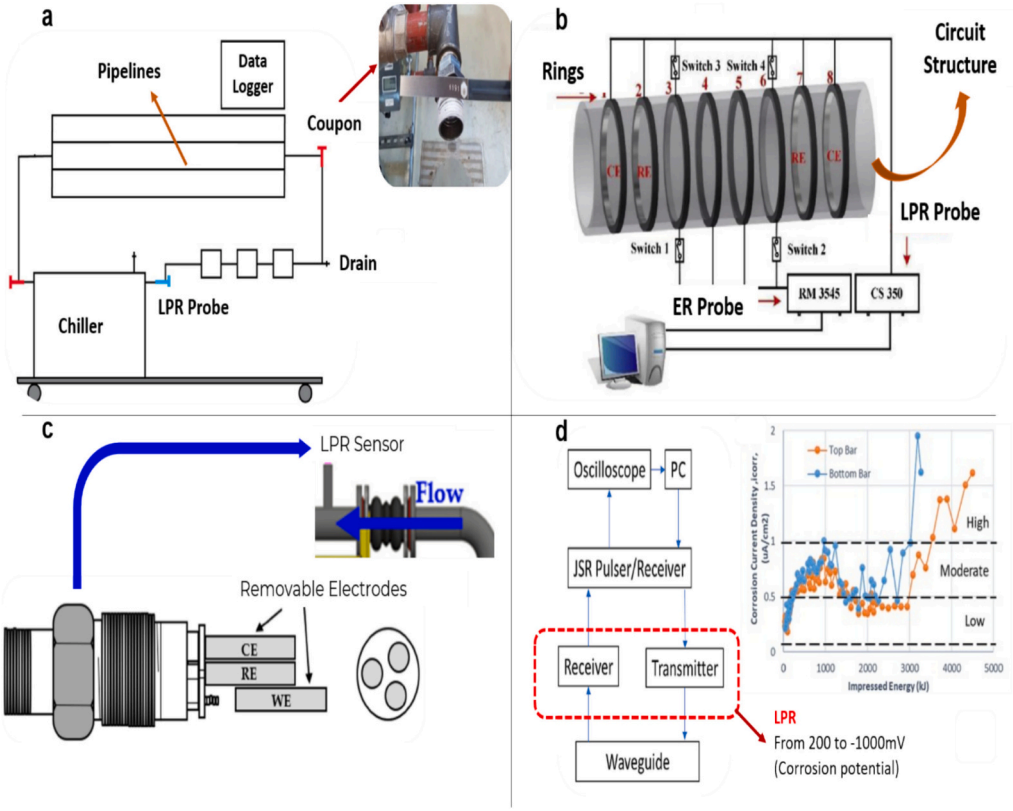

Fig. 3. **a)** Schematic pipeline with coupon and LPR probe locations used to measure the corrosion using LPR and gravimetric, adapted from [69]. **b)** Scheme of the erosion-corrosion device system with the measuring circuit and the pipeline structure used in the flow circuit, adapted from [70]. **c)** Schematic representation of LPR device with three removable electrodes and its position in the pipeline test, adapted from [71]. **d)** Schematic diagrams of the instrumentation used to monitor the corrosion specimen and I_{corr} measurements corresponding to corrosion levels from low to high, adapted from [72].

