DOI: 10.1002/maco.200905346

Embeddable reference electrodes for corrosion monitoring of reinforced concrete structures

G. S. Duffó*, S. B. Farina and C. M. Giordano

Mixed-metal oxide (MMO), graphite and laboratory-made Ag/AgCl electrodes were electrochemically characterized to be used as reference electrodes embedded in concrete structures. Electrodes were studied in both, aqueous solutions of pH ranging from 7 to 13.5 and embedded into cement mortars; and the electrochemical studies were carried out in the absence and presence of chloride ions. Potential evolution, polarisation behaviour, galvanostatic pulse response and impedance characteristics of the electrodes were carried out in aqueous solutions. Besides, the electrochemical stability of the electrodes embedded in mortar was studied for an exposure period of two years. It was found that the MMO pseudo-reference electrode is pH-sensitive, the graphite pseudo-reference electrode is oxygen sensitive and the Ag/AgCl pseudo-reference electrode is chloride sensitive. Then, regarding the corrosion monitoring of steel rebars, care should be taken to avoid misleading interpretations of the corrosion potential measurements. However, any of them can be used to measure the corrosion rate of the rebars by means of traditional electrochemical techniques.

1 Introduction

Reinforced concrete structures such as bridges, dams, and buildings involve large construction efforts, costing a great deal of money and spanning several years. Such structures are vital to the standard of living of millions of people worldwide and premature or unexpected failures of these structures are often catastrophic in terms of time, money and, in some cases, lives. This leads to the need for periodic evaluations of the structures. Concrete can undergo physical deterioration (cracking, frost, fire, etc.), chemical deterioration (sulphate attack, acid attack, sea water attack, alkali-aggregate reaction, leaching, etc.) and reinforcement corrosion [1, 2].

Corrosion of reinforcement bars (rebars) in concrete is recognized as a major problem in the maintenance of the structural integrity of structures. The concrete pH, usually in the range 12–13.5, provides chemical protection to the rebars due to steel passivation. However, with time, severe corrosion problems may occur in reinforced structures. The most important causes of corrosion initiation of reinforcing steel are the ingress of chloride ions and carbon dioxide to the steel surface. Chloride ion causes local destruction of the passive film leading to localized corrosion. Carbon dioxide, on the other hand, reacts with the hydrated cement matrix, leading to a pH decrease and subsequent loss of steel passivity and to corrosion initiation [3–5]. The corrosion of reinforcing steel in concrete is a major problem facing civil engineers and surveyors today as they maintain an ageing infrastructure. Potentially corrosion rehabilitation is a very large market for those who develop the expertise to deal with the problem. It is also a major headache for those who are responsible for dealing with structures suffering from corrosion [3].

The complexity of different types of corrosion makes corrosion monitoring difficult. A corrosion measurement system must be capable of making accurate measurements not only of electrochemical parameters related to corrosion rate (e.g., corrosion potential and/or polarisation resistance), but also of other important environmental parameters such as temperature, chloride ion concentration, concrete conductivity and oxygen

G. S. Duffó, C. M. Giordano
Comisión Nacional de Energía Atómica, Av. Gral. Paz 1499, (1650) San Martín, Buenos Aires, (Argentina)
E-mail: duffo@cnea.gov.ar

S. B. Farina, G. S. Duffó
Consejo Nacional de Investigaciones Científicas y Tecnológicas, Avda. Rivadavia 1917 - CP C1033AAJ - Cdad. de Buenos Aires (Argentina)

G. S. Duffó, S. B. Farina, C. M. Giordano
Universidad Nacional de Gral. San Martín, Campus Miguelete, Edificio de Gobierno: 25 de Mayo y Francia. CP 1650. San Martín, Provincia de Buenos Aires, (Argentina)

availability [5–7]. Then, the specialist can use all this information to assess the situation and take a decision concerning what mitigation strategies, if any, to apply.

The monitoring and control of corrosion of reinforcing steel in concrete requires reliable measurement of potentials, and embedded reference electrodes are essential elements of the sensor system [8]. Glass membrane electrodes are not fit for in situ measurements at the steel/concrete interface due to the very high alkaline environment at the interface and its fragility. A perfect embeddable electrode must obey several conditions: it must be stable, invariant to chemical and thermal changes in concrete, able to pass small currents with a minimum of polarisation and hysteresis effects, display long term performance, cost effective and result from an environmentally safe manufacturing. The long-term stability of reference electrodes is a critical issue, and in some cases pseudo-reference electrodes are used.

Reference electrodes used in reinforced concrete structures were reported by several authors [6, 9, 10]. Saturated calomel electrodes and saturated copper sulphate electrodes are conventionally used for most laboratory studies in alkaline environments due to its compatibility and easy use, and they are even used for in-situ measurements. Ag/AgCl reference electrodes are commonly used in concrete structures to measure the rebar corrosion potential [11–13]. The use of Ag/AgCl electrodes to determine the chloride content in solutions simulating the concrete interstitial electrolyte has been previously described [6, 11, 14–16]. It was reported [11] that Ag/AgCl electrodes embedded in mortar specimens are stable only for a short period. However these electrodes still remain a potentially interesting choice in what concerns chloride ion monitoring in reinforced concrete structures [16]. In some cases pseudo-reference electrodes are used. This type of electrodes is so named because it does not maintain a constant potential, therefore, by definition, it is not a true reference electrode. However, its potential depends on conditions in a well-defined manner: if the conditions are known the electrode can be used as a reference electrode. Manganese dioxide embedded electrodes are used as pseudo-reference electrodes and also as pH and humidity sensors [8, 17–20]. Finally, titanium bars activated with mixed-metal oxide and graphite electrodes are also used as embedded pseudo-reference electrodes in concrete [8, 21, 22].

This work is part of a project [23] oriented towards the development of an inexpensive, embeddable sensor system to perform measurements of corrosion potential of rebars, corrosion current density of rebars, chloride ion concentration, etc. inside a concrete structure. To that purpose full characterisation of different materials to be used as reference electrodes was needed, together with the advantages and disadvantages of each type of electrode. Unfortunately, there is a lack in literature of a complete comparative analysis, under equivalent conditions, of different types of electrodes. In the present work, a systematic electrochemical characterisation of different materials to be used as solid reference electrodes to be embedded in concrete structures was carried out. The electrodes, selected because their low cost and because they are easy to obtain or manufacture, are: rods of titanium activated with mixed-metal oxide (MMO) commercially produced for permanent impressed-current anodes in cathodic protection of reinforcing steel in concrete; bars of graphite; and laboratory-made silver/silver chloride electrodes. Tests were performed in both, aqueous solutions of different pHs and embedded in mortar, where their stability in the presence and absence of chloride ion was examined for a two year exposure period.

