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Electrochemical studies on the solid embeddable reference sensors for corrosion monitoring in concrete structure

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Abstract

Alkaline manganese dioxide (MnO_2), metal–metal oxide (MMO) and graphite reference sensors are fabricated in the laboratory as suitable as an embeddable use into the concrete structures. Sensors are embedded into the cement mortars and the electrochemical studies were carried out in the absence and presence of chloride ions. The electrochemical stability of the sensors was examined for the exposure period of one year. Polarisation behaviour and impedance characteristics of the sensors embedded in mortar was carried out in three aqueous solutions, namely distilled water, 3% NaCl and natural sea water.

Keywords: Sensor; Embeddable use; Concrete; Corrosion monitoring

1. Introduction

Monitoring and control of corrosion of reinforcing steel in concrete requires reliable measurement of stable potentials. Embeddable reference electrodes are very useful in corrosion monitoring of concrete structures for long-term monitoring and potentiostatically controlled cathodic protection 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. A perfect embeddable electrode must obey the following conditions: it must be stable, invariant to chemical and thermal changes in concrete, tolerant to climatic conditions and have the 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. The role of sensors in corrosion monitoring and durability assessment in concrete structures has been reviewed recently [1]. Reference electrodes for use with reinforced concrete structures were reported by several authors [2–5]. SCE 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 [6–8]. Manganese dioxide was tried as pH and humidity sensor [9–11]. The present investigation deals with the systematic studies on the performance characteristics of solid sensor electrodes embedded in mortar and their stability in the presence and absence of chloride ion was examined for one year exposure period.

2. Experimental

2.1. Sensor electrodes

Manganese dioxide, metal–metal oxide (MMO) and graphite were used as sensor electrodes. Commercially available graphite rod was used. MMO electrode used was produced

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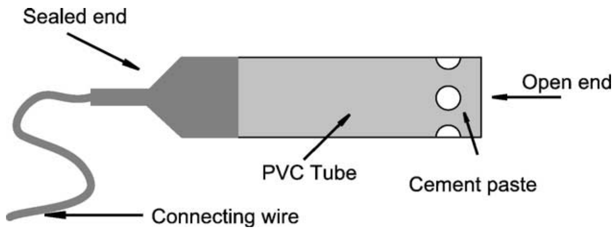

Fig. 1. Schematic of the embeddable reference sensor for concrete.

commercially for permanent impressed-current anodes in cathodic protection of reinforcing steel in concrete and the surface was covered with a precious mixed-metal oxide applied by a proprietary process. The coating mainly consists of Ir with Ru, Ta and Si is in lower quantities. MnO_2 electrode is fabricated as reported elsewhere [1] and briefly given as follows. It consists of three compartments, namely a porous hydrated cement paste as bottom layer, conductive alkaline slurry as middle layer and a powdered MnO_2 as top layer. The whole assembly is encapsulated in a plastic container and connections were made. Fig. 1 shows the schematic of the embeddable type reference sensor for concrete structures. Electrical contact with the surrounding concrete is through the bottom layer consisting of hydrated cement paste. The top of the assembly was sealed with epoxy and connections were made.

2.2. Materials

The ordinary Portland cement (OPC) conforming to KS: L 5201-1989 was used. The composition of OPC used was in wt. %: CaO 63.8, SiO_2 21.8, Al_2O_3 5.1, Fe_2O_3 3.0, MgO 1.7, SO_3, LOI 0.8 and others 0.1. The Bogue potential compound composition of cement in the range as follows: C_3S (45–55%), C_2S (20–30%), C_3A (8–12%) and C_4AF (6–10%). A natural fine aggregate of normal gravity conforming to KS: F 2526: 2002 was used.

2.3. Methods

2.3.1. Potential-time behaviour studies

Cylindrical mortar [cement (1) : sand (3)] specimens of size 15 cm height and 5.5 cm diameter were cast. Sensors were embedded centrally on the mortar specimens. Mortar was prepared using 1 : 3 mix with a w / c ratio of 0.45. The specimens were mechanically vibrated. After 24 h, the mortar specimens were demoulded and cured for 28 days in distilled water. Specimens were cast with 0% and 3% chloride by weight of cement. All the specimens were placed in the exposure yard for testing. Monitoring of potential was carried out for one year exposure period.

