

Electrochemical study on the macrocell corrosion mechanism between two adjacent common steel electrodes in immersion environment

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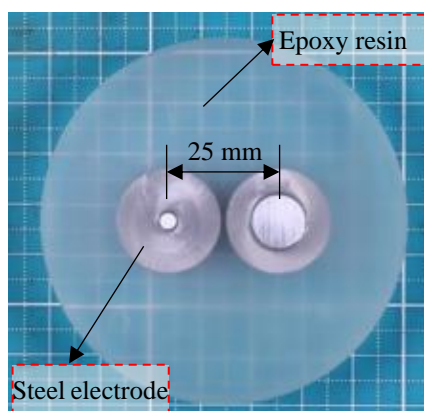
1. Introduction For painted steel structures, the coating can deteriorate due to ultraviolet radiation and environmental water pooling as well as salt, leading to corrosion of steel structures¹⁾. This kind of corrosion tends to occur not only from individual coating defects, but also from multiple adjacent coating defects. When the base steel under coating defects were connected in same circuit by rain and/or dew condensation water, then there may be mutual interaction between adjacent coating defects. Previous accelerated corrosion test showed that the corrosion degree of specimen with multiple coating defects was greater than that with single coating defects, which verified the mutual interaction effect between adjacent coating defects²⁾. However, the mechanism of interaction between plural coating defects is unclear yet. Various sizes of artificial circular defects were fabricated on the surface of steel electrode to simulate coating defects in this paper. The macrocell currents between adjacent defects were measured under immersion environment by Zero Resistance Ammeter (ZRA). The results showed that the steel electrode with larger defect was always anode, and there was a linear relationship between corrosion current and coating defects area ratio, which was consistent with catchment principle.

2. Test method Since there are various variables corresponding to real coating conditions, such as coating thickness, type, etc., to elucidate the mutual interaction between coating defects, the uncoated electrodes were firstly tested from the perspective of controlling variables. Two circular electrodes was applied to simulate the defects. The electrode was made of JIS G 4051 carbon steel with a diameter of 20 mm. Fig. 1 illustrates the configuration of the specimens. 3.5 wt % NaCl aq. was adopted to simulate the antifreezing agent. The distance between coating defects was 20 mm and the diameter of coating defects was 2, 3, 5, 7, 9 and 10 mm. The macrocell corrosion current was measured by zero-resistance ammeter. The microcell current density was determined by the stern-geary equation: $i_{micro} = k/R_{ct}$, where the stern-geary constant k is 0.00209V a commonly adopted value in engineering, and the charge transfer resistance R_{ct} was measured by the electrochemical impedance spectroscopy (EIS) method.

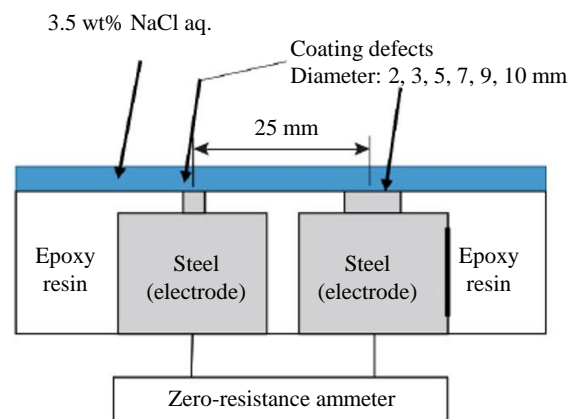
3. Test results The current density remained almost constant and positive regardless of the area of the electrodes. The results indicated that when two electrodes with different areas were short-circuited, the electrode with the larger area always acted as the anode. Besides, it can be inferred that the larger the ratio of cathode area and anode area, the larger the corrosion current density. The measured macrocell current density versus the ratio of cathode area and anode area for different electrode pairs is given in Fig. 2. The macrocell current was obtained by calculating the average current value during 24-hrs testing. Linear relationship between macrocell current density and the ratio of electrode area (Cathode area divided by anode area) was obtained with high correlation factor is 0.987. Mansfeld found that when the corrosion rate of the active metal is controlled by the oxygen diffusion rate, its galvanic current density with the noble metal is positively proportional to the anode-to-cathode area ratio which is the so-called catchment principle³⁾. Therefore, the linear relationship between macrocell current density and the ratio of electrode area could be explained by the catchment principle. The illustration of the catchment principle applied to the two electrodes in this paper is shown in Fig. 3. The reduction of oxygen takes place on both cathodic area and anodic areas, while the anodic reaction only takes place at the anode. Thus, the total cathodic reaction current can be obtained as Eq. (1), where $I_{cathode}$ and $i_{O_2}^L$ are the current density of cathode and limiting current density for oxygen diffusion; S^C and S^A are the cathode area and anode area respectively.

