Nickel ferrite (NiFe$_2$O$_4$): A possible candidate material as reference electrode for corrosion monitoring of steel in concrete environments

S. Muralidharan [a,*], V. Saraswathy [a], L. John Berchmans [a], K. Thangavel [a], Ki Yong Ann [b]

[a] Central Electrochemical Research Institute, Karaikudi 630006, Tamil Nadu, India
[b] Concrete Materials Mechanics and Engineering, School of Civil and Environmental Engineering, Yonsei University, Seoul 120-749, Republic of Korea

ARTICLE INFO

ABSTRACT

Nickel ferrite (NiFe$_2$O$_4$) was tried first time as a possible candidate material as embeddable reference sensor in concrete environments. NiFe$_2$O$_4$ was synthesized in the laboratory and assembled reference cell which consists of three compartments. The sensor performance was evaluated in concrete environments such as saturated calcium hydroxide solution, synthetic concrete pore solution and ordinary Portland cement (OPC) extract. The consistency test and electrochemical stability test of the sensor were studied in the said concrete environments and the half cell potential was found to be within ±5 mV, which was very well within the limit as sensor material for concrete. The polarization and impedance tests of NiFe$_2$O$_4$ sensor in concrete environments showed the stability of the sensor material in the highly alkaline concrete environments.

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1. Introduction

Ferrite compounds are very important because of their optical, electrical and magnetic properties. Moreover, many papers related to their development as possible gas sensor. Such an application required a high surface activity, and consequently a small crystallite size and a large surface area. The physical vapor deposition (RF-sputtering) is widely used for thin film synthesis. These nanostructured cobalt–manganese–ferrite films appear to be quite suitable for an application as gas sensors [1,2].

The importance of reference electrodes is undisputed practically in all electrochemical analytical methods. Particularly, the results rendered by potentiometry are all highly dependent on quality performance of the reference electrodes. Thus, the actual development of novel electrodes selective to ions goes hand in hand with studies oriented to optimization of the former [3].

Apart from all the classical features that reference electrode should have, namely, to provide a constant potential that is stable with respect to the indicator electrode, that it should not be polarizable, it should return quickly to the correct imposed potential after an accidental polarization, its behaviour should follow the Nernst Law for the pertinent species depending on the sort of electrode, that the potential be independent of the solution's composition and that the solid compound of the electrode have small solubility in the electrolyte [4]. Presently, it is required also that these electrodes are amenable to miniaturization and that they may be readily adapted to varied configuration as demanded by the analytical system.

Ives and Janz [5] 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 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 electro deposition 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 powdered 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 draw back for metal–metal oxide

* Corresponding author at: Central Electrochemical Research Institute, Corrosion Protection Division, CECRI Nagar, Karaikudi 630006, Tamil Nadu, India.
Tel.: +91 4565 227550–59; fax: +91 4565 227779.
E-mail address: corrmurali@yahoo.com (S. Muralidharan).

Table 1
Chemical composition of ordinary Portland cement.

Compound	OPC (wt%)
SiO_2	20–21
Al_2O_3	5.2–5.6
Fe_2O_3	4.4–4.8
CaO	62–63
MgO	0.5–0.7
SO_3	2.4–2.8
Loss on ignition (LOI)	1.0–1.5

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 the use of $Cu/CuSO_4$ as reference electrode for measurement of rebar potential in concrete. The drawback of such surface mounted electrode is that the seepage of copper sulfates 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 is well known that the most common reference electrodes are based on calomel, on sulfates and on Ag/AgCl, where the latter clearly exhibit superior characteristics regarding the miniaturization possibilities [6–10]. The use of polymers [11–15], membranes [16] instead of water to immobilize the chloride ions. Recently MnO_2 were reported as a best sensor electrode in concrete environments [17–19]. But for the modern technological changes new materials are come day-by-day and their uses also in variety of applications. It can be clearly seen from the foregoing that there is an utmost need to develop and evaluated the performance of reliable and maintenance-free systems for use in concrete.

In this aspect, $NiFe_2O_4$ was tried as first time in the reference sensor application to monitor reinforcement corrosion in concrete structures due to the specific advantages as follows:

- Environment-friendly O_2 gas was produced during electrolysis instead of green house gases. Hence nickel ferrite is called as green anode material.
- Nickel ferrite is called as life saving material.
- It is cost effective and easy to prepare.
- Nickel ferrite is commonly used in many electronic and magnetic devices due to their high magnetic permeability and low magnetic loss.
- It also used in electrode material for high temperature applications because of their high thermodynamic stability, electrical conductivity and electrode catalytic activity.
- It is resistance to corrosion.

