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Spinel $NiFe_2O_4$ based solid state embeddable reference electrode for corrosion monitoring of reinforced concrete structures

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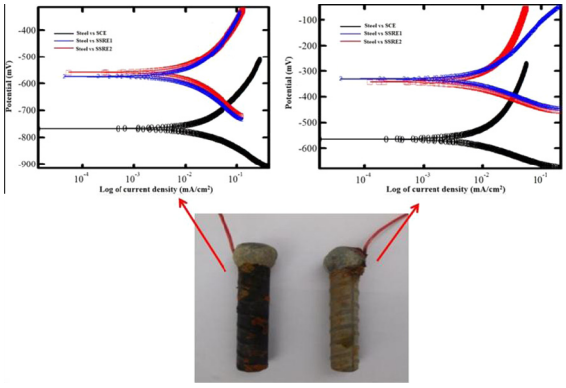
HIGHLIGHTS

- Solid state reference electrodes were fabricated using synthesized $NiFe_2O_4$.
- Potential stability of SSRE was studied in alkaline medium.
- Half cell potential of fabricated SSRE was characterized through the CV.
- Suitability of SSREs for corrosion monitoring of RC were studied.

GRAPHICAL ABSTRACT



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ABSTRACT

In this study, solid state embeddable reference electrode was fabricated and examined for their potential stability in high alkaline environment for the application of corrosion monitoring in reinforced concrete structure. Further, the fabricated solid state reference electrodes (SSREs) were studied in the presence and absence of chloride ion in aqueous solution in order to ensure their potential stability. The results showed that the fabricated SSRE gave stable potential in alkaline medium even in the presence of chloride ions. Steel rebar corrosion assessment studies were carried out in alkaline solution and real concrete medium using the fabricated SSRE and the results were compared with conventional saturated calomel electrode (SCE). The results indicate that the fabricated SSREs have the ability to differentiate the passive and active state of steel rebar similar to SCE.

1. Introduction

Concretes with reinforced steel that are frequently used in building structures are known as reinforced concretes (RC). The steel in RC structures has high tensile strength and increased stability. But corrosion of rebar in concrete structures reduces their lifespan. Hence corrosion monitoring of the rebar gives valuable information regarding the stability of the structure and also helps in further rehabilitation and remediation of the concrete structures. Some of the most commonly used electrochemical corrosion monitoring/measurement techniques are half-cell potential (E_{corr}) measurement, linear polarization resistance (LPR), and electrochemical impedance spectroscopy (EIS) [1]. These techniques essentially need reference electrodes/sensors to measure the corrosion rate. In half-cell potential measurement, the steel rebar potential was measured with respect to the external reference electrodes, such as SCE, Ag/AgCl, $Cu/CuSO_4$ as per the ASTM

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C876. But these external reference electrodes used for surface mounted techniques comes with certain limitations. For example the leakage of liquid from the reference electrode, contaminates the measurement system giving erratic signals owing to the resistance from the concrete structure [2–7]. In addition to that, the periodic maintenance and refilling of electrolyte may not be possible in all cases. Further, there is limitation in size miniaturization of the electrodes because of the glass body and the electrolytes. The liquid part also restricts the orientation of the working position of electrodes [8]. So, the development of liquid free reference electrodes has been of increasing interest in corrosion monitoring applications. Solid state reference electrodes (SSREs) have a promising future in these aspects and several groups have studied the effective use of corrosion monitoring of steel reinforced concrete structures [1,9–12]. Recently Guth et al., and Michalska reviewed several designs and characteristics of SSRE for various applications [13,14]. In electrochemical studies, an ideal electrode should be non-polarizable, zero current potentiometry and it should not contaminate the sample and the system must have long life [15].

Mn/MnO_2, Ce doped $NiFe_2O_4$ solid embeddable electrode systems were investigated by Muralidharan et al. and Guofu et al. [16–20]. These studies describe the basic platform of the solid potential reference electrode (sensor) for the application of corrosion monitoring in the reinforced concrete structures.

