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Sensor for oxygen evaluation in concrete

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Abstract

This paper includes results from a research work carried out for developing and optimising a sensor to measure the limiting current of oxygen reduction in concrete.

Platinum, stainless steel and carbon steel materials were tested as working electrodes in saturated $Ca(OH)_2$ solution. Linear correlations were obtained between the limiting currents of oxygen reduction and the oxygen concentration in solution.

The measurements of the limiting current density due to oxygen reduction have been made in concrete specimens with a sensor consisting of platinum and stainless steel, as working electrodes, graphite, as a counter electrode, and activated titanium, as a reference electrode, under different conditions of water and oxygen accessibility to the concrete. The results show that this sensor detects oxygen content variations in the interstitial solution of the concrete, providing qualitative information about the evolution of oxygen availability in concrete.

Keywords: Concrete; Durability; Corrosion monitoring; Oxygen sensor; Limiting current for oxygen reduction

1. Introduction

The implementation of a maintenance strategy together with the adequate monitoring procedures is considered as essential to prevent the premature corrosion of reinforcements and its consequences on the durability of concrete structures.

Sensors and associated monitoring systems can provide a realistic assessment of the service life of a structure giving information about both a spatial distribution and a temporal change in concrete cover properties, and concerning the reinforcement state [1].

The oxygen transport is one of the different measures that must be considered in the assessment of cover zone quality [1]. Vennesland [2], in a study dedicated to the evaluation of maintenance methods at Gimsøystraumen Bridge, points out this determination as the most conclusive one of the electrochemical monitoring methods used.

In submerged structures, for which the degree of saturation will generally be very high, the rate of steel corrosion is primarily controlled by diffusion of dissolved oxygen through the concrete cover [2–4]. The availability of oxygen at the reinforcement steel surface, as well as the mechanism and kinetics of oxygen reduction can thus be considered as essential factors for the corrosion of steel in concrete.

Significant attention has been paid to the subject of oxygen transport in concrete [2,4–8]. The oxygen transport evaluation using electrochemical techniques is based on the assumption that when a sufficiently negative potential, within a limited potential domain, is applied to the working electrode, the only cathodic reaction is the reduction of oxygen and, then, the oxygen transport may be recorded as an electrical current.

There are also some articles that address the mechanism and kinetics of oxygen reduction on iron, in alkaline solutions [9–14]. These papers propose an oxygen reduction mechanism on iron that involves the mediation of surface Fe(II) sites, formed by reduction in the passive film, which act as adsorption centres promoting the oxygen reduction reaction.

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Although the generalized opinion that the absence of oxygen in the vicinity of iron interrupts the corrosion, recent studies have disclosed that other reduction reactions will be able to assure its progression [4,15,16]. Alonso et al. [4] reported that once corrosion has been initiated, this process might be developed with a certain activity, even if there is a lack of oxygen.

Other research studies have been devoted to the cathodic reduction of oxygen in alkaline solutions simulating concrete and in concrete [17–19], reporting its influences on the reinforcement steel corrosion.

Considering the role of oxygen reduction on the reinforcement steel corrosion and the stated importance of monitoring systems, the main objectives of the present study are to develop and to evaluate a sensor to be used for monitoring the oxygen availability in concrete. When integrated in a corrosion monitoring system, this sensor would be able to provide complementary information about the main cathodic reaction and also concerning the external factors that may limit it.

2. Experimental

2.1. Studies performed in solution

Potentiodynamic tests were performed to study the influence of the working electrode material on oxygen reduction. Platinum (wire of 0.45 cm^2), AISI 316 stainless steel ($l = 13$ mm, diameter = 10 mm) and low carbon steel ($l = 13$ mm, diameter = 10 mm) were tested as working electrodes. Platinum was used as a counter electrode and the reference electrode was a Hg|HgO (0.1 M KOH) XR400, from Radiometer Copenhagen. The potentials were converted to the Standard Hydrogen Electrode (SHE) scale.