Hence considering the importance of ferrites, in this present investigation Ce^{3+} substituted nickel ferrite form an important class and it is used as a sensor material to monitor reinforcement corrosion in concrete environments.

2. Materials and methods

2.1. Cement

Ordinary Portland cement (OPC) conforming to IS: 8112-1989 (equivalent to ASTM C150-Type-1) was used throughout this investigation. The chemical composition (wt.%) of OPC used is given in Table 1.

2.2. Solutions used

(1) Saturated calcium hydroxide solution [pH 13.00]
(2) Synthetic Concrete pore solution [pH 13.0]
(3) Cement extracts [pH 12.5]

2.3. Solution preparation

2.3.1. Preparation of saturated calcium hydroxide solution

AR grade calcium oxide (CaO) was heated for a long time to remove any carbonate present in the sample. About 1.85 g of CaO is dissolved in distilled water to get a saturated calcium hydroxide solution.

2.3.2. Preparation of concrete pore solution

Synthetic concrete pore solution consists of 7.4 g sodium hydroxide (NaOH) and 36.6 g potassium hydroxide (KOH) per litre of saturated calcium hydroxide solution.

2.3.3. Preparation of cement extracts

Ordinary Portland cement was sieved through 150 μm sieve and extract was prepared as follows:
To 100 g of the cement, added 200 ml of distilled water and shaken vigorously for about 1 h. The extracts were then collected by filtration.

2.4. Preparation of sensor material ($NiFe_2O_4$)

2.4.1. Material synthesis

Fine crystalline nickel ferrite powders were synthesized using citrate gel process with appropriate amounts of high purity nickel nitrate [$Ni(NO_3)_2 \cdot 6H_2O$], ferric nitrate [$Fe(NO_3)_3 \cdot 9H_2O$] and citric acid [$C_6H_8O_7 \cdot H_2O$] as starting materials. The stoichiometric quantities of nitrate salts were dissolved in triple distilled water and required amount of citric acid was added as chelating agent. Dilute ammonia solution was poured slowly into the nitrate–citrate mixture to adjust the pH 6.5. The mixed solution was heated at 100 °C for 5 h with uniform stirring and evaporated to obtain a highly viscous gel. Thus obtained gel was placed in a hot plate and maintained at 300 °C; the gel was swelled and ignited with the evolution of large amounts of gaseous products resulting with the desired ferrite in the form of foamy powder.

The powder was compacted with the desired shape by mechanical pressing using a hydraulic press at 4 tons cm^{-2} to get the pellets of 1–2.5 cm diameter. Then the fabricated electrodes were sintered at 1000 °C in air for 50 h continuously and slowly cooled to ambient temperature [20].

2.4.2. Preparation of sensor assembly

Alkaline nickel ferrite ($NiFe_2O_4$) sensors were fabricated in the laboratory as follows. $NiFe_2O_4$ electrode consisted of three compartments namely a porous hydrated cement paste as bottom layer, a conductive alkaline slurry as middle layer and a $NiFe_2O_4$ as top layer.

2.5. Characterization of sensor

2.5.1. Reliability test

A newly assembled $NiFe_2O_4$ sensor was placed in a 75 ml of the test solution. Another $NiFe_2O_4$ sensor was also inserted into the saturated calcium hydroxide solution. The inner electrode spacing between the first sensor and the second sensor is maintained as 2.5 mm. The potential between these two sensors is monitored at room temperature (35 ± 1 °C).

2.5.2. Consistency test for NiFe$_2$O$_4$ reference sensor

A newly assembled NiFe$_2$O$_4$ sensor was placed in a 75 ml of the saturated calcium hydroxide solution. Saturated calomel electrode (SCE) was also inserted into the test solution. The inner electrode spacing between the first sensor and the second sensor is maintained as 2.5 mm. The potential between these two electrodes is monitored at room temperature (35 ± 1 °C).

