Int. J. Electrochem. Sci., 12 **(2017)** 7547 – 7556, doi: 10.20964/2017.08.15

International Journal of
ELECTROCHEMICAL
SCIENCE
www.electrochemsci.org

Effect of Air Humidity on the Diffusion Rate of Migrating Corrosion Inhibitor in Mortars

Xiangyu Lu[1,*], *Yunxia Guo*[1], *Pei Zhang*[2], *Chuanbo Zheng*[1]

[1] School of Materials Science and Engineering, Jiangsu University of Science and Technology, Zhenjiang 212003, Jiangsu, China
[2] College of Chemistry and Food Science, Yulin Normal University, Yulin 537000, Guangxi, China
[*]E-mail: luxiangyu2013@163.com

Received: 5 April 2017 / *Accepted:* 31 May 2017 / *Published:* 12 July 2017

The diffusion rate of a migrating corrosion inhibitor in mortars under dry air and humid air conditions was studied by electrochemical impedance spectroscopy. The results suggest that the impedance values of mortars increased with the concentration of the inhibitor. On the other hand, the impedances of the mortars maintained in the dry air are significant higher than the ones in the humid air condition. The fitting results show that the resistances of the concrete cover layer were obviously enhanced by the brushed corrosion inhibitor on the mortar surface. Meanwhile, the diffusion rates of the inhibitor in mortars also were accelerated by the high humidity of air.

Keywords: migrating corrosion inhibitor, electrochemical impedance spectroscopy, Warburg impedance, diffusion.

1. INTRODUCTION

Corrosion of reinforcing steel is one of the main factors to induce the degradation of concrete structure [1-3]. Corrosion inhibitor is widely used to prevent the corrosion of rebar in concrete for its exceptional performance and economically profitable [4]. Especially, migrating corrosion inhibitors attract many attentions for its convenience on the old structures [5-8]. Miksic [5] used the ultraviolet spectrophotometric method to detect the diffusibility of an amino-carboxylate based migrating corrosion inhibitor. The results show that the inhibitor can migrate to a depth of more than 76 mm after the concrete was immersed in the inhibitor solution for five weeks. Drew [6] studied the aminoalcohol and amine carboxylate based corrosion inhibitors on the old cracked and spalled concrete structures. The results show that the corrosion of reinforcing steel was significantly reduced by the inhibiting admixtures, and the authors attributed this situation to the high affinity and diffusibility of the inhibitors. Ormellese [7] also studied the effectiveness of a commercial amine based migrating corrosion inhibitor in concrete. The authors reported that inhibitor penetrated concrete mainly through the capillary absorption. Meanwhile, the inhibitor reacts with the constituents of the cement paste, which leads to a reduction of the concrete porosity and a retard of its penetration. Similarly, Chaussadent [8] also has reported that the interaction between monofluorophosphate and calcium ions would limit the diffusion of monofluorophosphate in the concrete. Trabanelli [9] investigated the corrosion inhibition of benzoic acid, 2-amino benzoic acid, and N-phenyl-2-amino benzoic acid on carbon steel in a carbonated concrete by using electrochemical impedance spectroscopy. The results suggest that only the benzoic acid and 2-amino benzoic acid exhibited some inhibitive effect towards the rebar corrosion process. Dhouibi [10] studied the long-term effectiveness of calcium nitrate and alkanolamine on the corrosion of rebar in concrete. The authors noticed that the both two inhibitors were not effective, when chloride is present on the steel-concrete interface. A brief review indicates that the previous studies mainly focus on the effective of the migrating corrosion inhibitor. Actually, migrating corrosion inhibitor is more suitable for the old structures for its convenient application (applied on the concrete surface). Thus, it is important to investigate the effect of environment factors on the diffusibility of the migrating corrosion inhibitor. In the present study, the humidity of air condition on the diffusibility of migrating corrosion inhibitor in concrete was studied by electrochemical impedance spectroscopy.