For the potentiodynamic studies, a Solartron system (SI 1287 interface, SI 1260 frequency response analyser) was used. Negative potential scans at 0.5 $mV\,s^{-1}$ were carried out from the open circuit potential to −0.90 V and −1.07 V, respectively, with platinum (Pt) and with carbon (CS) and stainless steel (SS) working electrodes. The experiments were conducted in an electrochemical cell (ASTM G5) filled with an unstirred saturated aqueous solution of $Ca(OH)_2$, pH 12.6, at 25 °C. According to Page and Treadaway [20], this solution may be taken as an approximate electrolyte to concrete pore solution. The levels of O_2 in the solution were reduced in a controlled way by bubbling N_2 through the solution in the cell before each electrochemical experiment. A galvanic WTW oxi 330 oxygen sensor with a cellox 325 probe was used for the measurements of the oxygen concentration in the solution.

2.2. Studies performed in concrete

A sensor was prepared consisting of either platinum ($l = 20$ mm, diameter = 0.5 mm) or stainless steel ($l =$ 26 mm, diameter = 6 mm) as working electrodes, graphite ($l = 30$ mm; diameter = 12 mm) as a counter electrode, and activated titanium (wire of $l = 26$ mm) as a reference electrode ($E_e = +0.143$ V (SHE)) [21]. The electrode materials were connected to a cable of four electrical conductors and inserted into a plastic mould. Araldite and epoxy resin were used to isolate the contacts and to define the working areas of the electrode materials.

Concerning the reference electrode, the use of activated titanium has been reported for this purpose [1,21] and previous experiments in solution have been quite satisfactory concerning its reproducibility and stability [22].

The sensors were embedded in concrete prisms ($10 \times 10 \times 12$ cm), which were prepared with concrete made of cement type I, with a cement content of 300 $kg\,m^{-3}$ and a water to cement ratio of 0.5, were cured for seven days in a chamber with a degree of humidity of 95 ± 5%. The sensors (I, II and III) were set to provide a concrete cover thickness of 15 mm with respect to the working electrode materials.

The concrete prisms with the embedded oxygen sensors were then submitted to the exposure conditions given in Table 1, in order to evaluate the performance and also the durability of the sensor in concrete under different oxygen access conditions.

To evaluate the influence of chloride, one of the sensors was immersed in a 10% NaCl aqueous solution and compared with another one that was kept during the same period immersed in distilled water. Before the electrochemical measurements, both sensors were submitted to similar conditions at room temperature. The concrete prisms were previously immersed for 10 days in dearated water (C6) and then dried for seven days in a chamber at 60% RH (C7).

For the electrochemical experiments, a PC4 Gamry system equipped with a potentiostat was used. The cathodic currents were determined potentiodynamically and the electric resistance of concrete by electrochemical impedance spectroscopy (EIS). Automatic ohmic compensation was applied during the potentiodynamic measurements.

Potentiodynamic scans at 1 $mV\,s^{-1}$ were performed from open circuit potential to −0.90 V (Ti_A) and −1.20 V

Table 1
Exposure conditions of concrete prisms

Conditions	
C1	Immersion in dearated distilled water at room temperature ($T = 20 \pm 2$ °C) for 18 days
C2	Drying in a chamber at room temperature ($T = 20 \pm 2$ °C; RH = 65 ± 5%) for 2 days
C3	Drying in a dearated atmosphere for 12 days at room temperature followed by 6 days at 40 °C, and by 1 day at room temperature ($T = 20 \pm 2$ °C)
C4	Immersion in dearated distilled water at room temperature ($T = 20 \pm 2$ °C) for 42 days, after a 12-month drying period in a chamber at RH = 60% and at room temperature ($T = 20 \pm 2$ °C)
C5	Exposure to the laboratory atmosphere ($T = 20 \pm 2$ °C; RH = 65 ± 5%) for 3 days, after a 7-month immersion period in water at room temperature ($T = 20 \pm 2$ °C)

(Ti_A), with platinum and stainless steel working electrodes, respectively. The EIS tests were carried out with a 10 mV ac modulation at open circuit potential, in the frequency range from 10^5 to 1 Hz.

3. Results and discussion

3.1. Studies performed in solution

Plots of the limiting current densities, i_L, as a function of the O_2 concentration for platinum, stainless steel and carbon steel electrodes are given in Fig. 1. These results were obtained from the potentiodynamic curves of each electrode in a saturated $Ca(OH)_2$ aqueous solution, at room temperature, with different concentrations of dissolved oxygen. Examples of such cathodic polarization curves of platinum and stainless steel working electrodes can be observed in Fig. 2.

