

# Electrochemical studies on the performance characteristics of alkaline solid embeddable sensor for concrete environments

S. Muralidharan<sup>\*</sup>, V. Saraswathy, K. Thangavel, N. Palaniswamy

*Corrosion Protection Division, Central Electrochemical Research Institute, Karaikudi 630006, Tamilnadu, India*

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## Abstract

In this study, alkaline solid embeddable  $\text{MnO}_2$  is used as a reference sensor for concrete environments. The performance characteristics are evaluated in a saturated calcium hydroxide solution, a synthetic concrete pore solution and ordinary Portland cement (OPC) extracts which correspond to the concrete environments. The electrochemical stability of the  $\text{MnO}_2$  electrode is studied in the said concrete environments. The uniformity of the  $\text{MnO}_2$  sensor is tested in concrete environments. The reversibility of  $\text{MnO}_2$  sensor in three alkaline solutions is within  $\pm 10$  mV, which is very well within the limit as sensor for concrete. The polarization behaviour of  $\text{MnO}_2$  electrode in concrete environments is carried out potentiodynamically and impedance behaviour showed the stability of sensor. All the studies revealed that  $\text{MnO}_2$  as a suitable sensor electrode for concrete structures. © 2007 Elsevier B.V. All rights reserved.

**Keywords:** Embeddable sensor; Rebar corrosion; Corrosion monitoring; Electrochemical techniques

## 1. Introduction

Steel reinforcements embedded in reinforced or pre-stressed concrete bridges and structures need continuous monitoring because of their susceptibility to corrosion. Since corrosion process is electrochemical in nature, various electrochemical techniques are being adopted to monitor reinforcement corrosion. In all these cases continuous monitoring of the half-cell potentials of embedded steel becomes a prerequisite. Such a situation calls for a stable and rugged reference electrode, which can be permanently embedded in concrete as close as possible to the embedded steel so as to generate reliable data. Locke and Dehghanian [1] used Mo/MoO<sub>2</sub> reference electrodes in concrete containing 0.1–0.2% of Cl were within a standard deviation of 10 mV whereas the potential differed by 30–40 mV in 0.5% Cl. Manning and Schell [2] on the other hand observed that molybdenum electrodes can produce erratic signals and become unstable at lower temperatures say 278 K. Dehghanian et al. [3] have found that Hg/HgO reference electrode can remain stable and give reproducible readings. However, Gurusamy and Geoghegan [4] have reported that Hg/HgO sys-

tem produced erratic potential within 6 months of embedment in concrete. Schell and Manning [5] have examined five different types of reference electrodes and according to them, carbon and lead appeared stable in all normal temperatures and humidities. Mo/MoO<sub>2</sub> and Ag/AgCl cells did not appear to offer any specific advantages and become unstable under cold temperatures. Gurusamy and Geoghegan [4] have evaluated the long-term performance of Ag/AgCl cells in chloride contaminated and chloride uncontaminated concrete up to a period of 4.5 years and reported a mean potential difference of 30–35 mV with respect to SCE in 3% CaCl<sub>2</sub> contaminated concrete. Oskar Klinghoffer et al. [6] have developed a system based on MnO<sub>2</sub> and evaluated its long-term performance. Climent-Llorca [7] reported the possibility of using Ag/AgCl wire electrodes as in situ sensors of chloride concentration in concrete was studied by embedding them in a series of mortar specimens with different admixed NaCl contents. They show a sensitive potentiometric response to overall Cl<sup>-</sup> concentrations. The stability of the potential readings depends on the Cl<sup>-</sup> concentration and allows these electrodes to be used as Cl<sup>-</sup> content sensors in short-term tests.

Ives and Janz [8] have described the construction and working of different reference electrode systems. The following drawbacks have been identified. Calomel electrodes and other mercury–mercurous electrodes are formed from mercury and hence any leakage may lead to pollution hazard. Further use of

<sup>\*</sup> Corresponding author. Tel.: +91 4565 227550–59; fax: +91 4565 227779.  
E-mail address: [corrnmurali@yahoo.com](mailto:corrnmurali@yahoo.com) (S. Muralidharan).