2. MATERIALS AND EXPERIMENTS

2.1 Materials

Carbon steel rods, with a diameter of 10 mm, which chemical composition (wt.%) was: 0.37% C, 0.16% Si, 0.32% Mn, 0.053% S, and 0.026% P were used in the present study. The steel samples were cut to a length of 60 mm and ground with emery paper up to No. 600. Copper wires were welded at one end of each sample. Then, the both ends were coated with silica gel and leaving a 50 mm length exposed zone in the middle of sample. The steel samples were degreased with alcohol, rinsed with deionized water, and dried in hot air. After that, the prepared samples were maintained in a drying vessel. Ordinary Portland cement (P.O 42.5) and river sand was used to mix mortars. The sand-cementitious material ratio and water-cement ratio (W/C) of the mortar were maintained at 3 and 0.5, respectively. The steel samples were embedded in the middle of a cylindrical mold with a size of $\Phi 40 \times 70$ mm, and mortar was poured into the mold and vibrated for 1 min. After curing for 24 h, the mortar samples were removed from the molds.

2.2 Experiments

Different concentrations of N,N-Dimethylethanolamine (DMEA) solution, including 0%, 1.5%, 3.0%, and 4.5% (wt.%) were brushed on the surface of the mortars. Every mortar sample was brushed for fifteen times and the brushing was performed after the previous processed surface has dried. For studying the effects of air humidity on the diffusion rate of migrating corrosion inhibitor in concrete, a home-made apparatus (figure .1) were used to control the humidity of environment. For comparing, a group of mortars were maintained in room condition (20±5 ℃, RH 60%), defined as the dry air condition. The other group of samples were kept in the apparatus (figure .1), which was moisturized by the humidifier every 8 h for 5 min, is defined as the humidity air condition. Two electrodes were used for the electrochemical impedance spectroscopy test [11, 12]. The carbon steel sample was the working electrode, and the reference and counter electrodes are connected with a Cu/CuSO4 electrode, and the Cu/CuSO4 electrode is glued to the mortar samples with complete wet absorbent cotton. EIS test was measured by a CS350 electrochemical workstation, the sweeping frequency is from 11520 Hz to 10 mHz with an AC perturbation of 10 mV.

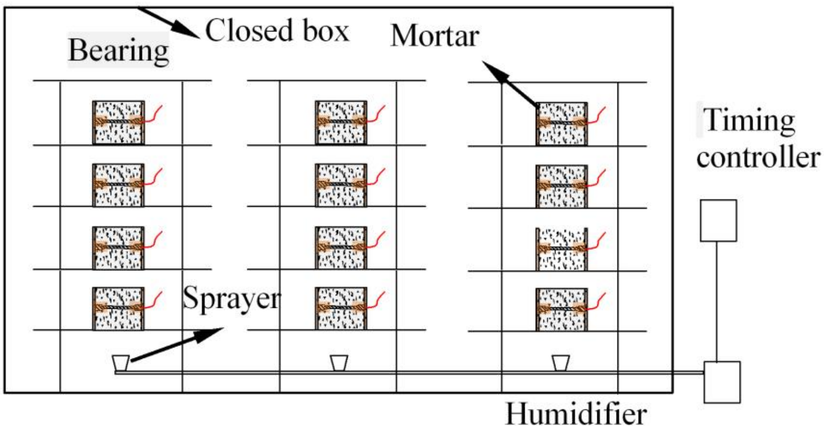


Figure 1. Schematic of the mortar sample and the air humidity control system.

3. RESULTS AND DISCUSSION

3.1 Electrochemical impedance spectroscopy

The electrochemical impedance spectroscopy of samples was tested 72 h, 240 h, and 720 h after the brushing process, and the results are presented in figure 2 to figure 4, respectively. It is easy to notice that the impedance of mortars in the humid air is much lower than those in the dry air condition. The value of the former almost is lower an order of magnitude than that of the latter. Similarly, Sagüés [13] reported that the impedance of samples apparently decreased when the concrete column were changed from dry condition to a partly immersed condition. The authors attributed this situation to the decrease of the resistance of concrete when the column was partly immersed. In the present study, the humid air also decreased the resistance of mortar in the closed box (as shown in figure 1). Thus, the impedance of samples in the humid air is significantly lower than that in the dry air.