2 Experimental technique

2.1 Reference electrodes

Three different types of electrodes were tested: activated titanium with mixed-metal oxides (MMO), graphite, and silver/silver chloride (Ag/AgCl) electrodes. The MMO electrodes were made from activated titanium rods (3 mm diameter) produced commercially for permanent impressed-current anodes in cathodic protection of reinforcing steel in concrete (WWI Procat, S.L., Spain). The surface of the activated titanium rod was covered with a precious mixed-metal oxide applied using a proprietary process. Energy-dispersive X-ray spectroscopy (EDS) of the MMO electrodes identified Ir and Ta as the main metallic species (Fig. 1). MMO electrodes were prepared by cutting the rod in 5 cm segments, drilling a 1 mm diameter hole 6 mm deep at one end in the axis direction, and crimping the stripped end of an insulated

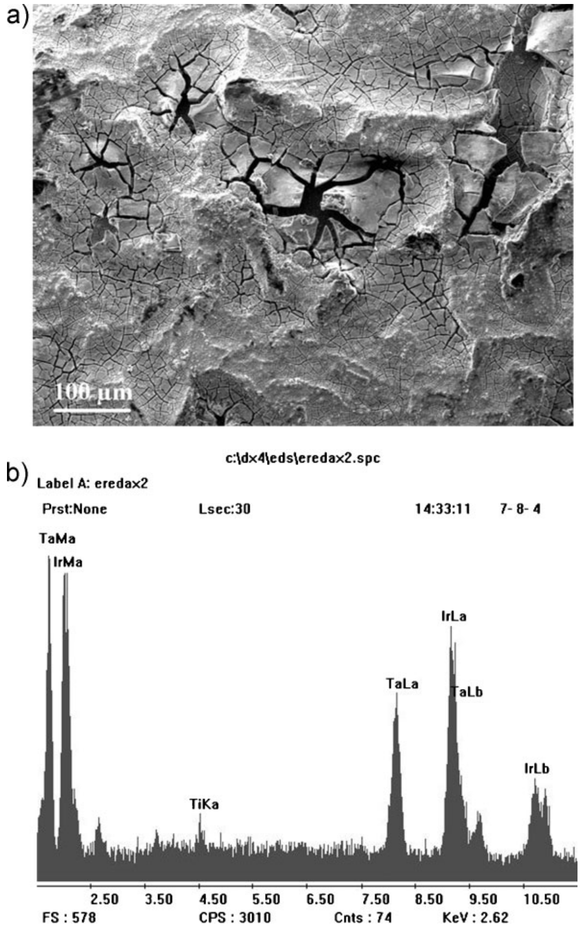

Figure 1. Surface (a) and energy-dispersive X-ray spectroscopy (b) of the activated titanium electrodes

braided Cu cable in the hole. The crimped and opposite ends of the bar were covered by epoxy resin, leaving an exposed surface area of approximately 4 cm^2.

Graphite electrodes were prepared using 4 mm diameter as-received commercial rod stock for dry-cell batteries (Carbograf S.R.L., Argentina). A Cu wire was inserted in a hole at the end of a graphite rod 3 cm long, and the junction was sealed with epoxy resin. The exposed surface area was $\sim$2.5 cm^2.

Silver/silver chloride electrodes used in this work were manufactured from 99.99% pure silver wires (1 mm diameter). Prior to the anodizing process, the wires were degreased with acetone; immersed in 28% ammonium hydroxide (NH_4OH) for 5 h; rinsed with high purity water (18 MΩ·cm); immersed in concentrated nitric acid (HNO_3) for 1 min and rinsed again with high purity water. Then the wires were anodised galvanostatically in 0.1 M hydrochloric acid (HCl) plus saturated potassium chloride (KCl). The electrode stability is strongly influence by the anodisation current density, being more stable when the anodisation procedure is carried out at an increased current density [24]. The normal anodising conditions in the present work were a current density of 6 mA/cm^2 for 10 min. After anodising, electrodes were kept in chloride solution (1 M KCl) out of direct sunlight until required. Prior to use the electrodes were rinsed with acetone and dried. The electrical connection was made through a Cu wire and the junction was sealed with epoxy resin. The exposed area was $\sim$1 cm^2.

2.2 Tests in aqueous solutions

The pH value of a fresh concrete may vary in the range 13.5–12.5, approximately. As carbonation proceeds, the pH value of the concrete pore solution decreases. In the present work, aqueous buffer solutions of pH ranging from 13.5 to 7.4 were used. The solutions abbreviation, constituents and pH are given in Table 1. Solution A, the so called simulated concrete pore solution (SPS), and solution B account for the pH of a fresh concrete. Solution C has a lower pH value and was chosen to account for a carbonated concrete; while solutions D and E were chosen to investigate the effect of lower pH values. All solutions were at room temperature (25 °C) and exposed to laboratory air.

2.2.1 Open-circuit potential measurements

The evolution of the electrode potentials was followed during 40 days by placing the electrodes in a polyethylene cell (500 cm^3 in volume) containing the test solutions A to E. Three different electrodes of each type were tested simultaneously in each solution.

Table 1. Composition and pH of the solutions used in the present work

Solution	Composition	pH
A	7.4 g NaOH + 35.6 g KOH per litre of saturated $Ca(OH)_2$ solution (SPS = saturated pore solution)	13.5
B	Saturated $Ca(OH)_2$ solution	12.5
C	0.025 M $NaHCO_3$ + 0.025 M Na_2CO_3	10
D	0.01 M $Na_2B_4O_7$	9.2
E	0.0087 M KH_2PO_4 + 0.0302 M Na_2HPO_4	7.4

In another set of tests, the effect of deaeration was investigated in saturated $Ca(OH)_2$ solution by bubbling alternatively air or high-purity nitrogen gas (N_2) into the cell. The electrode potentials measured under these conditions were compared to those measured under natural conditions of aeration.

The potential of the electrodes was also measured in the presence of chloride ions, added as KCl, in concentrations ranging from 10^{-5} to 1 M. In all cases, the potential measurements were made against a saturated calomel electrode (SCE) and they were taken with an electronic voltmeter Keithley 177 Microvolts DMM.

The same kind of cell was used for electrochemical impedance spectroscopy (EIS) tests in all liquid solutions. The EIS tests were conducted at the rest potential in the frequency range 100 kHz to 10 mHz using a signal amplitude of 10 mV. These electrochemical tests were performed with a Gamry PCI4 – 750 mA Potentiostat and analysed with a Gamry EIS300 Software (V. 4.35). Tests were made by triplicate using three different samples.

