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Short Communication

Evaluation on Protective Performance of Organic Coatings by Analyzing the Change Rate of Phase Angle at High Frequency

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Some parameters are valuable in analyzing the organic coating performance such as coating resistance, coating capacitance, charge transfer resistance, double layer capacitance, while their extraction from EIS data is usually time-taking, furthermore, there may be some errors in calculating EIS data with equivalent circuit method. In this paper an attempt is made to introduce a new parameter obtained from the change rate of phase angle of Bode at high frequency in the electrochemical impedance spectroscopy (EIS) data. The new parameter (μ) then proved to be effective when evaluating the protective performance of a kind of grey organic coating used in vehicle equipment. The results indicated that this parameter has a good agreement with the phase angle at middle frequency of 10 Hz and the phase angle at high frequency of 10k Hz, respectively. It is concluded that the parameter can be used for fast evaluation of organic coatings in practical application.

Keywords: Corrosion; Organic coating; Fast evaluation; Electrochemical impedance spectroscopy

1. INTRODUCTION

Not long after electrochemical impedance spectroscopy (EIS) found its way in corrosion studies, its power in impedance measurement at a very wide range of frequencies makes it possible to provide abundant information about degradation degree of metals coated polymers [1-7]. Some parameters about corrosion can be obtained such as coating resistance, coating capacitive, double capacitance and charge transfer resistance [8-11] by electrochemical equivalent circuit model (EECM) fitting, but the problem comes that the measured data points are not usually completely fitted with the EECM, to be exact, the exact EECM is sometimes difficult to select and time-consuming at least. For example, when studied a kind of complicated multilayer coating exposed to electrolyte, great changes in calculated data can be observed reflecting the EIS characteristics, the range of which sometimes reach up to more than 2 orders of magnitude. What's more, signal draft and scattered data often occur when measured at low frequencies. On the other hand, some other parameters from Bode plots can also be used to evaluate the performance of protective organic coating without long time and errors in calculation. Mansfeld *et al* [12] proposed two parameters, the minimum phase angle θ_{min} and its frequency $f_{\theta min}$. It's shown that θmin and the ratio fb /$f_{\theta min}$ are both dependent on the delaminated area between coating and metal. Sekine *et al* [13] found that there is a linear relation between $f_{\theta max}$ and Rc, where $f_{\theta max}$ is the frequency at which the phase angle is maximum and Rc the coating resistance. The relationship can be served as a criterion of coating resistance, since $f_{\theta max}$ can be measured quickly. Haruyama and Sudo [14] proposed the concept of breakpoint frequency fb, at which the phase angle firstly falls to 45°, and found a good correlation between the breakpoint frequency and the delaminated area of coating from the metal substrate. Mahdavian and Attar [15] analyzed the difference in performance of zinc chromate and zinc phosphate coating with the phase angles at 10 kHz (θ_{10kHz}). Zuo *et al* [16] observed that the phase angle at 10Hz (θ_{10Hz}) may qualitatively reflect the coating performance. Xia *et al* [17] proposed a new parameter of coating degradation coefficient by analyzing the changing rate of impedance which correlates well with the protective performance of organic coating. The advantage of above methods is that the parameters are mainly obtained in middle and high frequency domains of EIS, as a result, the measurements in low frequency domains and complicated fitting and calculation for EIS data can be avoided. It is possible to develop fast coating evaluation methods with the parameters above from Bode plot. However, compared with equivalent circuit analysis, more studies on different coating systems are necessary to establish the relationship between parameters from Bode plot and coating performance.

In this paper, a characteristic parameter μ named availability coefficient is described and extracted directly from Bode plot. The extraction process of the parameter μ in high frequencies domain will be analyzed theoretically, followed by practical evaluation example with a kind of grey organic coating, which made better understood the interconnection between the change rate of phase angle of organic coating and its performance.

2. THEORETICAL ANALYSIS

For an organic coating with high coating resistance, the ECCM can be simplified to a parallel circuit with only coating resistance Rc and coating capacitive Cc when supposing the solution resistance Rs is negligible (Fig.1) , and the impedance Z is given by Eq.(1).

