Numerical Approach for Atmospheric Corrosion Monitoring Based on EIS of a Weathering Steel

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Abstract Electrochemical impedance spectroscopy (EIS) and film thickness measurement have been employed to study the atmospheric corrosion of a weathering steel covered with a thin electrolyte layer in a simulated coastal–industrial atmosphere. The results indicate that the corrosion rate is a function of the covered electrolyte thickness and the wet/dry cycle. Within each wet/dry cycle, the increased corrosion rate is related to the increased Cl^- and SO_4^{2-} concentration and an enhancement of oxygen diffusion rate with the evaporation of the electrolyte. In addition, the corrosion rate increases during the initial corrosion stage and then decreases as the wet/dry cycle proceeds. Moreover, one mathematical approach based on the numerical integration method to obtain corrosion mass loss of steel from the measurements of EIS has been developed, and this would be useful for the development of indoor simulated atmospheric corrosion tests.

KEY WORDS: Weathering steel; Atmospheric corrosion; Electrochemical impedance spectroscopy; Steel rust; Coastal–industrial atmosphere

1 Introduction

The atmospheric corrosion behaviour of steel can be greatly affected by the thickness of its surface condensation electrolyte, especially with the presence of chlorides and sulphur dioxide in the surrounding atmospheric environment [1]. The change in the electrolyte thickness affects the atmospheric corrosion kinetics in several complicated ways. For example, the evaporation process of the electrolyte accelerates the transportation rate of dissolved oxygen through the electrolyte layer, promoting the cathodic reaction rate, but it causes a decrease in the intersection area of the electrolyte, enhancing the

electrolyte resistance. Besides, an increase in the existing anion concentration and the electrolyte conductivity can take place during the evaporation process of the thin electrolyte layer. When the electrolyte layer thins out, the concentration of anion rises to saturation and it recrystallizes into very fine crystal particles, such as NaCl or Na_2SO_4 . Moreover, after being subjected to several repeated cycles of wetting and drying, the steel surface will be covered with a thick rust layer, which undoubtedly affects the path of the atmospheric corrosion process. For example, the rust layer can resist the diffusion of aggressive anions to steel substrate, and $\gamma\text{-FeOOH}$, a common constituent of the rust layer, can be reduced to magnetite during the rusting process [2]. In addition, the covered rust layer affects the wetting time of the rusted steel surface, and Thee et al. [3] reported that it took a longer time to evaporate the same amount of water layer on the rusted steel surface than on the un-rusted steel surface.

In fact, the amount of the condensation electrolyte on steel surface is closely related to the surrounding atmospheric environment temperature and relative humidity

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(RH), which cannot be controlled in the traditional field exposure tests for atmospheric corrosion studies. The field exposure test can provide actual information on atmospheric corrosion behaviour of steels. However, it takes about 8–16 years just for one field exposure test, which makes it difficult to assess the long-term atmospheric corrosion resistance of steels [4]. Wet/dry cyclic corrosion test (CCT), based on saltwater spray followed by drying, can simulate the atmospheric corrosion under the conditions of controlled RH and temperature [5]. Dong *et al.* [6–8] studied the corrosion evolution behaviour of carbon steel and MnCuP weathering steel submitted to the CCTs in simulated atmospheric environments and found that the corrosion kinetics of steels had a great relevance to that of steels exposed to field atmospheric environments. Up to now, both field exposure test and indoor simulated test for atmospheric corrosion research are mainly focused on the corrosion kinetics of steels [9–11], which applies to the widely accepted power function model [12]. However, the corrosion kinetics cannot offer details about the evolution of electrochemical characteristics of the rust layer, which is also important for determining the long-term corrosion behaviour of the rusted steels.

