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Electrochemical studies on the performance characteristics of solid metal–metal oxide reference sensor for concrete environments

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Abstract

Cylindrical titanium surface activated with mixed metal–metal oxides (MMO) (though similar to permanent impressed current titanium anodes used in cathodic protection) was used as a reference sensor for concrete environments. The performance characteristics were evaluated in a saturated calcium hydroxide solution (pH 12.5), a synthetic concrete pore solution (pH 13.5) and ordinary Portland cement (OPC) extracts (pH 13.0), which correspond to the concrete environments. The electrochemical stability of the MMO electrode was studied in the said concrete environments and in various buffer solutions (pH 4, 7 and 10) for an exposure period of 180 days. Simultaneous experiments were carried out to realize the performance of the MMO electrode in various solutions containing different concentration of chloride. The self-corrosion studies of the MMO electrode both in concrete environments and in other solutions with and without addition of chloride were carried out gravimetrically for an exposure period of 180 days. The polarization behavior of the MMO electrode in the concrete environments was carried out potentiodynamically with a progressive addition of chloride. All the studies revealed that the MMO was a suitable sensory electrode for concrete structures both in the absence and presence of chloride ions.

Keywords: MMO sensor; Electrochemical stability; Concrete environments; Chloride ions

1. Introduction

Embeddable reference electrodes are very useful for long-term corrosion monitoring of concrete structures and potentiostatically controlled cathodic protection (CP) of reinforcement in concrete. Their use in laboratory work and field exposure tests is advisable for the purpose of ensuring valid exchange of data between laboratory and field work. The increasing use of remote monitoring also requires for reference electrodes to be capable of delivering reliable stable performance over an extended period of time. Use of reference electrodes in concrete presents several challenges. Ideally, an embedded electrode should be placed as close to the steel surface. The fixing arrangement of an internal reference electrode into the concrete is shown in Fig. 1 and the schematic drawing of corrosion monitoring using an embeddable reference is shown in Fig. 2. A perfect embeddable electrode must obey the following conditions: it must be stable, be invariant to chemical and thermal changes in concrete, be tolerant to climatic conditions, have ability to pass small currents with a minimum of polarization and hysteresis effects, display long-term performance, be cost effective and result from an environmentally safe manufacturing process. Recently, Ha et al. [1] reviewed the role of sensors in corrosion monitoring and durability assessment in concrete structures. Reference electrodes for use with reinforced concrete structures were reported by several authors [2–5]. Muralidharan and co-workers [6–11] studied the monitoring of reinforcement corrosion by various electrochemical techniques.

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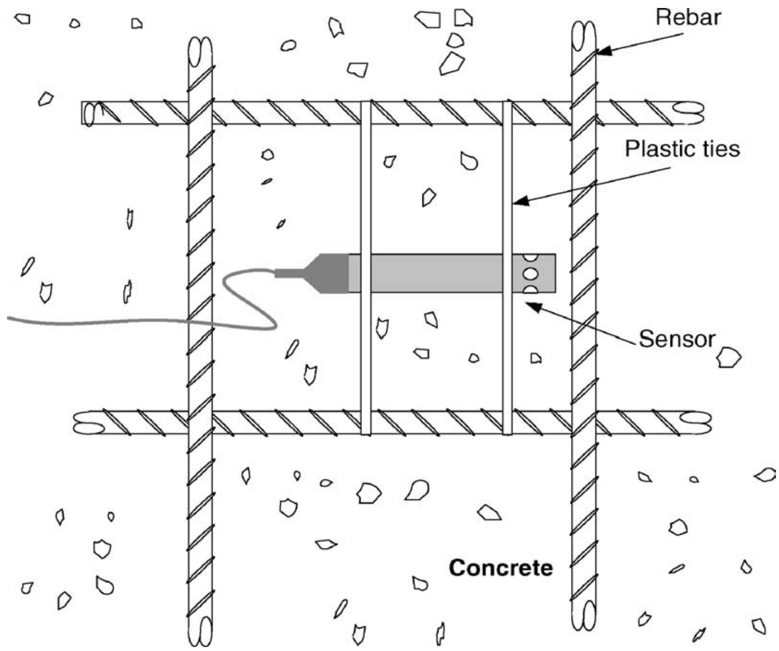

Fig. 1. Fixing arrangement of internal reference electrode into the concrete.