The plots of i_L, as a function of $[O_2]$, yield linear correlations that are defined by the following equations: i_L $(\mathrm{A\,cm^{-2}}) = 9 \times 10^{-6}$ $[O_2]$ and i_L $(\mathrm{A\,cm^{-2}}) = 4 \times 10^{-6}$ $[O_2]$ for the platinum (Pt) and stainless steel (SS) electrodes, respectively, with $[O_2]$ given in $\mathrm{mg\,l^{-1}}$.

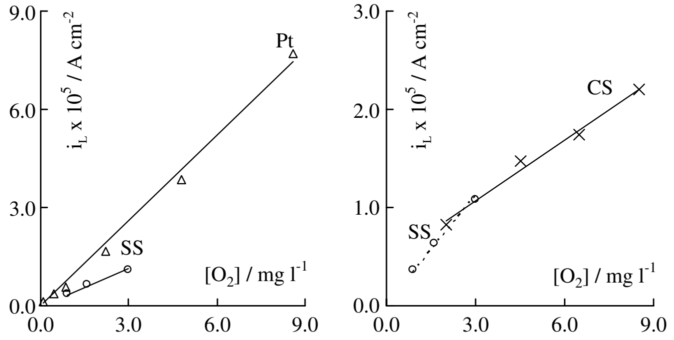

Fig. 1. Plots of limiting current density, i_L, vs oxygen concentration, $[O_2]$, obtained by cathodic polarization of platinum, carbon steel and stainless steel electrodes in $Ca(OH)_2$-saturated aqueous solution. $v = 0.5\ \mathrm{mV\,s^{-1}}$.

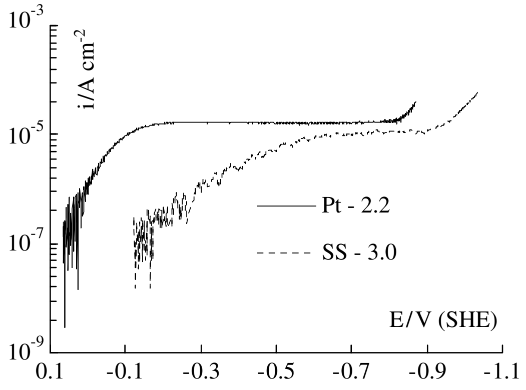

Fig. 2. Cathodic polarization curves of platinum (Pt) and stainless steel (SS) electrodes in $Ca(OH)_2$-saturated aqueous solution with different dissolved O_2 concentrations as indicated. $v = 0.5\ \mathrm{mV\,s^{-1}}$.

The limiting current densities of oxygen reduction for equivalent oxygen contents in solution are different on the platinum, carbon steel and stainless steel working electrode materials. Apparently, the oxygen reduction is inhibited on the steel electrodes, and particularly on carbon steel. For carbon steel electrode, the plot of the limiting current densities, as a function of the O_2 concentration, yield as well a linear relation although defined by i_L $(\mathrm{A\,cm^{-2}}) = (2[O_2] + 4) \times 10^{-6}$, with $[O_2]$ given in $\mathrm{mg\,l^{-1}}$. However it persists some doubts concerning the linear behaviour of carbon steel working electrode at low oxygen concentrations, because in those domains the experimental results does not allow a clear relation between the current limit density and the oxygen concentration in solution. This was the main reason to perform the tests with the stainless steel working electrode in a low oxygen concentration domain.

Analogous differences for the current densities, in the charge transfer control region, on platinum, carbon steel and stainless steel working electrode materials were also reported by Jäggi et al. [19]. The oxygen reduction inhibition on passive metals and a particularly lower exchange current density for carbon and stainless steels were the justifications given by these authors. It is also stated that such inhibition might cease once the steels started to corrode. However, comparable differences were not found in the diffusion limited region.