Since atmospheric corrosion of steels is mainly governed by electrochemical reactions on the wetting steel surface, the application of electrochemical technique would be suitable to study the atmospheric corrosion behaviour of steels [13]. Nevertheless, the difficulty related to this application is the fact that when the electrolyte is very thin, the solution resistance becomes very high, causing an inconvenient error in the measured corrosion rate [14]. In fact, electrochemical impedance spectroscopy (EIS) has been proven to be an effective and non-destructive method to study the electrochemical characteristics of steel samples [15]. There are many researches using EIS to study the effect of the electrolyte thickness on the mechanism of the atmospheric corrosion of metals [16–19]. Li *et al.* [14] used chip-shaped bi-electrodes to study the evolution of EIS of carbon steel in one wet–dry process. Fu *et al.* [15] utilised a chip-shaped multi-electrodes to monitor the corrosion of mild steel under an alternate wet–dry condition at a very low humidity. Nishikata *et al.* [16, 17] applied EIS to elucidate the effects of the thickness and the pH of the electrolyte films on the initial atmospheric corrosion stage of iron. However, there have been few studies trying to elucidate the atmospheric corrosion behaviour of weathering steel under an electrolyte film, especially in case of the rusted steels. Recently, the results from our previous work [15] have shown that the electrochemical characteristics evolution in the atmospheric corrosion of steels during the alternate wet/dry CCT can be continuously interpreted by EIS. Besides, the electrochemical behaviour of steel substrate and rusted steel

during the drying process of the covered thin electrolyte layer can also be monitored [3]. Based on the advantages of this test, it is of great interest to develop one calculation method from the measurements of EIS to estimate the long-term atmospheric corrosion process of steels. Moreover, the anticipated mathematical method may be an alternative to the traditional atmospheric corrosion assessment method of the field exposure tests and would be useful for the development of the indoor simulated atmospheric corrosion tests.

In this work, EIS and electrolyte layer thickness measurements have been employed to study the corrosion behaviour of a weathering steel with a thin electrolyte layer covering submitted to cyclic wet/dry exposure in a simulated coastal–industrial environment, and we paid particular attention to the development of one mathematical method from the EIS data to further analyse the atmospheric corrosion mass loss of the steel.

2 Experimental

2.1 Electrode Preparation

In this study, a weathering steel was used as the electrode material and its composition is (in wt%) as follows: 0.06 C, 0.0135 Si, 1.16 Mn, 0.38 Cr, 0.16 Ni, 0.24 Cu, 0.019 P, 0.005 S and balance of Fe. The steel was sectioned into a pair of comb-like electrodes [15], and then, the two electrodes were embedded in epoxy resin with the comb fingers crossing but not contacting each other [14], and the total exposure surface area was about 1 cm². After being ground on SiC paper to 1,000 grit, the two-electrode cell was stored in a desiccator for 24 h and then subjected to the wet/dry cyclic corrosion tests (CCT). During the EIS measurements, one electrode with an area of 0.5 cm² worked as working electrode, and the other one worked as reference electrode and auxiliary electrode [3].

2.2 Wet/Dry Cyclic Corrosion Test

A self-made chamber with temperature and relative humidity (RH) control units was used for the tests. The simulated environmental condition in the chamber was maintained at (30 ± 1) °C and (60 ± 2)% RH by using the humidity control system containing water–glycerol mixture, the ratio of which was prepared according to ASTM D 5032 [20]. Once the electrodes cell was placed in the chamber, the CCT was then performed. The first CCT was conducted by wetting the electrode surface with an electrolyte of 50 µL cm^{−2} and drying the electrode in the chamber for 12 h. The electrolyte solution contained 0.05 mol L^{−1} NaCl + 0.005 mol L^{−1} Na₂SO₃ solution

and its pH value was 4.0 (simulating a coastal–industrial environment [21]). For other CCT cycles, the same working steps as the first CCT were repeated, but a same volume of distilled water was used as a solution to keep a constant amount of chloride and sulphate ions during the whole test. First CCT refers to the period from wetting the surface with electrolyte to its drying, followed by the subsequent CCT cycle. Clearly, at the beginning of the first CCT, $0.05 \text{ mol L}^{-1} \text{ NaCl} + 0.005 \text{ mol L}^{-1} \text{ Na}_2\text{SO}_3$ solution was added on the steel surface; however, from the second CCT, the constant volume of distilled water was added. The whole corrosion test of the cell was performed for 60 CCT numbers.

2.3 Electrolyte Thickness and EIS Measurements

During the whole test, the electrode cell is placed on an analytic balance BS 224 S, Satorius with accuracy $d = 0.1 \text{ mg}$, and its USB interface is connected with a computer for recording the data of the weight change. When the electrolyte is laid on the surface of the cell, the observed weight of the electrolyte is read and recorded in the computer.

