*Int. J. Electrochem. Sci.*, 8 **(2013)** 773 - 779

International Journal of
ELECTROCHEMICAL
SCIENCE
www.electrochemsci.org

# Investigation the Deterioration Process of Organic Coating Using Changing Rate of Phase Angle at High Frequency United to Neural Network

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*Received:* 6 November 2012 / *Accepted:* 1 December 2012 / *Published:* 1 January 2013

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Electrochemical impedance spectroscopy (EIS) of an organic coating system in 3.5% NaCl solution was measured and a new parameter $k(f)$ named changing rate of phase angle at high frequency is extracted directly from Bode plots. The changing rate of phase angle at high frequency $k(f)$ was selected as the training sample for neural network. According to characteristics of EIS, changing rate of phase angle at high frequency $k(f)$ and the classification results by neural network, the deterioration process of organic coating can be divided into three stages. It is concluded that changing rate of phase angle at high frequency $k(f)$ is a helpful parameter and combined with neural network can be used for studying the deterioration process of organic coating.

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**Keywords:** neural network; organic coating; changing rate of phase angle; EIS

## 1. INTRODUCTION

Electrochemical impedance spectroscopy is one of the main methods to study protective performance and deterioration process of organic coating because it can provide abundant information [1-5]. By fitting equivalent circuit models, the method can give many electrochemical parameters such as coating resistance, coating capacitance, double layer capacitance and charge transfer resistance which are related to protective performance and deterioration process of organic coatings. However, it is difficult to select satisfactory equivalent circuit models for some coating systems. Also, signal drift and data scatter often occur during the time-taking measurements in low frequency. Therefore, other methods and parameters need to be used to study the protective performance and deterioration process of organic coating [6-11].

Neural network has been a simple and effective method for studying the deterioration process of coating systems for its strong adaptation ability and learning ability [12]. Gao et al [13] studied the changing rate of impedance of the simulated damage specimens with different coatings, and separated the deterioration process into five sub-processes by using Kohonen neural network. Zhao et al [14] analyzed the EIS characteristics, changing rate of impedance and the classification results by SOM neural network of organic coating under cyclic wet-dry conditions, and divided the entire deterioration process into three main stages.

However, these analyses were based on changing rate of impedance, so choosing a new parameter as the training sample for neural network is very necessary. In this paper, a new parameter $k(f)$ named changing rate of phase angle at high frequency is extracted directly from Bode plot and then put the parameter $k(f)$ as the training sample for neural network. The purpose of this study was to further understand the interconnection between changing rate of phase angle at high frequency $k(f)$ and deterioration process of organic coating, which may lead to a new evaluation method for coating deterioration process.

## 2. EXPERIMENTAL METHODS

The metal matrix used was hot-rolled steel panel T610L, with a size of 60×60×1mm. The mental matrix was firstly treated with zinc phosphate, and then was electrophoresed with crylic acid and polyester, and finally coated with hydrophilic topcoat. And the coating with 32.25±0.1μm thickness was used in this paper.

The EIS measurements were carried out in 3.5% NaCl solution at room temperature with PARSTAT 2263 electrochemical workstation. Impedance spectra were obtained at open circuit potential with a 10mV amplitude signal. The measuring frequency range was $10^5$ Hz to $10^{-2}$ Hz and the working area was 3.14cm$^2$. A three-electrode cell was used which the organic coating as the working electrode, a saturated calomel electrode as the reference electrode and a ruthenium electrode as the counter electrode.