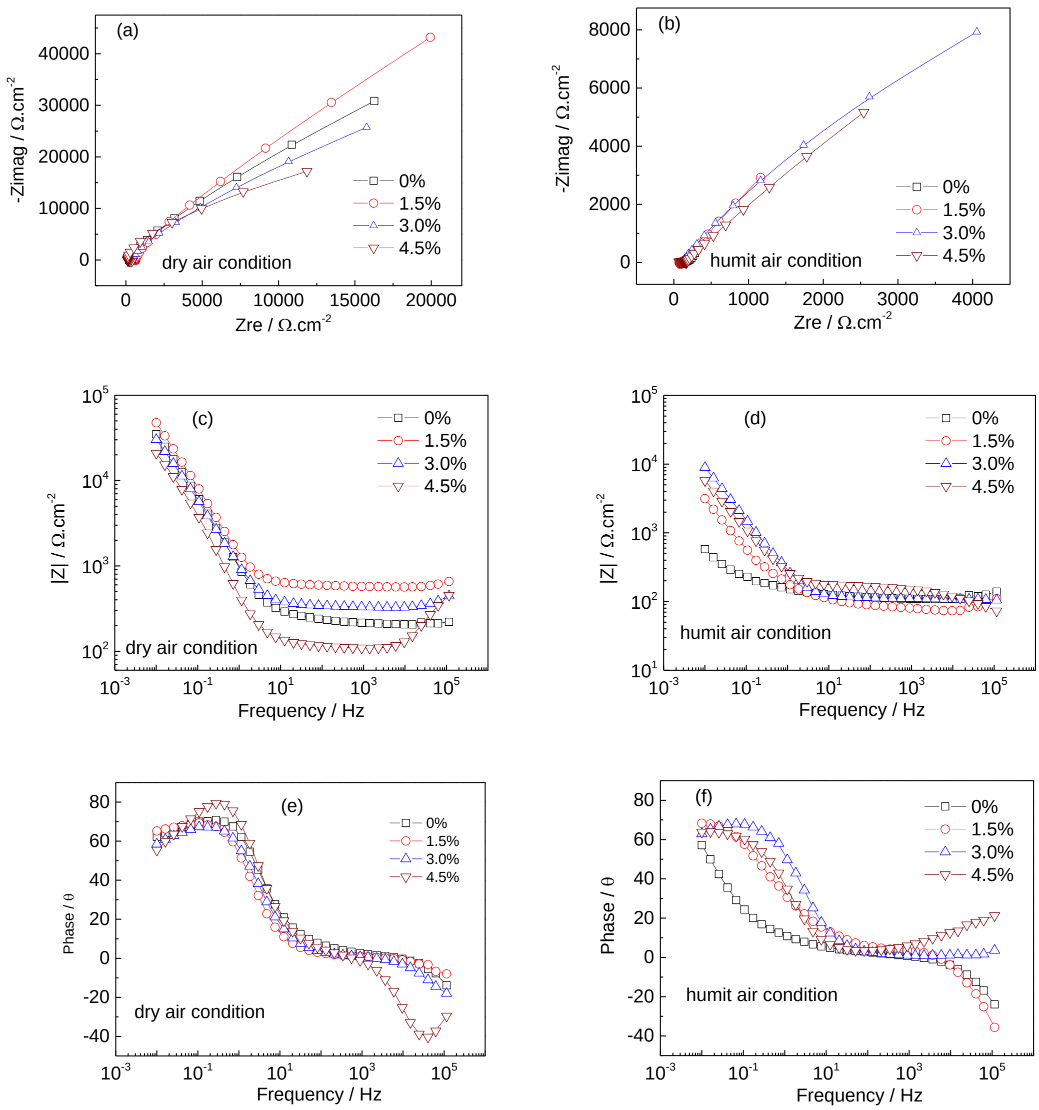


Figure 2. EIS results of mortars at 72 h, (a) Nyquist polts, (c) and (e) Bode polts of mortar in dry air condition, (b) Nyquist polts, (d) and (f) Bode polts of mortar in humid air condition.

On the other hand, in the whole experiment period (720 h), the impedance of mortars in the humid air increases with the concentration of DMEA solution from the initial time (figure 2(d)). However, the impedance of mortars in the dry air does not show significant influence by the DMEA concentration in the initial 240 h (figure 3(c)). After the brush process 720 h (figure 4 (c)), the value of impedance of samples in the dry air also increases with the DMEA concentration. This situation is further confirmed by the impedance results at the low frequency (0.01 Hz), as shown in figure 5. The DMEA solution was brushed on the surface will gradually permeate through the mortar layer by the pores and micro-cracks in the mortar [14, 15], which will increase the impedance of samples. As the concentration increasing, more DMEA content would coagulate on the surface and fill into these defects in mortars.