The weight of the electrolyte film (W_e) can be obtained as follows:

$$W_e = W_s - W_d, \quad (1)$$

where W_s stands for the observed weight of the cell during the evaporation process, and W_d is the initial weight of the cell for the first CCT and is also the weight of the dried rusted cell when a new CCT cycle starts. The thickness of electrolyte film (X) can be monitored by Eq. (2):

$$X = \frac{W_e}{\rho S}, \quad (2)$$

where ρ and S are the density and surface area of the electrolyte film, respectively. In this study, ρ is regarded as 1 g cm^{-3} and S is considered to be 1 cm^2 .

Cyclic EIS measurements have been continuously carried out during the evaporation of the electrolyte until the surface is completely dried. The frequency range for EIS is from 100 kHz to 10 mHz with an amplitude of 5 mV (rms) at open-circuit potential.

3 Results and Discussion

3.1 Electrolyte Thickness and EIS Measurements on Steel Substrate Electrode Cell

Figure 1 exhibits the changes in the electrolyte film thickness and the concentration of Cl^- and SO_4^{2-} during the electrolyte evaporation process on the steel substrate

Fig. 1 Variation in the electrolyte film thickness and the concentration of Cl^- and SO_4^{2-} during the electrolyte evaporation process on un-rusted steel sample during the first CCT. The ordinary numbers 1–16 in the plot denote the sequence of the cyclic EIS measurements with the calculated electrolyte film thickness results

sample in the first CCT. Obviously, the electrolyte film thickness shows a linear decrease to zero with its evaporation. When the corrosion proceeds to 1.85 h, the weight becomes zero, indicating the completed thinning out of the electrolyte film, and the thickness of which is denoted by 0 μm . In addition, Fig. 1 also shows the changes in concentration of Cl^- and SO_4^{2-} during the thin electrolyte film evaporation process. Apparently, the concentration of Cl^- and SO_4^{2-} increases at a lower rate and then significantly increases with the electrolyte layer thinning out. When the electrolyte layer is approaching thinning out, the concentration of Cl^- and SO_4^{2-} rises to saturation or oversaturation, and NaCl and Na_2SO_4 recrystallized as very fine particles precipitated on the steel substrate surface.

EIS was employed to investigate the corrosion process of the steel with the thin electrolyte layer covering during the drying process. Figure 2 shows the Bode plots of the EIS results in the 16 test periods within the first CCT cycle. The numbers 1–16 in Fig. 2 mean the sequence of the cyclic EIS measurements, and the corresponding electrolyte film thickness has also been given. After this cycle, there was little corrosion product formed, and the surface of substrate was exposed. Generally, for the impedance of the Bode plot measured on the steel substrate, the solution resistance is dominated at high frequency and the sum of solution resistance and charge transfer resistance is dominated at low frequency [22, 23].

Figure 2a reveals that, as the evaporation process of the electrolyte film proceeds, the impedance at both high frequency and low frequency firstly tends to decrease until the 13th EIS measurement and then sharply increases for the 14th EIS measurement. The 15th and 16th EIS measurements were carried out with a calculated electrolyte film thickness of 0 μm , respectively, and both results were

Fig. 2 Evolution of the Bode results for EIS measurement on un-rusted steel sample in the first CCT. The sequence of the EIS data getting and the corresponding electrolyte film thickness are accompanied by the Bode results, respectively: **a** impedance plot; **b** phase angle plot