Other hypotheses can also be formulated. Calvo and Shiffrin [13] proposed an oxygen reduction on iron mechanism that involves the mediation of surface Fe(II) sites formed by reduction of the passive film, which act as adsorption centres. Several other research studies indicate that the electrocatalytic reaction of oxygen with these Fe(II) sites is an essential step in the reduction mechanism [9–11]. Thus, changes in the structure and composition of the oxide film can cause changes in the kinetics and in the reaction mechanism. It is also stated by Calvo and Shiffrin that if the reduction of Fe(III) to Fe(II) is somehow hindered the oxygen reduction will be inhibited. Since these studies are reported to iron, the dissimilar electronic structure of passive films formed on stainless steel can also be expected to interfere with the mechanism of oxygen reduction. As reported by several researchers, the stainless steel passive film can be described as a bi-layer consisting of a n-type outer region and a p-type inner region, respectively consisting of iron oxide and of hydroxide and chromium oxide [23,24].

In this study, the results may reflect the effect of the inhibition on the oxygen reduction by the passive layer formed on the stainless steel electrode, recently polished and introduced in the test solutions with low oxygen content. The results obtained with carbon steel electrode may also reflect the inhibitive effect of the oxide layer on the oxygen reduction reaction. Possible oxide modifications induced by polarization may also affect the oxygen reduction reaction.

According to the findings of different researchers [4,9–16], the modifications of oxide composition in the steel electrode are expected to influence the current values of oxygen reduction. Stratmann and Müller [15] demonstrate that the oxygen is predominantly reduced within the rust scale and that the kinetics of the electron transfer depends on the number of Fe(II) states inside the rust layer. Alonso et al. [4] reported that once the corrosion has been initiated, this process might develop with certain activity, even if there is a lack of oxygen. These results confirm the occurrence of more cathodic reactions than the oxygen reduction. According to these verifications, the condition of the electrode surface will affect the value of the current density of oxygen reduction measured with the carbon steel working electrode. Then, the measurements will reflect not only the oxygen reduction but also the passive film or the rust scale catalytic contribution, the latter under conditions that induce the steel depassivation.

The results obtained in this study also point to the occurrence of other reduction reactions and to their consequences on the oxygen reduction currents. The observation that the superficial condition of electrode surface affect the limiting current density values give further support to this hypothesis [25].

For embedded electrodes in concrete, the surface condition of the steel can easily change especially in chloride containing environments. Then, the low carbon steel is not suitable for the determination of the limiting current of oxygen reduction, since the oxygen reduction currents measured with it would include the contributions from other reduction reactions.

3.2. Studies performed with the oxygen sensor embedded in concrete

The values of the limiting currents measured from the plateaus of the potentiodynamic curves of two of the sensors embedded in concrete prisms (examples given in Fig. 3 for a specified condition) are reported in Fig. 4 for Pt and SS working electrodes. These figures show the oxygen reduction limiting current evolution during the conditions C1–C5 defined in Table 1. The exposure time for each condition is specified in the figures by the number of days following each condition initiation.

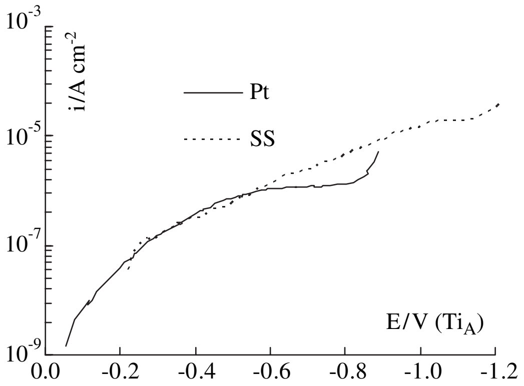

Fig. 3. Cathodic polarization curves of platinum (Pt) and stainless steel (SS) electrodes, after exposing the sensor to condition C3 (Table 1). $v = 1$ mV s^{-1}.

The evolution during the different steps of exposure was similar for Pt and SS, although the oxygen reduction limiting currents were quantitatively different for the two electrodes, as already observed in solution. However, the results in concrete are opposite to those obtained in solution with the same materials. According to these, the stainless steel working electrode originates limiting current density values considerably higher than the corresponding values obtained with platinum. It can only be assumed that, according to what has been previously described, in the concrete the passive oxide layer formed on the stainless steel surface must be different from that formed in solution. The results can then be explained if the passive film formed in concrete favours the reduction of the oxides and consequently the oxygen reduction as well. The increase in the