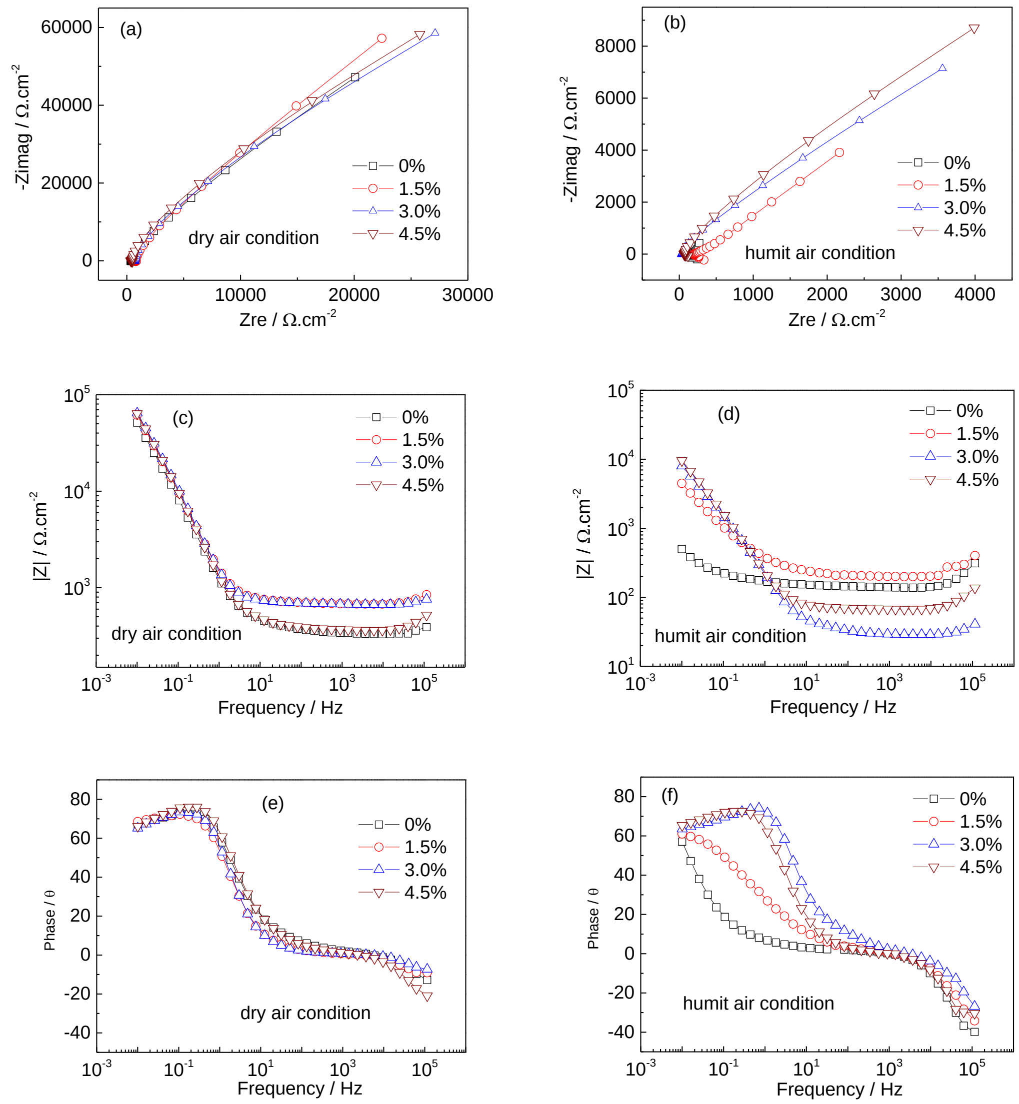
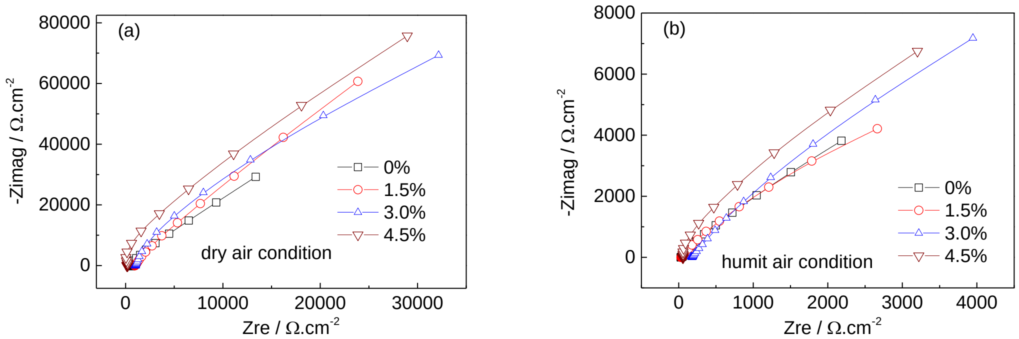