employed for comparison. For the steel substrate, the iron dissolution is balanced with the oxygen reduction [24], and during the period of 1st–13th EIS measurements, the oxygen reduction rate increases due to the ready availability of dissolved oxygen from the air to the thinning electrolyte film, leading to the increased corrosion rate and decreased high-frequency impedance and low-frequency impedance as the EIS measurement proceeds. Besides, the increased concentration of Cl^- and SO_4^{2-} in the thinning electrolyte film contributes to an enhanced electrical conductivity of the electrolyte, accelerating the steel corrosion process, which is an electrochemical one [25]. Therefore, the increased concentration of Cl^- and SO_4^{2-} in the thinning electrolyte film may also be responsible for the decreased high-frequency impedance and low-frequency impedance during the period of 1st–13th EIS measurements. For the 14th EIS measurement carried out with an electrolyte film thickness of 27 μm , the impedance at the high frequency significantly increases and subsequently shows an abrupt increase at frequency of 50.12 mHz, at which point the electrolyte thickness is about 15 μm . This impedance change can be explained as follows: when the remaining electrolyte film thickness is thinner than 15 μm , the electrolyte cannot be continuously distributed on the steel surface. In addition, the corrosion rate has reached a maximum value when the film thickness is thinner than 27 μm . According to the fundamentals of corrosion electrochemistry [26, 27], the almost no changes in impedance in Fig. 2a or phase angle in Fig. 2b for the 15th and 16th EIS measurements in nearly full frequency ranges also indicate the dry surface of the steel substrate sample at the two test periods.

Figure 2b shows that for the 1st–13th phase angle curves, the phase angle peak at the higher-frequency side exhibits a shift to the direction of higher-frequency side as the electrolyte evaporation proceeds, indicating a corrosion accelerating process of the steel sample under the effect of

Cl^- in the electrolyte layer [28]. In addition, the phase angle peak at the lower-frequency side exhibits a shift to the direction of lower-frequency side as the electrolyte evaporation proceeds due to the existence of SO_4^{2-} in the electrolyte layer [29]. Besides, a great decrease in the peak especially at the lower-frequency side of the phase angle curves of 14th EIS measurement is apparently observed, indicating a significant change in the sample surface condition [3]. The phase angle in the 15th and 16th curves shows a typical capacitance behaviour with a small current leakage resistor when the surface has no electrolyte covering [3].

3.2 Electrolyte Thickness and EIS Measurements on Rusted Electrode Cell

Figure 3 shows the changes in the electrolyte film thickness and the concentration of Cl^- and SO_4^{2-} during the

Fig. 3 Variation in the electrolyte film thickness and the concentration of Cl^- and SO_4^{2-} during the electrolyte evaporation process on rusted steel sample during the 54th CCT. The ordinary numbers 1–14 in the plot denote the sequence of the cyclic EIS measurements with the calculated electrolyte film thickness results

electrolyte evaporation process on rusted steel sample in the 54th CCT. The numbers 1–14 in Fig. 3 denote the sequence of the cyclic EIS measurements, and the corresponding electrolyte film thickness has also been given. Similar to the results shown in Fig. 1, the electrolyte thickness gradually becomes thinner and thinner until zero as the electrolyte film evaporation proceeds. Figure 3 also indicates that for the rusted steel sample during the 54th CCT, the thickness of initially 489- μm -thick electrolyte film does not drop to zero until the corrosion proceeds to 1.98 h. However, Fig. 1 indicates that for the steel substrate sample, it takes 1.85 h to evaporate out the initial thickness of 496- μm electrolyte. Usually, the amount of water associated with the surface is a function of temperature, porosity, degree of oxidation, grain structure and a variety of other surface-related properties [30, 31]. Therefore, the time of wetness on the rusted steel surface is prolonged due to the formation of rust layer. In addition, Fig. 3 shows the change in the concentration of Cl^- and SO_4^{2-} during the evaporation process of the thin electrolyte film. Obviously, the concentration of Cl^- and SO_4^{2-} firstly exhibits a gradual increase followed by a significant increase with the electrolyte layer thinning out. When the electrolyte layer approaches 0 μm , the concentration of Cl^- and SO_4^{2-} rises to saturation or oversaturation, and NaCl and Na_2SO_4 precipitated as very fine particles precipitated on the steel substrate surface.

