Int. J. Electrochem. Sci., 8 **(2013)** 1895 - 1902

International Journal of
ELECTROCHEMICAL
SCIENCE
www.electrochemsci.org

Investigation the Protective Performance of Organic Coatings with Different Breakage Degree Using EIS United to SOM Neural Network

Antao Xu[*], *Fan Zhang*[**], *Bing Luo, Fu Jin, Tianru Zhang*

Automobile Engineering Department, Military Transportation University, Tianjin 300161, China
[*]E-mail: xuantao428@163.com
[**]E-mail: 251249578@qq.com

Received: 4 December 2012 / *Accepted:* 3 January 2012 / *Published:* 1 February 2013

The protective performance of organic coatings with different breakage degree has been measured by electrochemical impedance spectroscopy (EIS) in 3.5% NaCl solution. The changing rate of impedance $k(f)$ was extracted directly from Bode plots and selected as the training sample for SOM neural network. According to the EIS characteristics and classification results of SOM neural network, the protective performance of organic coatings with different breakage degree can be divided into three levels of good, intermediate and poor, and the presence of small macro-pores only slightly influences the protective performance of organic coating. In addition, it is concluded that EIS united to SOM neural network is a helpful method for analyzing the protective performance of organic coatings with different breakage degree.

Keywords: SOM neural network; EIS; Damage degree; Changing rate of impedance; Organic coatings

1. INTRODUCTION

Electrochemical impedance spectroscopy (EIS) has been widely used in the investigation of the protective performance and degradation degree of organic coating for its ability to provide abundant information [1-7]. However, there are always some issues to select satisfied equivalent circuit to simulate the EIS results for some coating systems. Therefore, new methods and parameters [8-16] which can be extracted directly from Bode plots of impedance spectrum are useful for the evaluation of coating systems.

Neural network has become a new method for the evaluation of protective performance and degradation process of organic coating for its adaptation ability and learning ability [13]. Gao et al [14] studied the changing rate of impedance and separated the deterioration process of organic coating into five sub-processes by using Kohonen neural network. Zhao et al [15] analyzed the changing rate of impedance and divided the entire deterioration process of organic coating into three main stages by using SOM neural network. Xu et al [16] analyzed the deterioration process of organic coating by using the changing rate of phase angle at high frequency united to neural network. However, these neural network analyzes were based on immersion or cyclic wet-dry conditions, and it is time-taking to do these experiments for some complicated coating systems, so it will be a simple coating evaluation method for studying organic coatings with different breakage degree by using SOM neural network.

In this paper, organic coatings with different breakage degree were measured in 3.5% NaCl solution. The purpose of this paper are, firstly, to further understand the interconnection between breakage degree and protective performance, secondly, to investigate the influence of small macro-pores in organic coating, thirdly, to set up a new evaluation method for studying the protective performance of organic coating.

2. EXPERIMENTAL METHODS

2.1 Materials and samples preparation

The metal matrix used was Q/BQB403/ST14 cold-roll steel, with a size of 60×60×1mm. The mental matrix was firstly treated with zinc phosphate, then coated with epoxy ester primer, and then coated with polyurethane in the middle, and finally coated with acrylic acid topcoat. The thickness of the organic coating was 156.8μm and the working area was 19.6cm^2.

The breakage degree b of organic coating can be described as shown in Eq. (1),

$$b = \frac{S_p}{S} \qquad (1)$$

where S_p is the breakage area and S is the working area of organic coating.

A series of organic coatings with different breakage degree was prepared, as shown in Table 1.

