



# Fabrication of a cerium-doped nickel ferrite solid-state reference electrode and its performance evaluation in concrete environment

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## ABSTRACT

In this study, we fabricated a solid-state reference electrode (SSRE) using cerium (Ce) doping in nickel ferrite (NiFe<sub>2</sub>O<sub>4</sub>) nanoparticles (NPs) to monitor the corrosion of steel rebar in concrete. The process for synthesis of NPs was sol-gel combustion. The NPs were characterized by X-ray diffraction (XRD), field emission scanning electron microscopy (FESEM) probed with energy dispersive spectroscopy (EDS), and X-ray photoelectron spectroscopy (XPS). These techniques confirmed that the Ce doping was achieved successfully. The electrochemical stability of the fabricated SSRE was studied in buffer solution at different pH (7, 9, and 12) as well as in synthetic concrete pore solution (SCPS) and 3% NaCl-contaminated SCPS. Chloride ions do not affect the property of Ce-doped NiFe<sub>2</sub>O<sub>4</sub>. The stability of Ce-doped SSREs in different solutions as well as in concrete was constant throughout the exposure periods. The reversibility test results of Ce-doped NiFe<sub>2</sub>O<sub>4</sub> in SCPS solution for NiCe<sub>0.1</sub>Fe<sub>1.9</sub>O<sub>4</sub> (NFC1) and NiCe<sub>0.5</sub>Fe<sub>1.5</sub>O<sub>4</sub> (NFC5) showed 20 and 15 mV, respective differences in potential between the forward and reverse scan. This result indicates that Ce-doped NiFe<sub>2</sub>O<sub>4</sub> SSREs have better reversibility behavior than NiFe<sub>2</sub>O<sub>4</sub> in SCPS. The reliability of NFC5 SSRE is excellent in SCPS and a concrete environment, and the maximum difference in both conditions was 5 mV, which is within the range of acceptable values. This indicates that Ce-doped NiFe<sub>2</sub>O<sub>4</sub> SSRE can be used as a reliable embeddable sensor in concrete structures.

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## 1. Introduction

Corrosion of steel rebar embedded in concrete can lead to structural failure. There are many factors that cause the spalling and deterioration of concrete structures, e.g., ingress of chloride ions, carbonation of concrete, poor workmanship during construction, high water/cement ratio. Hence, the corrosion monitoring of steel rebar in concrete is imperative to identify and properly mitigate the corrosion of steel rebar. However, different processes must be implemented to determine the exact reason and mechanism of corrosion of embedded steel rebar in concrete. The main method through which the corrosion process can be understood is to measure the resistance and potential of steel rebar over time. Therefore, the corrosion monitoring of steel rebar in concrete structures through a reference electrode is key. Corrosion monitoring in concrete through a reference electrode is the best way to mea-

sure the potential and polarization resistance of embedded steel rebar. The most important factor to be considered in this process is the stability of the reference electrode in concrete. The reference electrodes provide information about the potential of steel rebar and measure the resistance produced at the interface of steel/electrolyte. The corrosion monitoring of embedded steel rebar in concrete has been performed using different electrochemical processes such as half-cell potential measurement, polarization resistance, and electrochemical impedance spectroscopy, all of which provide information about the phenomena occurring at the steel rebar/solution interface [1].

In an electrochemical study, the reference electrode is an essential device that actively participates in all potentiometric reactions. This electrode is highly dependent on the medium to be studied [2,3]. In addition to all of the classical features, the reference electrode should provide a constant potential [4], be non-polarizable (maximum  $\pm 20$  mV), and return quickly to the initial stage after an applied current [5]. This obtained potential should be independent of the solution composition. The most widespread types of reference electrodes are saturated calomel electrodes (SCEs) and

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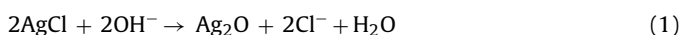
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**Table 1**  
Molar proportions of the reactants for the synthesis of SSREs.

System	Compound	Molar Proportion			
		Ni(NO <sub>3</sub> ) <sub>2</sub> ·6H <sub>2</sub> O	Ce(NO <sub>3</sub> ) <sub>3</sub> ·6H <sub>2</sub> O	Fe(NO <sub>3</sub> ) <sub>3</sub> ·9H <sub>2</sub> O	Urea
NFC0	NiFe <sub>2</sub> O <sub>4</sub>	1	0	2	6.67
NFC1	NiCe <sub>0.1</sub> Fe <sub>1.9</sub> O <sub>4</sub>	1	0.1	1.9	6.67
NFC5	NiCe <sub>0.5</sub> Fe <sub>1.5</sub> O <sub>4</sub>	1	0.5	1.5	6.67

silver–silver chloride electrodes, used to monitor the corrosion characteristics of steel rebar embedded in concrete. These types of electrodes are based on liquid material and have many complications in their production [6] such as contamination of electrodes by internal solution, periodic maintenance, liquid evaporation, and refilling of electrolyte. These process may not be acceptable during real exposure in concrete [7,8]. For example, the use of SCE is limited in clinical chemistry, cellular biology, and industrial process analysis. During the manufacturing process as well as in the service condition of SCE in concrete, the presence of Hg causes toxic effects on the ecosystem and human lives. The SCEs contain Hg and Hg<sub>2</sub>Cl<sub>2</sub> in the glass capillary of the electrode; during their embedding in concrete, the glass wall can break, releasing Hg<sub>2</sub>Cl<sub>2</sub> into the concrete. Because concrete is a porous material, the Hg<sub>2</sub>Cl<sub>2</sub> can diffuse out and enter the ground water.