2.2.2 Polarisation tests

Potentiodynamic polarisation curves were performed with the three types of electrodes and in all solutions A to E using a conventional glass cell (80 cm^3 in volume). The scan rate was 0.2 mV/s. Before drawing the curves, the systems were allowed to reach a stationary corrosion potential after a 90 min exposure to the solution. Ohmic drop effects were negligible in the range of current densities obtained. Potential sweeps went from −0.2 to 0.3 volts against the corrosion potential. A coil platinum wire (0.6 mm diameter) with an area 20 times greater than the working electrode was used as a counter electrode; a MMO, graphite or Ag/AgCl electrode as working electrode; and a SCE as reference electrode. The electrochemical tests were performed with an Autolab PGSTAT 30 Potentiostat.

Galvanostatic tests were performed with the three types of electrodes in all solutions in a polyethylene cell. A cathodic direct current density of 0.1 $\mu A/cm^2$ was applied to the electrodes for 3 to 5 days. After this, the current was interrupted, and the electrodes were kept in the solution at the rest potential.

2.3 Tests in mortar

MMO, graphite and Ag/AgCl electrodes were embedded in mortar cylinders (8 cm by 3.5 cm diameter) made of Ordinary Portland Cement (w/c = 0.6) and a cement/sand ratio 1/3. After an initial 28 day curing period immersed in water, the samples were exposed to two different conditions: laboratory environment (room temperature, 60–70% relative humidity), and immersed in 3.5% NaCl solution. The electrode potential readings were made against a SCE in contact with the external concrete surface at the lateral of the cylinder on a regular basis during 740 days. Tests were performed by triplicate.

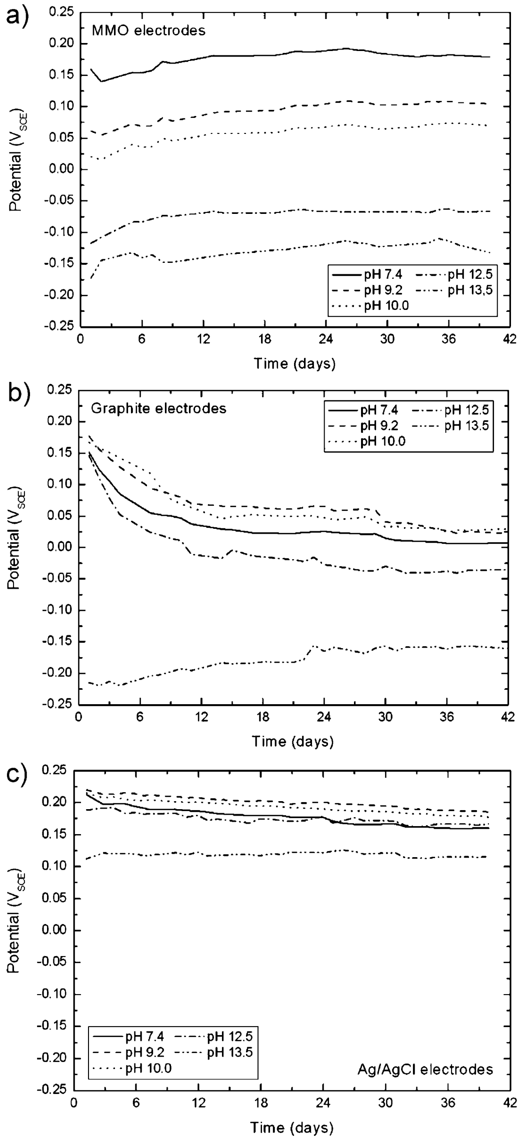

Figure 2. Potential evolution with time of MMO (a), graphite (b), and Ag/AgCl (c) electrodes in solutions of different pHs

3 Results

3.1 Tests in aqueous solutions

3.1.1 Open-circuit potential measurements

Potential evolution: Figure 2 shows the potential evolution with time of the three types of electrodes immersed in liquid solutions A to E. MMO electrodes (Fig. 2a) stabilise shortly (5/6 days) after immersion in the test solutions. Graphite electrodes (Fig. 2b) tend to stabilise after approximately 18 days of immersion. In this case the potential drift during the first days of immersion depends on the pH: at pH 13.5 the potential drift is lower than at lower pH values. Ag/AgCl electrodes (Fig. 2c) stabilize almost immediately at pH 13.5 but, at lower pHs, a slight but continuous decrease in potential is observed; and the potential tends to stabilise after approximately 32 days of immersion. Table 2 shows the minimum, maximum and average value of the potential of the electrodes after 40 days' exposure to solutions of different pHs. It can be observed that Ag/AgCl electrodes show the lower standard deviation.

Effect of deaeration: Figure 3 shows typical results of duplicate tests to determine the sensitivity of the electrodes to oxygen partial pressure variations at pH 12.5. The MMO and Ag/AgCl electrodes showed little or no effect (<20–25 mV drift) when switching from natural aeration at normal air pressure to bubbling N_2 gas through the test cell; or from bubbling air to bubbling N_2 gas. The change in potential of the graphite electrodes showed a more pronounced effect. It should be noted that graphite electrode potentials show a constant drift during the first 10 days of exposure to this solution (pH 12.5) even in natural conditions, as it is evident from Fig. 2b. However, an additional effect is observed when alternating the bubbling of N_2 and air into the cell. The potential shifted in the less noble direction when bubbling N_2, until a plateau was reached at a value ~45 mV lower. Upon air bubbling, the graphite electrode returned to the initial natural aeration potential. MMO and Ag/AgCl electrodes are almost insensitive to oxygen partial pressure.

Effect of Cl^- concentration: Table 3 shows the average potentials and standard deviation (over $n = 10$ measurements performed on 10 different electrodes) for MMO, graphite and Ag/AgCl

Table 2. Open circuit potential of MMO, graphite and Ag/AgCl electrodes vs. SCE after 40 days' exposure to various pH solutions

Electrode	pH 13.5	pH 12.5	pH 10	pH 9.2	pH 7.4
MMO					
Minimum	−0.167	−0.073	0.066	0.090	0.160
Maximum	−0.120	−0.056	0.072	0.119	0.180
Average	−0.132 ± 0.017	−0.066 ± 0.014	0.070 ± 0.001	0.105 ± 0.010	0.173 ± 0.007
Graphite					
Minimum	−0.175	−0.045	0.003	0.010	−0.009
Maximum	−0.137	−0.003	0.062	0.024	0.016
Average	−0.156 ± 0.019	−0.036 ± 0.008	0.030 ± 0.030	0.018 ± 0.007	0.005 ± 0.013
Ag/AgCl					
Minimum	0.114	0.164	0.172	0.185	0.158
Maximum	0.117	0.168	0.180	0.186	0.162
Average	0.116 ± 0.002	0.166 ± 0.002	0.177 ± 0.005	0.185 ± 0.001	0.160 ± 0.002