Figure 4 shows the Bode plots of the EIS results obtained on the rusted steel sample during the 54th wet–dry cyclic corrosion test, and the sequence of the cyclic EIS measurements is displayed by 1st–14th. Generally, for the impedance of the Bode plot measured on the rusted steel substrate, the rust layer resistance is dominated at high frequency and the sum of rust layer resistance and charge transfer resistance at the rust/steel interface is dominated at low frequency [32]. The fact that the phase angle in Fig. 4b

at high frequency is close to 0° also indicates the high-frequency-dominated rust layer resistance [33], which also refers to the solution resistance in penetrating the rust layer to steel substrate [34]. Figure 4a shows that the impedance at both high frequency and low frequency decreases as the evaporation process proceeds during the 1st–13th EIS measurements, indicating an accelerating corrosion process of the steel sample happens. However, for the 14th EIS measurement carried out with an electrolyte film of 41 μm thickness, the impedance at the high frequency obviously increases and then shows an abrupt increase at frequency of 19.05 mHz, at which point the electrolyte thickness is about 27 μm . This impedance change indicates that, when the remaining electrolyte film thickness is less than 27 μm , the electrolyte cannot be continuously distributed on the rusted steel surface and the corrosion rate of the steel sample sharply decreases. Besides, the corrosion rate has reached a maximum value when the layer thickness is thinner than 41 μm . Figure 4b shows that the phase angle peak shifted to the low-frequency side as the electrolyte evaporation proceeds, indicating an increase in the capacitance value of the rusted steel sample during this period of time [35]. For the 14th result, the phase angle greatly drops towards to 0° in the low frequency, indicating a capacitance behaviour with almost no current leakage resistor, i.e. a drying out surface. Figure 4b also shows the fact that the intermediate frequency phase angle decreases as the corrosion proceeds during the testing period due to the increased penetrability of the rust layer by corrosive anions of Cl^- and SO_4^{2-} .

3.3 EIS Evolution as a Function of CCT Number

The evolution results of the first EIS measurements as a function of CCT number are shown in Fig. 5. Figure 5a shows that the impedance at high frequency slightly

Fig. 4 Evolution of the Bode results for EIS measurement on rusted steel sample in the 54th CCT. The sequence of the EIS data getting and the corresponding electrolyte film thickness are indicated at the Bode results, respectively: **a** impedance plot; **b** phase angle plot

decreases as the corrosion process proceeds during the period from 1st CCT to 6th CCT, but the impedance for the 10th CCT shows a small increasing trend, and Fig. 5b shows that the impedance at high frequency obviously increases as the corrosion process proceeds. Moreover, Fig. 5a shows that the impedance at low frequency obviously decreases as the corrosion process proceeds during the period from 1st CCT to 10th CCT; however, Fig. 5b shows that the impedance at low frequency obviously increases as the corrosion process proceeds. As stated in the above context, for the impedance of the Bode plot measured on the rusted steel substrate, the rust layer resistance (also refers to the solution resistance for penetrating the rust layer to steel substrate) is dominated at high frequency and the sum of rust layer resistance and charge transfer resistance at the rust/steel interface is dominated at low frequency. Therefore, to further analysis the EIS results, the impedance at high frequency of 10 kHz (Z_{HF}) is regarded as the resistance of the electrolyte in the fine pores in the rust layer (R_{rust}), and the impedance at low frequency of 10 mHz (Z_{LF}) is regarded as the sum of the polarization resistance (R_p) and R_{rust} . Moreover, the reciprocal of the polarization resistance (R_p^{-1}) is considered as an indicator related to the changes in the corrosion rate, which can be described as [3]

$$R_p^{-1} = \frac{1}{Z_{LF} - Z_{HF}}. \quad (3)$$

3.3.1 Evolution in the R_{rust}

Figure 6 shows the evolution of the calculated R_{rust} as a function of CCT number. Clearly, during each EIS measurement, R_{rust} decreases as the electrolyte layer thickness decreases and then sharply increases when the electrolyte thins out. The increased electrolyte electrical conductivity

and enhanced oxygen reduction rate as the electrolyte evaporates are responsible for the decreasing of R_{rust} . In addition, Fig. 6a, b indicates that R_{rust} increases as the CCT number increases during the whole test duration, indicating the improved resistance of the rust layer as the corrosion process proceeds.

To further illustrate the evolution of R_{rust} as a function of the CCT number, Fig. 7 shows the changes in R_{rust} for the first EIS measurement in each CCT number during the whole corrosion process. Obviously, R_{rust} gradually increases as the CCT number increases during the whole corrosion test, indicating the enhanced rust layer resistance to further corrosion attack. Moreover, Fig. 7 shows that R_{rust} smoothly increases during the first 15 CCTs and then significantly increases during the period from 15 CCTs to about 45 CCTs and thereafter again smoothly increases until the end of the corrosion test. This is because that the initially formed rust layer is thin and loose with almost no resistance against the penetration of Cl^- and SO_4^{2-} , and as the corrosion process proceeds, the rust layer thickens with a growing compactness and enhanced corrosion resistance, and finally, the rust layer enters a steady state with a stable compactness and protective ability as the corrosion test further proceeds.