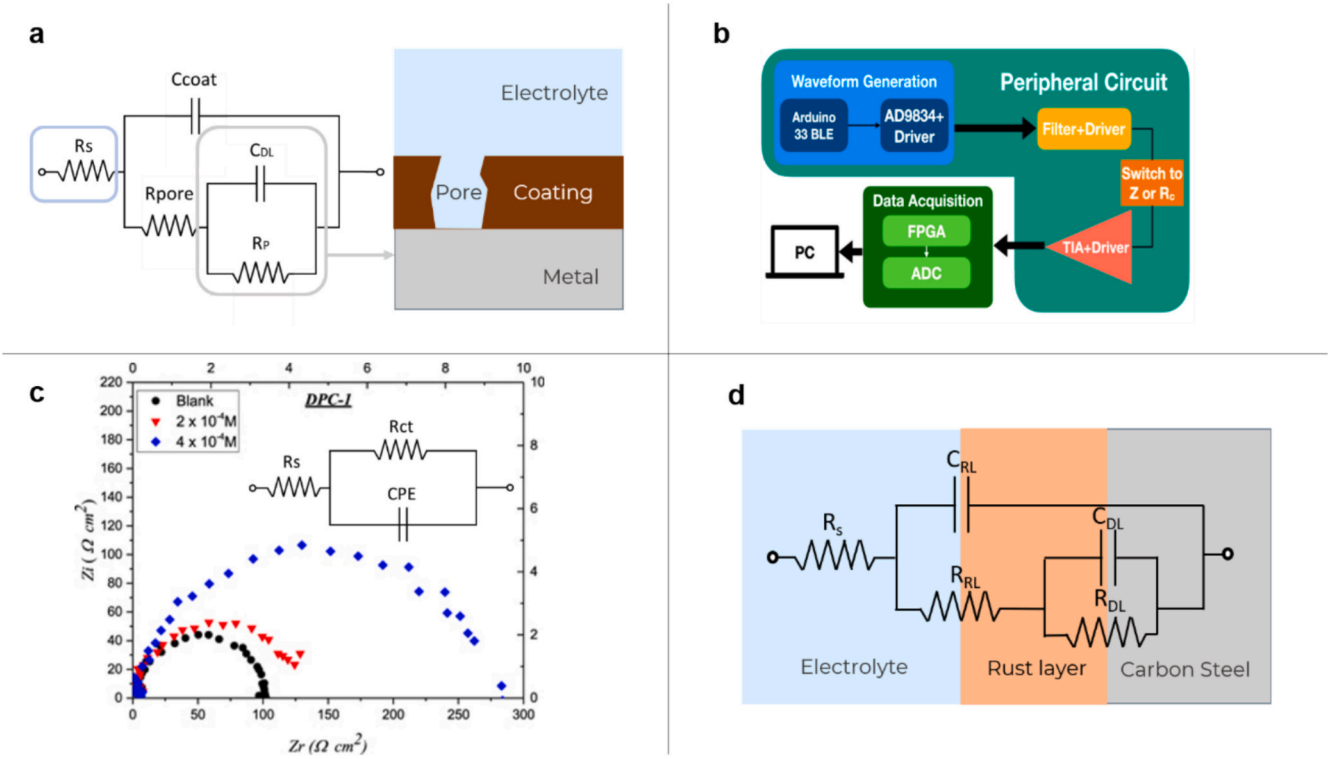

Fig. 4. **a)** Generic EEC model, where the capacitors are often replaced by CPEs when modeling real systems in practice. R_S models the electrolyte resistance; C_{DL} and R_P are the double-layer capacitance and polarization resistance that model corrosion at the metal surface, respectively; Ccoat is the coating capacitance, and Rpore models the resistance that hinders the electrolyte from reaching the metal surface through the pores in the coating, adapted from [73]. **b)** The block diagram of the proposed field deployable impedance-based corrosion sensor, adapted from [74]. **c)** EEC and Nyquist plots obtained for mild steel in 1 mol/L HCl solution, in the absence of corrosion inhibitor (black dots) and in the presence of two different concentrations (red and blue) of a pyrazole-based compound, at 303 K, adapted from [75]. **d)** EEC for carbon steel immersed in a simulated solution containing Fe^{2+}or Fe^{3+}, inspired by the reference [76]. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Yang et al. developed a novel electrochemical device [77] which involves the use of a steel pipeline encapsulated in thermal insulation. It consisted of an electrochemical device system with Pt-coated titanium wires in a three-electrode setup, which allows the continuous monitoring of corrosion rates and provides insights into the electrochemical behaviors of the materials under various environmental conditions. LPR was particularly crucial in the study as it enabled the real-time measurement of corrosion rates, crucial for comparing the effectiveness of traditional mass loss methods and the novel electrochemical approach in assessing the progression of CUI. Similarly, Shin et al. constructed a test bed to evaluate commercial corrosion devices for real-time monitoring of pipe wall thickness (Fig. 3c) [71]. The study explored the effectiveness of commercial corrosion devices, including LPR devices, in monitoring the integrity of piping systems under various operational conditions. These devices were capable of monitoring corrosion in the range from 0 to 200 mm per year maintaining a linear response between the measured electrochemical parameters. They are particularly suitable for assessing the early stages of corrosion, since under severe conditions of corrosion their response may become less reliable due to deviations from linearity and signal instability.