aqueous solutions either potassium chloride or other salts require careful maintenance as well as careful handling. The process of making silver–silver halide electrodes is quite tedious as it involves either electrodeposition or thermal decomposition. It is rather difficult to achieve stability, sensitivity, and reproducibility. The process of making metal–metal oxide electrode is also laborious as it involves using metal–powdered oxide in admixture. Sometimes aerial oxidation is employed but it will have only a very small electrochemical capacity. Anodic oxidation is also difficult process. In the case of silver–silver oxide electrode, it is rather difficult to secure adequate reproducibility. Electrode potential tends to be rather erratic. The major drawback for metal–metal oxide electrodes is that nobility of metal and stability of oxide do not run together. Hardness and polymorphism obstruct the attainment of reproducible standard states. It is also worthwhile to point out that ASTM C 876 specifies the use of Cu/CuSO<sub>4</sub> as reference electrode for measurement of rebar potential in concrete [9]. The drawback of such surface-mounted electrode is that the seepage of copper sulphate solution would contaminate the concrete and the copper ions would influence the steel behaviour. Further surface-mounted electrodes are subjected to ultraviolet radiation effect which can lead to erroneous data. IR drop within the concrete cover will also lead to erroneous interpretation. It can be clearly seen from the foregoing that there is an utmost need to develop and evaluate the performance of reliable and maintenance-free systems for use in concrete. Such embeddable electrodes should have the following features [10,11]: it should be rugged and maintenance-free, it should have desirable microreversibility and low-temperature coefficient, it should have negligible liquid junction potential, it should have adequate stability and reliability when compared to a standard reference electrode such as SCE, it should be capable of being embedded under any orientation, it should not lead to undesirable contamination of surrounding concrete. MnO<sub>2</sub> is chosen as a sensor material in this investigation due to the stability of MnO<sub>2</sub> in alkaline medium which is well known [12] and proved as a successful cathode material in alkaline batteries [13]. The present investigation deals with the electrochemical studies on the performance characteristics of alkaline solid embeddable MnO<sub>2</sub> sensor for concrete environments.

## 2. Materials used

Ordinary Portland cement (OPC) conforming to IS:8112–2989 [equivalent to ASTM C150-Type-1] was used. Manganese dioxide reagent grade  $\geq 90\%$  purity was used for making sensor. Solutions such as cement extracts (CE), saturated calcium hydroxide solution (SCS) and synthetic concrete pore solution (CPS) were used. TMT cylindrical rod of size 50 mm long and 10 mm diameter was used.

### 2.1. Solution preparation

Ordinary Portland cement was sieved through 150  $\mu\text{m}$  sieve and cement extract was prepared by filtration. AR grade CaO was ignited for a long time to remove any carbonate present in the sample and then cooled. About 1.85 g of CaO is dissolved

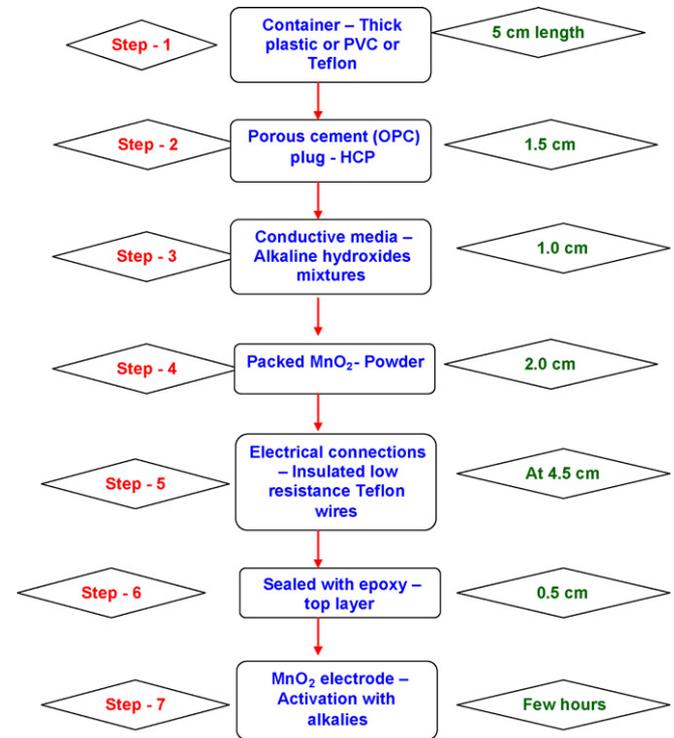


Fig. 1. Flow chart for the fabrication of embeddable MnO<sub>2</sub> sensor.

in distilled water to get a saturated calcium hydroxide solution. Synthetic concrete pore solution consists of 7.4 g NaOH and 36.6 g KOH per litre of saturated calcium hydroxide solution.