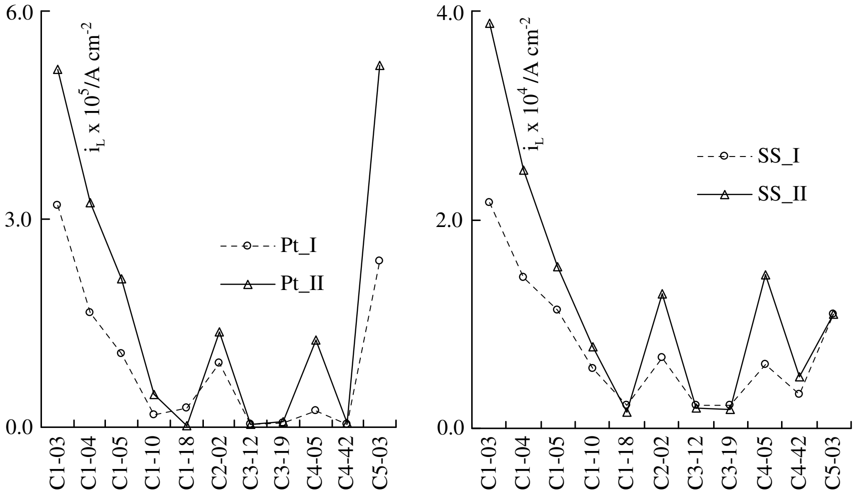

Fig. 4. Limiting current densities obtained from the polarisation curves on stainless steel (SS) and platinum (Pt) working electrodes from two of the sensors. $v = 1$ mV s^{-1}.

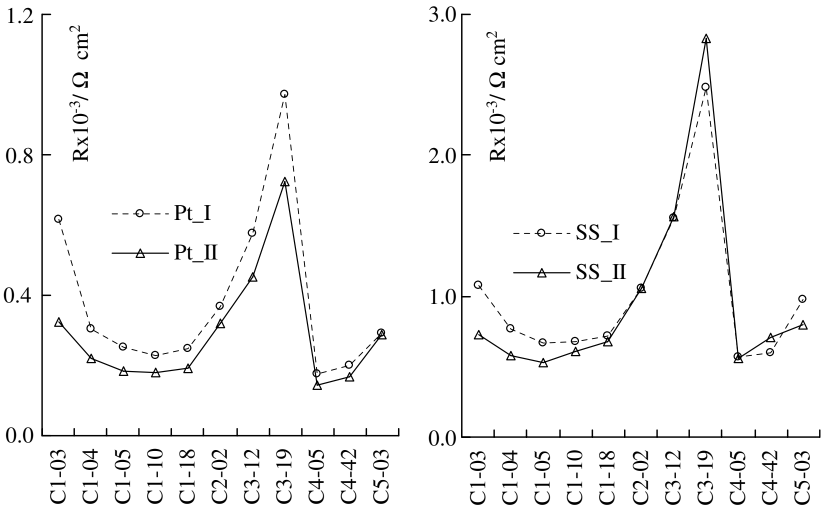

Fig. 5. Electric resistance determined from the EIS tests on stainless steel (SS) and platinum (Pt) working electrodes from two of the sensors.

oxygen reduction current may be explained by a catalytic effect possibly promoted by a larger amount of Fe(II) sites in the film formed in concrete than that created in solution.

Since it is also possible that the exposure conditions change the passive film characteristics in such a way that could modify the results over time, the experiments were performed as well after long periods of exposure time (C4 and C5). Nevertheless, the platinum and stainless steel working electrodes gave similar trends for the different conditions evaluated. Then it must be expected that, under conditions that do not induce the electrode corrosion, the stainless steel will be able to evaluate qualitatively the oxygen availability.

The results obtained for C4 and C5 conditions attest also to the durability of this oxygen sensor, since the electrochemical experiments after long periods of time still reproduce the previous ones (C1 and C2) under similar conditions.

Despite the similar limiting current evolution trends obtained with the two sensors, their different values are consequence of the concrete heterogeneity. In general, the differences between the sensor replicas are more significant for the smallest exposure periods than for the highest ones. The reproducibility of the tested sensor is generally improved by expanding the exposure period.