These findings highlighted the need for an additional study of intermeasurement cleanliness of the device to better clarify the real applicability and the need to map corrosion conditions before applying them.

In the realm of reinforced concrete corrosion monitoring, the LPR technique is widely employed. For instance, the research groups of Wang [72] and Mermerdas [78] used LPR in a different way, but with a shared goal: the early-stage corrosion detection. The former ones combined LPR with ultrasonic techniques and half-cell potential (Fig. 3d) to detect corrosion, showcasing its comprehensive assessment capabilities when integrated with other methods. This not only highlighted LPR's real-time capabilities, but also its effectiveness in complex environments, such as those with top-bar defects. In contrast, Mermerdas and coworkers focused on comparing different mineral admixtures' effectiveness in enhancing corrosion resistance, using LPR to evaluate their performance.

LPR proved crucial in quantifying the extent to which these additives could mitigate corrosion in various compositions and experimental conditions. Both studies underscored LPR's versatility and accuracy in real-time corrosion monitoring, making it a valuable tool for enhancing the durability of concrete structures.

In the challenging realm of stainless-steel monitoring, the LPR technique has been extensively investigated, as evidenced by the works of Mallco et al. [79] and Baltazar-Zamora et al. [80]. The former paper highlighted LPR's role in assessing corrosion resistance within high-temperature molten salt environments, demonstrating its efficacy in determining corrosion rates under extreme conditions. The corrosion rates measured by LPR provided valuable insights, showcasing its accuracy even in harsh environments. Similarly, the second article employed LPR to monitor AISI 304 stainless steel in concrete mixes subjected to saline solutions, emphasizing its role in enhancing corrosion resistance. These studies collectively exemplify LPR's broad application spectrum and its pivotal role in advancing corrosion-resistant materials and infrastructure.

2.4. *Electrochemical impedance spectroscopy*

EIS stands as a cornerstone in the study of carbon steel corrosion across various environments, offering comprehensive insights into corrosion mechanisms and protective film characteristics, as highlighted in the specialized literature [66]. Renowned for its high sensitivity, EIS

furnishes detailed information about the corrosion process, including the resistance of protective films. However, its widespread adoption is hindered by the requirement for specialized expertise in data interpretation [30]. Acknowledged as the primary electrochemical technique for corrosion investigations, EIS finds extensive application in assessing metal corrosion quality, such as rate, thickness, and heterogeneity, along with deciphering corrosion kinetics and evaluating corrosion inhibitor effectiveness [81]. In these analyses, EIS data are fitted with specific equivalent electrical circuits (EEC) to ascertain polarization resistance values (Rp), a crucial parameter inversely correlated with the corrosion rate of metals [73,74] (See Fig. 4a and b).This makes EIS responses crucial for developing high-performance corrosion monitoring tools that can be deployed in the field [82,75] (See Fig. 4c).