$$I_{cathode} = i_{O_2}^L \cdot (S^C + S^A) \quad (1)$$

In the same circuit, the anode current is equal to the cathode current, so the diffusion current density of the anode i_{anode} can be



a) Appearance of specimen



b) Elevation of specimen

Fig.1 Configuration of test set-up

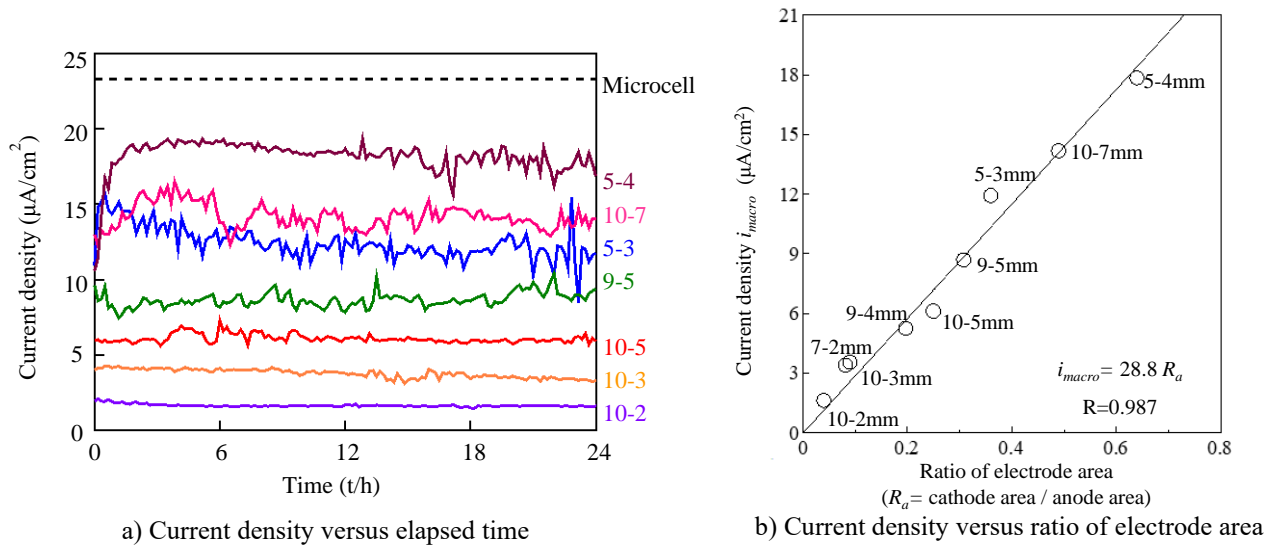


Fig.2 Measurement results of microcell and microcell current

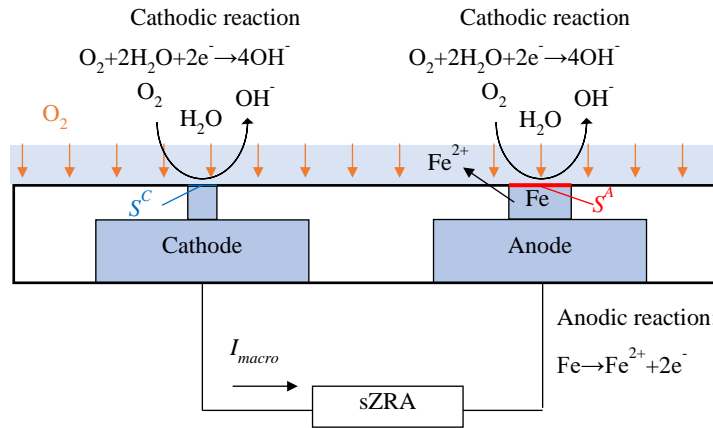


Fig.3 Illustration of catchment principle

expressed by Eq. (2):

$$i_{anode} = I_{anode}/S^A = I_{cathode}/S^A = i_{O_2}^L \cdot (1 + S^C/S^A) \quad (2)$$

Since all the reaction which takes place on cathode is the reduction of oxygen, then the macrocell current can be calculated by Eq. (3).

$$I_{macro} = i_{O_2}^L \cdot S^C \quad (3)$$

Herein we define the macrocell current density as the macrocell current divided by the anode area as given in Eq. (4).

$$i_{macro} = I_{macro}/S^A \quad (4)$$

Substituting Eq. (4) to Eq. (3), we have:

$$i_{macro} = i_{O_2}^L \cdot S^C/S^A = i_{O_2}^L \cdot R_a \quad (5)$$

Eq. (5) elucidates the reason for the linear relationship in Fig.2. Although the catchment principle was deduced from two different metals, for two electrodes with same material in immersion environment, when the cathodic reaction is limited by the rate of oxygen diffusion, the macrocell current is also proportional to the ratio of the cathode to the anode area. Besides, comparing Eq. (1) and Eq. (5), the diffusion rate of the anode will increase after shorting the two electrodes, and the increased part of the current density is the macrocell current density.

4 Summary 1) There was linear relationship between macrocell current density and the ratio of electrode area (Cathode area divided by anode area). 2) The linear relationship between corrosion current and coating defects area ratio could be explained by catchment principle.

References 1) M. Yang, S. Kainuma, S. Ishihar, A. Kaneko, T. Yamauchi: Corrosion protection of steel members using an Al-Zn base sacrificial anode and fiber sheet in an atmospheric environment, Construction and Building Materials, 234, 117405, 2020. 2) Kainuma, S., Kobayashi, J., Utsunomiya, K., & Sakamoto: Influence of size and proximity of paint coating defects on corrosion behavior of carbon steel plates. Journal of JSCE, 8(1), 87-102, 2020. 3) F. Mansfeld: Area Relationships in Galvanic Corrosion, Corrosion, 27(10), 436-442, 1971.