A saturated calomel electrode is conventionally used for all the laboratory studies in alkaline environments due to its compatibility and easy to use. Ag/AgCl reference electrodes are commonly used in concrete structures to measure the rebar potential, but their stability under cold conditions and their long-term performance are still questionable [12–14]. Each electrode has its own advantages and its disadvantages especially when used in the field. The present investigation deals with the performance evaluation of a solid type metal–metal oxides (MMO) electrode as a possible reference sensor for concrete structures. Studies are carried out in various buffer solutions of pH, namely, 4, 7 and 10 and also in concrete environments. Saturated calcium hydroxide solution (12.5), a synthetic concrete pore solution (13.5) and extracts derived from ordinary Portland cement (OPC) (13.0) are representing concrete environments. A simple electrochemical approach is adopted for characterizing the reference sensor used for corrosion monitoring of concrete structures.

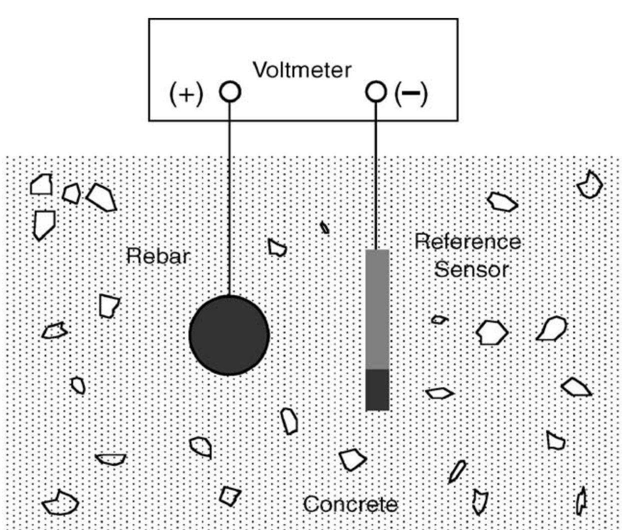

Fig. 2. Schematic drawing of corrosion monitoring of concrete structures (using embeddable reference).

2. Experimental

2.1. Sensor material

The MMO electrode examined was produced commercially for permanent impressed-current anodes in cathodic protection of reinforcing steel in concrete. Iridium coating by electrochemical deposition process was reported in literature [15]. The surface of the titanium was covered with a precious mixed metal oxide applied by a proprietary process. The MMO coating mainly consisted of IrO_x. Other metal oxides viz., Ru, Ta and Si were in lower quantities. The coating was done by the thermal decomposition of mixed metal oxides on the surface of the titanium. The Ti/(IrO_x + other metal oxides) coating was done in nitrate precursor mixtures dissolved in isopropanol. A sandblasted Ti substrate was degreased in isopropanol, followed by attack with boiling oxalic acid solution. The precursor solution was applied on the Ti substrate and calcinated at 550 °C. The procedure was repeated till the desired coating level required. The electrodes were subjected to final thermal treatment at the elevated temperature.

Table 1
Constituents of solutions used

Solution abbreviation	Constituents	pH
A	Potassium biphthalate	4.0
B	Potassium phosphate + NaOH	7.0
C	Potassium carbonate + potassium borate + KOH	10.0
D	Saturated calcium hydroxide	12.5
E	Synthetic concrete pore solution	13.5
F	Cement extracts	13.0

2.2. Chemicals

Potassium biphthalate (ACROS Organics, pure), potassium phosphate (Oriental Chemical Industries, Extrapure), sodium hydroxide (DSP chemicals, GR), potassium carbonate (DSP chemicals, GR), potassium borate (JUNSEI, Japan, GR), potassium hydroxide (DSP chemicals, GR), calcium oxide (Oriental Chemical Industries, Extrapure) and sodium chloride (DC chemicals Co. Ltd., GR) were used for preparing solutions. Calcium oxide was ignited for a long time to remove any carbonate present in the sample before use. The solutions abbreviation, constituents and pH are given in Table 1.