Table 1. The organic coatings with different breakage degree

breakage diameter(mm)	0	0.06	0.08	0.1	0.15	0.18	0.2	0.3
breakage degree	0	1.44E-6	2.56E-6	4.01E-6	9.02E-6	1.30E-5	1.60E-5	3.61E-5
breakage diameter(mm)	0.4	0.8	1	2	3	5	10	15
breakage degree	6.41E-5	2.56E-4	4.01E-4	1.60E-3	3.61E-3	1.00E-2	4.01E-2	9.02E-2

2.2 EIS measurements

The EIS measurements were carried out in 3.5% NaCl solution at room temperature with PARSTAT 2263 electrochemical workstation. EIS measurements were performed at the open circuit potential with a 10mV amplitude signal and the measuring frequency range was 10^5 Hz to 10^{-1} Hz. A three-electrode cell was used which the organic coatings with different breakage degree as the working electrode (WE), a saturated calomel electrode as the reference electrode (RE) and a Pt electrode as the counter electrode (CE).

3. RESULTS AND DISCUSSION

3.1 Analysis of EIS characteristics

As we know，the information from low frequency in Bode plots of impedance spectrum mainly reflects the impedance of the coating, so the maximum impedance at lowest frequency [17-21] can be used to evaluate the protective performance of the coating systems to a certain extent. The impedance spectrum measured for organic coatings with different breakage degree in 3.5% NaCl solution are shown in Fig.1, where Z_{im} is the imaginary part, Z_{re} is the real part, $|Z|$ is impedance module and θ is phase angle.

As shown in Fig.1 (A) and (a), when a tiny breakage degree appeared on the coating systems, only one time-constant was observed on Bode plots and the maximum impedance at lowest frequency remained no big change with a magnitude order around $10^{10}\Omega\bullet cm^2$. The reason might be that zinc phosphate on the metal matrix reacted and formed a tight protective film on the tiny breakage area of metal matrix, which protected the metal matrix from corrosion [22]. It is concluded that the protective performance of the coating systems was in a good condition. Along with the breakage degree kept on increasing, there were two time-constants observed on Bode plots and a diffusion tail appeared at low frequency on the Nyquist plots. It indicated that the corrosion process was diffusion control. At the same time, the maximum impedance at lowest frequency reduced suddenly and rapidly around $10^8\Omega\bullet cm^2$. It is concluded that the protective performance of the coating systems reduced quickly but still in an immediate condition, as shown in Fig.1 (B) and (b). As the breakage degree kept on increasing continuously, the diffusion tail on Nyquist plots disappeared and the capacitive radius semi-arc further reduced. It indicated that the corrosion process was translated from diffusion control into charge transfer control. And the maximum impedance at lowest frequency reduced below the magnitude order of $10^7\Omega\bullet cm^2$. It is concluded that the protective performance of the coating systems reduced quickly and in a poor condition, as shown in Fig.1 (C) and (c).