2.5.3. Stability test

The electro chemical stability of the NiFe$_2$O$_4$ sensor was assessed in different test solutions representing concrete environments. The conventionally used SCE was used as a reference electrode. The simulated concrete environments chosen for the tests are saturated calcium hydroxide solution (SCS), concrete pore solution (CPS) and cement extract (CE). Six sensors (S1–S6) were assembled and used for this study. Six numbers of polythene beakers (100 ml capacity) were taken. The particular sensor electrode and the saturated calomel electrode (SCE) were simultaneously kept immersed in 75 ml of test solution. An inner electrode spacing of 2.5 mm was maintained in all experiments. One terminal of the voltmeter was connected to the NiFe$_2$O$_4$ sensor and the other common terminal was connected to the saturated calomel electrode (SCE). The stability in maintaining the potential of the NiFe$_2$O$_4$ electrode was monitored with respect to SCE in concrete environments for the exposure of 30 days.

2.5.4. Polarization test

Potentiodynamic polarization studies were carried out for NiFe$_2$O$_4$ sensor as working electrode in OPC extracts, saturated calcium hydroxide solution and concrete pore solution. The different test solutions were prepared using distilled water. The polarization cell is a three-electrode glass cell assembly. A rectangular platinum foil was used as the counter electrode. The area of the counter electrode is much larger than the area of the working electrode. This will exert a uniform potential field on the working electrode. Reference electrode used was SCE. 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. Time intervals of 10–15 min were given for each of the system to attain a steady state and the OCP was noted. Both anodic and cathodic polarization curves were recorded potentiodynamically using ACM instrument, UK. This instrument itself is having provisions for programs to evaluate corrosion kinetic parameters such as I_{corr}, E_{corr}, b_a and b_c. The potentiodynamic condition corresponds to a potential sweep rate of 60 mV min^{-1} and potential ranges of −200 mV to +200 mV from the OCP. All the experiments were carried out at constant temperature of 35 ± 1 °C.

2.5.5. Reversibility test

A similar procedure as above was adopted for reversibility test also. The potentiodynamic condition corresponds to the potential sweep rate of 6 mV min^{-1} and potential ranges of −20 mV to +20 mV from the OCP. Here the experiment is run for two cycles. The difference in the shifting of potential from the first cycle and the second cycle was noted. Six sensors were used for the study.

2.5.6. Impedance test

A three-electrode cell assembly was used here also. For this NiFe$_2$O$_4$ sensor was as working electrode; saturated calomel electrode as reference electrode and platinum electrode as counter electrode. They were assembled and connections were made. A time interval of 10–15 min was given for the OCP to reach a steady value. The impedance measurements were carried out using ACM Instruments, UK. The real part (Z') and imaginary part ($-Z''$)
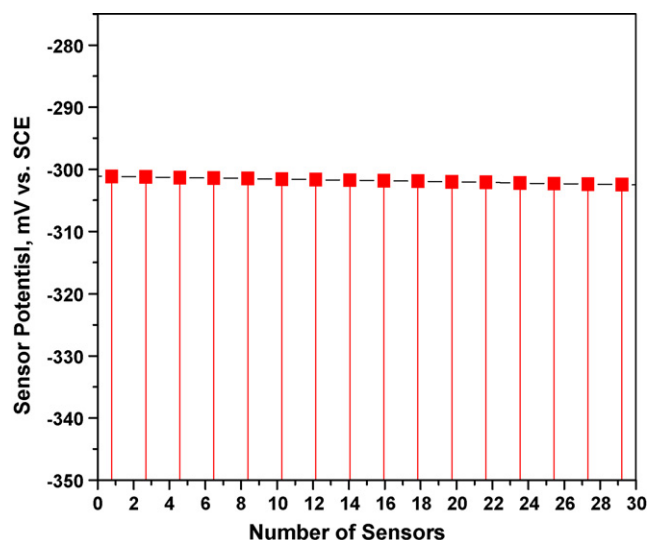

Fig. 1. Consistency test graph for NiFe$_2$O$_4$ reference sensor in saturated calcium hydroxide solution.

of the cell impedance were measured for various frequencies (30,000–0.1 Hz). Plots Z' vs. $-Z''$ were made. Impedance measurements were carried out for NiFe$_2$O$_4$ sensor in OPC extracts, saturated calcium hydroxide solutions and concrete pore solutions.

3. Results and discussion

3.1. Reliability test for NiFe$_2$O$_4$ reference sensor

Reliability of all the assembled NiFe$_2$O$_4$ sensor was tested in SCS at room temperature. Here it was observed that as expected, the potential difference between the any two NiFe$_2$O$_4$ sensors was found to be zero. This indicates that the reliability of all the assembled NiFe$_2$O$_4$ sensor was found to be excellent. All the sensors are subjected to this test before further characterization.