Nanocrystalline metal ferrites have a general formula of MFe_2O_4 with mixed spinel structure, where M represents divalent metal cations, such as Mn^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+} [21–23]. In the inverse spinel structure, Ni^{2+} ions and half of the Fe^{3+} ions occupy octahedral sites and the remaining Fe^{3+} ions occupy tetrahedral sites. Spinel type ferrites are commonly used in many electronic and magnetic devices. They are used as high temperature electrode materials due to their high magnetic permeability, low magnetic losses, and excellent chemical and thermodynamic stability. Nickel ferrite ($NiFe_2O_4$) material is used in many fields including energy storage electrochemical applications [24–26], catalysis, drug delivery systems, sensors [27–31]. Several possible methods are reported in literature for the synthesis of nano ferrite materials which includes sol–gel method [21,32], hydrothermal method [23,31], co-precipitation method, self-propagating high temperature synthesis [33] and high energy milling method [22,29,34]. Among these, the sol–gel auto combustion method is unique as it is simple and cost effective. In this method, the ignition and chemical gelatin processes gives ultrafine and homogeneous powder [32].

In the present work, nickel ferrite was synthesized by sol–gel auto combustion method. Synthesized samples were characterized by various analytical methods for ensuring their purity. Solid state reference electrodes were prepared and their potential stability, reversibility characteristics were studied electrochemically in high alkaline passive (chloride free) and active (with chloride) solution medium. Corrosion assessment of steel rebar was also investigated and the results were compared with the conventional saturated calomel electrode (SCE).

2. Experimental methods

2.1. Materials

All chemicals used were of analytical grade and were used as received form without any further purification. Distilled water was used for preparation of all solutions.

2.2. Synthesis of nickel ferrite

Sol–gel auto combustion method has been used for the synthesis of nickel ferrite ($NiFe_2O_4$). The procedure for synthesis is described elsewhere [35] and is described as follows. Stoichiometric amount of Ni $(NO_3)_2{\cdot}6H_2O$, Fe $(NO_3)_3{\cdot}9H_2O$ and citric acid (1:2:3) were dissolved in water separately. Nickel nitrate solution was added into iron nitrate solution and stirred for 1 h followed by the addition of citric acid solution. The pH of the solution was adjusted in the range of 6–7 using aqueous ammonia solution. Finally the mixture was directly heated on a hot plate at about 70–80 °C with constant stirring in order to remove the excess water. The removal of excess water results in the formation of viscous gel of brownish black metal nitrate and the continuous heating of the gel initiates self-combustion reaction. Large amounts of gaseous products evolved during this process and finally foamy powder of nickel ferrite was formed. The flow chart of preparation of nickel ferrite is shown in Fig. 1 along with the photographic images. The product was collected and crushed in an agate mortar and annealed at a high temperature of 800 °C for 5 h for ensuring the crystallinity of the sample.

2.3. Characterization techniques

The prepared sample powder was characterized by X-ray diffraction technique using PAN elliptical D8 advance Diffractometer, with a Cu Kα radiation (1.5406 Å) and a graphite monochromator, within a range of diffraction angle from 10° to

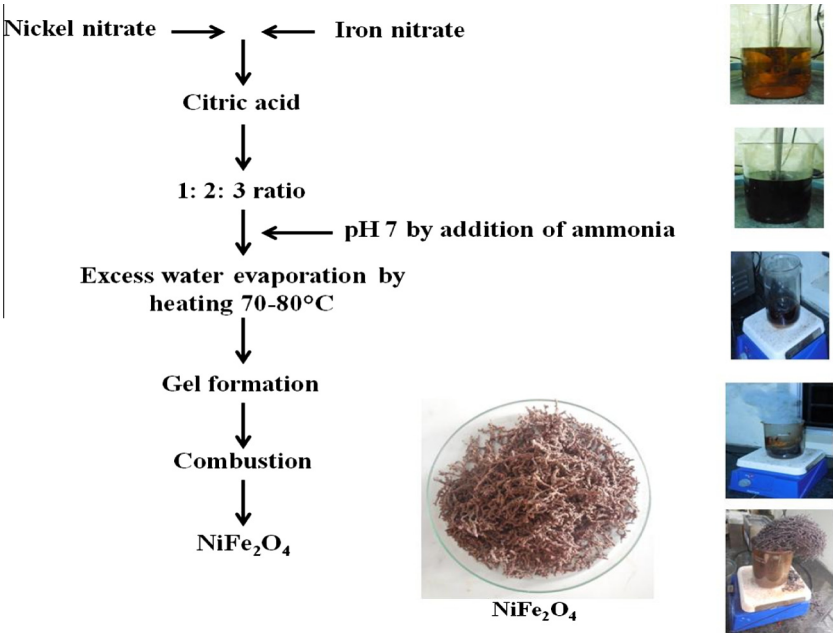

Fig. 1. Flow chart and photographic images of nano nickel ferrite ($NiFe_2O_4$) synthesis.