2.3.2. Polarization behaviour of sensing electrodes embedded in mortar specimens

The sensing electrode was embedded in cylindrical mortar specimens of size 5.5 cm diameter and 10 cm height were cast using w / c ratio of 0.45. Potentiodynamic polarization was carried out in three aqueous solutions, namely distilled water, 3% NaCl and natural sea water. Sensors embedded in mortar act as working electrode, perforated cylindrical stainless sheet act as counter electrode and SCE served as reference electrode. Polarization was carried out using Gamry Instruments, Inc. at an ambient temperature of 25 ± 1 °C.

2.3.3. Impedance behaviour of sensing electrodes embedded in mortar specimens

A similar procedure was adopted for making mortar specimens for impedance studies. Impedance measurements were carried out using Solartron 1480 Multistat electrochemical

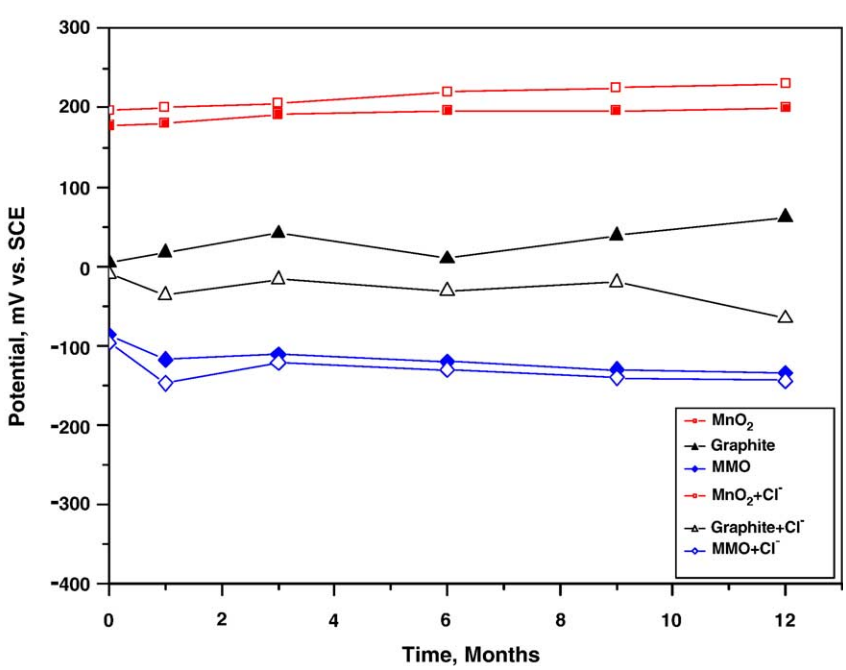

Fig. 2. Electrochemical stability of embedded sensors in mortar for one year exposure period with and without chloride.

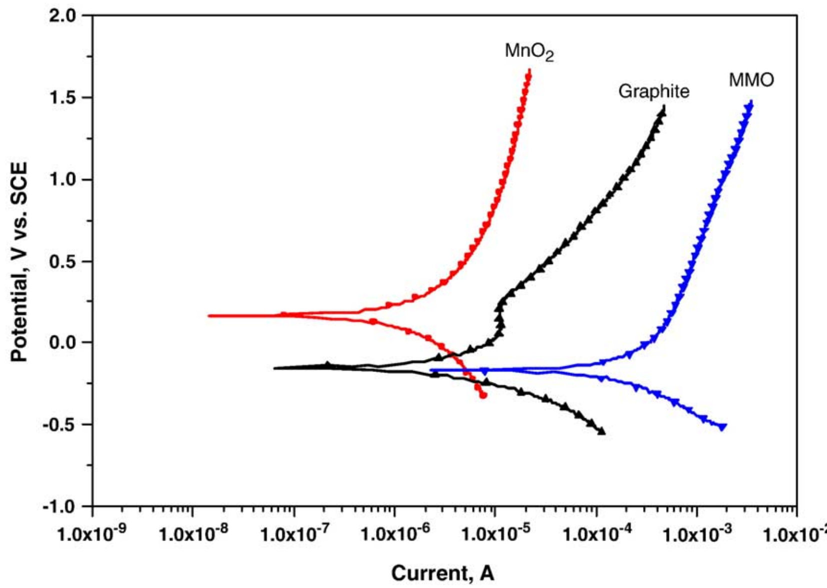

Fig. 3. Potentiodynamic scan of sensors embedded in OPC mortar–distilled water medium.

