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Development of solid state embeddable reference electrode for corrosion monitoring of steel in reinforced concrete structures

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Corrosion of steel reinforcement concrete structures is monitored through the surface mounting techniques using liquid based reference electrodes. Due to the limited usage of liquid based reference electrodes solid state reference electrode are introduced recently. In the present study, we fabricated and characterized Mn_3O_4 based pellet electrode for corrosion assessment of steel rebar in high alkaline medium through electrochemical methods and the results are compared with conventional saturated calomel reference electrode (SCE). The results indicate that the fabricated pellet electrode exhibits better characteristics suitable for high alkaline concrete environment and differentiate the passive and active status of steel rebar.

1. Introduction

Steel reinforced concrete structures are plays a vital role in civil infrastructures such as bridges, dams and buildings. Steel reinforcement gives structural strength, stability, durability etc. Usually the pH of concrete structures is found highly alkaline (~12.5–13.5). This high alkaline pH produces a passive film on the surface of steel and hinders the further corrosion [1]. Though, the effect of external pollutants in concretes such as chloride ions, sulphate ions and CO_2 ingression affect the pH and induced the localized corrosion on the surface of steel rebar and promote the corrosion [2,3].

Prior detection and monitoring corrosion of steel in reinforced concrete structures pave the way to evaluate the lifespan of civil structures and take appropriate rehabilitation aspect. The non-destructive electrochemical corrosion monitoring methods such as galvanic potential measurement [4,5] open circuit potential measurements, linear polarization measurements and electrochemical impedance provides effective information on corrosion status [6,7] of rebar in concrete. In these methods, the rebar potential was measured with respect of standard reference electrodes like Ag/AgCl, Hg/Hg_2Cl_2 and $Cu/CuSO_4$ [8]. This reference electrode is consist of liquid part of either saturated chloride or sulphate solutions and made up of glass body as one part of it. These types of glass based liquid filled reference electrodes are not suitable for in-situ measurements [2] because the liquid part chloride and sulphate ions of solution leakage contaminate the concrete structure and induce the localized corrosion. In another way, most of the measurements were carried out by surface mounting techniques as per ASTM C876. This surface mounting technique may produce the erratic signal, non-reliable potential etc. due to the large distance of steel in concrete structures and outer surface.

To overcome these issue, embeddable pseudo reference electrodes and solid state reference electrodes is introduced by several groups [9–16]. Pseudo reference electrode (Quasi reference electrode) is a kind of reference electrode, in which their potentials were not stable, were dependent on various factors and the potential was not usually defined (Thermodynamic equilibrium cannot exist) approximately constant under appropriate conditions. Pt and Mo wire, Ag wired covered by Ag-salt of chloride and bromide is used in this typically as pseudo reference electrode in various fields which includes of corrosion monitoring of concrete structure [14]. In solid state reference electrode, the major components of sensing materials and embodiments are solid and it is used to measure the potential of other components (i.e. to be used

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potential measurements instead of conventional reference electrodes) [17–21]. These embeddable reference electrode have numerous advantages than compared to the liquid based reference electrodes [2,22–25] and that are usable for in-situ measurements due to their, smaller size, quick response, long self-life, maintenance free use and applicable to non-aqueous medium applications.

In concrete structures, the embeddable reference electrodes for corrosion monitoring of steel attracted by many researchers due to its reliable status of rebar due to minimized large distance between outer cover and inner steel rebar surface (minimize i_R drops) and it can be usable for long term monitoring on the basis of maintenance free use and also suitable for online monitoring due to their maintenance free nature [13–15].

In this embeddable reference electrodes most of the system used metal-metal oxide one of the components and which serves as main functions to produce stable potential in particular medium. In the case of MnO_2 and $NiFe_2O_4$ embeddable reference electrode [9–12], MnO_2 and $NiFe_2O_4$ were used as main components in PVC tube substrate sealed with porous cement plug; high alkaline paste (mixture of KOH, NaOH and $Ca(OH)_2$) act as conducting medium. Here the active materials are also deviated from the real concrete medium and the high solubility of alkaline and alkaline earth metal creates lake of connectivity between the concrete and sensing materials. In another case, G. S. Duffo et al. developed embeddable multi probe sensor based on mixed metal oxide probe as one of main components [13,14]. In which, there, rare earth high cost Ir, Ta and graphite rod from dry cell are used. The high cost and low inadequate availability of Ir and Ta not favored to commercialization. The graphite rod producing potential is questionable in high alkaline medium. In these aspects, the development of another active corrosion monitoring reference electrode is important and interesting. This is offers new kind of reference electrodes in this field.