Despite these advantages, EIS does require expertise in data interpretation, which can limit its accessibility for routine use in industrial settings. However, the precision and detailed information it provides justify the use in critical applications where accurate corrosion monitoring is essential. This technique's ability to deliver real-time data on corrosion processes makes it invaluable for monitoring the integrity of protective coatings and understanding the kinetics of corrosion reactions under various environmental conditions [83,84]. Schindelholz explored real-time monitoring of corrosion using electrochemical methods, highlighting the practical applications and effectiveness of EIS in providing timely data for maintenance and prevention strategies. Their study emphasizes the real-time aspect of EIS, demonstrating its utility in dynamic environments where corrosion rates can change rapidly [83].

The development of portable EIS devices, which are compact, easy to operate, and capable of providing in-situ corrosion monitoring is making EIS more accessible [38,85]. The integration of EIS with water treatment plants presents a promising perspective for comprehensive monitoring of corrosion in water distribution systems. By combining EIS with the existing infrastructure of water treatment plants, continuous and real-time data on corrosion rates and the effectiveness of corrosion inhibitors can be obtained. This integration enhances the ability to maintain the integrity of water distribution systems, thereby ensuring safe and clean water supply [86,76].

Moreover, advancements in EIS have focused on improving the analysis of complex systems and enhancing the technique's sensitivity and accuracy. This progress includes the development of methodologies for analyzing EIS data using Kramers-Kronig transformations, which ensure the stability and linearity of the impedance measurements [87,88]. It also includes the ability to distinguish corrosion behavior under varied environmental conditions, revealing distinct corrosion patterns across atmospheric, splash, tidal, and immersion zones [89]. Furthermore, the interpretation and analysis of complex EIS data can be significantly augmented by artificial intelligence and machine learning algorithms, enabling more sophisticated pattern recognition and predictive modeling [31]. Overall, the continued development and refinement of EIS as a tool for corrosion analysis underscore its significant role in both research and practical applications. Its detailed insights into corrosion mechanisms and inhibitor performance, combined with its ability to monitor real-time changes, make EIS a cornerstone technique in the study and prevention of carbon steel corrosion [90,91].

2.5. Electrochemical noise (EN)

EN has emerged as a non-invasive and powerful technique for evaluating the corrosion and degradation of metals across diverse environments. Due to the electrochemical nature of corrosion, oscillations in