### 2.2. Preparation of sensor assembly

Alkaline manganese dioxide (MnO<sub>2</sub>) sensors were fabricated in the laboratory as follows. MnO<sub>2</sub> electrodes consists of three compartments namely a porous hydrated cement paste as bottom layer, a conductive alkaline slurry as middle layer and a powdered MnO<sub>2</sub> as top layer. The flow chart for making MnO<sub>2</sub> sensor is given in Fig. 1. The configuration of MnO<sub>2</sub> sensor is shown in Fig. 2. The fabrication of MnO<sub>2</sub> sensor consists of seven steps. The brief description of each step is as follows:

- Step-1: A suitable container made up of thick plastic or PVC or Teflon was chosen. The total length of the cell assembly used was 5 cm.
- Step-2: Ordinary Portland cement sieved through 150  $\mu\text{m}$  sieve was used. OPC mixed with a required quantity of double-distilled water to make a paste. This paste was applied in the bottom of the cell.
- Step-3: The conductive media consists of alkaline hydroxide based on sodium, potassium and calcium. The pH of the slurry is equal to that of pH of the concrete.
- Step-4: MnO<sub>2</sub> powder is tightly packed into the cell (compaction of about 2–3 psi) and about 2 cm length.
- Step-5: Electrical connection was taken from the top of the assembly. An insulated, low resistance Teflon wire was used.
- Step-6: The top of the cell was sealed with epoxy.

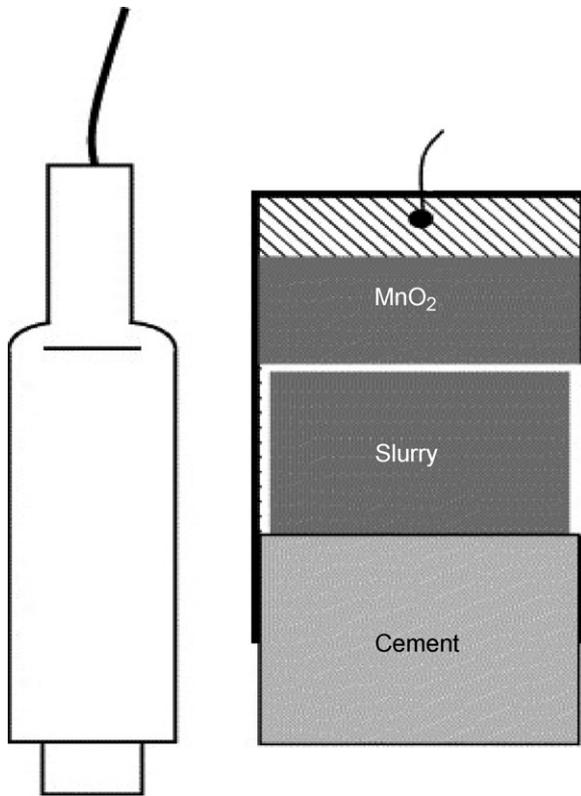


Fig. 2. A structure of MnO<sub>2</sub> reference sensor.

- Step-7: The MnO<sub>2</sub> sensor electrode was activated with saturated calcium hydroxide solution for few hours.

### 2.3. Characterization of sensor

#### 2.3.1. Stability test

The electrochemical stability of the MnO<sub>2</sub> sensor was assessed in different test solutions representing concrete environments. The conventionally used saturated calomel electrode (SCE) was used as a reference. Six sensors were assembled and used for this study. Six numbers of polythene beakers (100 ml capacity) were taken. The particular sensor electrode and SCE were simultaneously kept immersed in 75 ml of test solution. An inner electrode spacing of 2.5 mm was maintained in all the experiments. The potential of the MnO<sub>2</sub> electrode was monitored with respect to SCE over a period of 30 days.

#### 2.3.2. Reliability test

A newly assembled MnO<sub>2</sub> sensor was placed in a 75 ml of the test solution. Inserted another MnO<sub>2</sub> sensor in the same test solution. The inner electrode spacing between the first sensor and the second sensor is 2.5 mm. The potential between these two sensors is monitored at room temperature of  $35 \pm 1$  °C.

#### 2.3.3. Polarization characteristics

**2.3.3.1. Potentiodynamic polarization studies.** Potentiodynamic polarization studies were carried out using MnO<sub>2</sub> sensor in OPC extracts, saturated calcium hydroxide solution and concrete pore solution. The polarization cell is a three-electrode

glass cell assembly consists of MnO<sub>2</sub> sensor as working electrode, cylindrical platinum foil as counter electrode and SCE as reference electrode. A constant quantity of the test solution was taken in the polarization cell. Time intervals of 10–15 min were given for each system to attain a steady state and the OCP was noted. Both anodic and cathodic polarization curves were recorded potentiodynamically using ACM instrument, UK. The potentiodynamic condition corresponds to a potential sweep rate of 60 mV/min and potential ranges of –200 to +200 mV from the OCP. All the experiments were carried out at a room temperature of  $35 \pm 1$  °C.

**2.3.3.2. Cyclic polarization measurements.** A similar procedure as above was followed for cyclic polarization studies also. The potentiodynamic condition corresponds to the potential sweep rate of 6 mV/min and potential ranges of –20 to +20 mV from the OCP. The experiment is run for two cycles. The difference in the shifting of potential from the first cycle and the second cycle was noted.