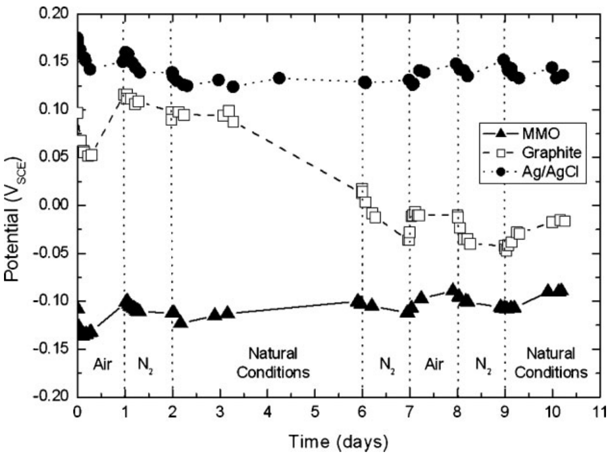

Figure 3. Potential evolution of MMO, graphite and Ag/AgCl electrodes during alternating periods of air bubbling, N_2 bubbling and natural conditions in saturated $Ca(OH)_2$ solution

electrodes immersed in solutions of KCl. No clear trend was observed for MMO electrodes: the potential shows high dispersion at low chloride concentrations, and the potential shifts to more noble values for higher chloride concentrations. Graphite electrode potentials show a tendency to decrease at chloride concentrations higher than 10^{-3} M. At lower chloride concentrations dispersion increases and no significant variation is observed in the potential values. Ag/AgCl electrode potentials follow a linear relationship with the logarithm of chloride activity in the range 10^{-4} to 1 M (Fig. 4), being the slope 52 mV/decade. For lower chloride concentrations, dispersion increases and the average potential reaches a limiting value.

Electrochemical impedance spectroscopy tests: The typical appearance of the Bode diagram for MMO electrodes in liquid solutions is shown in Fig. 5 (insert). The diagram, obtained in the SPS solution, is similar in shape and size to those in the other solutions (pH 7.4 to 13.5). The high-frequency limit impedance value agrees well with the value expected from each test solution conductivities and cell dimensions used. This type of spectra is usually interpreted by using a simple model consisting of a constant phase-angle element (CPE) in parallel with the polarisation resistance (R_p) in addition to the electrolyte resistance (R_e). In the present model, a CPE is used instead of a capacitance to account for the non-ideal capacitive response. The CPE is characterized by an admittance coefficient (Y_o) and a frequency exponent n. These parameters were used to compute the apparent capacitance according to the procedure described elsewhere [25]. MMO electrodes yield large admittance coefficients so that the electrode behaviour can be considered approximately as that of a large capacitor. The average apparent capacitance of MMO electrodes were computed and yielded values ranging from 0.9×10^{-2} to 1.4×10^{-2} F/cm^2, independently of the pH solution (Fig. 5).

Table 3. Average potentials and standard deviation (vs. SCE) for MMO, graphite and Ag/AgCl electrodes immersed in solutions of KCl

[Cl$^-$] (M)	MMO electrode	Graphite electrode	Ag/AgCl electrode
1×10^{-5}	0.195 ± 0.066	0.160 ± 0.018	0.195 ± 0.010
1×10^{-4}	0.189 ± 0.055	0.170 ± 0.011	0.192 ± 0.003
5×10^{-4}	0.212 ± 0.045	0.141 ± 0.017	0.164 ± 0.001
1×10^{-3}	0.206 ± 0.030	0.133 ± 0.012	0.153 ± 0.001
5×10^{-3}	0.225 ± 0.031	0.116 ± 0.007	0.119 ± 0.001
1×10^{-2}	0.223 ± 0.019	0.100 ± 0.007	0.100 ± 0.001
2×10^{-2}	0.231 ± 0.012	0.092 ± 0.005	0.085 ± 0.001
5×10^{-2}	0.269 ± 0.014	0.077 ± 0.005	0.061 ± 0.001
1×10^{-1}	0.273 ± 0.018	0.057 ± 0.004	0.046 ± 0.001
1	0.286 ± 0.011	-0.009 ± 0.008	0.002 ± 0.002

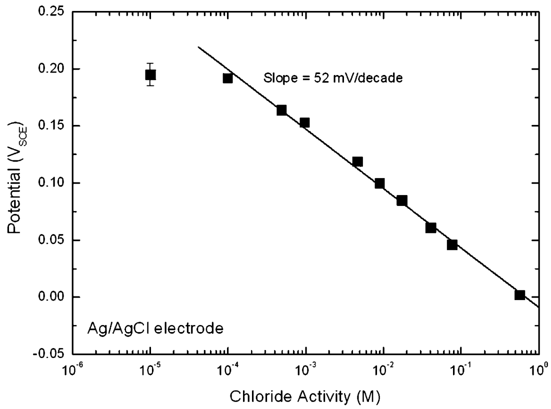

Figure 4. Effect of chloride activity on the potential of Ag/AgCl electrodes

This high equivalent capacitance implies a low electrode impedance. On the other hand, graphite electrodes show lower capacitance values (between 3×10^{-5} and 7×10^{-5} F/cm^{-2}) than MMO electrodes in all solutions. Ag/AgCl electrodes show a similar behaviour to that of graphite electrodes but the response is different at pH 13.5, at which the apparent capacitance increases more than one order of magnitude, being close to that observed for MMO electrodes. Values shown in Fig. 5 are the average

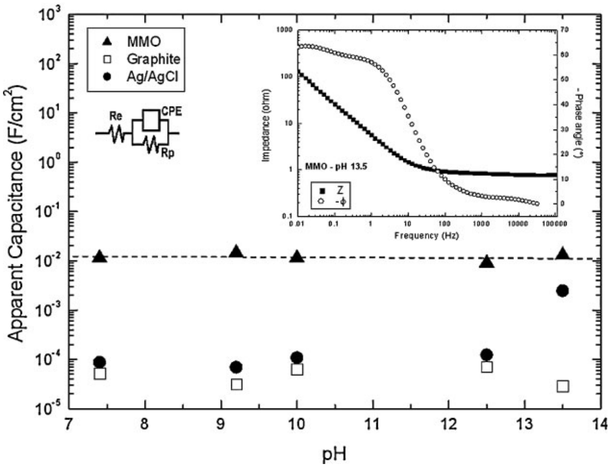

Figure 5. Apparent capacitance of MMO, graphite, and Ag/AgCl electrodes as a function of the pH solution as obtained from EIS measurements. Insert: Typical Bode diagram of a MMO electrode at pH 13.5

apparent capacitance values over three independent measurements; standard deviation was less than 10% in all cases. However, it should be noticed that, in the case of graphite and Ag/AgCl electrodes, the fitting was not as good as in the case of the MMO electrodes.