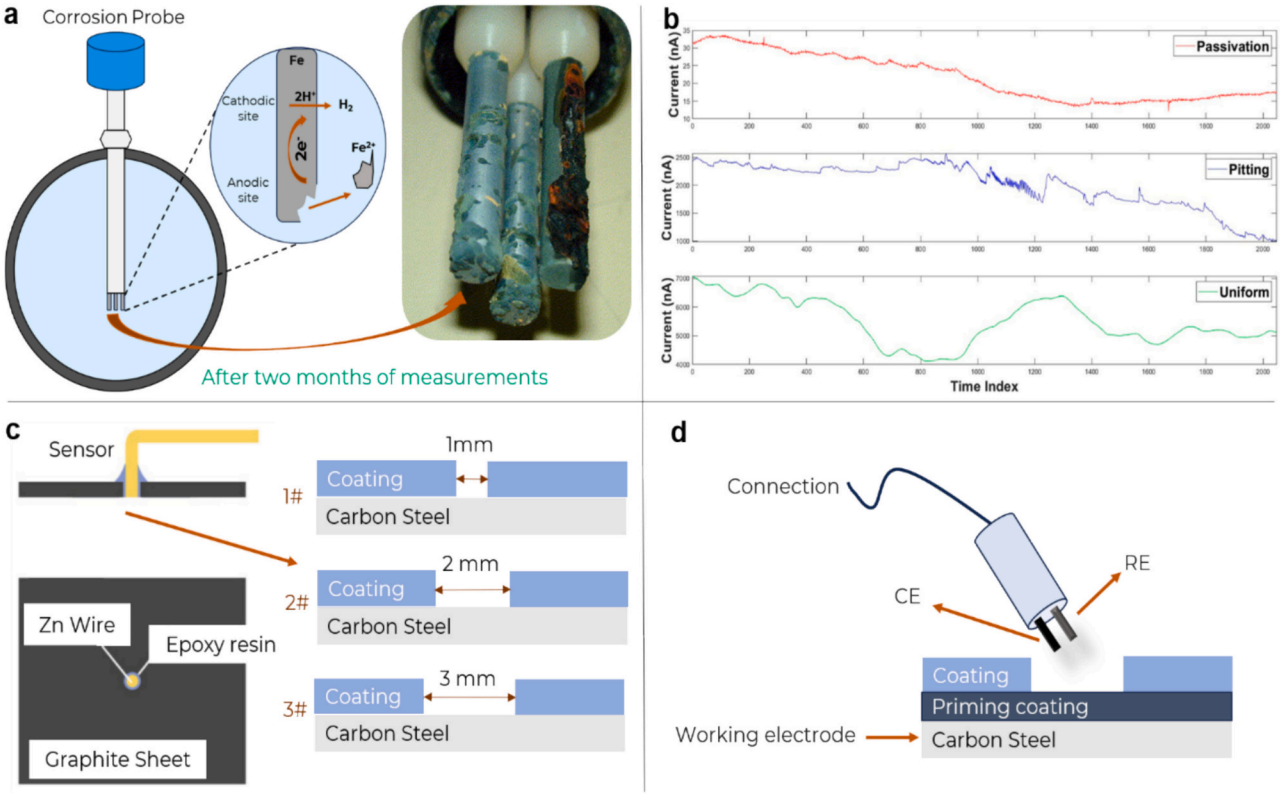

Fig. 5. a) Scheme of the insertion of the Corrosion Probe in the on-line pipeline monitoring and picture after two months of exposure, adapted from [93]. **b)** EN response associated with uniform corrosion (green), pitting corrosion (blue), and passivation (red), results from [94]. **c)** Diagram of the self-made detection sensor and three investigated defects in the coating, adapted from [97]. **d)** The electrochemical sensor used in corrosion detection with an organic coating/carbon steel working electrode sheet and the four investigated defect levels in the organic coating, adapted from [98]. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

potential and current were observed, caused by the formation of microcells on the metal surface (Fig. 5a) [92,93]. The detection of such fluctuations provides information about ongoing corrosive processes with details into corrosive dynamics on a microscopic scale, which serve as key indicators of localized corrosion events. By refining data interpretation methods, EN utility was bolstered making it a valuable tool for real-time corrosion monitoring and early detection of pitting corrosion (Fig. 5c) [94]. Despite its efficacy, EN data can be inherently complex to interpret, necessitating the use of advanced analysis techniques [30]. Nonetheless, EN remains highly advantageous due to its non-invasive nature and capacity to detect localized corrosion events promptly. Ongoing developments in EN methodology aim to enhance its sensitivity and accuracy, extending its applicability to monitor corrosion in complex systems and challenging environments [15,95,96].

EN allows collecting data which are essential for a comprehensive evaluation of the corrosive process and development of mitigation strategies. Although there are divergences about some specific aspects, the scientific community agrees that the EN signal contains valuable information that could enhance our understanding of corrosion and improve prevention and control strategies. An example is reported by Xia et al., where a summary table presents nine electrode systems that can be adopted for EN measurements directly in the field, eight of which can be applied to corrosion measurements in environments such as pipelines due to their non-destructive nature with minimal damage to the working electrode [12].

EN analysis is a rapid and non-destructive method that could overcome the complexity of localized corrosion evaluation [99], by simply acquiring signals from freely corroding systems without any external stimuli. Fluctuations in current or potential, associated with pitting initiation and passive layer breakdown, could be directly observed in experimental data. This made EN measurement a valuable tool for in-situ monitoring of these phenomena [100]. Indeed, the different states and mechanisms of corrosion occurring when carbon steel is exposed to different electrolytes, such as uniform corrosion, passivation, and localized corrosion, were successfully studied by EN [101], which allowed to define the characteristics of pitting corrosion behavior [102]. In particular, during the pit induction period in carbon steel, potential and current fluctuations occurred simultaneously, and the Faraday process was dominant. During pit nucleus formation, there was a phase difference between potential and current fluctuations, due to slow discharge of the electric double layer. During pit growth, most of the anodic current was consumed in the electric double layer, and a small part was involved in the film formation reaction [103]. The ability to detect pitting corrosion non-invasively and in real-time made EN a valuable technique for the industry, helping to improve the safety and durability of metallic materials in aggressive environments.

