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Electrochemical stability of embeddable MnO_2/Mn reference electrode and its AC impedance behavior

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A novel embeddable MnO_2/Mn reference electrode for corrosion monitoring is mainly prepared from a mixture of β type manganese dioxide and manganese by high-pressure molding in laboratory. The long-term electrochemical stability of electrodes was studied in cement mortar. AC impedance behavior of the MnO_2/Mn reference electrode was examined in synthetic concrete pore solutions after that. The long-term potentiometric measurements showed good stability and no apparent potential drift within 90 days continuous measurement. The electrochemical stability of MnO_2/Mn reference electrode is related to equilibrium established by double-phase oxides MnO_2 and MnO_x ($1 \le x < 1.5$). AC impedance behavior verified that the fabricated reference electrodes were sufficient to meet the requirement for corrosion monitoring in concrete environment.

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1. Introduction

Monitoring of the electrochemical potential of steel reinforcement in concrete is a well established technique for assessing the severity of corrosion and for controlling cathodic protection systems [1]. Embeddable reference electrode is the significant technology for health monitoring in the concrete structures, which enables long-term remote monitoring in time. Many kinds of reference electrodes suitable for concrete environment have been developed [2]. Copper-copper sulfate reference electrode is used as the standard electrode in ASTM C 876-91 [3]. Metal–metal oxide (MMO), graphite and laboratory-made Ag/AgCl electrodes were electrochemically characterized as reference electrodes embedded in concrete structures by G.S. Duffo *et al* [4]. Recently, MnO_2 electrode is proved to be a more stable and reliable electrode in concrete environment [5,6].

However, the origin of the electrochemical stability of the MnO_2/Mn electrodes hasn't been clarified yet. In this paper, β type manganese dioxide and pure manganese were selected as actives materials to prepare a novel embeddable reference electrode, and its electrochemical properties in synthetic concrete pore solution and cement mortar was investigated in this paper.

2. Materials and method

2.1 Materials

In this study, P·O 42.5 cement from Harbin Cement Co. LTD was used for all experiments. River sand with fineness modulus of 2.4 was used as fine aggregate. Synthetic concrete pore solution consisted of 0.2 mol NaOH and 0.6 mol KOH per litre of saturated calcium hydroxide solution.

2.2 Preparation of MnO_2/Mn reference electrode

The active materials used in the electrodes were mainly prepared by mixing β type manganese dioxide (4-7 μm particle size, reagent grade ≥99% purity), manganese (reagent grade ≥99.3% purity) in mass proportions: 90:10. This mixture was extensively ground and then molded at 10^5 N/cm^2 pressure for about 15 minutes. The electrode body was fabricated to 13.2 mm in diameter and 10 mm in height, and then was cured under 25±1 ℃ for 24 hours. After that, aging disposal of the electrode body should be employed in 1mol/L NaOH solutions for about 14 days. Three embeddable MnO_2/Mn reference electrodes (T_1, T_2 and T_3) were fabricated according to the procedure reported in our earlier publication [7] and briefly given as follows. A fiber mortar (10 mm high) with a proper porosity was formed as bottom layer of the entire electrode nylon shelter 20 mm in external diameter, 15 mm in internal diameter and 50 mm in length to embody the electrolyte in it. The fabricated electrode body was emerged in the eletrolyte, a kind of special alkaline gel (pH=13.75) with the similar components corresponded to that of pore water in normal concrete. The top end of the electrode body was connected to an anticorrosion cable (see Fig. 1).

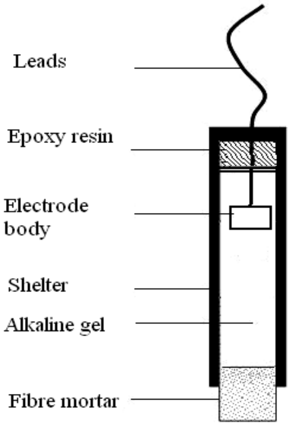

Fig. 1. Illustration of embeddable reference electrode.

2.3 Electrochemical measurement

All the electrochemical measurements were performed by RST5200 electrochemical system at an ambient temperature of 20 ± 1 ℃ and RH of 50% after the specimens cured for 28 days.

2.3.1 Stability of MnO_2/Mn reference electrode

The electrochemical stability of the MnO_2/Mn reference electrode was measured with respect to an ERE20 (Force, Inc) commercial reference electrode in the cement mortar (1:3 ratio cement: sand) with a w/c ratio of 0.5 for a period of 90 days. ERE20 was embedded 70 mm depth in the middle of the cement mortar 500 mm in diameter and 150mm in height (See Fig. 2), and three fabricated reference electrodes were embedded 100 mm far away from the ERE20 and kept the same height as ERE20.