The ordinary Portland cement conforming to KS:L 5201-1989 was used throughout this investigation. The composition of OPC used is listed in Table 2. The cement extracts were prepared as follows. One hundred grams of the ordinary Portland cement were dissolved in 200 ml of distilled water and then shaken mechanically for 1 h. The cement extract was then collected by filtration. The pH was measured by using a portable ISTEK pH meter (Model 76P) with a relative accuracy of ±0.002.

2.3. Methods

2.3.1. Determination of self-corrosion rate

Weight loss measurements were performed as described earlier [11,16]. A cylindrical MMO electrode of 0.6 cm diameter and 5 cm length were taken for this study. The initial weight of the sensor samples was noted using Ohaus Explorer four-digit electronic balance for gravimetric weight loss measurements. Triplicate specimen was tied from the hook of the glass stopper and introduced into a PVC see-through cell containing 250 ml of the various solutions above. The pH of the test solutions was maintained constant throughout the exposure period by adding appropriate constituents. All the tests were conducted at room temperature of 25 ± 1 °C. Weight losses were measured before and after immersion in test solutions at the end of exposure period of 180 days. On a separate experiment, the sensory specimens were introduced into the different test solutions with 30,000 ppm of chloride.

Table 2
Composition of ordinary Portland cement (OPC)

Constituents	wt.%
CaO	63.8
SiO_2	21.8
Al_2O_3	5.1
Fe_2O_3	3.0
MgO	1.7
SO_3	2.0
Loss on ignition (LOI)	0.8
Others	0.1

2.3.2. Visual observations

During weight loss measurements, the sensory specimens were taken out frequently and the surfaces were carefully examined with magnifying lens. After the end of the exposure period, the specimens were removed from the test solutions, washed with water and the surface was examined by using a graduated scale microscope.

2.3.3. Open-circuit potential measurements

Open-circuit potential (OCP) of the different systems was often monitored using a voltmeter with a high input impedance of 20 MΩ. A saturated calomel electrode was used as a reference electrode. The positive terminal of the voltmeter was connected to the working electrode, i.e., the sensory electrode and the common terminal were connected to the reference electrode. The corresponding potential was recorded. OCP for all specimens was monitored over an exposure period of 180 days.

An experiment was also conducted simultaneously in the presence of different concentration of chloride. The electrochemical stability of potential of the MMO sensory electrode in the presence of different concentration of chloride was measured with respect to the saturated calomel electrode at room temperature. In this study, a specimen in triplicate was used for each system and the average of these values was plotted against time.

2.3.4. Potentiodynamic polarization

A conventional three-electrode cell assembly was used for this study. The working electrode was a cylindrical rod of the MMO sensory electrode. Platinum foil of large area and a saturated calomel electrode served as the auxiliary and reference electrodes, respectively. Potentiodynamic polarization study was carried out in all the solutions with and without addition of chloride. A constant quantity of the test solution was taken in the polarization cell. The working, counter and reference electrodes were assembled and connections were made. The test solution was continuously stirred using a magnetic stirrer to avoid the concentration polarization. A constant time interval of about 10–15 min was given for each system to attain a steady state. Both cathodic and anodic polarization curves were recorded potentiodynamically using a Gamry Instruments, Inc., CMS 100 Framework software analyzer. All the experiments were carried out at room temperature of 25 ± 1 °C. Duplicate experiments provided essentially the same results.