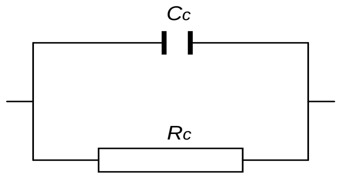


Figure 1. Simplified EECM for intact high impedance coating

$$Z = \frac{1}{Y} = \frac{1}{\frac{1}{R_C} + j\omega C_C} = \frac{R_C}{1 + j\omega R_C C_C} \tag{1}$$

Where angular frequency $\omega = 2\pi f$,and f is the frequency applied.

$$Z' = \frac{R_C}{1 + \left(\omega R_C C_C\right)^2} \tag{2}$$

Where Z′ is the real part of Z

$$Z'' = \frac{\omega R_C^2 C_C}{1 + \left(\omega R_C C_C\right)^2} \tag{3}$$

Where Z″ is the imaginary part of Z,

$$\vartheta = arctg(-\frac{Z''}{Z}) = arctg(\omega R_C C_C) \tag{4}$$

Where θ is the phase angle of Z,

$$k(f) = \left|\frac{\mathrm{d}\theta}{\mathrm{d}(\log f)}\right| \tag{5}$$

From the definition above, we know that k(f) equals to the slope of Bode phase angle. For the discrete EIS data, the differential form will be replaced by a derivative form:

$$k(f) = \frac{|\theta_{f_i} - \theta_{f_{i-1}}|}{\log f_i - \log f_{i-1}} = \frac{|\theta_{f_i} - \theta_{f_{i-1}}|}{\log 1.33}, \quad i = 1, 2, \ldots n \tag{6}$$

$$Z\mathrm{resistor} = \mathrm{Zre} + j\ \mathrm{Zim} = R \tag{7}$$

$$Z\mathrm{capacitor} = \mathrm{Zre} + j\ \mathrm{Zim} = j\ [-1 / (2\ \pi\ f\ C\mathrm{c})] \tag{8}$$

As shown in Eq. (7) and Eq.(8), a resistor's impedance does not change with frequency, but a capacitor's impedance is inversely proportional to the frequency. At very high frequency the impedance of a capacitor is nearly zero, the impedance of a capacitor becomes so much smaller than *R*c that all the current flows through the capacitor rather than *R*c, so the capacitor acts as if it were as a zero ohm impedance or as just a piece of wire. The overall impedance in the circuit equals to the impedance of *R*s. This leads to the resistive behavior at the very high frequency [18]. Beginning from this state, that the frequency decrease a little will cause a little increase of the impedance of *C*c accordingly, as a result, a very tiny current will be diverged from the capacitor, which will meantime cause the change of the phase at its frequency. If the *R*c is very large (vs the resistance of the capacitor), the change of the current flowing through the capacitor will be very little , as a result, a very little change of θ will be caused accordingly, for the denominator of *k*(f) is a constant (See equation (6)), *k*(f) will be also close to zero, on the contrary, if the *R*c is very small, the change of current flowing through the capacitor will be much ,accordingly, the change of θ will also be very much, meantime, *k*(f) will be large. But when *f* decline to the intermediate even low frequencies domain, the impedance of the capacitor cannot be ignored, so the frequencies will be confined near to the high frequency of 100 kHz. The 56 kHz, 75 kHz and 100 kHz will be set as a practical example in this paper. The analysis above indicates a direct relation between *k*(f) (i.e. the change of phase angle) and coating impedance reflecting coating performance, to be exact, *k*(f) at high frequency next to 100kHz can reflect the coating performance.

The next is to theoretically calculate the $\mathrm{Max}_{f(k)}$ of *k*(f) by formula derivation. Combining with Eq.(4) and Eq.(5), a derivative equation will be gained as follows,

$$k(f) = \frac{\ln 10}{\frac{1}{2\pi f \omega R_C C_C} + 2\pi f \omega R_C C_C} \times \frac{180^\circ}{\pi} \tag{9}$$

Then the range of *k*(*f*) can be described as follows,

$$0 \le k(f) \le 65.964^\circ , \tag{10}$$

Here unify the unit of angle as the slope of the phase angle curve in Bode.

Define the availability coefficient μ of coating performance:

$$\mu = 1 - \frac{|k(fi)|}{65.964^\circ} , \quad 0<\mu<1, \quad (i=1,2,\ldots n) \tag{11}$$

Where *k*(*f*i) is the derivative value when the frequency applied change range from 56k to 100kHz.

The relation between μ and the coating performance is explained as follows, At the initial stage of immersion, the *R*c of coating is very large, when the frequency descend from the 100kHz, the change of the current flowing through the capacitor will be very little, and the change of phase angle θ very little accordingly, therefore, *k*(f) will be close to zero, and μ close to 1 ,which indicates that the coating has a good performance; with the immersion time elapsing, the *R*c of coating decrease, when the frequency decrease from the 100kHz, the change of the current flowing through the capacitor will enhance, and the change of the phase angle θ increase accordingly, and *k*(f) will also gradually augment approaching the theoretical maximum of 65.964°, and μ will gradually be close to zero, which indicates that the coating performance is deteriorated.