3.1.2 Polarisation tests

Polarisation curves: Results of the potentiodynamic polarisation tests are shown in Fig. 6 for the MMO, graphite and Ag/AgCl electrodes. Duplicate experiments provided essentially the same results. All MMO electrode polarisation curves showed significant hysteresis. This fact became evident when comparing the rest potential (measured after a 90 min exposure time) with the corrosion potential observed in the polarisation curve. The difference between these two values was approximately 100 mV at pH 7.4 and 200 mV in the other solutions. MMO electrodes showed a passive region where the current densities depend on the pH of the solution: the higher the pH, the higher the current density of the passive region. Graphite and Ag/AgCl electrodes showed much less hysteresis than the MMO electrodes. In the case of graphite electrodes, the polarisation curves showed that at pH values lower than 13, the anodic current densities were low enough to guarantee that the electrodes do not undergo significant corrosion. At pH 13.5 high current densities were observed probably due to the fact that carbon is not thermodynamically stable in the presence of water at pH above 13 [26]. With further increasing of the electrode potential an increase in current density was observed, that corresponds to oxygen evolution. In the case of Ag/AgCl electrodes, anodic currents remained relatively low above the corrosion potential at pH values below 13. A slight increase in current density was then observed with further increasing of the potential. At pH 13.5, an anodic peak was observed at low overpotentials, followed by a region of constant current densities of the order of 30 μA/cm^2. This anodic peak is probably due to the formation of some silver oxides [27–29].

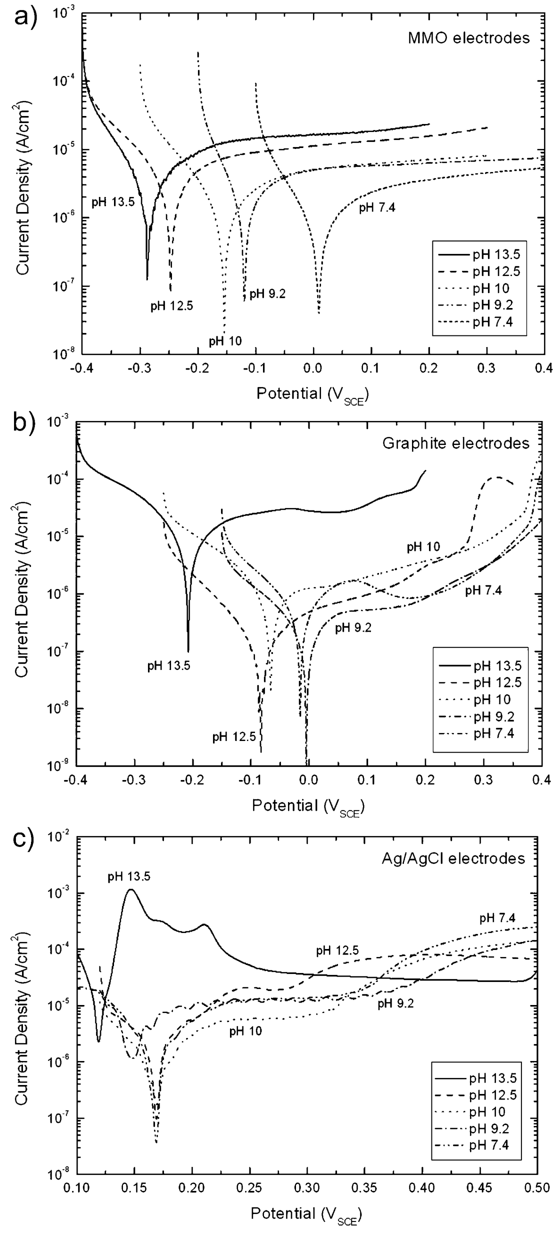

Figure 6. Potentiodynamic polarisation curves of MMO (a), graphite (b), and Ag/AgCl (c) electrodes in solutions of different pH values

Galvanostatic tests: The three types of electrodes were tested in all solutions A to E. After a quasi-stabilisation period that ranged from 2 to 4 days, a cathodic current density of 0.1 μA/cm^2 was applied for a period of 3–5 days. Then the potential was measured for another period of 3–5 days. Results were repetitive for each type of electrode in all solutions tested. However, significant differences were found in the behaviour of each type of electrode. Results of the representative galvanostatic tests are shown in Fig. 7. The potential of the MMO electrodes shifted ~50–100 mV more negative and approached a limiting value after 1 to 2 days. The potential recovered toward the initial values upon interruption of the current. The system exhibited a similar apparent time constant (~1–2 days) during current application and recovery.

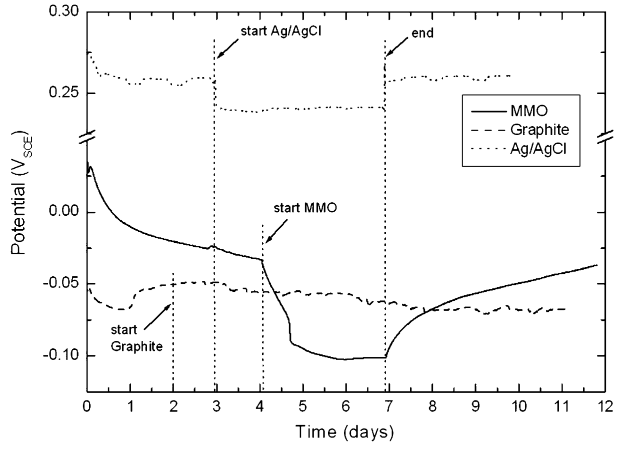

Figure 7. Potential of MMO electrodes in solution B (pH 12.5), graphite electrodes in solution C (pH 10) and Ag/AgCl electrodes in solution E (pH 7.4). Vertical dotted lines indicate the start and end of the galvanostatic pulse

Graphite electrodes showed no change in their potential when applying the cathodic pulse. The potential of the Ag/AgCl electrodes shifted ~20–25 mV in the less noble direction and recovered immediately after the interruption of the current. In this case the shift in the potential and the recovery were almost instantaneous as it is shown in Fig. 7.