3.2. Consistency test for NiFe$_2$O$_4$ reference sensor

The consistency of NiFe$_2$O$_4$ reference electrode in saturated calcium hydroxide solution is given in Fig. 1. It was observed that NiFe$_2$O$_4$ sensor showed their perfect consistency in the alkaline solution. The measured potentials were found to be in the range from −300 mV to −308 mV. The disparity between the various assembled sensors (30 numbers) in alkaline solution was as high as ±8 mV vs. SCE and the graph showed almost parallel to the x-axis indicating the consistency of NiFe$_2$O$_4$ sensor.

3.3. Stability test for NiFe$_2$O$_4$ reference sensor in concrete environments

The electrochemical stability of the sensor was monitored in different test solutions representing concrete environments with respect to SCE for the exposure period of 30 days. The potential of NiFe$_2$O$_4$ electrode in concrete environments such as saturated calcium hydroxide solution, synthetic concrete pore solution and OPC extracts was measured with respect to SCE. Typical data obtained for SCS is given in Fig. 2. The potential (−300 mV) of sensor was found to be almost constant throughout the exposure period of 30 days.
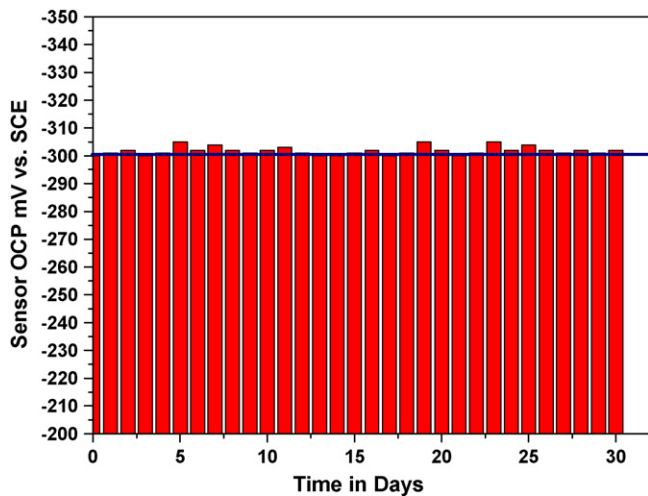
Fig. 2. Stability test for NiFe$_2$O$_4$ reference sensor in saturated calcium hydroxide solution.

Fig. 3. Reversibility (cyclic) curves for NiFe$_2$O$_4$ reference sensor in saturated calcium hydroxide solution.

3.4. Reversibility test for NiFe$_2$O$_4$ reference sensor in concrete environments

The reversibility characteristics of the NiFe$_2$O$_4$ reference sensor in concrete environments were carried out by cyclic sweep method. Cyclic polarization behaviour of NiFe$_2$O$_4$ sensor in concrete environments was found to be good. The maximum difference between the first cycle and second cycle is observed as ±5 mV vs. SCE and this difference in potential is acceptable as sensor electrode in concrete environments. The typical cyclic sweep curve of NiFe$_2$O$_4$ sensor in SCS is given in Fig. 3. The reversibility parameters of NiFe$_2$O$_4$ sensor in SCS derived from the cyclic polarization curves are given in Table 2. Here it was observed that, in SCS the sensors S2, S4 and S5 showed same potential difference between the first and second cycle. Sensors S1, S3 and S6 showed the difference of 2 mV, 2 mV and 1 mV, respectively. The average of difference in potential in first cycle and second cycle was found to be 0.8 mV. This difference was almost negligible for using NiFe$_2$O$_4$ sensor in SCS. The average E_{corr} value with standard deviation in SCS solution was found to be
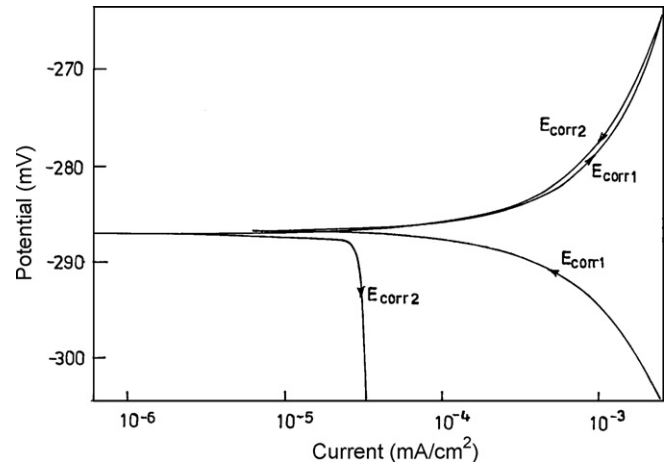
−300.5 ± 6.5 mV for forward scan and −299.5 ± 7.5 mV for reverse scan. The difference in potential was found to be 1 mV only.