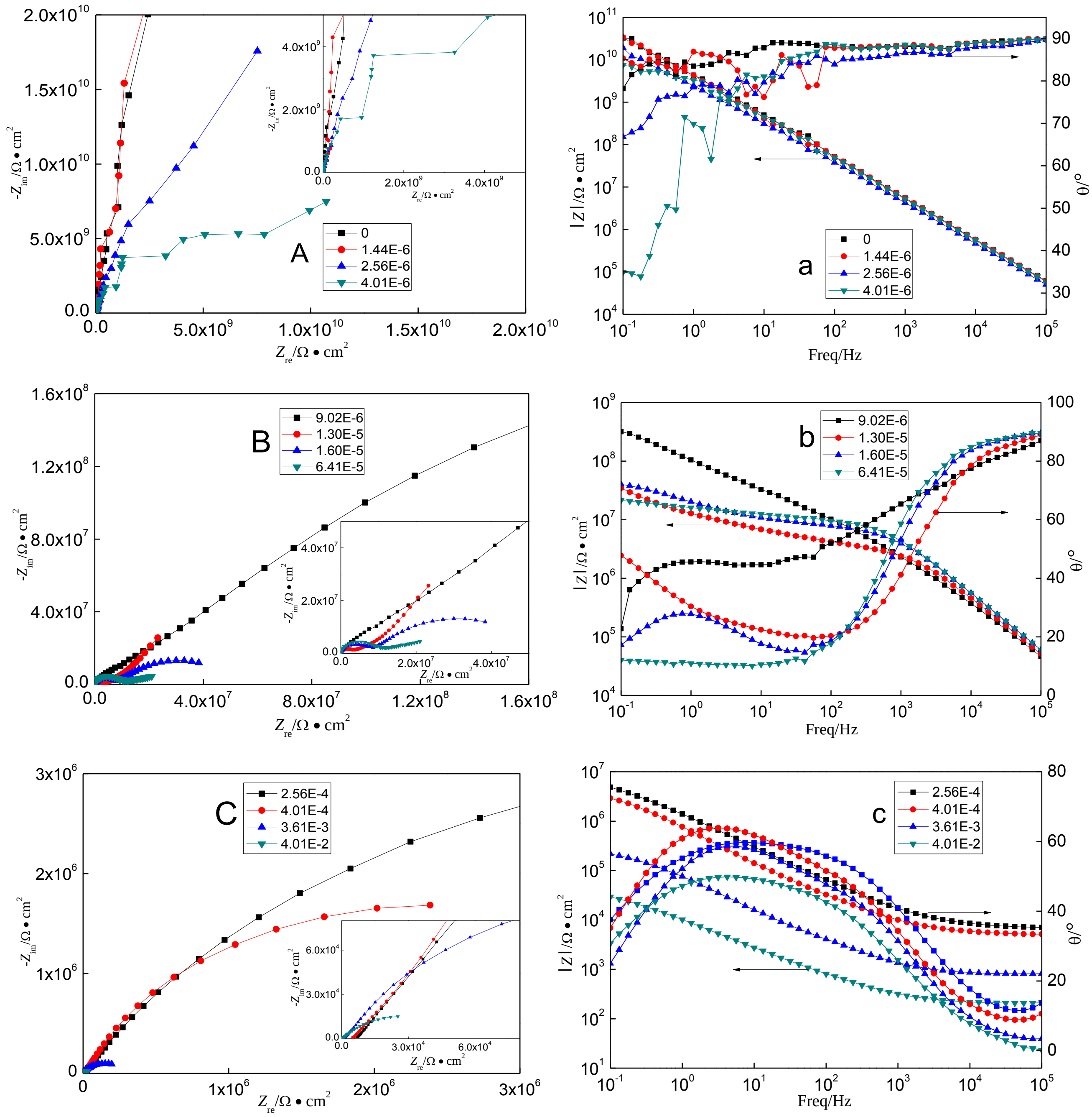

Figure 1. EIS plots of organic coatings with different breakage degree

From the above analysis, it is clear that the organic coating would keep its protective performance in a good condition when the breakage degree is slight, but as the breakage degree kept on increasing, its protective performance would reduce quickly until totally lost.

3.2 Analysis of parameter for training sample

The changing rate of impedance satisfying Eq. (2) [13-15] can reflect the breakage degree of organic coating clearly.

$$k(f) = \frac{d(|Z|)}{d(\log|f|)} \qquad (2)$$

For the discrete EIS data, the differential form will be replaced by a derivative form as follows:

$$k(f) = \frac{|Z_{f_i}| - |Z_{f_{i-1}}|}{\log f_i - \log f_{i-1}}, \quad i = 1, 2, \cdots, n \qquad (3)$$

Fig. 2 was typical Bode plots for organic coatings with different breakage degree, and according to the changing tendency, we can divide the Bode plots into three parts. But in the range of 10^1 Hz to 10^3 Hz (part 2), the tendency shows a remarkable change, which may relate to the breakage degree of organic coatings.