In addition, the Ag/AgCl electrode is the best and most applicable for free chloride ion detection in concrete [9]. However, there are many controversial findings regarding the stability of Ag/AgCl reference electrodes in highly alkaline environments [10,11]. These electrodes are stable for short-term exposure; however, after a longer duration, they have a stability problem due to conversion of AgCl into Ag<sub>2</sub>O [12] in alkaline solution.



The AgCl reacts with OH<sup>−</sup> and is partially or completely converted into Ag<sub>2</sub>O. The transformation of AgCl into Ag<sub>2</sub>O is a continuous process and generates a mixed potential at the electrode/solution interface. Therefore, this material is not good to use as a reference electrode in a concrete environment. S.Muralidharan et al. reported that the use of Cu/CuSO<sub>4</sub> as reference electrode for measurement of steel rebars potential in concrete. The drawback of such surface mounted electrode is that the seepage of copper sulfates solution would contaminate the concrete [13]. Graphite has also performed satisfactorily in concrete, but this is not a thermodynamically true sensor [14].

G.S. Duffo et al. have studied the electrochemical stability of the reference electrodes in mortar at embedded condition. It found that the MMO pseudo-reference electrode is pH-sensitive, the graphite pseudo-reference electrode is oxygen sensitive, and the Ag/AgCl pseudo reference electrode is chloride sensitive. Besides he reported that the solid Ag/AgCl reference electrode potential is also independent of the pH with the exception of pH 13.5 where a slightly lower potential was measured [10]. The drawbacks of SCE (toxic properties of Hg) and Ag/AgCl (conversion of AgCl into Ag<sub>2</sub>O) reference electrodes can be overcome by the development of liquid free SSREs [15–18]. These electrodes are free from storage problem to the inner filling of the solution in glass container. This system does not require solution to be refilled and can be easily fabricated in a miniaturized sensor, which is very useful in medicine, biological sciences [19], and corrosion monitoring of civil infrastructure.

MnO<sub>2</sub> and nickel ferrite have been reported as the best solid-state reference electrodes in a concrete environment [20–22]. However, MnO<sub>2</sub> also has a stability problem in highly alkaline environments after a longer duration of exposure due to liquid junction potential error. In such a case, the potential error is significant, and the material cannot be used as a reference electrode owing to the difference in mobility of hydroxyl ions of the solution and the

cations of the metal [23]. However, through modern technological changes, new materials have been developed and have been used in a variety of applications. Therefore, there is significant need to develop and evaluate the performance of reliable and maintenance-free reference electrodes to use in concrete structures in order to monitor the corrosion process at the steel rebar/concrete interface.

Nanostructure materials have attracted extensive attention owing to their unique properties and potential applications [24–26]. Nanocomposite metal oxides are model materials for chemical ion sensing due to their high active surface areas and are extensively employed as chemo-sensors for the detection, recognition, and quantification of various effective ions [27,28]. Recently, nano nickel ferrite and rare earth-doped materials have captured the attention and imagination of researchers due to their unique properties, such as high surface area, good optical properties, electrical and magnetic properties [29,30], high alkaline stability, excellent conductivity, good reversibility, ease of fiction-alization, robust mechanical properties, and low production cost. G. Dixit et al. have reported the enhancement of structural, electromagnetic, and electrical transport properties of cerium (Ce)-doped NiFeO<sub>4</sub> [31].

A literature search revealed that there is very little information available regarding the fabrication and electrochemical evaluation of rare earth metal-doped SSRE. In the present study, SSREs were fabricated using Ce-doped NiFe<sub>2</sub>O<sub>4</sub> to obtain good reversibility and long-term stability through electrochemical experiments in synthetic/simulated concrete pore solution (SCPS). Such SSREs are economical, very easy to implement and fix in hard concrete, and can be used to monitor the corrosion process at the steel rebar/concrete interface. The present fabricated SSRE was characterized at different pH and in synthetic concrete pore solution through different electrochemical processes.

## 2. Materials and methods

### 2.1. Synthesis of nickel ferrite and Ce-doped nickel ferrite

All chemicals in this study were analytical grade and used without further purification. NiFe<sub>2</sub>O<sub>4</sub> (NFC0), NiCe<sub>0.1</sub>Fe<sub>1.9</sub>O<sub>4</sub> (NFC1), and NiCe<sub>0.5</sub>Fe<sub>1.5</sub>O<sub>4</sub> (NFC5) nanoparticles (NPs) were prepared using urea which act as a combustion fuel. Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O, Fe(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O, and Ce(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O were dissolved in distilled water at a stoichiometric proportion with urea. Thus, the stoichiometric composition of the redox mixture is required in order to release the maximum energy for the reaction; therefore, 6.67 M urea was used [32]. The molar proportion is shown in Table 1. The above mixture was directly heated on a hot plate at 80 °C with constant stirring in order to remove the excess water. The resulting material was a viscous brownish-black metal nitrate gel. The gel was heated continuously at 120 °C to initiate self-combustion. A large amount of gaseous products was evolved during this process; finally, Ce-doped nickel ferrite NP powder was obtained. The product was collected, crushed in an agate mortar, and annealed at 800 °C for 5 h to ensure the crystallinity of the sample. A schematic of the preparation of the NP material is shown in Fig. 1. For comparison, nickel ferrite (NFC0) was synthesized without cerium nitrate

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