Figure 3. EIS results of mortars at 240 h, (a) Nyquist polts, (c) and (e) Bode polts of mortar in dry air condition, (b) Nyquist polts, (d) and (f) Bode polts of mortar in humid air condition.



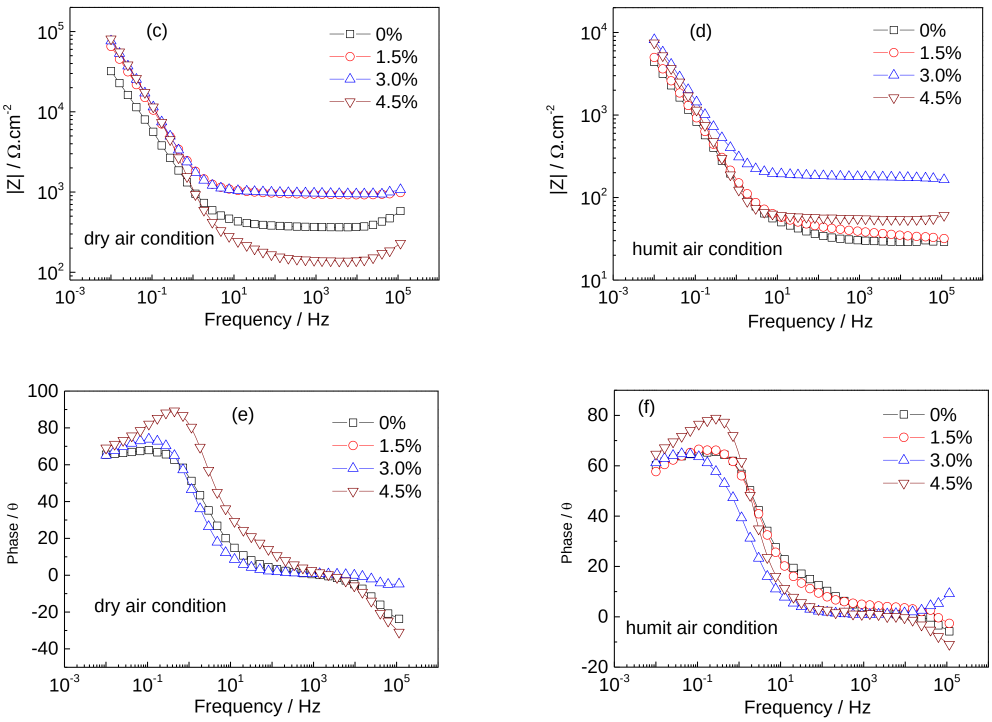


Figure 4. EIS results of mortars at 720 h, (a) Nyquist polts, (c) and (e) Bode polts of mortar in dry air condition, (b) Nyquist polts, (d) and (f) Bode polts of mortar in humid air condition.

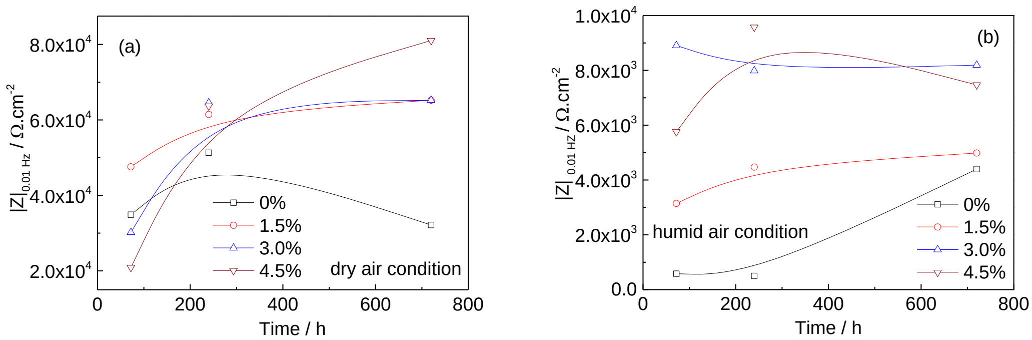


Figure 5. The impedance at 0.01 Hz for mortars at different time, (a) dry air condition, (b) humid air condition.

