



Short communication

Screen-printed electrode as a cost-effective and miniaturized analytical tool for corrosion monitoring of reinforced concrete

Alessandro Sassolini^{a,1}, Noemi Colozza^{b,1}, Elena Papa^b, Kersti Hermansson^c, Ilaria Cacciotti^d, Fabiana Arduini^{b,*}

^a ARPA Lazio, Via Salaria per L'Aquila 6-8, 02100 Rieti, Italy

^b Department of Chemical Science and Technologies, University of Rome Tor Vergata, Via della Ricerca Scientifica, 00133 Rome, Italy

^c Department of Chemistry-Ångström, Uppsala University, Box 538, S-75121 Uppsala, Sweden

^d Department of Engineering, University of Rome Niccolò Cusano, Via Don Carlo Gnocchi 3, 00166 Rome, Italy

ARTICLE INFO

Keywords:

Screen-printed reference electrode

Agar gel

Potentiometric measurement

Iron bar corrosion

ABSTRACT

Herein, we report the first electrochemical sensor based on a screen-printed electrode designed to evaluate the corrosion level in iron-reinforced concrete specimens. The combination of an Ag pseudoreference electrode with a gel polymeric electrolyte allows for fast, stable and cost-effective potentiometric measurements, suitable for evaluating the corrosion of iron bars embedded in concrete samples. The sensor was found to be capable of discriminating between a standard non-corroded sample and samples subject to corrosion due to the presence of chloride or carbonate in the concrete matrix. The potential in concrete-based specimens containing carbonate (pH 9, -0.35 ± 0.03 V) or chloride (4% w/w, -0.52 ± 0.01 V) was found to be more negative than in a standard concrete-based sample (-0.251 ± 0.003 V), in agreement with the ASTM standard C876 method which uses a classical Cu/CuSO₄ solid reference electrode. Our results demonstrate that a printed Ag pseudoreference electrode combined with KCl agar provides an efficient and reliable electrochemical system for evaluating the corrosion of iron bars embedded in concrete-based structures.

1. Introduction

In the 19th century, the introduction of reinforced concrete established a milestone in the construction industry, and it is now one of the most common building materials worldwide. The widespread use of concrete can be ascribed to its ability to be moulded into almost any shape, giving it an intrinsic advantage over other materials. To overcome its limited tensile strength, reinforced concrete was then produced, with steel bars embedded in concrete. One of the main limitations of reinforced concrete is the corrosion of the steel reinforcing bars, which can result in damage to concrete-based structures such as buildings, bridges, and highways. To cite an old example, in 1967 the sudden collapse of the Silver Bridge over the Ohio River at Point Pleasant resulted in the loss of 46 lives and costs of millions of dollars, while in more recent times, August 2018, the Morandi bridge in Genoa (Italy) collapsed with 43 deaths. One of the key points in preventing such disasters is the delivery of a fast, cost-effective, and easy to use corrosion monitoring system able to reveal the onset or progress of corrosion so that the necessary countermeasures can be taken in good

time.

Several techniques are currently in use for corrosion monitoring in both the laboratory and the field, including half-cell potential measurements, linear polarization resistance measurements, and electrochemical impedance spectroscopy [1]. Among these, the half-cell potential test is the only corrosion monitoring technique standardized by the American Society for Testing and Materials (ASTM), to determine the probability of corrosion within the rebar in reinforced concrete structures. The system is based on the measurement of the potential between the steel reinforcing bar and a Cu/CuSO₄ reference electrode, where the reference electrode is connected to the negative end of the voltmeter and the steel reinforcing bar to the positive end. The empirically obtained data supplies an indication of the relative probability of corrosion occurring [2,3], which forms the basis of the ASTM standard C876 method. In more detail: for measured potential values (vs the Cu/CuSO₄ electrode) lower than -0.200 V, the standard method infers a 10% probability of corrosion; values between -0.200 V and -0.350 V are associated with an increasing probability of corrosion; while values lower (larger in magnitude) than -0.350 V correspond to

* Corresponding author at: Dipartimento di Scienze e Tecnologie Chimiche, Università di Roma Tor Vergata, Via della Ricerca Scientifica, Rome, Italy.