measurement unit coupled with Solartron 1255-B Frequency Response Analyzer and multi media computer at an ambient temperature of 25±1 °C. The real part (Z′) and the imaginary part (−Z″) of the cell impedance were measured for various frequencies (100,000–0.01 Hz). Plots of Z′ versus −Z″ were made.

3. Results and discussion

3.1. Electrochemical stability of sensing electrodes embedded in mortar

Fig. 2 relates the potential in millivolts and time in months for sensor electrodes embedded in mortars for the exposure period of one year. It was observed from Fig. 2 that the potential measured with respect to MnO_2 sensor showed constant for the exposure period of one year. MMO stabilized the potential from the 2nd month of exposure and afterwards showed the stable potential through out the exposure period. On the other hand, for graphite cells, the swing in potential values was noticed throughout. The potential-time behaviour for the chloride contaminated mortar is also shown in Fig. 2. It was observed that the addition of chloride does not make any influence for the one year exposure period. This is to be observed in all the three sensor electrodes embedded in mortar.

3.2. Potentiodynamic polarization behaviour of sensing electrodes embedded in mortar

Polarization behaviour of sensor electrodes embedded in mortar was carried out in distilled water, 3% NaCl and natural sea water environments. The typical polarization graphs are given in Figs. 3–5.

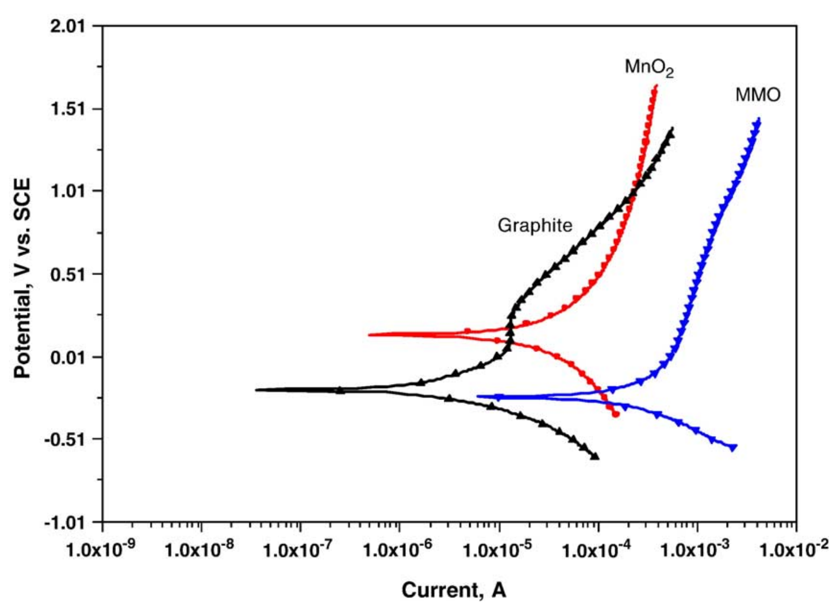

Fig. 4. Potentiodynamic scan of sensors embedded in OPC mortar–3% NaCl medium.