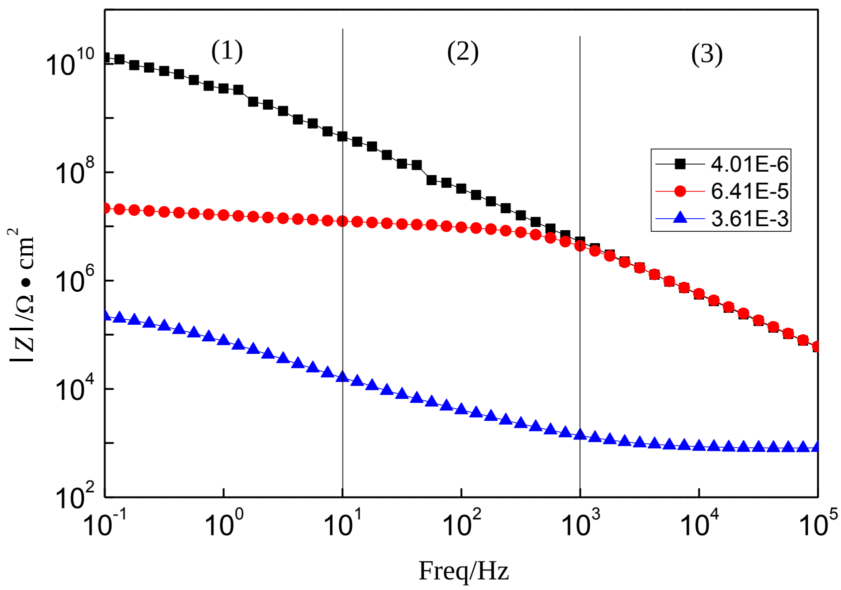

Figure 2. Typical Bode plots for organic coatings

All the *k*(*f*) data were extracted from Bode plots according to Eq. (3). And the typical *k*(*f*) data in the range of 10^1 Hz to 10^3 Hz for organic coatings with different breakage degree as shown in Fig. 3. It is clear that the changing rate of impedance *k*(*f*) almost close to a horizon linear as the breakage degree become bigger and bigger. So with the help of parameter *k*(*f*), the protective performance of organic coating can be distinguished effectively without fitting equivalent circuit[15]. Therefore, we use the changing rate of impedance *k*(*f*) in the range of 10^1 Hz to 10^3 Hz as the training sample for SOM neural network to analyze the protective performance of organic coatings with different breakage degree.

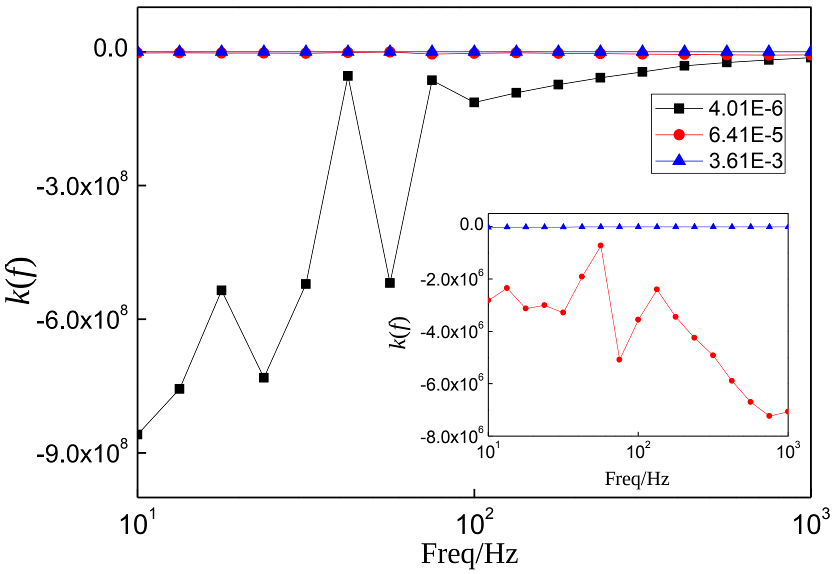

Figure 3. Typical $k(f)$ data in the range of 10^1 Hz to 10^3 Hz

3.3 Analysis of SOM neural network

All training samples of SOM neural network were parameter $k(f)$ in the range of 10^1 Hz to 10^3 Hz. The parameter $k(f)$ was analyzed using Neural Network Toolbox function based on the Matlab 7.0 [23].