## 3. RESULTS AND DISCUSSION

### *3.1 Analysis of EIS for coating system*

Fig. 1 was the Nyquist plots and Bode plots of coating system after immersed in 3.5% NaCl solution with different time, where $Z_{im}$ is the imaginary part and $Z_{re}$ is the real part. As shown in Fig.1, the deterioration process of organic coating can be divided into three main stages [15]. In the earlier stage, the single capacitive radius semi-arc in Nyquist plot is very large and low frequency impedance module $|Z|_{0.01Hz}$ [16,17] in Bode plot is around $10^7\Omega\bullet cm^2$, which means the stage of medium permeating process through the organic coating and the coating system has a good performance (Fig. 1(A) and (a)). In the middle stage, the capacitive radius semi-arc decreases quickly and gradually transitions to two time-constants, along with low frequency impedance module $|Z|_{0.01Hz}$ decreasing to around $10^6\Omega\bullet cm^2$, which means the stage of corrosion initiation and extending under organic coating and the coating system has certain protective performance(Fig. 1(B) and (b)). In the later stage, more than one time-constant and diffusion tail are observed, along with low frequency impedance module $|Z|_{0.01Hz}$ decreasing to around $10^5\Omega\bullet cm^2$, which indicates that the progress is dominated by diffusion and the protective performance of coating system is seriously deteriorated(Fig. 1(C) and (c)).