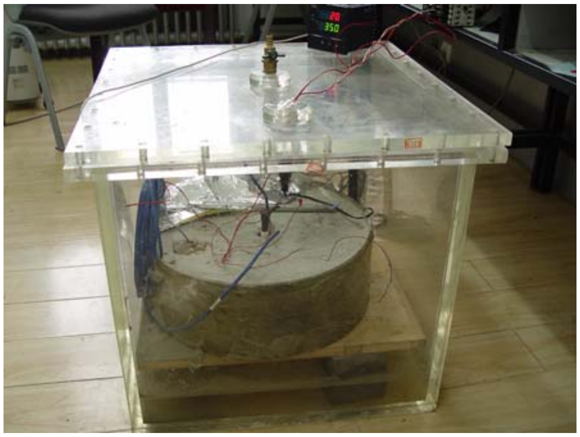

Fig. 2. Illustrative of electrodes array in cement mortar and its measurement enviroment.

2.3.2 AC impedance behaviors of MnO_2/Mn reference electrode sensor

AC impedance measurements were carried out in synthetic concrete pore solution at an ambient temperature of 25±1℃. For comparison, AC impedance behavior of the commercial saturated calomel electrode (SCE) was also studied. Fabricated reference electrodes or SCE act as working electrode, and the Ni plate (7 cm×7 cm) acts as counter electrode. Measurements were performed in the frequency range from 20,000 Hz to 0.01 Hz. Sinusoidal voltage of 10 mV was supplied, and direct current potential was set to the anode potential with respect to counter electrode. The real part (Z') and the imaginary part (Z'') of the cell impedance were recorded for the system studied.

3. Results and disscussion

3.1 Stability of MnO_2/Mn electrodes

Fig. 3 depicts the difference in the maximum and minimum measured potential value of fabricated MnO_2/Mn electrodes.

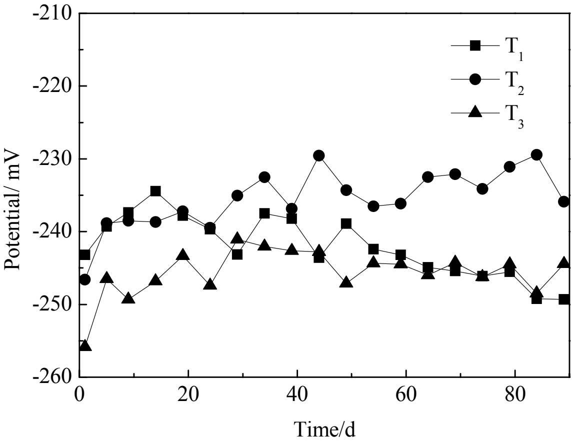

Fig. 3. Variation of potential vs. exposure period in synthetic pore solutions.

The initial potential value was -243 mV, -246 mV and -255 mV for T_1, T_2 and T_3, respectively. The fluctuation is found to be less than ±6 mV with regard to the initial potential of all three electrodes for a period of 90 days.

During the disposal period, the active material of the electrode, β type manganese dioxide will be partly reacted with H^+ ions according to the following reaction:

$$MnO_2 + H^+ + e \rightarrow MnOOH. \quad (1)$$

In the special case of the frequently observed oxide series $Mn(OH)_2$—MnOOH—MnO_2 which mostly form series of mixed crystals without miscibility gap, MnO_2 and MnOOH are mixed as a homogeneous phase solid solution and their chemical potentials are dependent on the composition of the phase [8]. Consequently, the potential E of such homogeneous phase species at 25 ℃ can be represented as follows regardless of the above mentioned equilibrium oxide MnO_x:

$$E = \frac{1}{F}(\mu^{\Theta}_{MnO_2} - \mu^{\Theta}_{MnOOH}) - 0.059\log\frac{\alpha_{MnOOH}}{\alpha_{MnO_2}} - 0.059pH \quad . (2)$$

where $\mu^{\Theta}_{MnO_2}$ and μ^{Θ}_{MnOOH} are the chemical potentials of standard states for subscript constituents, respectively. And α_{MnOOH} and α_{MnO_2} are the activities of these constituents, respectively. That's to say, the potential E is related to the pH value of the electrolyte and mass ratio of α_{MnOOH} and α_{MnO_2} in the electrode films. For the host lattice of present MnO_2 is of β crystalline type, the activity ratio of α_{MnOOH} and α_{MnO_2} will be relatively stable without environmental disturbance after aging disposal in 1 mol/L NaOH solution [8].

But unfortunately, to apply the reference electrode into practice, the most important requirement of electrodes is to exhibit well capacity of resisting disturbance. Therefor a double-phase heterogeneous oxides MnO_2—MnOOH/MnOx has been put forward to instead the MnO_2—MnOOH systems.