E-mail address: fabiana.arduini@uniroma2.it (F. Arduini).

¹ These authors contributed equally.

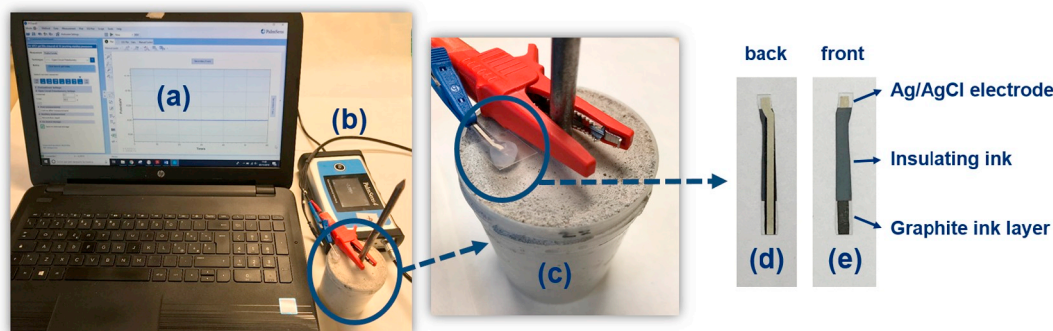


Fig. 1. Experimental set-up used in this work. In detail: (a) a laptop and (b) a portable potentiostat were used to analyse (c) concrete-based specimens by means of (d, e) a printed Ag/AgCl sensor.

a 90% probability of corrosion [4].

In recent years printing technology has boosted the development of miniaturized and mass-produced sensors for cost-effective and customised use in field measurement. A number of screen-printed electrodes and ink-jet printed electrodes have been widely reported in the literature for applications in the environmental field, with extensive tests of sensors in several matrices including river and lake water, soil, and plants [5,6].

For easy to use applications in the field of concrete, solid sensors are usually combined with wet interfaces. In the hunt to develop suitable sensors, some gel polymeric materials such as chitosan [7], pectin [8], and agar [9] have been investigated as polymeric electrolytes. They have several advantages, such as being easily customised and loaded with salt (e.g. NaCl) as well as being safe for human beings and the environment, although they have not yet been used for concrete monitoring.

Herein, we report the first application of a printed electrochemical reference electrode combined with a gel polymeric electrolyte for measurement of corrosion in reinforced concrete samples.

2. Experimental

2.1. Apparatus and reagents

Potentiometric measurements were performed using a PalmSens portable instrument (The Netherlands). All reagents used were analytical grade and obtained from Sigma (St. Louis, MO). Portland Buzzi Unicem II/B-LL R 32.5 and river sand Uni EN 12620 were used to produce the concrete sample.

2.2. Preparation of agar gel-based electrolyte

Agar powder was dispersed in electrolyte solution (KCl 0.1 M) to give a final concentration of 2.5% w/v, heated until the agar dissolved and then allowed to cool down in a petri dish (diameter 10 cm). The resulting gel was cut into cylindrical samples with a diameter of 7 mm and thickness of 5 mm. The gel cylinders were placed in contact with the reference electrode and the concrete surface.

2.3. Preparation of printed reference electrode

The reference screen-printed electrode was home-produced with a 245 DEK (Weymouth, UK) screen-printing machine, using a flexible polyester film (Autostat HT5) obtained from Autotype Italia (Milan, Italy) as substrate and silver chloride (Electrodag 6038 SS) as ink to produce the reference electrode [10].

2.4. Preparation of reinforced concrete specimens

Portland cement and river sand in a 1:2 (w/w) ratio were used to prepare concrete-based specimens (150 ml of water was added to 1 kg of powder). The concrete paste was then divided into four identical specimens for a reproducibility study. An iron rod (length 18 cm and diameter 1.8 cm) was embedded in the concrete paste of each specimen and after 28 days a solid concrete-based specimen was obtained. To study the chloride-based corrosion effect, three different groups of four specimens with different percentages of calcium chloride (1, 2, 4, %w/w) were produced by adding calcium chloride to the concrete paste. To evaluate carbonate-based corrosion, sodium bicarbonate (NaHCO_3) was added (around 40 g) until the initial pH of 13 decreased to pH 9 [11].