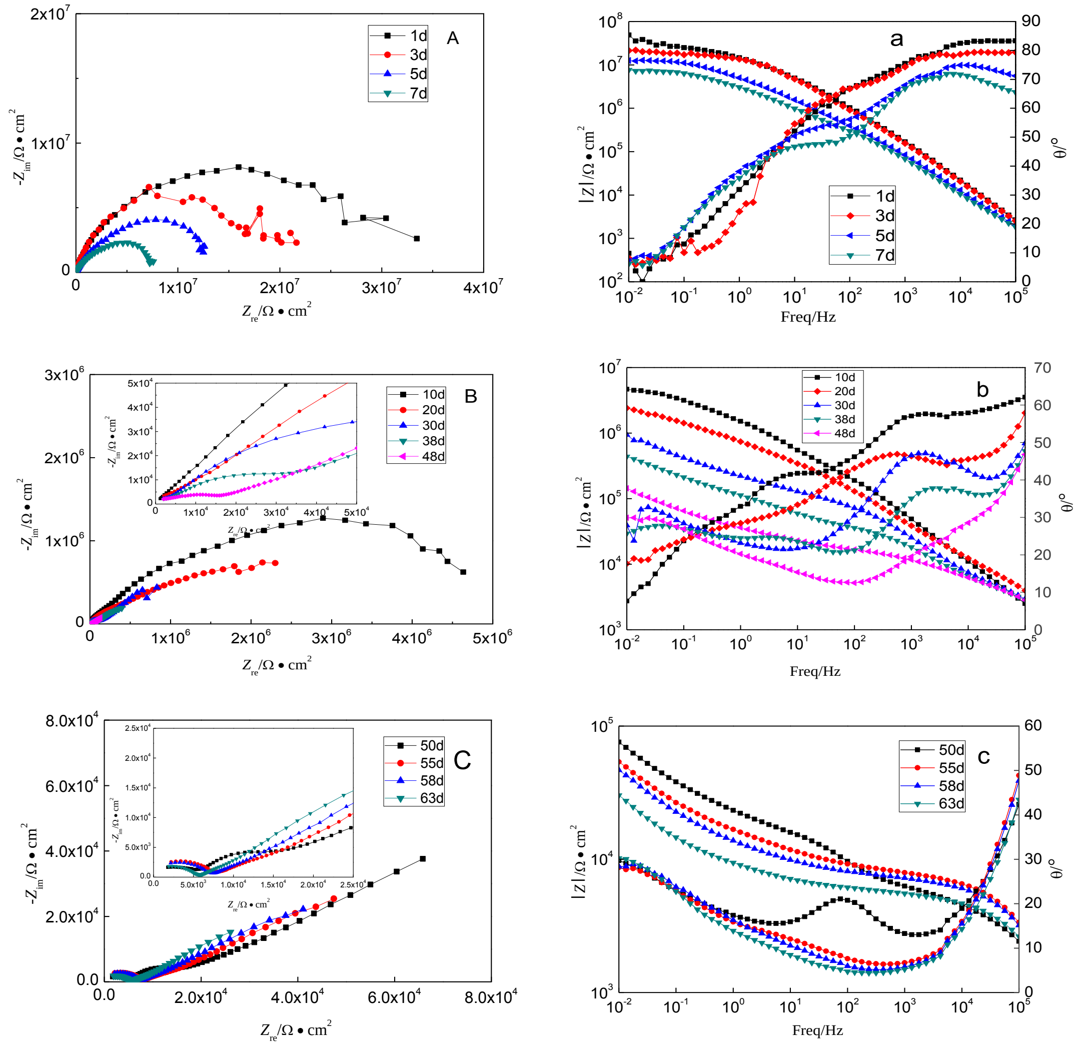


**Figure 1.** EIS plots of coating system after immersed in 3.5% NaCl solution with different time

### *3.2 The changing rate of phase angle at high frequency*

Fig. 2 shows the phase angle at high frequency of Bode plots of organic coating in different immersion time. It is clear that the phase angle at high frequency almost equal to a horizon linear in the earlier stage and the change becomes bigger and bigger along with the extension of immersion time, which indicates that the protective performance of coating system becomes worse and worse. So the changing rate of phase angle at high frequency satisfying Eq. (1) [11] can reflect the deterioration process of organic coating to a certain degree.

$$k(f) = \left| \frac{d\theta}{d(\log f)} \right| \quad (1)$$

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

$$k(f) = \frac{\left|\theta_{f_i} - \theta_{f_{i-1}}\right|}{\log f_i - \log f_{i-1}}, \ i=1,2\ldots n \quad (2)$$

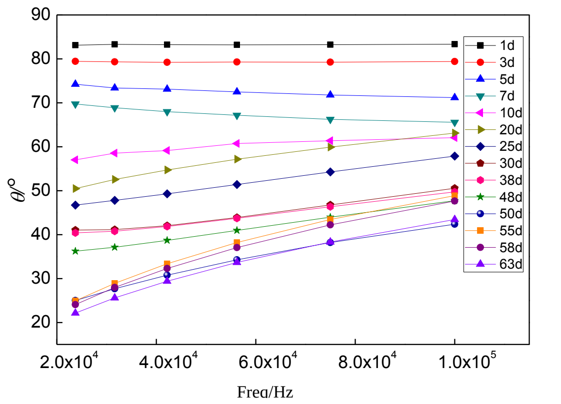


**Figure 2.** Bode plots of coating system at high frequency

Because of the impedance of capacitor cannot be ignored when frequency is intermediate or low, the frequency will be confined near to the high frequency of $10^5$ Hz. Otherwise, Eq. (1) and Eq. (2) are unavailable.

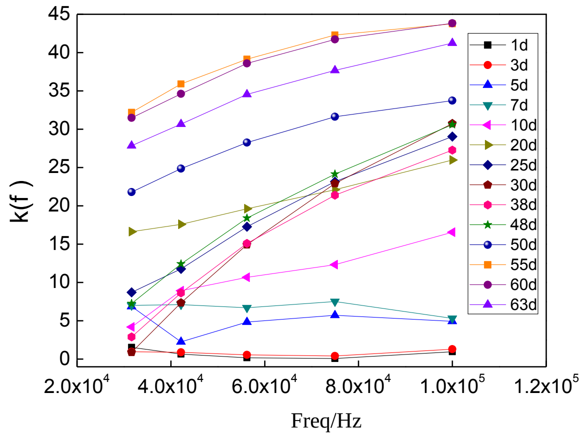


**Figure 3.** The changes of *k*(*f*) at high frequency with immersion time

All the $k(f)$ data were calculated by the Bode plot in the frequency range between $3.0\times10^4$ Hz and $10^5$ Hz everyday according to Eq. (2). As shown in Fig. 3, similar decreasing tendencies can be observed between phase angle at high frequency and the parameter $k(f)$. It is clear that the changing rate of phase angle at high frequency also almost equal to a horizon linear in the earlier stage and the change becomes bigger and bigger along with the extension of immersion time. So with the help of parameter $k(f)$, the deterioration process of organic coating can be distinguished effectively without fitting equivalent circuit and analyzing other parameters.