#### 2.3.4. AC impedance measurements

The impedance measurements were carried out using ACM Instruments, corrosion monitoring field machine. The real part ( $Z'$ ) and imaginary part ( $-Z''$ ) of the cell impedance were measured for various frequencies (30 000–0.1 Hz). Plots of  $Z'$  vs.  $-Z''$  were made. Impedance measurements were carried out for MnO<sub>2</sub> sensor in OPC extracts, saturated calcium hydroxide solutions and concrete pore solutions.

## 3. Results and discussion

### 3.1. Test for uniformity for MnO<sub>2</sub> reference sensor

The uniformity of MnO<sub>2</sub> reference electrode in saturated calcium hydroxide solution is given in Fig. 3. For this experiment, 30 numbers of MnO<sub>2</sub> reference electrodes were made and tested in saturated calcium hydroxide solution. It was inferred that, out of 30 numbers of electrodes, 17 numbers showed +200 mV, 8 numbers showed +202 mV and 5 numbers showed +205 mV

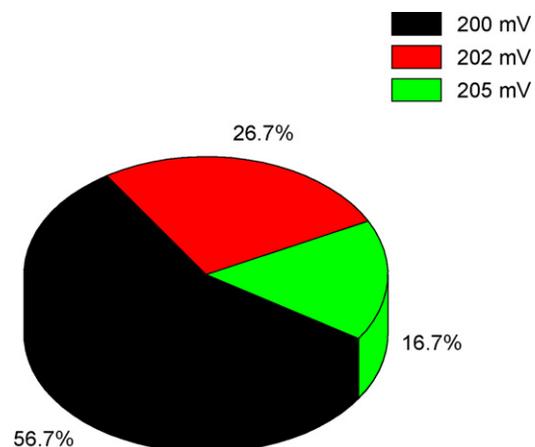


Fig. 3. Uniformity of measured potential of sensor in the saturated solution of calcium hydroxide.

vs. SCE. It is interesting to note that, not much variation was observed between these electrodes. The maximum variation observed was only  $\pm 5$  mV vs. SCE and this difference in potential is almost negligible indicating that MnO<sub>2</sub> electrodes showed uniformity in concrete environments under laboratory condition.

3.2. Reliability test of MnO<sub>2</sub> reference sensors

The reliability of developed MnO<sub>2</sub> sensor was tested in SCS at room temperature. Here it was observed that as expected the potential difference between the two MnO<sub>2</sub> electrodes was found to be zero. This indicates that the reliability of all the assembled MnO<sub>2</sub> sensor was found to be excellent. All the sensors are subjected to this test before further characterization.

3.3. Stability test for MnO<sub>2</sub> reference sensor in concrete environments

The electrochemical stability of the MnO<sub>2</sub> sensor was monitored in different test solutions representing concrete environments with respect to SCE for the exposure period of 30 days. The potential of MnO<sub>2</sub> electrode in concrete environments such as saturated calcium hydroxide solution, synthetic concrete pore solution and OPC extracts are given in Fig. 4. The potential were measured for the exposure period of 30 days. Interestingly, MnO<sub>2</sub> electrode in all the three solutions showed stable behaviour after 12 days. The stability of the MnO<sub>2</sub> electrode was maintained after 12 days up to 30 days of exposure. Here it was concluded that the MnO<sub>2</sub> reference sensor maintained the perfect stability in SCS, CPS, and CE extracts, which represents concrete environments for the exposure period of 30 days at room temperature  $35 \pm 1$  °C.

3.4. Cyclic sweep (reversibility) behaviour of MnO<sub>2</sub> reference sensor in concrete environments

The reversibility characteristics of the MnO<sub>2</sub> reference sensor in concrete environments were carried out by cyclic sweep method. It is interesting to note that cyclic polarization behaviour of MnO<sub>2</sub> sensor in concrete environments was found to be good. The maximum difference between the first and second cycle is +5 mV vs. SCE and this difference in potential is acceptable as

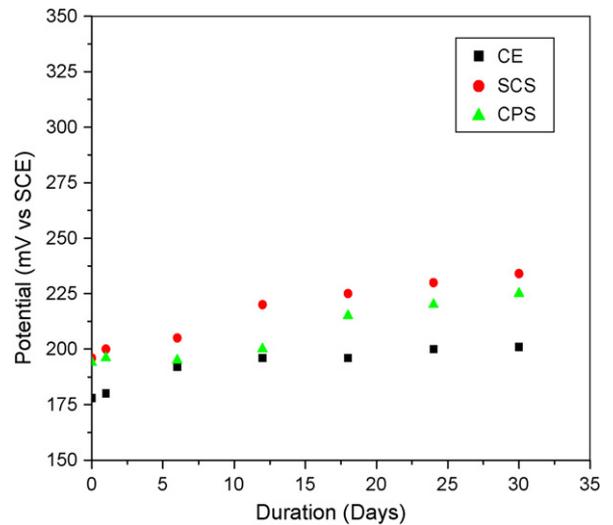


Fig. 4. Stability of MnO<sub>2</sub> reference sensor in concrete environments.