3.3.2 Evolution in the R_p^{-1}

In this study, R_p^{-1} (the reciprocal of R_p) is employed to indicate the corrosion rate of the rusted steel sample [3]. Figure 8 shows the evolution in R_p^{-1} for each EIS measurement in each wet/dry cycle as a function of CCT number. Generally, during each CCT cycle, R_p^{-1} gradually increases with the evaporation of the electrolyte and then sharply decreases when the electrolyte approaches drying out. The evaporation process of the electrolyte can enhance the dissolved oxygen transportation rate in the electrolyte film, leading to an increased oxygen reduction rate and an increasing R_p^{-1} as the electrolyte becomes thinner.

Fig. 5 Evolution in the impedance result for Bode plots of the first EIS measurement as a function of CCT number: **a** 1–6 CCT; **b** 15–58 CCT

Fig. 6 Evolution in the calculated R_{rust} during the electrolyte evaporation process as a function of CCT number: **a** 1–14 CCT; **b** 15–53 CCT

Fig. 7 Evolution in the calculated R_{rust} as a function of CCT number for the first EIS measurement during each wet-dry cyclic process

Figure 8a, b shows that R_p^{-1} gradually increases as the CCT number increases to 14 CCT and then R_p^{-1} gradually decreases as the CCT number further proceeds; that is to say, the corrosion rate of the rusted steel increases to a

maximum with increasing CCT number to a certain value and then decreases as the corrosion further proceeds. Dong *et al.* [21] studied the corrosion evolution of MnCuP weathering steel in simulated atmospheres and also found that the corrosion rate increases in the initial corrosion process and then decreases with the corrosion process prolonging. This kind of evolution is closely related to the characteristics of the rust layer. During the initial CCTs, the formed rust layer is very thin, loose, porous and discontinuous, and it facilitates the transportation of Cl^- and SO_4^{2-} to corrode the steel substrate leading to a higher corrosion rate. Besides the reduction in dissolved oxygen, the initially formed steel rust contains a large amount of substance such as $\gamma\text{-FeOOH}$ and $\beta\text{-FeOOH}$ that can be reduced into Fe_3O_4 in the cathodic corrosion reaction. So, the corrosion rate greatly increases at the initial corrosion stage [36]. However, as corrosion process further proceeds, the rust layer has become compact and adhesive to steel substrate, and its barrier effect has been come into being. Therefore, the corrosion rate decreases during this corrosion period.

Fig. 8 Evolution in R_p^{-1} as a function of CCT number for each EIS measurement during wet-dry cyclic process: **a** 1–14 CCT; **b** 15–53 CCT

3.4 Numerical Method for EIS Data Interpretation

The above discussion indicates that EIS is one useful electrochemical method in investigating the corrosion evolution of steel with a thin electrolyte layer covering. In this section, one calculation method has been developed to estimate the atmospheric corrosion kinetics of steel based on the EIS measurements. As stated, R_p^{-1} can be thought as an indicator in reflecting the changes in corrosion rate. In fact, R_p^{-1} is a function of the electrolyte thickness (T) and CCT number (N), expressed as:

$$R_p^{-1} = f(T, N). \quad (4)$$

From this function, we firstly deal with the relationship between R_p^{-1} and the electrolyte thickness to obtain the average R_p^{-1} of each CCT, as shown in the following equation:

$$\left[R_p^{-1} \right]_{\text{CCT}} = \left[\frac{\int_a^b R_p^{-1} dT}{(b-a)} \right]_{\text{CCT}}, \quad (5)$$

where a and b represent the initial and final thickness, respectively.