Consequently, the impedance of samples increases with the concentration of DMEA in solution. The impedance increment of the mortar in the humid air is earlier than the one in dry air condition, which suggests that the permeation of DMEA in mortar is closely related to the humidity condition. That is, the permeation rate of the DMEA is enhanced by the humidity of concrete.

To further study the effect of air humidity on the diffusibility of DMEA in mortars, an equivalent circuit, as shown in figure 6, was used to fit the EIS results by applying the Zsimpwin software. R_s is the resistance of the solution that connects the mortars and the $Cu/CuSO_4$ electrode,

R_{con} and Q_{con} separately represent the resistance and capacitance of the mortar cover layer, R_{ct} and Q_{ct} are the polarization resistance and the double layer capacitance, respective [16]. Warburg impedance, represented by Z_w, is introduced to fit the smearing phenomenon in the high frequency [17]. Similar with the earlier study, the Warburg impedance is thought to be closely related to the diffusion of the DMEA in the mortar in the present study.

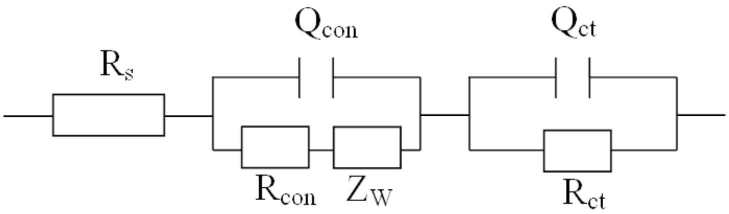


Figure 6. Equivalent electrical circuit used for modelling of the impedance data.

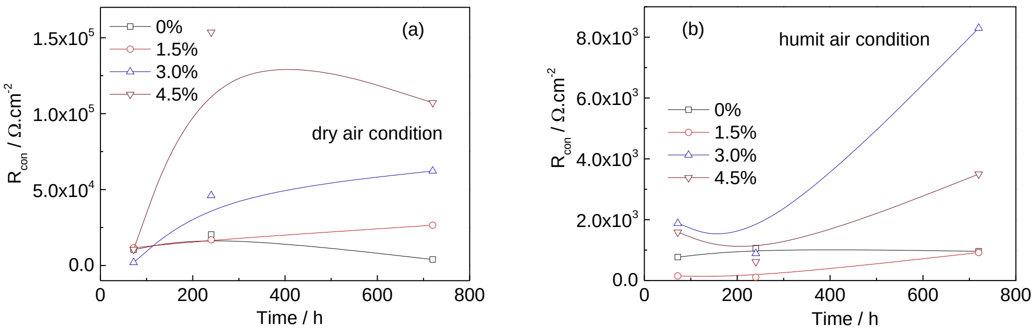


Figure 7. Equivalent electrical circuit used for modelling of the impedance data, (a) dry air condition, (b) humid air condition.

As many studies reported, the smearing phenomenon appears in the Nyquist plot suggests that the diffusion of oxygen is the controlling process. Warburg impedance Z_w in equation (1) is often applied to describe the semi-infinite plane diffusion's characteristic of oxygen [16, 17].

$$Z_w = Y_{ow}\varpi^{-1/2}(1-j) \qquad (1)$$

where Y_{ow} is the Warburg coefficient, the fitting results of Y_{ow} are presented in figure 8. It is easy to notice that the value of Y_{ow} for the samples in humid air condition (figure 8 (b)) is much higher than those in the dry air condition (figure 8 (b)). Meanwhile, the Y_{ow} values also gradually increase with the concentration of DMEA increasing. Furthermore, the diffusion coefficient of oxygen can be get from the Warburg coefficient (Y_{ow}) by equation (2) [14, 15].

$$D_{oxy} = \left[\frac{RT}{\sqrt{2}AF^2Y_{ow}C}\right]^2 \qquad (2)$$

where D_{oxy} is the diffusion coefficient of oxygen; R represents the gas constant; T is the temperature; A is the area of electrode; F is the Faraday constant; C is the concentration of oxygen on the mortar surface.