2.5. Experimental measurement set-up

Potentiometric measurements were carried out on the reinforced concrete specimens by connecting the steel bar with crocodile clip to the printed reference electrode with a contact to the potentiostat. To close the electrochemical cell, the printed reference electrode was placed in contact with the concrete surface by means of an agar gel-based electrolyte (KCl in agar gel) (Fig. 1).

3. Results and discussion

Steel embedded in concrete encounters a favourable environment (alkaline conditions) for iron passivation as a consequence of the production of an iron oxide film (i.e. Fe_2O_3) on the surface; this acts as a protective layer. However, the resistance to corrosion due to this protective layer tends to drastically decrease when the reinforced concrete is exposed to chlorides or CO_2 (carbonation reaction), resulting in the steel becoming depassivated and the observation of active corrosion. To evaluate the suitability of our new sensor system, several studies were carried out using the different concrete specimens prepared in the presence and absence of CaCl_2 and NaHCO_3 , as described below.

First, the sensor was tested with a pristine concrete specimen and a potential value equal to 0.218 V was obtained. This figure is in agreement with the value reported by the ASTM standard C876 method corresponding to only 10% probability of corrosion. It should be taken into account that we have used a Ag pseudo-reference electrode which has a slightly lower potential (0.285 vs NHE) with respect to the Cu/ CuSO_4 reference electrode (0.314 V vs NHE).

To deliver a successful sensor, the repeatability and the robustness of the analytical device are of prime importance and these aspects were evaluated for the reinforced concrete sample in the absence of CaCl_2 and NaHCO_3 (Fig. 2). We thus tested the same device in 10 successive measurements, obtaining an intra-electrode repeatability (RSD%) equal to 0.5% (Fig. 2A). We also evaluated the repeatability in an inter-electrode procedure by testing the same concrete-based sample with

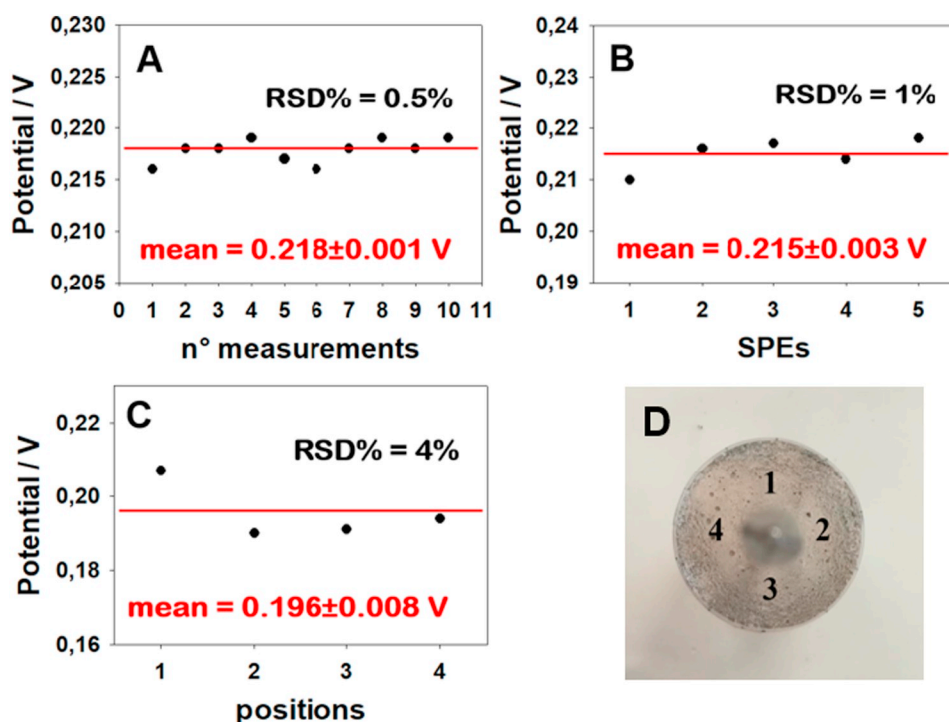


Fig. 2. (A) Study of the intra-electrode repeatability, measuring the potential using the same printed reference electrode and the same piece of gel. (B) Study of inter-electrode repeatability using different printed reference electrodes and piece of gel. (C and D) Evaluation of the homogeneity of the sample, to study if the position of the reference electrode can affect the measurement.

different gel-based electrolytes and different printed reference electrodes, obtaining a RSD% equal to 1% (Fig. 2B). Thus, outstanding repeatability was demonstrated, especially when bearing in mind that both the gel-based electrolyte and the printed reference electrodes were produced manually. Fig. 2C and D show the results of our tests of the homogeneity of one of our samples, and confirms that the samples exhibit satisfactory homogeneity.