3. EXPERIMENTAL METHODS

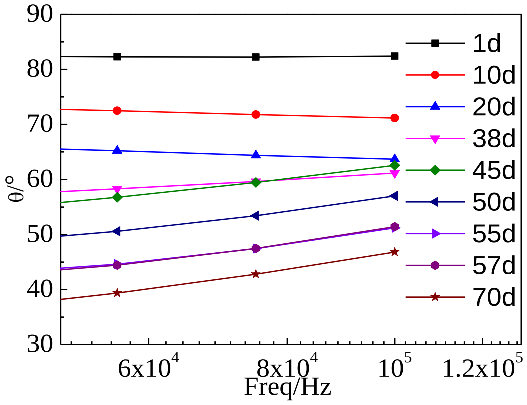
In order to verify the theoretical analysis above, experiments on a kind of grey organic coating were carried out.

The mental substrate was made from hot-rolled steel panel T610L, with a size of 60×60×1mm. The mental substrate was firstly treated with zinc phosphate, and then is electrophoresed with grey crylic acid and polyester, and finally coated with hydrophilic topcoat. The thickness of the coating was 35.34±0.1μm and the working area was 7.07cm^2.

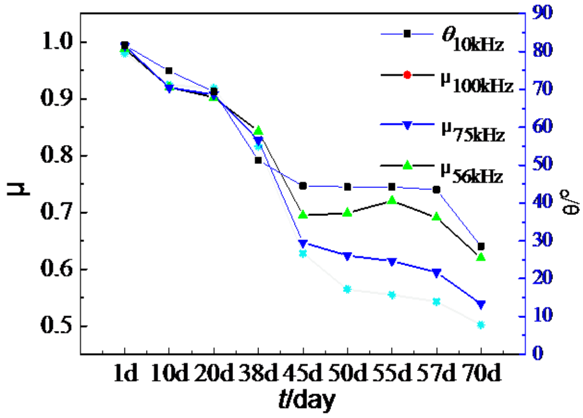
The EIS measurements were carried out in an electrolytic cell using a PARSTAT 2263 electrochemical workstation (Princeton Applied Research, USA).EIS measurements were performed at the open-circuit potential with a 10 mV amplitude signal and the applied frequency ranged from 100 kHz to 10mHz.The sample was immersed in 3.5% NaCl solution at room temperature (23±2℃) examined periodically. A Three-electrode cell was used which the grey organic coating as the working electrode (WE), a saturated calomel electrode (SCE) as the reference electrode (RE) and a ruthenium electrode as the counter electrode (CE).

4. RESULTS AND DISCUSSIONS

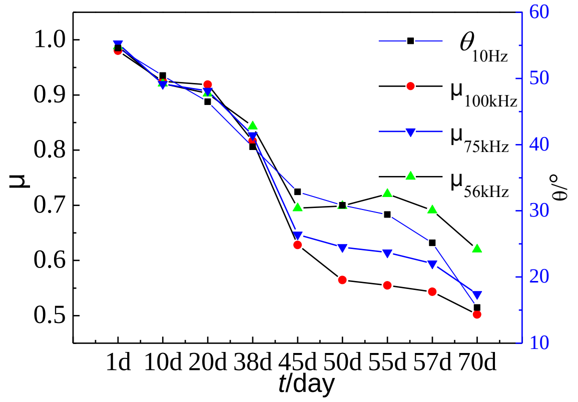
Fig.2 (a) shows the Bode phase plot of grey organic coating in high frequency domain in different immersion time. It is clear that the slope of organic coating ｜*k*(f)｜increase gradually with different immerse time. It can be observed that the impedance at low frequency on the first day keep at the magnitude order of 10^7Ω•cm^2 indicating a good coating performance [19], and the change rate of phase angle curve in Bode at high frequency with immersion time almost gradually increased while corresponding impedance at low frequency continually decreased (Fig.3). It fallen down to the magnitude order of 10^5Ω•cm^2 on the 70th day, indicating a very low coating performance. It discloses that the *k*(f) (i.e. the change rate of phase angle curve) reflects the performance of this kind of organic coating.