A variable κ, is defined as shown in equation (3). Then, the diffusion coefficient of oxygen (D_{oxy}) can be get from Y_{ow} according to equation (4).

$$\kappa = \frac{RT}{\sqrt{2}AF^2C} \qquad (3)$$

$$D_{oxy} = \left[\frac{\kappa}{Y_{ow}}\right]^2 \qquad (4)$$

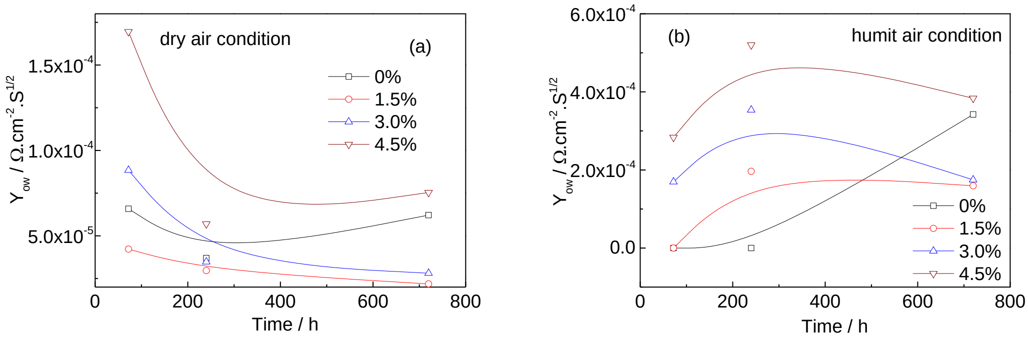


Figure 8. Fitting results of Y_{ow} values for samples brush with different concentrations of DEMA.

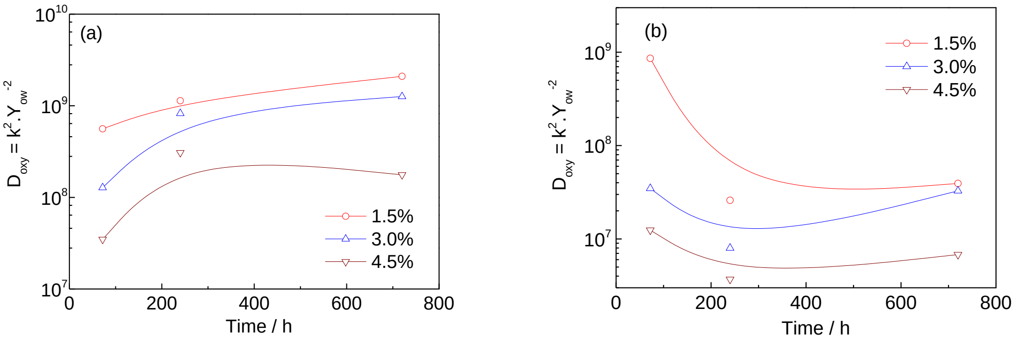


Figure 9. Values of $\kappa^2.Y_{ow}^{-2}$ for samples brush with different concentrations of DEMA. (a) dry air condition, (b) humid air condition.

In the present study, all the electrochemical impedance spectroscopy was tested at room temperature. The fluctuation of temperature (T) and the concentration of oxygen (C) of the samples can be ignored. Thus, as equation (4) shows, the diffusion coefficient of oxygen D_{oxy} in the mortars is mainly controlled by the Warburg coefficient (Y_{ow}). As the result in figure 9 shows, the value of D_{oxy} significantly decreased with the concentration of DEMA. This situation indicated that the diffusion of oxygen in mortars is significantly blocked by the brushed DEMA. As the concentration increasing, more DEMA migrates in the mortar layer and fill into the pores and micro-cracks of the inner cementitious materials. Thus, the diffusion coefficient of oxygen in mortars was significantly decreased with the concentration of DEMA. On the other hand, the value of D_{oxy} for the mortars in the dry air condition (figure 9 (a)) is obvious higher than those ones in the humidity condition (figure 9 (a)). Besides the humidity of mortars, this result is also closely related to the migration of the DEMA. The migration of the corrosion inhibitor on the surface were accelerated by the high humid, then the diffusion of oxygen in the mortars in the humid air condition was delayed. As a result, the D_{oxy} of samples in the dry condition is much higher than the ones in the humid condition. Similarly, Vedalakshmi [16] used the Warburg impedance in EIS results to study the diffusion of chloride in concrete. The authors also noticed that the diffusion coefficient of chloride decreased with the compressive strength of concrete. That result, together with the result in here, suggests that the Warburg impedance is one of the effective methods to study the diffusion process in mortars.