The reversibility parameters for sensor in CPS also given in Table 2. It was observed that, sensors S3–S6 showed the same potential difference in the first and the second cycle. Sensors S1 and S2 showed the difference of 5 mV and 4 mV respectively. The average difference between the first and second cycle for NiFe$_2$O$_4$ sensor in CPS solution was found to be 2.2 mV indicating that NiFe$_2$O$_4$ electrode showed better reversibility in CPS. The average E_{corr} value with standard deviation in CPS solution was found to be −300.5 ± 7.5 mV for forward scan and −302 ± 5 mV for reverse scan. The difference in potential was found to be 1.5 mV only.

The reversibility parameter for sensor in CE is given in Table 2. The average of the potential difference of first cycle and second cycle in CE was found to be 1.2 mV. This value is also within the limit of potential of NiFe$_2$O$_4$ electrode in concrete environments. Here it was interesting to note that the average E_{corr} value with standard deviation in CE solution was found to be same for both forward scan and reverse scan.

Table 2
Reversibility (cyclic) parameters of NiFe$_2$O$_4$ reference sensor in concrete environments.

Sensor number	E_{corr1} (mV vs. SCE)	E_{corr2} (mV vs. SCE)	Difference between E_{corr1} & E_{corr2} (mV vs. SCE)
Saturated calcium hydroxide solution			
S1	−294	−292	2
S2	−297	−297	0
S3	−301	−300	2
S4	−307	−307	0
S5	−296	−296	0
S6	−296	−295	1
Average value with standard deviation	−300.5 ± 6.5	−299.5 ± 7.5	1
Concrete pore solution			
S1	−294	−299	5
S2	−293	−297	4
S3	−305	−304	1
S4	−299	−298	1
S5	−308	−307	1
S6	−308	−307	1
Average value with standard deviation	−300.5 ± 7.5	−302 ± 5	1.5
Cement extracts			
S1	−303	−302	1
S2	−305	−305	0
S3	−302	−300	2
S4	−301	−300	1
S5	−302	−301	1
S6	−300	−301	2
Average value with standard deviation	−302.5 ± 2.5	−302.5 ± 2.5	0

Fig. 4. Polarization curve for NiFe$_2$O$_4$ reference sensor in saturated calcium hydroxide solution.
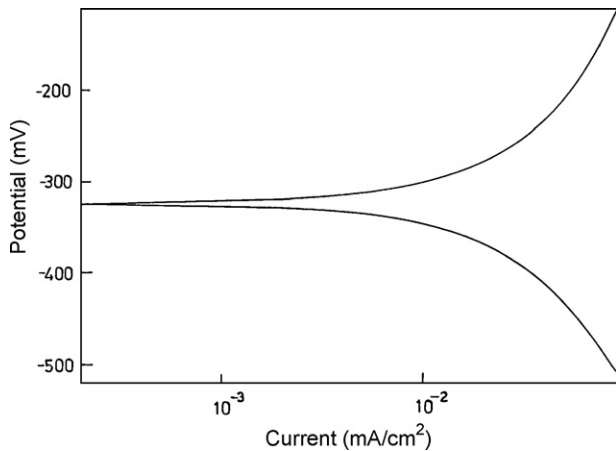

Fig. 5. Impedance curve for NiFe$_2$O$_4$ reference sensor in saturated calcium hydroxide solution.