3.2 Tests in mortar

Figure 8 shows the MMO, graphite and Ag/AgCl electrode potentials as a function of time over a 2 year interval, when exposed to two different conditions (laboratory environment and immersed in 3.5% NaCl solution).

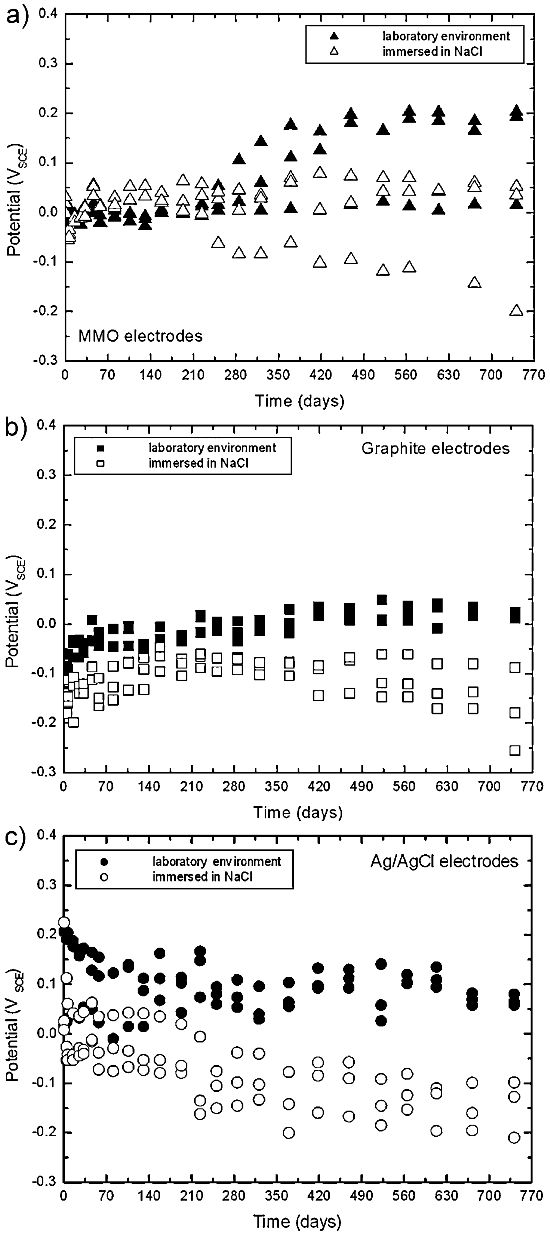

Figure 8. Potential evolution with time of MMO (a), graphite (b), and Ag/AgCl (c) electrodes in mortar, exposed to air and immersed in NaCl solutions

MMO electrode potentials show good short-term stability, independently of the test environment (Fig. 8a). After 250 days of exposure, potential readings become less reproducible, both in laboratory conditions and immersed in 3.5% NaCl solution.

Graphite electrode potential evolution (Fig. 8b) shows that this type of electrode is very stable in the long-term interval. Dispersion is very low for electrodes exposed to laboratory environment, and as for the samples immersed in chloride solutions, the dispersion increases with time, but the mean values remain almost constant. The potential drift is approximately 50 mV/year in air and 3 mV/year in aqueous solution.

Figure 8c shows the Ag/AgCl electrode potential evolution. During the first days of testing, no significant differences were observed between the potential of the air-exposed electrodes and the immersed electrodes. After approximately 10 days of exposure, electrodes immersed in NaCl showed a tendency to decrease the potential, with a drift of 88 mV/year. The specimens exposed to air showed an almost negligible drift of 22 mV/year.

After two years of testing, the mortar specimens were broken apart and the morphology of the electrodes was observed under the electronic microscope. The aspect of the electrodes was essentially the same as before the tests. EDS showed the presence of chloride in those specimens immersed in NaCl, revealing that the chloride ions had reached the surface of the electrodes. The chloride concentration after two years of immersion into NaCl solution was determined in a zone adjacent to the electrode and up to 5 mm far from it. The result was 1.56 ± 0.07 percent by weight of mortar ($n = 4$). The chloride content of the original mortar was 0.06 percent by weight of mortar. Phenolphthalein tests performed on the fresh surface of the broken mortar specimens exposed to laboratory environment revealed that the mortar was completely carbonated.

4 Discussion

The data obtained in the present work allow the following analysis, in which the three reference electrodes are compared regarding the following features: their stability in aqueous solutions, considering the behaviour with pH and the influence of the oxygen partial pressure; their stability in mortar; their polarisability; and their response to chloride content variations in the medium.

4.1 Stability in aqueous solutions

MMO electrodes are stable in time when immersed in aqueous solutions of pH ranging from 7.4 to 13.5. Figure 9 represents the electrode potential after a 40 days exposure time as a function of pH. The potential variation with the pH is determined by the following reaction

$$2\,IrO_2 + 2\,H^+ + 2e^- = Ir_2O_3 + H_2O \qquad (1)$$

as it can be observed in Fig. 9. Then, this type of electrodes, besides being useful as reference electrodes in concrete, can also be suitable as pH sensors. The basis for metal oxide electrodes serving as hydrogen ion-selective electrodes is that the redox reaction at mixed–metal oxide is reversible in aqueous solutions.

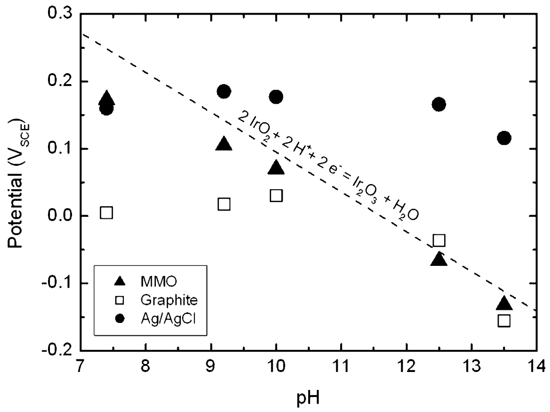

Figure 9. Potential measurements of MMO, graphite and Ag/AgCl electrodes in liquid solutions with partial Pourbaix diagrams for the Ir/H_2O system [26]

The metallic oxide as a H^+-selective electrode must possess excellent corrosion resistance and stable potential response in the test solutions. The metal oxide electrodes developed for this purpose include oxides of Ir, Pt, Pd, Rh, Ti, Sn, Al, Ru, Os, Ta, Mo, W, Co, etc., among which iridium oxide is followed with the most interest because, compared with other metal oxide electrodes, iridium oxide electrodes exhibit better stability in a wide pH range, higher resolution, and quicker response in high-temperature, high-pressure, and aggressive media [30]. It was found that MMO electrodes are insensitive to variations in oxygen partial pressure, which is consistent with the fact that the potential is determined by Equation (1).