(a) Bode plot of grey organic coating in high frequency



(b) Availability coefficient μ at 56 kHz,75 kHz and 100 kHz compared with θ_{100kHz} with different immersion time



(c) Availability coefficient μ at 56 kHz, 75 kHz and 100 kHz compared with θ_{10Hz} with different immersion time

Figure 2. Bode plot and calculated availability coefficient μ compared with θ_{100kHz} and θ_{10Hz}

Fig.2 (b) and (c) show the relationship between the availability coefficient μ calculated at 56 kHz, 75 kHz and 100 kHz with different immersion time respectively. It is observed that μ_{56kHz}, μ_{75kHz} and μ_{100kHz} show the similar decreasing tendencies. Moreover, compared with change trend of the phase angle at 10Hz and 10kHz (i.e. θ_{10Hz} and θ_{10kHz}), it is seen for the studied coating that the decreasing tendencies of μ_{56kHz}, μ_{75kHz} and μ_{100kHz} are also close to the decreasing tendencies of θ_{10Hz} and θ_{10kHz} respectively with different immersion time which both proved to be the efficient evaluation parameters by others listed before. Therefore, the good correlation observed between μ and θ_{10Hz} and θ_{10kHz} leads us to believe that μ is another parameter which could be used to evaluate coating performance quickly.

The measured EIS plots of grey organic coating are shown in Fig.3 with different immersion time, where *Z*im is the imaginary part of *Z* and *Z*re is the real one of *Z* . On the first day, the capacitive radius semi-arc is very large with only one time-constant in the Bode and the large impedance of $5.0\times10^7\Omega\bullet cm^2$ at the low frequency (Fig. 3(a) and (a′)), meantime $\mu > 0.98$， which indicates the organic coating has a good performance. After 10 days, the semi-arc in Nyquist decreases quickly, there exists 2 time-constants in the Bode (Fig. 3(a′)). The time-constant at the high frequency is the result of interface capacitance and pore resistance of organic coating, the one at the low frequency come from double layer capacitance and charge transfer resistance caused by mental substrate, which discloses that the electrolyte has permeated through the pore of the organic coating. At this time, the impedance at low frequency has decreases to $1.2\times10^7\Omega\bullet cm^2$, reflecting a better coating performance (Fig. 3(a)), meantime $\mu > 0.90$. With the passage of exposure time, on the 38th day, three time-constants in the Bode plot is observed (Fig. 3(b′)), the impedance at low frequency has fallen down to the magnitude order of $10^6\Omega\bullet cm^2$, and the capacitive radius at low frequency is raising, reflecting an increasing corrosion resistance under the organic coating during the degraded progress for some time (Fig. 3(b)). When it comes to the 70th day, an apparent diffusion tail is observed on the Bode plot (Fig. 3(c)), which indicates that the corrosion progress is dominated by diffusion, and severely corrosion occurred under the coating. Combining with the impedance of $10^5\Omega\bullet cm^2$ at the low frequency (Fig. 3(c′)), it's found that the coating system is seriously deteriorated and basically lose its protection performance, at this time, $\mu < 0.7$.

As is known, impedance at low frequencies [17, 20-24] is often used to evaluate coating performance, but it is always time-taking, and sometimes errors occur in measurement for the drafting signal (fig.3(a)), while, the parameters such as *f*b, $f_{\theta max}$, θ_{min} listed before are just more applicable for comparison among different coatings, and the change range of the parameters θ_{10Hz} and θ_{10kHz} from time to time vary wildly with different coating system, which will cause barriers to evaluate coating performance. Compared with the parameters mentioned above, the change of the availability coefficient μ is relatively more mildly, furthermore the change rate of phase angle at high frequencies for the experimenter can be quickly, directly and vividly observed on the Bode plot when testing, which is convenient to arrive at a fast and right conclusion about the coating performance [25-30].