With the attempt to obtain the integrated value of the relationship between R_p^{-1} and thickness, the trapezoidal rule [37], one of the well-known numerical methods for integration, is then applied. Based on this integration method, Eq. (6) can be provided:

$$\int_a^b R_p^{-1} d(T) = \sum_{n=1}^n A_n, \quad (6)$$

where A is the area of a segment and n is an order of segments. Combining Eqs. (5) and (6), the modified equation can be obtained:

$$R_p^{-1} = \frac{\sum_{n=1}^n A_n}{T}. \quad (7)$$

Figure 9 shows an example for application of Eqs. (5–7) for the 6th CCT result. Calculated by MATLAB program (R2011b) [38], the sum of the segment area from 1 to 13 is around $6,365.07 \times 10^{-4} \mu\text{m} \Omega^{-1} \text{cm}^{-2}$. The total electrolyte thickness of this CCT is $463 \mu\text{m}$. So, the average R_p^{-1} is $13.747 \times 10^{-4} \Omega^{-1} \text{cm}^{-2}$.

The above steps are repeated for all CCT numbers, and we can obtain the relationship between the average R_p^{-1} and CCT as shown in Fig. 10. To further understand the corrosion evolution of the steel in the simulated atmospheric environment, the accumulation of corrosion mass loss during the whole corrosion process should be obtained.

Fig. 9 Relationship between R_p^{-1} and the electrolyte thickness of 6th CCT with the application of the numerical integration using the trapezoidal rule. A_1 – A_{13} indicate the segments of the numerical integration

For these relationships, the following principal equations are taken for calculation [26].

Stern–Geary equation:

$$I_{\text{corr}} = K \left(R_p^{-1} \right). \quad (8)$$

Corrosion rate (by Faraday’s law):

$$\frac{d\Delta W}{dt} = \left(\frac{M_{\text{Fe}}}{2F} \right) I_{\text{corr}}. \quad (9)$$

The CCT number per day:

$$\frac{dN}{dt} = 2. \quad (10)$$

Corrosion rate can be indicated as:

Fig. 10 Evolution in the calculated average R_p^{-1} as a function of CCT number, and the area under the curve is divided into 59 segments for further integration

$$\frac{d\Delta W}{dN} = \left(\frac{d\Delta W}{dt} \right) \left(\frac{dt}{dN} \right). \quad (11)$$

By substituting Eqs. (8), (9) and (10) into Eqs. (11) and (12), the following equation can be obtained:

$$\frac{d\Delta W}{dN} = \left(\frac{M_{\text{Fe}} K R_p^{-1}}{2F} \right) \left(\frac{dt}{dN} \right), \quad (12)$$

where I_{corr} is corrosion current density (A cm^{-2}), K is proportional constant (V), ΔW is corrosion mass loss (g cm^{-2}), t is time of exposure (s), $M_{\text{Fe}} = 55.9 \text{ g mol}^{-1}$, and $F = 96,500 \text{ C mol}^{-1}$ is Faraday's constant. In this work, K is assigned to be 0.017 V, which has been presented in our previous work [14]. The constant values were calculated by Eq. (12), and then, the following equation was obtained:

$$d\Delta W = 0.216(R_p^{-1}dN). \quad (13)$$

Equation (13) is integrated to derive the simple form of corrosion mass loss as shown by Eq. (14):

$$\Delta W = 0.216 \int_1^N R_p^{-1} dN. \quad (14)$$

The integration term in Eq. (14) can be derived by the integrated area under the relationship curve between R_p^{-1} and CCT. To deal with this integration problem, we again apply the Trapezoidal rule [38] as can be seen in Fig. 10, with the area under the curve being divided into 59 segments, the integrated area (A_{int})

$$A_{\text{int}} = \int_1^N R_p^{-1} dN = \sum_1^N A_N. \quad (15)$$

The final numerical form of the mass loss during atmospheric corrosion process can be obtained as follows:

$$\Delta W = 0.216 \sum_1^N A_N. \quad (16)$$

Figure 11 shows the calculated corrosion mass loss of the steel as a function of CCT number, and clearly, the corrosion mass loss continuously increases as the CCT number proceeds. The above context provided one mathematical method from the EIS data to gain the corrosion mass loss of steel submitted to atmospheric corrosion. Although field exposure test can provide actual information on atmospheric corrosion behaviour of steels, it usually takes about 8–16 years just for one field exposure test, which makes it difficult to assess the long-term atmospheric corrosion resistance of steels [39]. Besides, field exposure test is usually a kind of one of time and