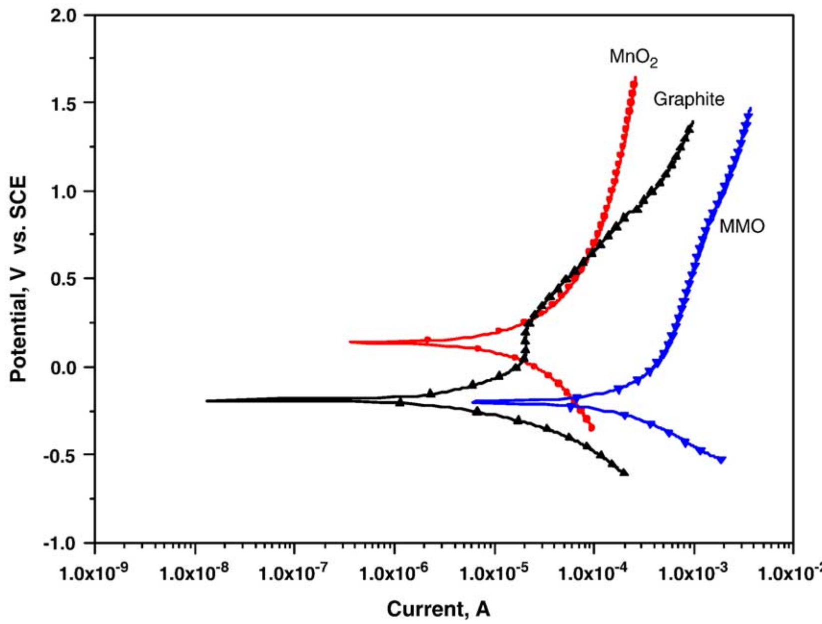

Fig. 5. Potentiodynamic scan of sensors embedded in OPC mortar–natural sea water medium.

It was observed from figures that, graphite electrode showed almost similar behaviour in all the three media investigated. Interestingly, MMO showed a stable passive region in the anodic direction in all the three media. Among all, MnO_2 electrode showed very negligible current both in the presence and absence of chloride in solutions indicating the tendency towards minimum of polarization. Not much variation was noticed either in the cathodic or in the anodic polarization curves. In addition, a stable potential passive region was observed in the anodic direction. The presence of chloride also does not having any influence on the anodic direction. A good agreement in potential and current values was noticed in the case of 3% NaCl and natural sea water medium.

3.3. AC impedance behaviour of sensing electrodes embedded in mortar

The typical Nyquist plot for mortar embedded with sensor electrodes is shown in Figs.6–8. Interestingly, distorted semicircle was recorded for all the systems but the Warburg line was obtained in the lower frequency region. The impedance diagram obtained in the distilled water medium was similar in shape and size to those in other solutions. The high frequency limit impedance value agreed well with the value expected from the test solution conductivities and mortar dimensions used. The high frequency arc did not vary greatly from solution to solution. The low frequency response was dominated by a constant phase angle element. No other admittance elements could be identified clearly at the low frequencies. The impedance behaviour of MnO_2, MMO and graphite sensor electrodes embedded in mortar was found to be similar in all the three aqueous media studied. The same observation was already observed in potentiodynamic polarization studies also. For graphite, the potential is partially dependent on the oxygen level in the concrete. In the case of long-term exposure, the homogeneity of concrete is affected due to the alternate wetting and drying process of concrete due to the environmental changes in the surrounding region. This will lead to

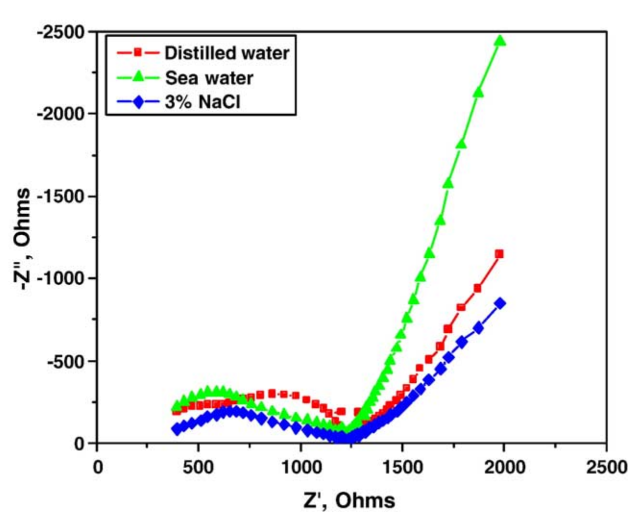

Fig. 6. Impedance behaviour of graphite sensor embedded in mortar.