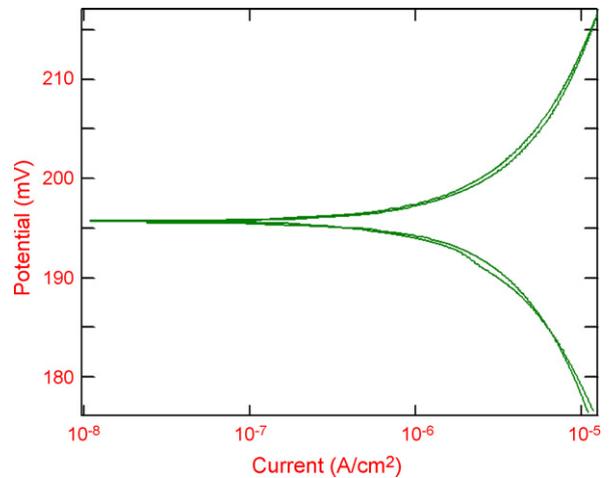


Fig. 5. Typical cyclic polarization curve for MnO<sub>2</sub> sensor in SCS.

sensor electrode in concrete environments. The typical cyclic sweep curve of MnO<sub>2</sub> sensor in SCS is given in Fig. 5. The reversibility parameters of MnO<sub>2</sub> sensor in SCS derived from the cyclic polarization curves are given in Table 1. Here it was observed that, in SCS the sensor Nos. 2–4 showed same potential between the first and second cycle. Sensor Nos. 1, 5 and 6

Table 1  
Reversibility characteristics of MnO<sub>2</sub> sensor in concrete environments

Sensor	SCS (mV vs. SCE)			CPS (mV vs. SCE)			CE (mV vs. SCE)		
	1st	2nd	Difference	1st	2nd	Difference	1st	2nd	Difference
1	210	214	4	219	222	3	212	214	8
2	213	214	1	194	196	2	189	193	4
3	196	196	0	197	199	2	193	198	5
4	193	194	1	194	196	2	194	197	3
5	194	198	4	194	194	0	192	194	2
6	222	227	5	198	198	0	196	191	5
	Average 2.5			Average 1.5			Average 4.5		

showed the difference of 4 mV, 4 mV and 5 mV, respectively. The average of difference in potential in first cycle and second cycle was found to be 2.5 mV. This difference was almost negligible for using  $\text{MnO}_2$  sensor in SCS. The reversibility parameters for sensor in CPS also given in Table 1. It was observed that, sensor Nos. 5 and 6 showed the same potential in the first and the second cycle. Sensor Nos. 2–4 showed the difference of only 2 mV. The average difference between the first and second cycle for  $\text{MnO}_2$  sensor in CPS solution was found to be 1.5 mV indicating that  $\text{MnO}_2$  electrode showed better reversibility in CPS. The difference in potential was also less than SCS. The reversibility parameter for sensor in CE is given Table 1. The reversibility parameter, i.e. the difference between the potential of the first cycle and the second cycle in CE is more than that of SCS and CPS. The average of the potential of first cycle and second cycle in CE was found to be 4.5 mV. This value is also within the limit of potential of  $\text{MnO}_2$  electrode in concrete environments. The trend in the existence of the reversibility of the  $\text{MnO}_2$  electrode in three alkaline environments is as follows: CPS > SCS > CE.

### 3.5. Polarization behaviour of $\text{MnO}_2$ reference sensor in concrete environments

A small amount of current is involved during the remote corrosion monitoring of embeddable sensors. Even these small current should not polarize an ideal embeddable sensor. It was noticed that the anodic and cathodic polarization curves are almost similar in all the cases. On the other hand, the appreciable passive region was noticed in the anodic polarization curves. The typical polarization curve for  $\text{MnO}_2$  sensor in SCS is given in Fig. 6. The polarization parameters for  $\text{MnO}_2$  sensor in three solutions are given in Table 2. It was observed from Table 2 that in SCS, except sensors 4 and 6, all other sensors almost showed the less polarization current values. In CPS, except sensors 3 and 5 all other sensors almost showed the less polarization current values. In CE, except 3 and 5, all other sensors showed negligible polarization current values. Among six sensors studied, the maximum of four sensors showed similar polarization behaviour in three alkaline solutions. In addition, no significant change in corrosion potential values were observed. Even a small current is induced during polarization, the corrosion potential of the  $\text{MnO}_2$  sensor not changed. This behaviour is quite suited for our interest to choose  $\text{MnO}_2$  as an embeddable sensor for concrete environments.