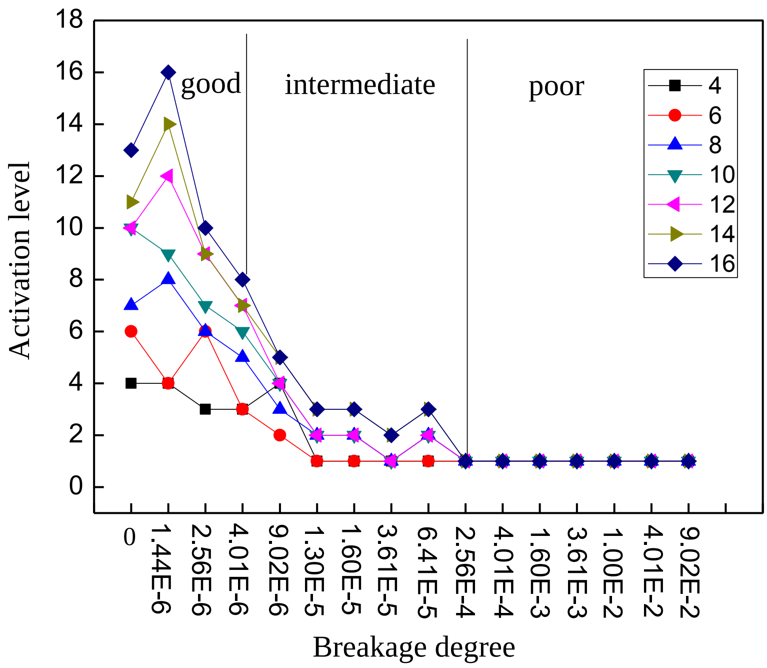

Figure 4. Tendency of activation level with different breakage degree

The function of net=newsom(minmax(P),[n 1]) was used to build a self-organizing feature map, and the functions of train and sim were used to train and emulate for 16 (the number of coating samples in this experiment) training samples, respectively. P was the parameter $k(f)$ and [n 1] was the dimension of the output layer.

After the network was trained, the variation trend of activation level of output layer could reflect the protective performance of organic coatings [15]. Different activation level in the output layer was obtained under different n values after 400 times of network training. When n was greater than or equal to 4, the classification result showed a similar law. The changes of activation level in the output layer obtained along with different breakage degree were given in Fig. 4 under the condition that n=4, 6, 8, 10, 12, 14, 16, respectively. The general trend of activation level in the output layer along with different breakage degree could be divided into three levels of good, intermediate and poor [12] as shown in Fig. 4.

(1) Level of good: When a tiny breakage degree appeared on the organic coatings, the activation level in the output layer tended to decline but still in a high level. It is concluded that the protective performance of the coating systems was in a good condition and the presence of small macro-pores [24] only slightly influences the protective performance of organic coating.

(2) Level of intermediate: As the breakage degree kept on increasing, the activation level in the output layer decreased suddenly and rapidly, which means that the protective performance of the coating systems reduced quickly but still in an immediate condition.

(3) Level of poor: As the breakage degree kept on increasing continuously, the activation level in the output layer dropped to 1 and closed to a horizon linear, which means that the protective performance of the coating systems had lost and in a poor condition.

4. CONCLUSTIONS

The result indicates that EIS characteristics show the similar law with classification results of SOM neural network. And according to the EIS characteristics and classification results of SOM neural network, the protective performance of organic coatings with different breakage degree can be divided into three levels of good, intermediate and poor, and the presence of small macro-pores only slightly influences the protective performance of organic coating. It is concluded that EIS united to SOM neural network is a helpful method for analyzing the protective performance of organic coatings with different breakage degree.

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