Table 3
Gravimetric weight loss data for the MMO sensory electrode in various buffer solutions and in concrete environments with and without chloride (180 days of exposure)

Solution	pH	Without chloride			With chloride		
		Weight loss (g)	Weight gain (g)	*n*	Weight loss (g)	Weight gain (g)	*n*
A	4.0	0.0016 ± 0.0004	–	3	0.0044 ± 0.0005	–	3
B	7.0	0.0015 ± 0.0002	–	3	0.0027 ± 0.0002	–	3
C	10.0	0.0013 ± 0.0001	–	3	0.0026 ± 0.0002	–	3
D	12.5	–	0.0325 ± 0.006	3	–	0.0085 ± 0.002	3
E	13.5	–	0.0249 ± 0.009	3	–	0.0053 ± 0.005	3
F	13.0	–	0.0303 ± 0.007	3	–	0.0091 ± 0.004	3

n = number of replicate experiments.

3. Results and discussion

3.1. Weight loss measurements

Triplicate experiments ($n = 3$) were carried out for each system and the average weight loss data for the MMO sensory electrode in solutions A–F with and without addition of chloride are given in Table 3.

It was observed from Table 3 that the weight loss increased when the pH was moving towards acidic. For example, the weight loss was 0.0016 g at pH 4, 0.0015 and 0.0013 g at pH 7 and 10, respectively. On the other hand, the MMO electrode showed a weight gain in other three concrete environments (solutions D–F). The performance of the MMO electrode in the solutions D–F are encouraging.

The influence of addition of chloride (30,000 ppm) in different test solutions on the self-corrosion of the MMO electrode are also given in Table 3. From this table, it was observed that again the MMO showed a slight weight loss in solutions A–C and no weight loss in other test solutions D–F, indicating the better performance in concrete environments. The weight loss observed for solutions A–C in the chloride added solutions followed a similar trend to that already observed in the case of plain solutions. The weight loss values were almost doubled in chloride added solutions, compared to plain solutions due to the aggressive nature of chloride ions. The MMO electrode showed a better performance in solutions D–F even in the presence of a large amount of chloride.

The weight gain is due to the adsorption of species from the stagnant electrolyte, which blocks the active areas and improves the corrosion performance of MMO electrode especially in concrete environments. It is a fact that the OH^- ions existing in the cement extracts and in alkaline solutions may act as a mild anodic inhibitor, which prevents the competitive adsorption of chloride ions [6].

A good reference sensor must have two important prerequisites, namely: (i) it should not lose its identity by dissolution or self-corrosion in the environment and (ii) it should demonstrate a stable potential throughout. In this aspect, the self-corrosion of the MMO electrode was nil in the concrete environments even in the presence of a large amount of chloride.

3.2. Visual observations

A stable thin layer was formed on the MMO surface in saturated calcium hydroxide solution, a synthetic concrete pore solution and cement extracts. The MMO electrode did not show any rust products or deformation of coating in the concrete environments.

3.3. Open-circuit potential measurements

The electrochemical stability of the MMO sensory electrode in various pH media with and without addition of chloride was measured with respect to a saturated calomel electrode for an exposure period of 180 days.

In plain solutions, a swing in potential value was observed in the case of solutions A–C. On the other hand, a stable potential value was observed in the case of solutions D–F throughout the exposure period. The measured potential values of the MMO electrode against the concrete environments showed almost linear behavior throughout the exposure period. This indicates that the MMO electrode has perfect electrochemical stability in these media. This behavior is quite suited for our interest and makes the MMO electrode be a stable reference for concrete environments. The MMO electrode was able to stabilize within 20 days of exposure in representative concrete environments.

Fig. 3 relates the potential–time behavior of the MMO electrode in solutions A–F in the presence of various concentrations of chloride. As already observed in plain solutions, again the MMO electrode displayed a stable potential behavior in all the chloride levels especially in solutions D–F, but it failed to show a stable behavior in solutions A–C.

The difference in the maximum and minimum measured potential values for an exposure period of 180 days was found to be ±20 mV versus saturated calomel electrode in the case of solutions D–F and ±100 mV versus saturated calomel electrode in the case of solutions A–C, respectively. The anomaly may be due to the fact that commonly iridium is in a +4 oxidation state, but iridium is able to easily assume +2, +3 or +6 in addition to +4. The change in oxidation state would shift the oxide–metal-solution equlibria.