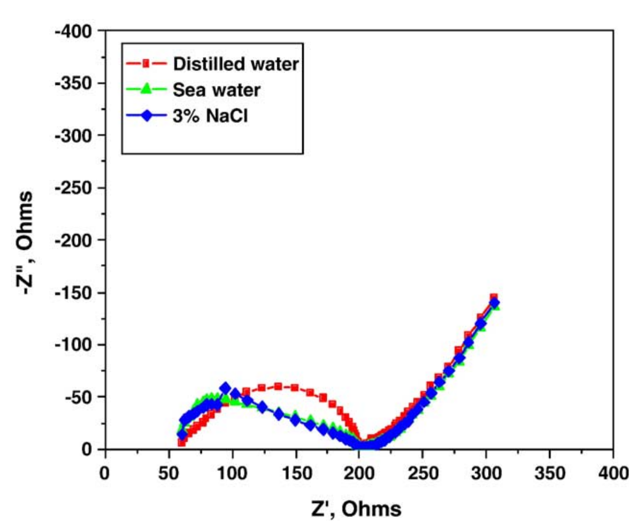

Fig. 7. Impedance behaviour of MMO sensor embedded in mortar.

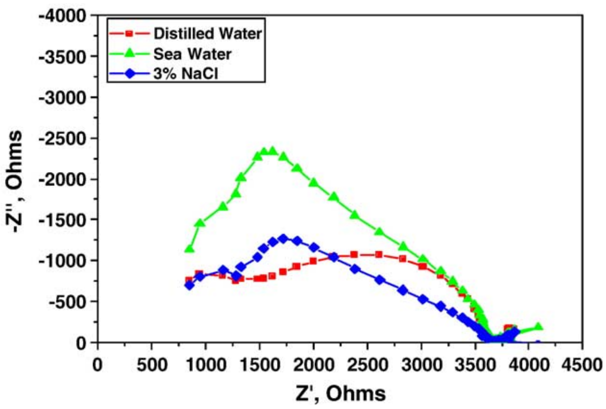

Fig. 8. Impedance behaviour of MnO_2 sensor embedded in mortar.

the continuous variation in the potential. The stability of the potential of MMO electrode is expected from the dependence of the iridium–water system in aqueous solutions. As per Pourbaix diagram of the Iridium–H_2O system, the pH dependence of the MMO electrode potential in the liquid solutions by an equilibrium between Ir oxides at the electrode surface of the type to obey the possible reaction is as follows:

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

The stability of MnO_2 electrode is due to the following reasons. The half-cell potential of MnO_2 is a complex function of the reduction state of manganese dioxide. But the potential being determined by MnO_2/Mn_2O_3 equilibrium potential. In MnO_2 electrodes, the middle layer is a slurry of pH 13.5 corresponding to the pH of normal pore water and will take care of the chemical balance with the surrounding concrete. This is the most advantageous of the manganese dioxide electrode which is chloride free when compared to the well known Ag/AgCl electrode which is always surrounded with chloride. The electrolytic contact of MnO_2 to the concrete environments is through the bottom layer which is made up of a diffusion barrier of cement paste, giving a good protection to the electrode unlike other electrodes. This will sufficiently give a good bond to the concrete as well as to the all important interface between the electrode and the concrete environments. The liquid junction potential across this interface is very minimal because the pH is nearly the same in the bottom plug and in the cell interior. This will not be expected to develop any junction potential at the plug/concrete interface, if this sensory electrode is used in the field. The additional advantage of embeddable type MnO_2 is free from harmful elements like mercury or corrosion accelerators like chloride and sulphate. The better performance of MMO and the superior performance of MnO_2 indicate that they are reliable embeddable type electrodes for the corrosion monitoring of concrete structures.

The stability of potential maintained by various sensor electrodes with and without chloride follows the order: $MnO_2 > MMO > Graphite$.

MMO was chosen as the material of the sensor as it is physically strong and has desirable electrochemical polarization characteristics. MnO_2 is the true reference electrode for concrete. Graphite will give a relative potential of the system.

4. Conclusions

The following conclusions were drawn from the present investigations:

1. MnO_2 sensor seems to be a more stable and reliable electrode in mortar medium.
2. MMO electrode also appears to be better for mortar medium.
3. Graphite electrode is less stable and more sensitive to the environmental changes in concrete. Graphite electrode may be utilized for short-term monitoring applications.
4. Very low polarization current is noticed in all the three sensors embedded in mortar.
5. The addition of chloride does not make any influence on the performance of sensors for one year exposure period.

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