Using EN measurement, it was also possible to study in detail the effectiveness of inhibitors and organic coatings (Fig. 5c and d) in preventing pitting corrosion in steels [97,98]. The application of corrosion inhibitors could be optimized based on information obtained through EN analysis. By quickly identifying the effectiveness of different inhibitors under varied conditions, industries could select the most suitable compounds to protect their equipment. EN could also be used to continuously monitor the condition of metal surfaces in industrial environments, allowing early detection of passive layer failures and implementation of corrective measures before significant corrosion occurs [104].

3. Comparison among electroanalytical methods

3.1. Complementarity of the information achieved

The electroanalytical techniques used for corrosion monitoring differ fundamentally in the type of electrical signal applied, which directly influences the nature and depth of the information obtained (Table 2). Direct voltammetric methods, such as LPR and PDP, involve the application of a fixed or slowly varying potential and are widely used to quantify corrosion rates by estimating the corrosion current density. These techniques, although relatively simple and informative, can disturb the electrochemical equilibrium of the system, particularly in systems with unstable or evolving interfaces.

In contrast, alternating current techniques, such as EIS, apply small amplitude sinusoidal perturbations over a range of frequencies, allowing the characterization of interfacial processes, such as charge transfer resistance and double layer capacitance, with minimal disturbance to the system. EIS is particularly useful for studying corrosion under protective coatings or inhibitor films, where subtle interfacial changes must be monitored without altering the surface condition.

EN presents a complementary and non-invasive approach that records spontaneous fluctuations in current and potential over time, typically without any external disturbance. This makes EN especially valuable for monitoring localized corrosion, including pitting and crevice corrosion, in real time.

By combining methods based on direct current, alternating current and noise signals, it is possible to obtain a more comprehensive understanding of corrosion processes. The complementary use of these techniques helps to overcome the limitations inherent in each method individually, increasing reliability in complex environments and aiding more accurate diagnostics in corrosion monitoring programs, justifying why several articles use more than one method in corrosion monitoring.

3.2. Analytical performance in comparison with traditional methods

Electroanalytical approaches, such as EIS and EN analysis, offer substantial advantages in terms of precision, sensitivity, and real-time monitoring capabilities [105] with respect to conventional analytical

Table 2
Overview and comparison of corrosion monitoring methods for field application described in the literature and reported in this review.

Method	Sensitivity	Accuracy	Range of measurement	Field applications	Ref
PDP	Moderate. Defines active, passive and transpassive regions.	Moderate. Accurate for system stability.	From mA to μA	Used for measuring corrosion in reinforcements and stainless steel; also applied in the evaluation of corrosion inhibitors and protective coatings.	[52,55,56,61]
LPR	Moderate. Linear variation in ±30 mV	Moderate. Accurate for uniform corrosion; overestimates pitting.	From mA to nA	Applied for monitoring uniform and localized corrosion, including real-time and in-situ monitoring along pipelines; also used for assessing inhibitors and coatings.	[69,70,71,78]
EIS	High. Detects passive films, diffusion, micro-corrosion.	High. Depends on complex EEC.	From 100 kHz to 0.1 Hz	Suitable for pipelines and marine structures; used for real-time monitoring of coating integrity and effectiveness of corrosion inhibitors.	[74,75,83,76]
EN	High. Pitting and passive failures.	Moderate. Qualitative; difficult to quantify precisely.	From mA to μA	Applied to monitor corrosion rates in harsh environments (e.g., high temperatures, stainless steel); effective for detecting localized corrosion (e.g., pitting), assessing pipeline integrity, and offshore/marine applications.	[12,95,97,98]

methods used for corrosion detection (see Table 1). These techniques allow for a more detailed and accurate assessment of corrosion processes, capturing intricate details about the rate, nature, and kinetics of corrosion, as well as the effectiveness of protective coatings and inhibitors [106]. EIS, for instance, provides detailed information about the corrosion process, including the resistance of protective films, and can be used to model corrosion behavior using EECs to determine polarization resistance values, which are inversely proportional to corrosion rates [107].