Graphite electrode potentials require some days before stabilizing in aqueous solutions. The electrode potential after a 40 days exposure time is independent of pH in the range 7–10 (Fig. 9). At higher pH values, a slight decrease in potential is observed. This type of electrode is sensitive to variations in oxygen partial pressure and, even though these variations are not very important, they constitute a disadvantage when performing potentials measurements in media where local variations of oxygen are expected, as it is the case of concrete structures. The fact that the electrode potential is sensitive to the oxygen partial pressure is consistent with the fact that the electrode potential is partially determined by the oxygen/water equilibrium reaction [12]. In particular, when deaerating the solutions a shift towards less noble potential values is observed in concordance with the fact that the oxygen availability is reduced.

Ag/AgCl electrodes show good stability in liquid solutions and they show excellent reproducibility, in comparison with MMO and graphite electrodes. The electrode potential is independent of the pH of the solution (Fig. 9), with the exception of pH 13.5 where a slightly lower potential was measured. The Ag/AgCl electrode potential is given by the following equilibrium reaction:

$$AgCl + e^- = Ag + Cl^- \tag{2}$$

so that the electrode potential is only fixed by the chloride concentration and the temperature, and independent of the pH value. Besides, Ag/AgCl electrodes proved to be insensitive to variations in oxygen partial pressure, as expected from Equation (2).

4.2 Stability in mortar

Tests in mortar show good short-term stability for MMO electrodes but, after almost 1 year, the electrode behaviour becomes less reproducible, both in laboratory environment and immersed in NaCl solution. For those specimens exposed to laboratory conditions, it could be assumed that the increase in the electrode potential observed in some cases after 280 days is due to the carbonation process that lowers the pH and consequently shifts the potentials of the MMO electrodes towards higher values. In fact, phenolphthalein tests confirmed that specimens exposed to laboratory environment were completely carbonated after 2 years. However, significant dispersion of values is observed, not only for the specimens exposed to laboratory environment but also for those immersed in NaCl. This behaviour is probably due to heterogeneities in the metal oxide coating that in some cases can be observed at naked eye. As it was stated above, the material used in the present work is commercially produced for anodes in cathodic protection of concrete structures and the lack of homogeneity in the coating is a consequence of the manufacturing process. To obtain more reliable and stable long-term measurements, different methods of fabrication of iridium oxides electrodes should be tested, as those proposed in the literature [30–32]. The fact that these electrodes are robust in structure, and quick in response made them a good candidate to be used as reference electrodes in concrete.

Tests in mortar show relatively good stability of graphite electrodes along the whole testing period (2 years). Contrary to what was observed for MMO electrodes, and as expected from results in Fig. 9, no significant potential changes were observed due to the pH decrease due to concrete carbonation in specimens exposed to laboratory environment. Specimens immersed in aqueous solutions show less noble potential values than those exposed to laboratory conditions, probably due to the fact that the oxygen availability is reduced under these conditions.

Ag/AgCl electrodes tested in mortar reveal relatively good stability along the whole testing period when exposed to laboratory environment. Those specimens immersed in NaCl solution show a decrease in potential after approximately 210 days of exposure, revealing the moment when chloride ions reach the electrode surface.

4.3 Polarizability

From EIS tests it was found that MMO electrodes show high equivalent capacities, which implies low electrode impedance. This capacitive behaviour provides tolerance to brief current incursions to the electrode, as a result from accidental improper connections. Following the procedure of *Sagüés* et al. [21] [31] MMO electrodes with apparent capacities of 4×10^{-2} F (sample area of 4 cm^2) yield impedance values close to 200 Ω at a typical frequency of some mHz. Then, for a current incursion of 5 μA during 1 min, the electrode will polarize only 1 mV. Then, this kind of electrode has the ability to pass brief small currents with a minimum of polarisation which is advantageous when conducting electrochemical measurements on steel rebars.

EIS tests performed on graphite electrodes show lower equivalent capacities than MMO electrodes, which imply higher impedance values, a non desirable feature for a reference electrode. For instance, graphite electrodes with apparent capacities of the order of 10^{-4} F (sample area of 2.5 cm^2) yield impedance values close to 100 kΩ at a typical frequency of some mHz. Then, for a current incursion of 5 μA during 1 min, the electrode will polarize as much as 0.4 V.

As well as for graphite electrodes, Ag/AgCl electrodes show high impedance values, a fact that constitutes a clear disadvantage in the case that non desirable current incursions occur.

From polarisation tests it can be concluded that MMO electrodes show some hysteresis, and a measurable change in potential after the application of a long cathodic pulse. A polarisation resistance was computed, from the applied current density during the galvanostatic pulse (0.1 $\mu A/cm^2$) and the measured potential change (Fig. 7) in each solution; and the resulting values ranged from 100 to 250 kΩ. Then, for a typical input bias current of 1 nA (typical input bias currents of operational amplifiers are 40 nA, but for potentiostat circuits, input bias currents of less than 5 nA are recommended, being in most cases as low as some pA), potential shifts lower than 0.25 mV are obtained. Then, it is concluded that this type of electrode resists the long-term effect of the application of small bias currents commonly found in electrochemical instruments.

On the contrary, hysteresis effects and potential shifts after the application of a prolonged galvanostatic pulse were negligible for graphite electrodes.

Ag/AgCl electrodes show little hysteresis and a small shift in potential when a cathodic current is applied, being the recovery almost instantaneous. When computing the polarisation resistance, values of 200–250 kΩ were found, indicating that - as with MMO electrodes -, bias currents of 1 nA generates potential shifts of no more than 0.25 mV.

4.4 Response to chloride content variations

In chloride solutions, it was found that the Ag/AgCl electrode potential is linear with the log $[a_{Cl-}]$ in the range 10^{-4} to 1 M with a slope of 52 mV/decade, a value that is close to the theoretical value of 59 mV/decade predicted by Equation (2), revealing a Nernstian behaviour. At lower chloride concentrations (or activities) the electrode potential remains constant, deviating from the theoretical value. However, according to the variation range of chloride concentration when the concrete is contaminated, the prepared Ag/AgCl electrode is able to monitor the chloride concentration in an actual corrosion system [30,33].

From the previous analysis the main issues are

- the MMO reference electrode potential depends on the pH;
- the graphite reference electrode potential depends on the oxygen concentration; and
- the Ag/AgCl reference electrode potential depends on the chloride content.