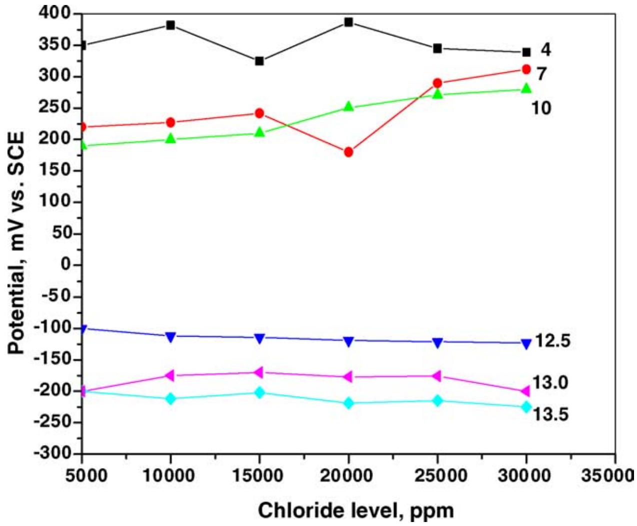

Fig. 3. Electrochemical stability of the MMO sensory electrode in various pH media in the presence of chloride.

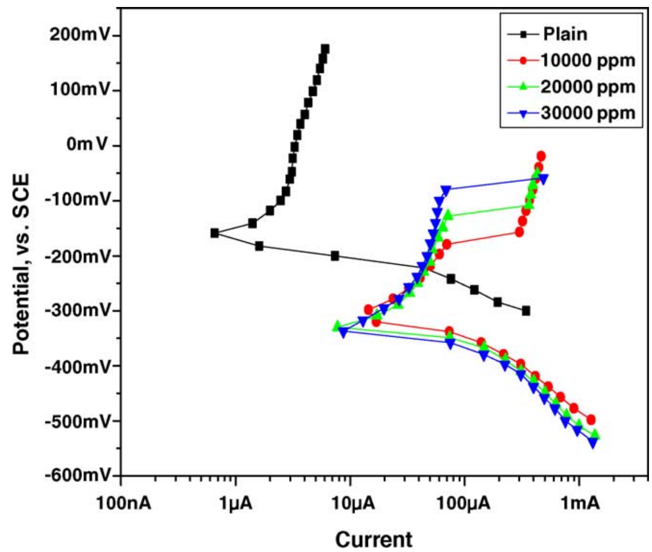

Fig. 4. Polarization behavior of the MMO sensory electrode in saturated calcium hydroxide solution with and without chloride.

The stability of the potential of the MMO electrode is expected from the dependence of the iridium–water system (Ir–H_2O system) in aqueous solutions. Gottesfeld and McIntyre [17] demonstrated a reversible behavior of the iridium electrode surface. As per the Pourbaix diagram of the Ir–H_2O system, the potential of the MMO electrode in the liquid solutions depends on the equilibrium between iridium oxide and the electrode surface, and the possible reaction is

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

3.4. Potentiodynamic polarization

Potentiodynamic polarization studies were carried out only in the saturated calcium hydroxide solution, a synthetic concrete pore solution and in ordinary Portland cement extracts.

Fig. 4 shows the polarization behavior of the MMO electrode in a saturated calcium hydroxide solution with and without addition of chloride. It is noted in the figure that MMO in a plain saturated calcium hydroxide solution showed a stable passive region in the anodic direction and the corrosion current was found to be 1 μA. The addition of chloride showed no influence on polarization curves and only the corrosion current was increased to 10 μA. But still a passive region was observed in the anodic direction. The same observation was already noticed in the weight loss and OCP measurements.

Fig. 5 depicts the polarization curves for the MMO electrode in a synthetic concrete pore solution with and without addition of chloride. No significant change was observed on the cathodic and anodic polarization curve pattern among the various systems studied. Here again, a stable passive region was noticed in the anodic direction. The chloride added system showed the corrosion current values less than 10 μA in this solution.