Mn_3O_4 is a unique mixed metal oxide spinels due to coexistence of Mn in different valence state of Mn^{2+}, Mn^{3+} and used in many technological applications such as gas sensor, molecular adsorption, catalyst [25], lithium ion batteries [26] and used in various other aqueous, non-aqueous and high alkaline medium [27] due to their excellent physicochemical stability, non-toxic nature, low cost and high abundance.

Major objective of this work is to develop and characterize a solid state metal oxide reference electrode for corrosion assessment of steel in reinforced concrete structure. Hence, we described the fabrication of Mn_3O_4 based solid state metal oxide pellet reference electrode preparation and its electrochemical characterization in high alkaline environment and the effective use of corrosion monitoring of steel in reinforced concrete structures. Based on this study, the Mn_3O_4 pellet electrode provides unique and reliable potential applications with respect to SCE.

2. Materials and methods

2.1. Mn_3O_4 preparation

All the reagents used in this work were analytical grades and were used without further purifications. Double distilled water was used in all the experiments. Mn_3O_4 was synthesized through the metal chloride precipitation method and typically described as follows.0.22 mol of $MnCl_2 \cdot 2H_2O$ and 0.44 mol NaOH were separately dissolved in distilled water. Then NaOH solution was added to the $MnCl_2$ solution with constant stirring. After that, 1.37 m mol of cetyltrimethylammonium bromide (CTAB; cationic surfactant it enhances the formation of nanoparticles and suppress the reunion of nanoparticles [28]) was dispersed into the mixtures. The resulting precipitate was collected and washed with distilled water until the washing water amperes as neutral pH and then washed with ethanol. Finally the prepared sample was dried at 60° C for 24 h.

2.2. Characterizations

Structural characterization was performed by X-ray diffractometry using PAN elliptical D8 advance Diffractometer Cu Kα radiation with wavelength of 1.5406 Å. Fourier transform infrared spectra (FTIR) was recorded by Bruker-tensor 27 with opus 6.5 version software. The surface morphology of prepared sample was observed by scanning electron microscopy (SEM) through VEGA3 SB TESCAN SEM and Field-emission scanning electron microscopy (FE-SEM) using a Carl Zeiss AG Supra 55VP with an acceleration voltage of 5–30 kV. Phase composition were studied by Energy dispersive X-ray spectroscopic (EDS) method; which was collected using X-Flash Detector 410M with Bruker ESPRIT QUANTAX EDS analyzing software.

2.3. Fabrication of solid reference electrode

Solid state reference electrodes were prepared in PVC epoxy mold as follows. As prepared 0.5 g of Mn_3O_4 powder was mixed with 1% PVA in water (Polyvinyl alcohol) in agate mortar until got homogeneous dryness and then pressed into a pellet of 10 mm dia with thickness ~3 mm through hydraulic pressing machine (10 MPa). The electrical connection was made using Teflon coated copper wire with silver paste glue and embedded into PVC (polyvinylchloride) body using epoxy resin and it can be shown in Fig. 5a. Before evaluating the performance of Fabricated Pellet Electrode (FPE), which was polished by fine grade emery, papers in order to get the homogeneous exposure in test solutions.

2.4. Potential stability measurements for FPE

Potential stability of FPE in different pH solution (phosphate buffer), synthetic concrete pore solution (SCPS) (0.3 M KOH, 0.1 M NaOH and 0.01 M $Ca(OH)_2$; pH ~13) and 0.1 M NaOH were measured with respect to SCE in two electrode setup with help of high impedance multimeter. The FPE were immersed in test solution throughout the measured periods in a beaker and then salt bridge were used between the connection of working electrode (FPE) and the reference electrode of SCE. In each reading were taken out after attain the stability of ± 5 mV.

2.5. Steel corrosion monitoring in solution medium

In order to evaluate the practical utility of fabricated electrode in concrete environment, we took steel rebar (5 cm length and 8 mm dia) in high alkaline pH medium of 0.1 M NaOH for passive medium and 0.1 M NaOH with 1% and 2% of NaCl for active medium.

2.6. Electrochemical studies for corrosion monitoring of steel rebar in solution medium

Potential of steel rebar (working electrode) was periodically measured with respect to the SCE (Saturated Calomel Electrode) and FPE through the two electrode cell setup. All the potential studies were measured in room temperature (30 ± 2 °C).

Potentiodynamic polarization and impedance studies were done using Gill automated potentiostat (ACM instrument, UK) in three electrode cell setup in which steel rebar served as working electrode, Pt foil (1 cm^2) served as counter electrode and SCE served as reference electrode. Similar experiments were also performed using FPE instead of SCE for the comparison purpose. In each measurement, the open circuit potential (OCP) was measured for