These facts led to conclude that the potential of the three reference electrodes studied will change with changes in the environment. Then the application of these electrodes to measure the corrosion potential of the steel reinforcement is limited. However, if these electrodes are used to determine the corrosion rate of the steel rebar by means of the linear polarisation resistance technique, or the electrochemical impedance spectroscopy technique [3–5] [34], where the steel is polarized ±20 mV from the corrosion potential, this limitation is overcome.

5 Conclusions

In the present work, it was found that the MMO pseudo-reference electrode is pH-sensitive, the graphite pseudo-reference electrode is oxygen sensitive and the Ag/AgCl pseudo-reference electrode is chloride sensitive. Then, regarding the corrosion monitoring of steel rebars, care should be taken to avoid misleading interpretations of the corrosion potential measurements. However, any of them can be used to measure the corrosion rate of the rebars by means of traditional electrochemical techniques.

Acknowledgements: The authors acknowledge the technical assistance and suggestions of *E. A. Arva* and *C. J. Lafont*. The financial support of the Consejo Nacional de Investigaciones Científicas y Técnicas (CONICET), of the FONCYT, Secretaría para la Tecnología, la Ciencia y la Innovación Productiva and of the Universidad Nacional de General San Martín (Argentina), is also acknowledged.

6 References

[1] P. Kumar Mehta, P. J. M. Monteiro, *Concrete. Microstructure, Properties and Materials*, McGraw-Hill, New York **2006.**
[2] M. Gani, *Cement and Concrete*, Chapman & Hall, London **1997.**
[3] J. P. Broomfield, *Corrosion of Steel in Concrete. Understanding, investigation and repair*, E & FN SPON, London and New York **1997.**
[4] A. Bentur, S. Diamond, N. S. Berke, *Steel Corrosion in Concrete: Fundamentals and Civil Engineering Practise*, Taylor & Francis, London **1997.**
[5] P. Pedeferri, B. Polder, L. Bertolini, B. Elsener, *Corrosion of Steel in Concrete: Prevention, Diagnosis, Repair*, Wiley-VCH, Weinheim **2004.**
[6] W. J. McCarter, O. Vennesland, *Constr. Build. Mater.* **2004**, *18*, 351.
[7] J. P. Broomfield, K. Davies, K. Hladky, *Cem. Concr. Compos.* **2002**, *24*, 27.
[8] S. Muralidharan, T. H. Ha, J. H. Bae, Y. C. Ha, H. G. Lee, K. W. Park, D. K. Kim, *Mater. Lett.* **2002**, *60*, 651.
[9] H. Arup, B. Sorenson, *Corrosion/92*, paper 208, NACE International, Houston, 1992.
[10] J. E. Bennett, T. A. Mitchell, *Corrosion/92*, paper 191, NACE International, Houston, 1992.

[11] M. A. Climent-Llorca, E. Viqueira-Perez, M. M. Lopez-Alataya, *Cem. Concr. Res.* **1996**, *26*, 1157.

[12] F. J. Ansuini, J. R. Dimond, *Corrosion/2001*, paper 01296, NACE International, Houston, 2001.

[13] T. Villela, A. Souza, H. Abdel-Rehim, *Corrosion* **2002**, *60*, 342.

[14] C. P. Atkins, J. D. Scantelbury, P. J. Nedwell, S. P. Blatch, *Cem. Concr. Res.* **1996**, *26*, 319.

[15] C. P. Atkins, M. A. Carter, J. D. Scantelbury, *Cem. Concr. Res.* **2002**, *31*, 1207.

[16] M. F. Montemor, J. H. Alves, A. M. Simoes, J. C. S. Fernandes, Z. Lourenço, A. J. S. Costa, A. J. Appleton, M. G. S. Ferreira, *Cem. Concr. Compos.* **2006**, *28*, 233.

[17] L. Telli, B. Brahimi, A. Hammouche, *Solid State Ionics* **2000**, *128*, 255.

[18] C. N. Xu, K. Miyazaki, T. Watanabe, *Sensor Actuat B-Chem.* **1991**, *46*, 87.

[19] Z. Rogulski, H. Siwek, I. Paleska, A. Czerwinski, *J. Electroanal. Chem.* **2003**, *543*, 175.

[20] H. Arup, O. Klinghoffer, J. Mietz, *Corrosion/97*, paper 243, NACE International, Houston, **1997**.

[21] P. Castro, A. A. Sagüés, E. I. Moreno, L. Maldonado, J. Genescá, *Corrosion* **1996**, *52*, 609.

[22] S. Muralidharan, T. H. Ha, J. H. Bae, Y. C. Ha, H. G. Lee, K. W. Park, D. K. Kim, *Sensor Actuat B-Chem.* **2006**, *113*, 187.

[23] G. S. Duffó, S. B. Farina, E. A. Arva, C. M. Giordano, C. J. Lafont, in: *Integral Service Life Modelling of concrete Structures*, R. M. Ferreira, J. Gulikers, C. Andrade, (eds.), RILEM Publication S.A.R.L, Bagneaux, France **2007.**

[24] L. A. Simion, M. Mistrianu, A. Manoiu, D. I. Vaireanu, *Proceedings of the 12th Romanian International Conference on Chemistry and Chemical Engineering*, 13–15 Sept. **2001**, Bucharest, Ed. Printech, vol. ''Quality Control and Analytical Chemistry, Corrosion and Electrochemistry'', pp. 281–286, ISBN: 973-652-384-5.

[25] C. H. Hsu, F. Mansfeld, *Corrosion* **2002**, *57*, 747.

[26] M. Pourbaix, *Atlas of Electrochemical Equilibria in Aqueous Solutions*, NACE-CEBELCOR, Houston and Bruxelles **1974.**

[27] R. D. Giles, J. A. Harrison, *J. Electroanal. Chem.* **1970**, *27*, 161.

[28] N. Sato, Y. Shimizu, *Electrochim. Acta* **1973**, *18*, 567.

[29] M. López Teijelo, J. R. Vilche, A. J. Arvía, *J. Electroanal. Chem.* **1984**, *162*, 207.

[30] R. G. Du, R. G. Hu, R. S. Huang, C. J. Lin, *Anal. Chem.* **2006**, *78*, 3179.

[31] A. A. Sagüés, S. C. Kranc, E. I. Moreno, *Corros. Sci.* **1995**, *37*, 1097.

[32] M. Wang, S. Yao, M. Madou, *Sensor Actuat B-Chem.* **2002**, *81*, 313.

[33] M. F. Montemor, A. M. P. Simoes, M. G. S. Ferreira, *Cem. Concr. Compos.* **2003**, *25*, 491.

[34] C. Andrade, J. A. González, *Werkst. Korros.* **1978**, *29*, 515.

(Received: April 15, 2009) W5346
(Accepted: May 4, 2009)