To challenge the sensor towards samples subjected to a corrosion process, a concrete-based specimen prepared with NaHCO_3 with a final pH equal to 9 was evaluated with the aim of simulating environmental

carbonation [12]. As expected, we observed a decrease in the potential (to -0.35 ± 0.03 V), ascribed to carbonation-based corrosion (Fig. 3A). As a consequence of the carbonation process an increase in the Fe oxidation reaction occurs. Furthermore, satisfactory repeatability was also observed in this case, with intra-electrode RSD% equal to 0.3% (Fig. 3B).

To evaluate the capability of the sensor to monitor the corrosion generated by chloride, three concrete samples prepared with different amounts of CaCl_2 (1, 2 and 4% w/w) were tested. We found that when the amount of chloride content in the concrete matrix was increased, a

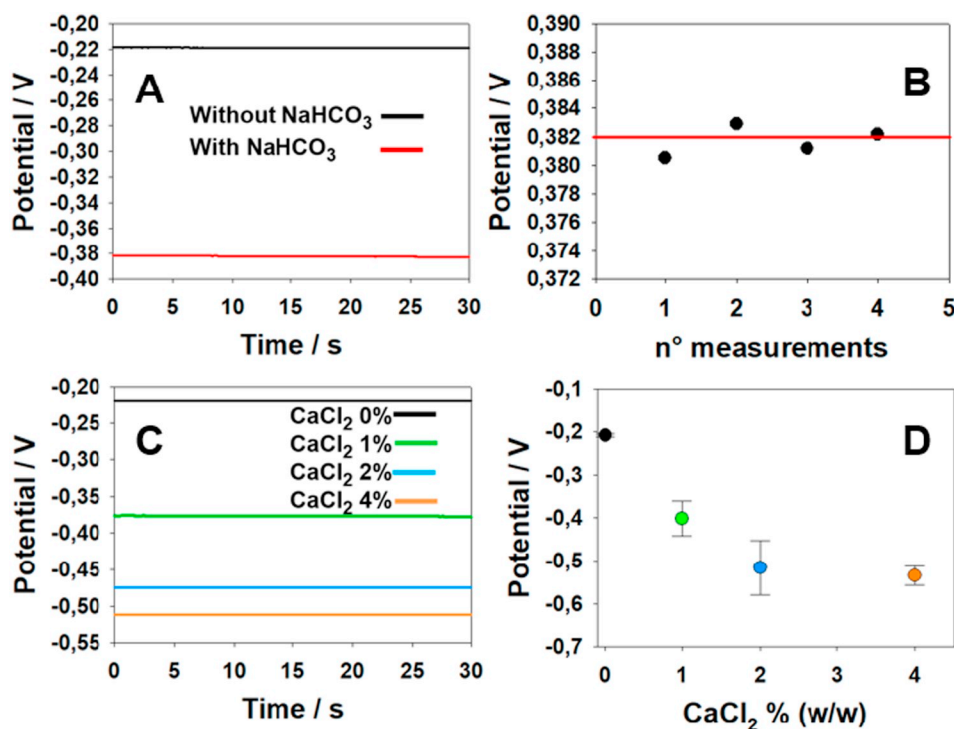


Fig. 3. (A) Potentiometric measurements using concrete-based specimen in the absence (black line, pH = 13) and in presence of carbonate (red line, pH = 9). (B) Repeatability measures of samples with carbonate. (C) Typical potentiometric measurements in the presence and absence of different amount of chloride. (D) Potential obtained with different amounts of chloride, measurements carried out in triplicate. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

more negative potential was observed (Fig. 3C, D). As in the case of the carbonation process, the presence of chloride boosts the corrosion with the consequent oxidation reaction of Fe at the steel bars, giving rise to a more negative potential [13].