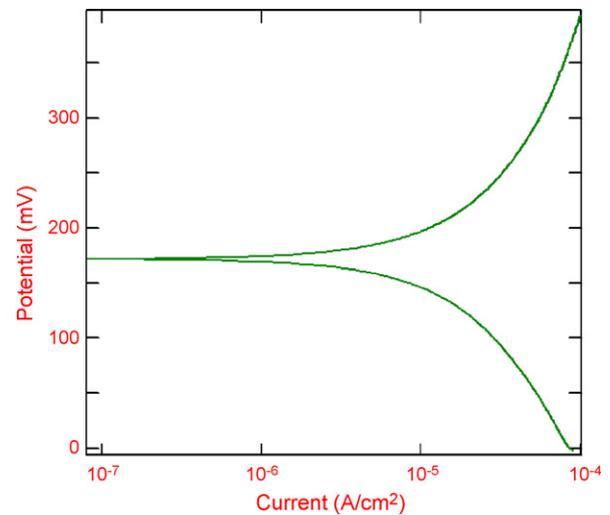


Fig. 6. Typical potentiodynamic polarization curve for  $\text{MnO}_2$  sensor in SCS.

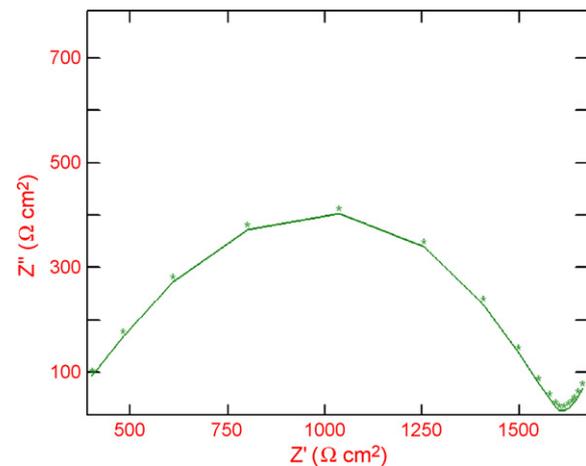


Fig. 7. Typical impedance diagram for  $\text{MnO}_2$  sensor in SCS.

### 3.6. AC impedance behaviour of $\text{MnO}_2$ reference sensor in concrete environments

Impedance diagram obtained for the frequency range 30 000–0.1 Hz at the open circuit potential of  $\text{MnO}_2$  in concrete environments are shown in Fig. 7. In most of the cases, impedance diagram obtained is perfect semicircle along with Warburg impedance at the lower frequencies. The charge transfer resistance has been calculated from the difference in impedance

Table 2  
Polarization parameters for  $\text{MnO}_2$  sensor in concrete environments

Sensor no.	SCS		CPS		CE	
	OCP (mV)	$i_{\text{corr}}$ ( $\text{mA cm}^{-2}$ )	OCP (mV)	$i_{\text{corr}}$ ( $\text{mA cm}^{-2}$ )	OCP (mV)	$i_{\text{corr}}$ ( $\text{mA cm}^{-2}$ )
1	208	0.0020	209	0.0020	201	0.0022
2	206	0.0021	207	0.0020	202	0.0020
3	203	0.0018	204	0.0045	204	0.0040
4	203	0.0076	203	0.0018	208	0.0019
5	208	0.0020	202	0.0080	209	0.0079
6	202	0.0071	205	0.0023	203	0.0022

Table 3  
Impedance parameters for MnO<sub>2</sub> sensor in concrete environments

No.	SCS			CPS			CE		
	OCP (mV)	$R_{ct}$ ( $\times 10^2 \Omega \text{ cm}^2$ )	$C_{dl}$ ( $\times 10^{-3} \text{ F}$ )	OCP (mV)	$R_{ct}$ ( $\times 10^2 \Omega \text{ cm}^2$ )	$C_{dl}$ ( $\times 10^{-3} \text{ F}$ )	OCP (mV)	$R_{ct}$ ( $\times 10^2 \Omega \text{ cm}^2$ )	$C_{dl}$ ( $\times 10^{-3} \text{ F}$ )
1	208	2.597	7.153	207	2.129	2.947	203	2.902	5.281
2	202	1.073	1.977	201	3.672	1.686	201	3.242	2.080
3	206	9.340	0.825	202	4.720	4.983	202	6.445	9.890
4	202	1.527	1.282	206	4.588	2.156	205	2.722	4.387
5	201	6.632	3.806	208	3.632	1.306	203	2.235	3.148
6	208	2.063	8.560	208	2.161	1.656	207	1.222	1.477
	Average	3.872	3.933	Average	3.483	2.455	Average	3.128	4.377