### *3.3 Analysis of neural network for coating system*

Training sample of neural network was based parameter $k(f)$ obtained in a frequency range between $3.0\times10^4$ Hz and $10^5$ Hz [11,13], include $3.162\times10^4$ Hz, $4.217\times10^4$ Hz, $5.623\times10^4$ Hz, $7.499\times10^4$ Hz and $10^5$ Hz. The parameter $k(f)$ was analyzed using Neural Network Toolbox function based on the Matlab 7.0 [18]. First, the function of net=newsom(minmax(P),[n 1]) was used to build a self-organizing feature map, then, the functions of train and sim were used to train and emulate for 63(days in this experiment) training samples, respectively. $P$ was 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 changes of deterioration process of organic coating [14]. After 400 times of network training, activation level in the output layer was obtained under different $n$ values. When the value of $n$ was excessively big, activation level in the output layer would be more and the classification would be more specific, and there would be no need for classifying the failure state of coating too specifically. But when the value of $n$ was excessively small, the classification difference generated would be very small, and the change of activation level in the output layer would be small as well so that it could not reflect the failure state of coating detailedly. When $n$ was equal to 35, the classification result was already able to offer the classified information about the deterioration process of organic coating clearly.

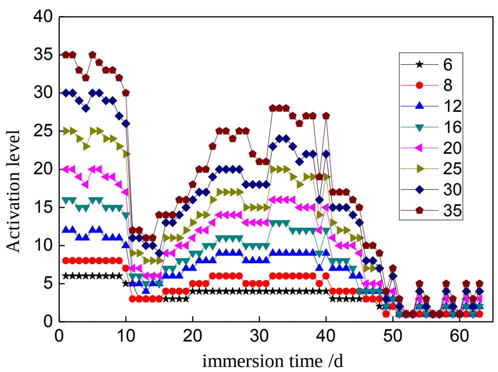


**Figure 4.** Tendency of activation levels with the immersion time

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 the immersion time were given in Fig. 4 under the condition that n=6, 8, 12, 16, 20, 25, 30, 35. The general trend of activation level in the output layer along with the changes of immersion time could be divided into three stages [14,19] as follows:

Stage Ⅰ (1-9 days), as the extension of immersed time, activation level in the output layer tended to decline by degrees, but the fluctuation was not wild. In addition, the capacitive radius semi-arc decreased by degrees, and low frequency impedance module $|Z|_{0.01Hz}$ decreased by degrees as well. This indicated that the micropores become more and larger in the coating. The coating was degraded little by little, but the corrosion medium did not reach to the interface of coating/matrix [9,15]. At this moment, the coating was an isolated layer and it could insolate between matrix metal and water. It indicated that this stage was medium permeating process through the organic coating and the coating system has a good performance [20].

Stage Ⅱ (10-47 days), the neuron in output layer dropped to a lower activation level suddenly and rapidly, and it rose to a certain activation level after a short time. EIS transferred to two time-constants gradually, and low frequency impedance module $|Z|_{0.01Hz}$ tended to keep declining, which indicated that the corrosion medium had spilled over into the interface of coating/matrix, and then corrosion reaction started to come up. The cause of the rising of activation level was that there was reaction between zinc phosphate and corrosion medium. It indicated that this stage was corrosion initiation and extending under organic coating and the coating had a particular barrier property.

State Ⅲ (48-63 days), the neuron in output layers dropped to a very low level suddenly and rapidly, and tended to be stable and constant. EIS showed multiple time constants, which indicated a rapid corrosion process under the coating, and the coating appeared to peel off. It indicated that this stage was corresponded to coating peeling and failure and the coating had lost its protective performance.

## 4. CONCLUSTIONS

According to characteristics of EIS, changing rate of phase angle at high frequency *k*(*f*) and the classification results by neural network, the deterioration process of organic coating can be divided into three stages: Stage Ⅰ: medium permeating process through the organic coating, Stage Ⅱ: corrosion initiation and extending under organic coating, State Ⅲ: coating peeling and failure. The result indicates that the changing rate of phase angle at high frequency show the similar decreasing tendencies with the phase angle at high frequency, which means that the parameter *k*(*f*) is a helpful parameter and combined with neural network can be used for studying the deterioration process of organic coating.

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