3.5. Polarization test for NiFe$_2$O$_4$ 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, an appreciable passive region was noticed in the anodic polarization curves. The typical polarization curve for NiFe$_2$O$_4$ sensor in SCS is given in Fig. 4. The polarization parameters for NiFe$_2$O$_4$ sensor in all the three solutions derived are given in Table 3. It was observed from Table 3 that NiFe$_2$O$_4$ sensors almost showed the less polarization current values. For example in SCS, the I_{corr} values observed for six sensors (S1–S6) were found to be in the range 0.00020–0.00026 mA cm^{-2}. Among six sensors studied, maximum of four sensors showed similar polarization behaviour in the three alkaline solutions. The average corrosion potential values with standard deviation are found to be −301.5 ± 6.5 mV, −299.5 ± 8.5 mV and −303.0 ± 3.0 mV for SCS, CPS and CE systems respectively. Here it was observed that no signifi-
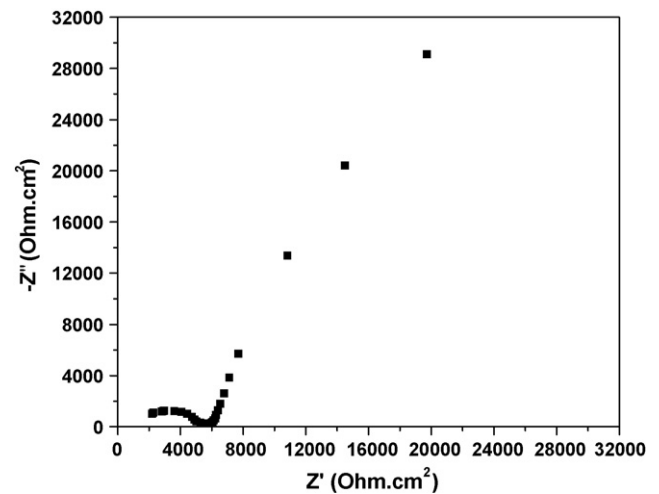
cant change in corrosion potential values among the three systems studied. Even though a small current is induced during polarization, the corrosion potential of the NiFe$_2$O$_4$ sensor was not changed. This behaviour is quite suited for our interest to choose NiFe$_2$O$_4$ as an embeddable sensor for concrete environments.

3.6. Impedance test for NiFe$_2$O$_4$ reference sensor in concrete environments

Impedance diagram obtained for the frequency range 30,000–0.1 Hz at the open circuit potential of NiFe$_2$O$_4$ sensor in concrete environments were carried out. In most of the cases, impedance diagram showed Warburg impedance at the lower frequencies. The charge transfer resistance has been calculated from the difference in impedance 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 NiFe$_2$O$_4$ electrode in SCS solution is given in Fig. 5. The impedance parameters for

Table 3
Polarization parameters of NiFe$_2$O$_4$ reference sensor in concrete environments.

Sensor number	E_{corr} (mV vs. SCE)	I_{corr} (mA cm^{-2})	b_a (mV dec^{-1})	b_c (mV dec^{-1})
Saturated calcium hydroxide solution				
S1	−297	0.00020	24	30
S2	−298	0.00026	24	28
S3	−308	0.00025	23	30
S4	−307	0.00021	20	30
S5	−295	0.00023	21	28
S6	−295	0.00024	22	28
Average value with standard deviation	−301.5 ± 6.5			
Concrete pore solution				
S1	−291	0.00025	23	29
S2	−291	0.00028	36	30
S3	−295	0.00026	47	30
S4	−299	0.00034	46	30
S5	−308	0.00025	49	31
S6	−308	0.00030	32	30
Average value with standard deviation	−299.5 ± 8.5			
Cement extracts				
S1	−303	0.00024	14	29
S2	−306	0.00035	12	30
S3	−300	0.00029	10	30
S4	−301	0.00029	18	30
S5	−302	0.00040	18	31
S6	−304	0.00038	18	29
Average value with standard deviation	−303.0 ± 3.0			

Table 4
Impedance parameters of $NiFe_2O_4$ reference sensor in concrete environments.

Sensor number	OCP (mV vs. SCE)	R_{ct} (Ω cm^2)	C_{dl} (F cm^{-2})
Saturated calcium hydroxide solution			
S1	−293	2.168×10^2	1.111×10^{-3}
S2	−290	3.718×10^2	1.482×10^{-3}
S3	−309	4.545×10^2	1.176×10^{-3}
S4	−307	2.388×10^2	3.256×10^{-3}
S5	−295	2.736×10^2	2.111×10^{-3}
S6	−294	2.651×10^2	4.017×10^{-3}
Average value with standard deviation	−299.5 ± 9.5		
Concrete pore solution			
S1	−291	5.811×10^2	1.566×10^{-3}
S2	−302	3.391×10^2	1.148×10^{-3}
S3	−305	6.064×10^2	1.673×10^{-3}
S4	−309	1.852×10^2	1.850×10^{-3}
S5	−308	1.846×10^2	1.013×10^{-3}
S6	−308	1.833×10^2	1.288×10^{-3}
Average value with standard deviation	−300.0 ± 9.0		
Cement extracts			
S1	−302	2.588×10^2	1.674×10^{-3}
S2	−306	5.187×10^2	1.144×10^{-3}
S3	−301	5.422×10^2	1.611×10^{-3}
S4	−301	2.596×10^2	2.116×10^{-3}
S5	−302	2.239×10^2	2.980×10^{-3}
S6	−303	2.069×10^2	1.774×10^{-3}
Average value with standard deviation	−303.5 ± 2.5		