While traditional methods continue to provide economical and practical solutions for many scenarios, the superior performance of electroanalytical approaches justifies their investment, particularly in critical applications where precise data is essential [108]. These methods are not only capable of delivering precise, detailed, and environmentally friendly data but also enhance the ability to monitor and mitigate corrosion in real-time, thus preventing potential failures and extending the lifespan of critical infrastructure [109]. The ongoing advancements in electroanalytical techniques, coupled with the integration of machine learning and artificial intelligence for data analysis, further underscore their potential to revolutionize corrosion monitoring [110].

In essence, while traditional corrosion monitoring methods have their place in the industry due to their cost-effectiveness and practicality, electroanalytical approaches represent the future of corrosion monitoring. Their ability to provide comprehensive, real-time data and adapt to various environmental conditions makes them indispensable tools in the ongoing effort to protect and maintain vital infrastructure. Investing in these advanced methods is a strategic decision that aligns with the goals of sustainable development and the need for high-performing, reliable corrosion monitoring systems.

4. Electrochemical sensors as new tools for the corrosion monitoring

Among electroanalytical methods for corrosion monitoring, electrochemical sensors are particularly promising due to their cost-effectiveness, user-friendliness, and portability. These characteristics make them ideal for real-time, on-site detection of corrosion in a variety of environments. A landmark study in this field was published by Sassolini et al. which marked the first investigation into miniaturized electrochemical sensors for corrosion monitoring [111]. In this study, the authors employed silver screen-printed electrodes to monitor corrosion by detecting the spontaneous potential occurring in reinforced concrete as a key indicator of the probability for corrosion occurrence. This novel approach provides an effective means for the early detection of corrosion, offering a practical and economic tool for structural integrity monitoring. The sensor was firstly tested in the laboratory using reinforced concrete samples and then applied on the real outdoor artwork *Music Collection Session* by Arman (Milan, Italy) [112].

Despite the promising potential demonstrated in laboratory studies, bridging the gap between these studies and large-scale applications remains a significant challenge [113]. Also based on our personal experience, we can assume that several factors limit the successful technological transfer of electroanalytical methods, particularly electrochemical sensors, for corrosion monitoring in real-world settings. Among the primary obstacles are issues related to the lifespan, repeatability, and reliability of these sensors under varying environmental conditions [114].

The lifespan of electrochemical sensors, especially in harsh environments where corrosion rates can fluctuate, can be a major concern. Sensors must maintain their sensitivity and accuracy over extended periods, which is critical for long-term monitoring of infrastructure. Additionally, repeatability — i.e. the ability of the sensor to provide consistent results across multiple measurements or devices — is crucial for ensuring reliable data. In many cases, sensors that perform well in controlled laboratory conditions may struggle to maintain their effectiveness in more variable, complex, or dynamic real-world environments. Furthermore, the reliability of these sensors is paramount; any failure or deviation in their performance could lead to incorrect corrosion assessments, which could jeopardize the safety of the structures being monitored.

Addressing these challenges requires ongoing research and development, particularly in improving sensor materials, enhancing calibration techniques, and developing more robust sensor designs that can withstand the diverse conditions encountered in real applications. For instance, Souza et al. investigated the diffusion of iron in a 0.5 M HCl solution, a medium commonly employed in studies of carbon steel corrosion and the evaluation of corrosion inhibitors [115]. The study quantified diffusion coefficients for Fe^{2+}/Fe^{3+} ions by fitting experimental current data, introducing a parameter not previously reported in the literature. These results hold potential for advancing electroanalytical methods to monitor Fe^{2+}/Fe^{3+} concentrations in HCl solutions associated with carbon steel corrosion.