4. CONCLUSIONS

Using different concentrations of N,N-Dimethylethanolamine (DMEA) solutions as the migrating corrosion inhibitor, the diffusibility of the inhibitor in the mortars under dry air and humid air conditions are studied by electrochemical impedance spectroscopy, respectively. The following conclusions can be drawn from the results of this study.

(1) Both in the dry air and humid air condition, the impedance of mortars increased with the concentration of DEMA. On the other hand, the value of impedance for samples in the dry air condition is much higher than the ones in the humid air condition.

(2) Comparing with the fitting concrete resistances of the samples in humid air, those for samples in the dry condition are much higher. Meanwhile, the resistance of the concrete cover layer is also increased with the concentration of the corrosion inhibitor.

(3) The fitting results of Warburg impedance indicate that the permeation of the migrating corrosion inhibitor is obviously increased with the humidity of air, which means that the high humid air condition accelerates the migration of inhibitor in concrete.

ACKNOWLEDGEMENT

This work is supported the National Natural Science Foundation of China (51601074), the Key Laboratory of Advanced Civil Engineering Materials (Tongji University), Ministry of Education (201701), State Key Laboratory of High Performance Civil Engineering Materials (No. 2015CEM006), the Natural Science Foundation of Jiangsu Province, China (No. BK20141292), and Jiangsu Provincial Department of Education Fund (15KJB430009).

References

1. X. Feng, X. Lu, Y. Zuo , N. Zhuang, D. Chen, *Corros. Sci*., 103 (2016) 223
2. X. Feng, X. Lu, Y. Zuo , N. Zhuang, D. Chen, *Corros. Sci*., 103 (2016) 66
3. X. Feng, X. Lu, Y. Zuo, D. Chen, *Corros. Sci*., 82(2014) 347
4. C. Xie, H. Yan. *Materials Review*, 28 (2014) 101
5. B. AMiksic, M. Shen, J. Hicks, *Mater. Performance*, 52 (2013) 48
6. M. S. Drew, J. J. Meyer, J. Hicks, *Mater. Performance*, 51(2012) 8
7. M. Ormellese, F. Bolzoni, S. Goidanich, M. P. Pedeferri, A. Brenna, *Corros. Eng. Sci. Techn.*, 46 (2011) 334
8. T. Chaussadent, V. Nobel-Pujol, F. Farcas, I. Mabille, C. Fiaud, *Cem. Concr. Res*., 36 (2006) 556

9. G. Trabanelli, C. Monticelli, V. Grassi, A. Frignani, *Cem. Concr. Res*., 35 (2005) 1804
10. L. Dhouibi, E. Triki, A. Raharinaivo, *Cem. Concr. Compos*., 24 (2002) 35
11. D. V. Ribeiro, C. A. C. Souza, J. C. C. Abrantes, D. V. Ribeiro, C. A. C. Souza, *Rev. Ibracon Estrut. Mater*., 8 (2015) 529
12. S. P. He. Beijing University of Chemical Technology (thesis), 2010
13. A. A. Sagüés, M. A. Pech-Canul, A. K. M. S. Al-Mansur, *Corros. Sci*., 45 (2003) 7
14. R. Vedalakshmi, K. Rajagopal, N. Palaniswamy, *Corros. Eng. Sci. Tech*., 44 (2013) 20
15. A. Królikowski, J. Kuziak, *Electrochim. Acta*, 56 (2011) 7845
16. R. Vedalakshmi, V. Saraswathy, H. W. Song, N. Palaniswamy, *Corros. Sci*., 51 (2009) 1299
17. G. Qiao, J. Ou, *Electrochim. Acta*, 52 (2007) 8008