$NiFe_2O_4$ sensor in all the three alkaline solutions are given in Table 4. It was found from Table 4 that, not much variation was noticed in the average R_{ct} values of $NiFe_2O_4$ sensor in three test solutions. For example, the average R_{ct} values for $NiFe_2O_4$ sensor in SCS, CPS and CE are $3.026 \times 10^2 \,\Omega$ cm^2, $3.466 \times 10^2 \,\Omega$ cm^2 and $3.350 \times 10^2 \,\Omega$ cm^2, respectively. The average C_{dl} values for $NiFe_2O_4$ sensor are 2.192×10^{-3} F cm^{-2} in SCS, 1.423×10^{-3} F cm^{-2} in CPS and 1.883×10^{-3} F cm^{-2} in CE. A comparable trend was obtained between charge transfer resistance and double layer capacitance values of different sensors which indicated the better impedance characteristics of $NiFe_2O_4$ sensor in the three test solutions.

3.7. Mechanism of $NiFe_2O_4$ reference sensor in concrete environments

$NiFe_2O_4$ reference sensor consisted of three compartments namely a bottom layer of hydrated porous cement paste protecting the sensor from physical damage during concrete construction and also acts as an electrolytic contact with the reinforcing steel. Middle layer is a gel having pH equal to that of concrete and top layer is the sensor material. The pH of the gel corresponds to that of pore water in a normal concrete. So errors due to diffusion of ions through the porous plug are eliminated.

The galvanic potential of the sensor originate as Ni^{2+}/Ni^{3+} redox coupling. Advantage of using $NiFe_2O_4$ electrode in concrete is free from polluted elements like Hg and free from corrosion accelerators like chlorides and sulfates. It is not only containing no harmful elements but also cost effective and environmentally safe manufacturing process. It is a solid type electrode so it is easy to handle and movable in any direction.

4. Conclusions

$NiFe_2O_4$ sensor showed the perfect consistency in saturated calcium hydroxide solution at room temperature. $NiFe_2O_4$ sensor seems 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 (±20 mV) test for $NiFe_2O_4$ sensor in saturated calcium hydroxide solution, concrete pore solution and cement extracts medium

indicated a maximum difference of 5 mV between forward scan and reverse scan. This test certified the better reversibility characteristics of $NiFe_2O_4$ reference electrode in concrete environments. Tafel polarization (±200 mV) test for $NiFe_2O_4$ sensor in saturated calcium hydroxide solution, concrete pore solution and cement extract medium indicated a very low polarization current. This test confirmed the good polarization behaviour of $NiFe_2O_4$ reference electrode in concrete environments. AC impedance test for $NiFe_2O_4$ in saturated calcium hydroxide solution, concrete pore solution and cement extract medium indicated a comparable trend between charge transfer resistance and double layer capacitance. These results further confirmed the stability of the $NiFe_2O_4$ reference electrode in concrete environments.

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Biographies

S. Muralidharan was born in Tamil Nadu, India on June 03, 1966. He received PhD 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 durable concrete, fly ash utilization, nano-materials for corrosion prevention etc.

V. Saraswathy was born in Tamil Nadu, India on April 15, 1966. She received PhD 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.

L. John Berchmans was born in Tamil Nadu, India on May 05, 1960. He received PhD in Materials Engineering from Bharathidhasan University, Trichy. He has been working at CECRI since 1988. His research areas include green anode materials for metallurgical applications etc.

K. Thangavel was born in Tamil Nadu, India on January 12, 1956. He received PhD 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, admixtures etc.

Ki Yong Ann presently a professor, School of Civil and Environmental Engineering, Yonsei University, Seoul, 120-749, Republic of Korea. His research interest includes development of high durable and multifunctional concrete, embeddable sensors for corrosion monitoring etc.