Fig. 11 Calculated corrosion mass loss of the steel as a function of CCT number during the whole corrosion process

labour consuming, such as data sampling at various intervals. However, the provided EIS measurement on self-made comb-like steel electrodes is easy in operation and time saving. Moreover, one mathematical method based on EIS measurements to elucidate the corrosion mass loss result has been developed. In fact, from the corrosion mass evolution result as shown in Eq. (16), corrosion kinetics evolution parameters such as average corrosion rate and instantaneous corrosion rate can also be obtained [40], and such kind of parameters are closely related to the rust layer characteristics such as composition, structure and electrochemical properties. The relationship between atmospheric corrosion kinetics evolution of steels and the covered rust layer characteristics can be found in details in our previous work [6–8]. Therefore, the provided mathematical method may be an alternative to the traditional atmospheric corrosion assessment method of the field exposure tests and would be useful for the development of indoor simulated atmospheric corrosion tests.

3.5 Corrosion Mechanism

The atmospheric corrosion of steel can be regarded as corrosion of iron under thin electrolyte film containing corrosives, that is, formation of rust layer by oxidation of ferrous ions dissolved from steel surface via anodic reaction in corrosive environment. For the steel without rust covering, the oxygen reduction and iron dissolution dominate the corrosion process. Due to the ready availability of oxygen to the cathodic sites and the increasing concentration of Cl^- and SO_4^{2-} during thinning out of the electrolyte film, the corrosion rate increases as indicated in Fig. 2. For steel in the initial corrosion stage, the rust contains a

considerable amount of FeOOH substance that can be reduced as part of the cathodic reaction [41–43]. Therefore, the reductions in oxygen and rust contribute to an increasing corrosion rate during the initial stage as shown in Fig. 5 [37]. However, at the same time, the active rust islands over the steel surface have been gradually transformed into electrochemically stable deposits consisted of Fe₃O₄, and this thin rust layer can grow to cover the whole steel surface and the protective ability of the rust layer improves. When the protective effect of the rust layer is in the balance with the corrosion effect, the corrosion rate reaches the maximum as indicated in Fig. 8. Then, as the rust layer grows and becomes more compact, the protective ability is predominant over the corrosion deterioration effect, and the corrosion rate begins to decrease greatly as the CCT cycle proceeds [44, 45]. Thicker and denser rust layer generally results in higher corrosion resistance because the transportation of ions is more greatly restricted [46]. In addition, when the corrosion products grow in thickness, especially when those products possess poor electric conductivity properties, the ionic transportation may become lower [47]. This potentially points out that when the stable rust forms on the steel substrate, it can provide a retarding effect on the transportation of oxygen and Cl[−] and SO₄^{2−} through the rust layer to steel substrate [48], and thus lowers the corrosion rate.

4 Conclusions

The corrosion evolution of a weathering steel covered with a thin electrolyte layer has been carried out for various wet–dry cycles in a simulated coastal–industrial atmospheric environment by using EIS method on comb-like electrodes. The results indicate that the corrosion rate of the steel is a function of the covered electrolyte layer thickness and the CCT cycle, and the following conclusions have been obtained:

1. Within each CCT cycle, the deceased impedance at high frequency with the evaporation of the electrolyte layer is related to an increase in the concentration of Cl[−] and SO₄^{2−} and an enhancement of oxygen diffusion during the thinning out of the electrolyte layer.
2. Due to the ready availability of oxygen to the cathodic sites and higher concentration of Cl[−] and SO₄^{2−} during thinning out of the electrolyte layer, R_p^{-1} increases in the initial corrosion stage. When the protective effect of the rust layer is in the balance with the corrosion effect, R_p^{-1} reaches a maximum. Then, as the rust layer grows in thickness and compactness and the protective ability is predominant over the corrosion

deterioration effect, R_p^{-1} begins to greatly decrease as the CCT number proceeds.

3. The provided mathematical approach based on the numerical integration method to obtain corrosion mass loss of steel from the measurements of EIS may be an alternative to the traditional atmospheric corrosion assessment method of the field exposure test and would be useful for the development of the indoor simulated atmospheric corrosion tests.

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