Fig. 5 shows the concrete electric resistance measured with two of the sensors (I and II) on both working electrodes by impedance spectroscopy. The resistance values were taken in each case as the real component of impedance at high frequencies for which the phase angle is nearly zero and the impedance module is frequency independent. The resistance results reflect very well the changes in the concrete wetness corresponding to the various experimental conditions.

The external humidity variations and its consequences on the concrete saturation degree influence the oxygen availability in concrete. In fact, when the concrete sample is fully saturated with water (after long periods of immersion) the oxygen transport is difficult, and consequently the oxygen would be depleted, the current densities reaching a minimum value (see C1 and C4). When dry concrete is exposed to open atmosphere, the concentration of oxygen in the interstitial solution should be at a maximum (see in particular data corresponding to the conditions C2 and C5). However, if the drying is carried out under an inert atmosphere of N_2, then, the oxygen concentration in the interstitial solution is minimal and a significant reduction in the limiting current of oxygen reduction (see data corresponding to the C3 condition) is likely to occur. These last results reflect essentially the oxygen concentration restriction since the concrete electric resistance is similar. Then, the concrete conditioning under restrict oxygen accessibility conditions may limit the primary reduction reaction of the steel reinforcement corrosion process. According to these results, this sensor would be able to

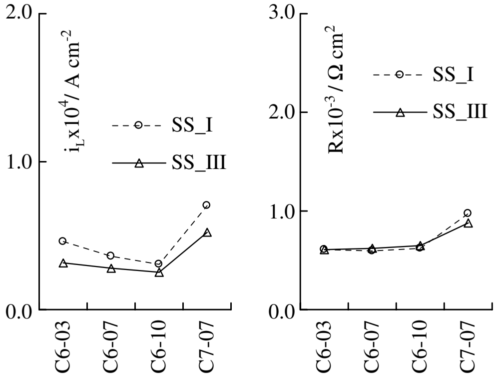

Fig. 6. Limiting current densities for oxygen reduction and concrete electric resistance measured with the stainless steel (SS) working electrode from two of the sensors after exposing the concrete prisms to the specified conditions (C6 and C7) at room temperature ($T = 20 \pm 2$ °C). $v = 1$ mV s^{-1}.

provide complementary information about the main cathodic reactions of the corrosion process, and also concerning the external factors that may limit it. As an example, this sensor may be useful to evaluate the effectiveness of superficial treatment processes for concrete that prevent the access of oxygen.

To verify the sensor durability under aggressive conditions, one of the sensors (III) was exposed to a 10% NaCl aqueous solution and the limiting currents were compared with those obtained with another sensor (I). The comparison of the two sensors was done by submitting the two sensors to 10 days in dearated water followed by seven days in a chamber at 60% RH at room temperature. The results exposed in Fig. 6 show that both sensors have a lower limiting current density in immersed conditions than after drying, and show an increase past the drying period. Sensor III, even after being submitted to contamination with chlorides, maintained a similar performance to sensor I. This result gives further support to the hypothesis that the stainless steel electrode will be able to give information about the oxygen availability in concrete even under conditions that normally induce the carbon steel corrosion.

4. Conclusions

The limiting current of oxygen reduction measured by potentiodynamic polarization with either platinum or stainless steel working electrodes proves to be an adequate methodology to evaluate the oxygen availability in solution, since linear correlations between the limiting currents and the O_2 concentration were obtained with these electrodes. However, the oxygen reduction on stainless steel may be influenced by the passive film reduction inhibition or by the electrocatalytic action of reduced oxide states existent on the electrode surface.

The carbon steel is not recommended for evaluating the availability of oxygen in concrete, because the superficial oxides modifications, induced either by exposure conditions or by polarization, influence the reduction currents.

The tests performed to evaluate reliability of the oxygen sensor showed that this electrochemical sensor, made of stainless steel, graphite and activated titanium, had a good performance. This sensor was sensitive to the changes in the oxygen concentration corresponding to various experimental conditions (wetting/drying conditions or absence/presence of oxygen). The limiting currents registered with both stainless steel and platinum showed similar trends, even under aggressive conditions.

As well, the good performance of the sensor during the long term tests even when under severe exposure conditions attests its durability.

The tested oxygen sensor can also give complementary information about the concrete saturation degree, since it allows the measurement of the concrete electric resistance.

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