at low and high frequencies. The double layer capacitance ( $C_{dl}$ ) has been calculated from the frequency at which the imaginary component of the impedance  $-Z''$  is maximum. The typical Nyquist plots for MnO<sub>2</sub> electrode in SCS solution is given in Fig. 7. The impedance parameters for MnO<sub>2</sub> sensor in three alkaline solutions are given in Table 3. It was found from Table 3 that, not much variation was noticed in the average  $R_{ct}$  values of MnO<sub>2</sub> sensor in three test solutions. For example, the average  $R_{ct}$  values for MnO<sub>2</sub> sensor in SCS, CPS and CE are  $3.872 \times 10^2 \Omega \text{ cm}^2$ ,  $3.483 \times 10^2 \Omega \text{ cm}^2$  and  $3.128 \times 10^2 \Omega \text{ cm}^2$ , respectively. The average  $C_{dl}$  values for MnO<sub>2</sub> sensor are  $3.933 \times 10^{-3} \text{ F}$  in SCS,  $2.455 \times 10^{-3} \text{ F}$  in CPS and  $4.377 \times 10^{-3} \text{ F}$  in CE. A comparable trend was obtained between charge transfer resistance and double-layer capacitance values of different sensors indicated the better impedance characteristics of MnO<sub>2</sub> sensor in three test solutions.

### 3.7. Comparison of half-cell potential of MnO<sub>2</sub> reference sensor in concrete environments by different techniques

The comparison of half-cell potential of MnO<sub>2</sub> sensor during electrochemical measurements such as cyclic polarisation, potentiodynamic polarisation and AC impedance technique is given in Table 4. Here it was observed that MnO<sub>2</sub> sensor showed more or less the same half-cell potential values from different techniques. Interestingly, the stability of potential of MnO<sub>2</sub> sensor by ac technique is agreed very well with dc techniques. The average half-cell potential MnO<sub>2</sub> sensor in three test solutions by different techniques is given in Table 5. It was observed

Table 4  
Comparison of half-cell potential of MnO<sub>2</sub> sensor by various techniques

No.	Half-cell potential (mV vs. SCE)								
	SCS			CPS			CE		
	CP	PP	Imp.	CP	PP	Imp.	CP	PP	Imp.
1	209	208	208	209	209	207	204	201	203
2	205	206	202	204	207	201	206	202	201
3	203	203	206	200	204	202	205	204	202
4	206	203	202	200	203	206	200	208	205
5	202	208	201	206	202	208	207	209	203
6	203	202	208	205	205	208	201	203	207

CP: cyclic polarization, PP: potentiodynamic polarization, Imp.: ac impedance.

that the average half-cell potential of MnO<sub>2</sub> sensor by different techniques showed their uniformity, stability, reliability and reversibility of MnO<sub>2</sub> sensor in concrete environments.

### 3.8. Mechanistic aspects of sensor in concrete environments

The electrochemical stability of sensor electrodes in simulated concrete environments was measured with respect to saturated calomel electrode. The stability of the any sensor electrode depends on the measure of the activity of the reactive species. If the activity of the species reacting at the sensing electrode varies, the potential also may vary. So all the sensor electrodes depend on how far they maintain the stability and the stability depends on the activity of the sensing element. In the case of MnO<sub>2</sub> the galvanic-coupling between the reference sensor and the embedded steel in concrete is a measure of the MnO<sub>2</sub>/Mn<sub>2</sub>O<sub>3</sub> equilibrium potential and Fe/Fe<sup>2+</sup>. The half-cell potential of MnO<sub>2</sub> is a complex function of the reduction state of manganese dioxide. But the potential being determined by a MnO<sub>2</sub>/Mn<sub>2</sub>O<sub>3</sub> equilibrium potential. In MnO<sub>2</sub> electrodes, the middle layer is slurry of pH of 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 advantage of the manganese dioxide electrode which is chloride-free. The electrolytic contact of MnO<sub>2</sub> to the concrete environments is through the bottom layer which is made up of diffusion barrier of cement paste gives a good protection to the electrode unlike other electrodes made up of glass. This will sufficiently give a good bond to the concrete and also means that all important interface between the electrode and to the concrete environments. The liquid junction potential across this interface is very minimum because of the pH is nearly the same in the bottom plug and in the cell interior. This will expect not to develop any junction potential at the plug/concrete interface, if this sensor electrode is used in

Table 5  
Average half-cell potential of MnO<sub>2</sub> sensor in concrete environments

Technique	Half-cell potential (mV vs. SCE)			Average (mV vs SCE)
	SCS CPS CE			
	Cyclic polarization	204	204	
Potentiodynamic polarization	205	205	204	204
AC impedance	204	205	203	204

the field. The advantage of MnO<sub>2</sub> is very compact, easy to use in the field, chloride-free, sulphate-free and mercury-free sensor for concrete structures.