4. Conclusion

In this work, a cost-effective and miniaturized electrochemical sensing tool has been designed and produced with the aim of evaluating the corrosion of steel bars embedded in concrete. The combination of a silver-based printed pseudoreference electrode with a gel-based electrolyte (KCl in agar gel) makes it possible to perform the measurement directly on the concrete sample without any sample treatment. Since the printed electrochemical reference sensor has been conceived as a miniaturized electrode, the sensing tool can easily be embedded in a concrete structure for on-line monitoring at low cost. Since concrete is the most widely used manufactured material globally, and climate change can accelerate the deterioration of concrete infrastructure, much work is being done to reduce the economic impact of concrete testing. In this overall scenario, the sensing tool that we have presented here could pave the way for a cost-effective sensing system, expanding the application of printed electrodes to the construction-engineering sector.

Acknowledgments

This work was supported by INNOCONCRETE project “Innovative tools for conservation and monitoring of artworks in concrete by exploiting electrochemical paper-based sensors, functionalized nanomaterials, and modelling”, financed by the Executive Program on Scientific and Technological Cooperation between Italian Republic and Sweden,

through Ministry of Foreign Affairs and International Cooperation and the Swedish Research Council (VR).

References

- [1] J. Gao, J. Wu, J. Li, X. Zhao, Monitoring of corrosion in reinforced concrete structure using Bragg grating sensing, *NDT E Int.* 44 (2011) 202–205.
- [2] D.L. Spellman, R.F. Stratfull, *Concrete Variables and Corrosion Testing*, (1972).
- [3] R.F. Stratfull, *Half-Cell Potentials and the Corrosion of Steel in Concrete*, No. 433, (1973).
- [4] A.S.T.M. Standard, C876: Standard Test Method for Corrosion Potentials of Uncoated Reinforcing Steel in Concrete, ASTM International, West Conshohocken, PA, 2009.
- [5] F. Arduini, S. Cinti, V. Scognamiglio, D. Moscone, G. Palleschi, How cutting-edge technologies impact the design of electrochemical (bio) sensors for environmental analysis. A review, *Anal. Chim. Acta* 959 (2017) 15–42.
- [6] A. Antonacci, F. Arduini, D. Moscone, G. Palleschi, V. Scognamiglio, Nanostructured (Bio) sensors for smart agriculture, *Trends Anal. Chem.* 98 (2017) 95–103.
- [7] A. Pawlicka, M. Danczuk, W. Wiczorek, E. Zygadło-Monikowska, Influence of plasticizer type on the properties of polymer electrolytes based on chitosan, *J. Phys. Chem. A* 112 (2008) 8888–8895.
- [8] J.R. Andrade, E. Raphael, A. Pawlicka, Plasticized pectin-based gel electrolytes, *Electrochim. Acta* 54 (2009) 6479–6483.
- [9] E. Cano, A. Crespo, D. Lafuente, B.R. Barat, A novel gel polymer electrolyte cell for in-situ application of corrosion electrochemical techniques, *Electrochem. Commun.* 41 (2014) 16–19.
- [10] N. Colozza, M.F. Gravina, L. Amendola, M. Rosati, D.E. Akretche, D. Moscone, F. Arduini, A miniaturized bismuth-based sensor to evaluate the marine organism *Styela plicata* bioremediation capacity toward heavy metal polluted seawater, *Sci. Total Environ.* 584 (2017) 692–700.
- [11] C. Andrade, J.A. González, Quantitative measurements of corrosion rate of reinforcing steels embedded in concrete using polarization resistance measurements, *Mater. Corros.* 29 (1978) 515–519.
- [12] A. Goyal, H.S. Pouya, E. Ganjian, P. Claisse, A review of corrosion and protection of steel in concrete, *Arab. J. Sci. Eng.* 43 (2018) 5035–5055.
- [13] M. Manera, Ø. Vennesland, L. Bertolini, Chloride threshold for rebar corrosion in concrete with addition of silica fume, *Corros. Sci.* 50 (2008) 554–560.