After metal Mn and MnO_2 mixed together, only one oxide can exist in a thermodynamic equilibrium with the own metal at a constant defined temperature [9]:

$$MnO_2 + Mn \rightarrow MnO_x \qquad (3)$$

where x value genarally depends on the temperature. In this case, the metal ion equilibrium at the phase boundary metal/oxide has to be established. By analogy the preceding evaluation (2) and (3), if only two heterogeneous phases (MnO_x and MnO_2—MnOOH) could be in equilibrium with each other, the potential of electrode will not depend on the ratio of the quantities of the phases. The potential will remain constant during the oxidation until the MnO_2 or MnO_x is consumed. Such provision has been approved by the electrochemical stability of the MnO_2/Mn reference electrodes shown in Fig. 3, thus $1 \leq x < 1.5$ could be defined after all.

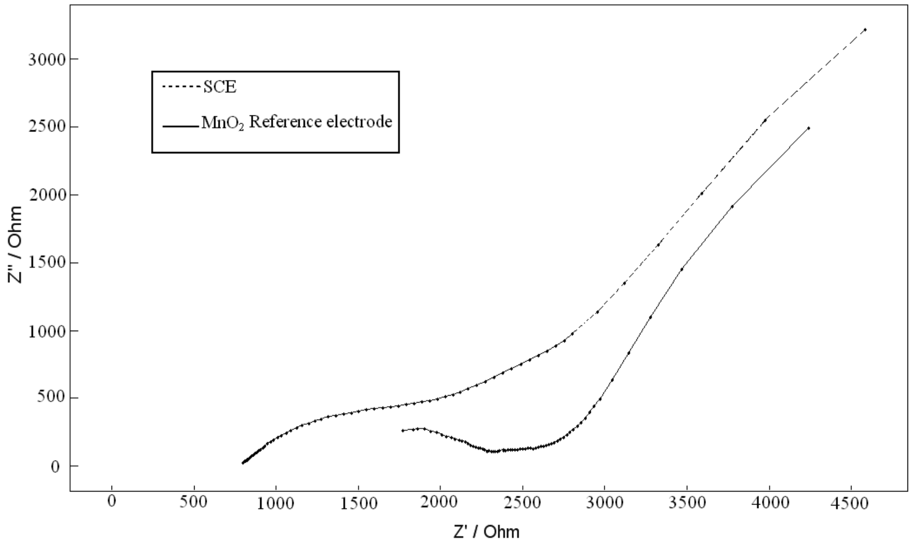

Fig. 4. Impedance behavior of MnO_2/Mn electrode.

3.2 Electrochemical impedance spectroscopy test

Impedance diagram obtained in various frequencies (20,000 to 0.01 Hz) at the open-circuit potential of fabricated MnO_2/Mn electrode and SCE (vs. Ni plat) in synthetic concrete pore solutions were shown in Fig. 4. The high frequency impedance plots of SCE agree with a pure resistance (Z''=0). Hence SCE could provide a precise solution potential at high frequency. The high frequency response of fabricated electrode was dominated by a decayed capacitive reactance arc. The double layer capacitance can be obtained from the following equation:

$$C_{dl} = \frac{1}{2\pi f X_c} \quad (4)$$

where f is the frequency (in Hz), X_c is the capacitive reactance (in Ω). When a high frequency 20,000 Hz is adopted, the X_c value is about 200 Ω (Fig. 4), and the calculated C_{dl} value of the fabricated electrode is about 40000 pF. The lower C_{dl} may be due to the smooth surface of the embedded electrode body in the electrode shelter. From the trend of the decay capacitive reactance arc, the magnitude of R_s (including resistance of fiber mortar, gel solution and electrode bodies′ Ohm resistance) in fabricated electrode can also be obtained. As expect, R_s in the fabricated electrode is a little higher (about 1500 Ω) than that in SCE. Such difference is a complex function of the permeability of fiber mortar, diffusion ability of ions in gel and electrode body properties etc.

As the frequency decreases, the plots of SCE have exhibited an obvious sudden upward trend, which indicated the charge transfer process or the diffusion of reactants to the surface of SCE is difficult. In view of the narrow glass tip of such SCE electrode, the difficult diffusion process could be the decision factors. However, more tight data points nearby the R_s were observed in the lower frequency region of the fabricated electrode. That's to say, the charge transfer process and the diffusion of reactants of the latter will not be the "bottlenecks" until the frequency becomes low enough. To sum up, relatively small modulus of impedance $|Z|$ of the fabricated reference electrode was observed in various measurement frequencies, and the R_s associated with the real part (Z') of the fabricated electrode will be further reduced by increasing the effective area of the electrode body, improving the ionic conductivity of alkaline gel, etc.

4. Conclusions

MnO_2/Mn reference electrode exhibits a stable potential in cement mortar for 90 days. The electrochemical stability of MnO_2/Mn reference electrode is related to equilibrium established by double-phase oxides MnO_2 and MnO_x ($1 \leq x < 1.5$). The AC impedance behavior further confirmed that the fabricated electrode had a suitable modulus of impedance. All these results showed that the fabricated MnO_2/Mn reference electrode was sufficient to meet the requirements of electrochemical measurement in concrete.

Acknowledgements

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