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Nickel ferrite ($NiFe_2O_4$): 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*

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ABSTRACT

Nickel ferrite ($NiFe_2O_4$) was tried first time as a possible candidate material as embeddable reference sensor in concrete environments. $NiFe_2O_4$ 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 -300 mV vs. SCE. The reversibility of sensor in the three alkaline solutions 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 $NiFe_2O_4$ sensor in concrete environments showed the stability of the sensor material in the highly alkaline concrete environments.

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

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* 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).

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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).