Fig. 6 depicts the polarization behavior of the MMO reference electrode in the cement extracts with and without addition of chloride. Interestingly, the MMO electrode in plain cement extracts showed a unique passive behavior and the corrosion current value was in the order of 100 nA. After adding chlorides, the corrosion current was shifted approximately to the order of 10 μA.

In fact, cement extracts was a real representative of concrete, the MMO reference sensor in cement extracts showed a very negligible current, indicating that the MMO electrode did not polarize to a great extent for a very small current applied during remote corrosion monitoring. This is an essential requirement for a good embeddable reference sensor in concrete for the field measurements.

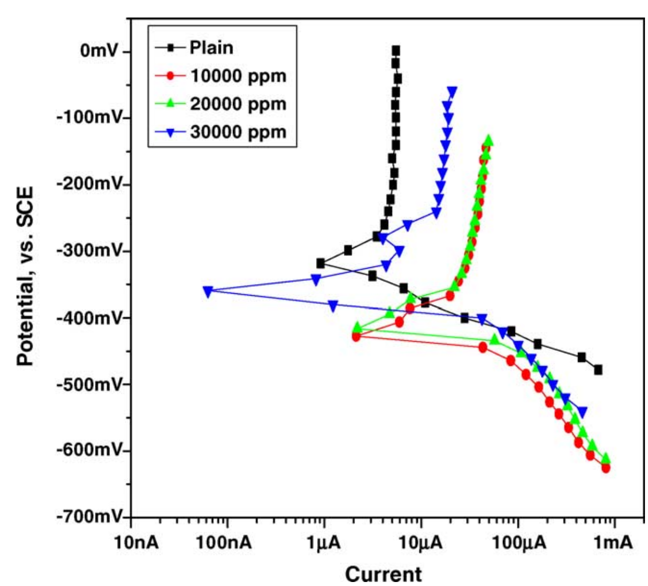

Fig. 5. Polarization behavior of the MMO sensory electrode in a synthetic concrete pore solution with and without chloride.

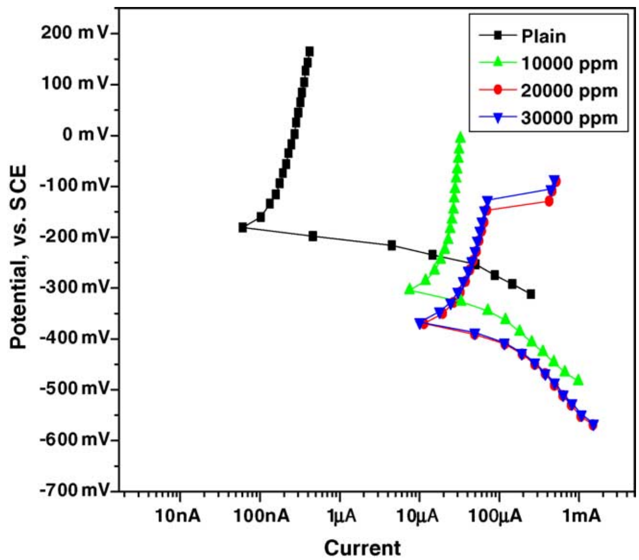

Fig. 6. Polarization behavior of the MMO sensory electrode in cement extracts with and without chloride.

Among the three concrete environments studied, the performance of the MMO reference sensor with respect to self-corrosion, electrochemical stability and a lower polarization current value follows the order of cement extracts > a synthetic concrete pore solution > saturated calcium hydroxide solution.

Even though these studies are restricted only to the solutions representing concrete media, but the effective use of this embeddable MMO electrode in concrete under laboratory conditions is currently under investigation.

4. Conclusions

Self-corrosion of the MMO electrode was almost negligible in the solutions representing concrete environments. The MMO electrode showed better performance characteristics in concrete media and exhibited an excellent stability. The electrochemical stability in the concrete environments exploited the MMO electrode as a suitable, embeddable potential sensor for corrosion monitoring in concrete structures. The MMO sensory electrode was suitable both in the absence and presence of chloride ions.

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