#### 4. Conclusions

MnO<sub>2</sub> sensor showed the perfect uniformity in saturated calcium hydroxide solution at room temperature. MnO<sub>2</sub> electrode also showed the reliability with respect to saturated calomel electrode. MnO<sub>2</sub> sensor proved to be more stable and reliable sensor electrode in concrete environments such as saturated calcium hydroxide solution, concrete pore solution and cement extracts. Cyclic polarization ( $\pm 20$  mV) test for MnO<sub>2</sub> sensor in saturated calcium hydroxide solution, concrete pore solution and cement extracts medium indicated a maximum difference of 5 mV between the forward and reverse scans. This test certified the good reversibility of MnO<sub>2</sub> sensor in concrete environments. Tafel polarization ( $\pm 200$  mV) test for MnO<sub>2</sub> sensor in saturated calcium hydroxide solution, concrete pore solution and cement extract medium indicated a very low polarization current confirmed the better performance of MnO<sub>2</sub> sensor in concrete environments. AC impedance test for MnO<sub>2</sub> in saturated calcium hydroxide solution, concrete pore solution and cement extract medium indicated the same double-layer capacitance values confirmed the perfect stability of the MnO<sub>2</sub> sensor in concrete environments.

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#### References

- [1] C.E. Locke, C. Dehghanian, *Mater. Perform.* 18 (1970) 70–73.
- [2] D.G. Manning, H.C. Schell, *Transportation Research Record*, 1041 Transportation Research Board, National Research Council, Washington, DC, 1985.
- [3] C. Dehghanian, C.R. Root, C.E. Locke, *Corrosion* 81, NACE Conference, Ontario, Canada, Paper 45, April 1981, p. 6.
- [4] K.N. Gurusamy, M.P. Geoghegan, in: C.L. Page, K.W.J. Treadway, P.M. Bamforth (Eds.), *Corrosion of Reinforcement in Concrete*, Elsevier Applied Science, 1990, p. 346.
- [5] H.C. Schell, D.G. Manning, *Corrosion* 85, NACE Conference, Massachusetts, Paper 263, March 1985, p. 17.
- [6] O. Klinhoffer, H. Arup, J. Mietz, *Eur. Corr.* 97, Trendheim, September, 1997.
- [7] M.A. Climent-Llorca, E. Viqueira-Pérez, M.M. López-Atalaya, *Embeddable Ag/AgCl sensors for in situ monitoring chloride contents in concrete*, *Cement Concr. Res.* 26 (1996) 1157–1161.
- [8] D.J.G. Ives, G.J. Janz, *Reference Electrodes Theory and Practice*, Academic Press, 1961, p. 60.
- [9] *Annual Book of ASTM Standards*, C876, 1995.
- [10] W.J. McCarter, O. Vennesland, *Sensor systems for use in reinforced concrete structures*, *Constr. Build. Mater.* 18 (2004) 351–358.
- [11] M. Raupach, P. Schießl, *Macrocell sensor systems for monitoring of the corrosion risk of the reinforcement in concrete structures*, *NDT&E Int.* 34 (2001) 435–442.
- [12] N.N. Greenwood, A. Earnshaw, *Chemistry of the Elements*, 2nd ed., Butterworth–Heinemann, Oxford, 1997.
- [13] D. Linden, *Handbook of Batteries*, McGraw–Hill, Maidenhead, 1995.

#### Biographies

**S. Muralidharan** was born in Tamilnadu, India, on 3, June 1966. He received his Master's degree (Chemistry) from Bharathidasan University and Ph.D. from Madurai Kamaraj University, India. He has been working at CECRI since 1997. His research interest includes sensors for corrosion monitoring in concrete structures, admixtures for concrete, fly ash utilization, nanomaterials, etc.

**V. Saraswathy** was born in Tamilnadu, India, on 15 April 1966. She received her Bachelor's degree (Civil) from Madurai Kamaraj University and Ph.D. from Alagappa University, India. She has been working at CECRI since 1988. Her research areas include corrosion monitoring, repair and rehabilitation, cathodic protection, waste product utilization, etc.

**K. Thangavel** was born in Tamilnadu, India, on 12 January 1956. He received his Master's degree (Chemistry) from Madurai Kamaraj University and Ph.D. from Alagappa University, India. He has been working at CECRI since 1980. His research interest includes corrosion monitoring and control in concrete structures, high-performance concrete, nanomaterials, admixtures, etc.

**N. Palaniswamy** was born in Tamilnadu, India, on 19 August 1952. He received his Master's degree (Chemistry) from Madras University and Ph.D. from Madurai Kamaraj University, India. He has been working at CECRI since 1976. His research interest includes cathodic protection, anodic protection, bio-corrosion, corrosion protection in concrete, etc.