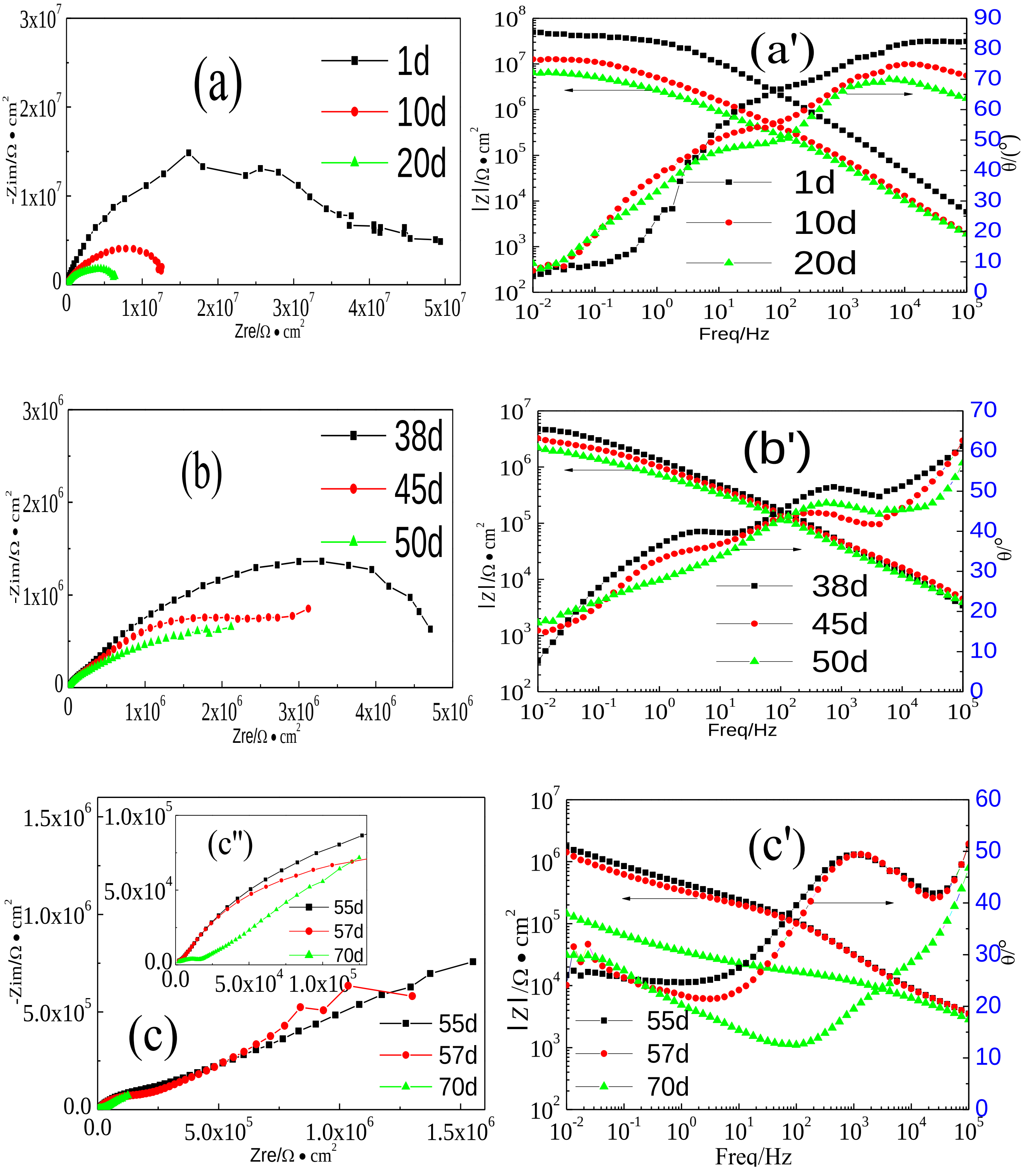


Figure 3. EIS plots of grey coatings of vehicle equipment after immersed in 3.5%NaCl solution with different time

According to the availability coefficient μ, the entire degradation progress of the organic coatings system could be fallen into three main stages. Stage Ⅰ is the medium penetration into coating, which corresponds to $\mu > 0.90$; stage Ⅱ is the initial corrosion stage under organic coating, which corresponds to μ > 0.70; stage Ⅲ is the corrosion extending and coating become invalid, which corresponds to μ < 0.70. From the analysis above, it can be concluded that there is a good decreasing tendencies between μ and coating performance. It should be emphasized that it is the variation tendencies of the phase angle next to highest frequencies, not their values, play the major role in reflecting the coating performance. The conclusion above is mainly applicable for the grey organic coating studied. However, for other coating systems, the value of availability coefficient μ in high frequency domain at different corrosion stage may be more or less different. If the coating system and corrosive medium is determined, it also possible to evaluate the protective performance of organic coating to be studied. More work is underway.

5. CONCLUSIONS

A new method of fast evaluation of the organic coating performance was proposed without EECM fitting and complicated calculation for EIS data. The availability coefficient μ was used to evaluate the organic coating performance which was extracted from Bode phase plot at the high frequency next to 100 kHz. The result indicates that the parameter μ show the similar decreasing tendencies with the performance evaluation parameters of organic coating $\theta_{10\text{Hz}}$ and $\theta_{10\text{kHz}}$, which discloses that μ is fast and effective to evaluate the protective coating performance of grey organic coatings. However, it still needs to be verified further by more samples.

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