Transitioning from laboratory-based studies to field implementations necessitates careful validation and calibration of electroanalytical methods under realistic operating conditions, considering factors like environmental variability and sensor longevity [116]. Collaborative efforts between researchers, industry stakeholders, and regulatory bodies are indispensable for streamlining the technological transfer process and facilitating the widespread adoption of electrochemical methods for carbon steel corrosion monitoring [117]. These efforts will ultimately contribute to the resilience and sustainability of infrastructure worldwide by providing more accurate and timely data on corrosion processes, thereby informing maintenance and prevention strategies [118].

5. Conclusions

This review underscores the paramount importance of corrosion monitoring, particularly employing electroanalytical methods, in comparing the pervasive threat of electrochemical corrosion, which exacts substantial and often irreparable damage to both infrastructure and human safety. In this frame, electroanalytical techniques offer several advantages for corrosion monitoring, including in-situ applicability, although their application implies to overcome important challenges. Indeed, techniques such as EIS and PDP often require complex data interpretation and modeling. For example, EIS data must be fitted to appropriate equivalent circuit models to extract meaningful parameters, which can introduce uncertainties and subjective results. This fitting process demands expertise and may lead to inconsistencies, especially when multiple valid models can describe the same data.

Furthermore, accurate corrosion quantification using voltammetric and amperometric methods relies on robust calibration curves and well-characterized reference systems. However, calibration is strongly affected by the wide variability of the matrix composition, temperature, or flow conditions, which limit the application of these techniques in the real environment. Long-term operation under corrosive conditions remains also a significant obstacle. Electrodes may suffer from surface fouling, drift, or degradation over time, particularly in multiphase systems containing solids, microorganisms, or aggressive ions such as Cl^-. These factors impair sensor repeatability and may require frequent maintenance or replacement. Moreover, long-term exposure to corrosion inhibitors or coating leachates can interfere with the electrode response.

Despite all these challenges, the latest advances in miniaturization technology allowed the realization of compact instrumental devices that can be installed in the pipeline, also ensuring waterproofness, power autonomy, wireless communication, and data integrity under variable conditions, especially for long-term unattended monitoring.

Therefore, while electroanalytical methods hold great promise for corrosion monitoring, these limitations must be acknowledged and addressed. Continued research is needed to develop more robust

analytical devices, automated data interpretation algorithms, and standardized deployment protocols tailored for industrial environments to facilitate technological transfer from the laboratory to the field. These are other reasons why we should opt and invest in electroanalytical approaches for corrosion monitoring. By facilitating the adoption of electroanalytical methods, particularly in regions or industries where such expertise may be lacking, technological transfer initiatives can catalyze improvements in corrosion management practices, thereby reducing economic losses and enhancing safety standards. Moreover, investing in the dissemination of these methods ensures that emerging economies and smaller enterprises can leverage cutting-edge technologies to address corrosion challenges effectively, aligning with broader goals of sustainable development and inclusive growth. In essence, prioritizing technological transfer in electroanalytical methods represents a strategic investment in the resilience and longevity of infrastructure worldwide, underscoring its indispensable role in safeguarding critical assets and fostering socio-economic progress.

CRediT authorship contribution statement

Michael D.P. Souza: Writing – original draft, Conceptualization. **Giulia Moro:** Writing – original draft, Conceptualization. **Rodrigo S. Melo:** Writing – original draft. **Ligia M. Moretto:** Writing – review & editing, Supervision. **Simone L.D.C. Brasil:** Writing – review & editing, Supervision. **Chiara Zanardi:** Writing – review & editing, Supervision.

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.

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Data availability

Data will be made available on request.

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