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The Evaluation of Coating Performance by Analyzing the Intersection of Bode Plots

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In this paper, a new parameter named as IBP (intersection of Bode plots) was proposed to evaluate the coating performance by directly analyzing the Bode plots. The electrochemical impedance data of three coating systems in 3.5% sodium chloride solution were measured and the IBP correlated well with the results of coating resistance R_c and low frequency impedance $|Z|_{0.1Hz}$. It is concluded that IBP can be used for the evaluation of coating performance in practical applications.

Keywords: electrochemical impedance spectroscopy; coating performance; intersection of Bode plots

1. INTRODUCTION

The electrochemical impedance spectroscopy (EIS) has been widely used in the investigation of the performance and degradation degree of coatings because of its good ability to provide abundant information [1-7]. As we know, by fitting electrochemical equivalent circuit (EEC) models, some electrochemical parameters related to the coating performance can be obtained, such as coating resistance, coating capacitance, double-layer capacitance and transfer resistance, and these parameters are very useful in analysis of the protective performance of coatings. However, it is difficult to select satisfied equivalent circuit models for some complicated coating systems, and an equivalent circuit involving three or more circuit elements can often be rearranged in various ways and still yield exactly the same impedance [8, 9].

In certain cases, the evaluation of coating performance by extracting the characteristic parameters from Bode plots of the electrochemical impedance spectroscopy has a useful theoretical and practical value. Shiro et al [10] found a good relationship between the breakpoint frequency f_b and the disbanded area of coating. Isao et al [11] observed a linear correlation between $f_{\theta max}$ and R_c, where $f_{\theta max}$ is the frequency at which the phase angle is maximum and R_c is the coating resistance. Mahdavian et al [12] used the theta at high frequency (10 kHz) to evaluate the performance of zinc phosphate and zinc chromate coatings. Zuo et al [13] used the phase angle at 10 Hz to evaluation the performance of several multi-layer coating systems. Akbarinezhad et al [14] found that decreasing percentages (DP) of the areas under Bode plots are convenient parameters for evaluating coating degradation.

In this paper, the possibility of using a new parameter IBP named intersection of Bode plots extracted directly from Bode plots as the discrimination indicator of the protective performance of coatings is described. The extracting process of parameter IBP is analyzed theoretically. The purpose of this paper is to further understand the interconnection between the IBP and coating properties, which may lead to a new evaluation method for coating performance in practical applications.

2. THEORETICAL ANALYSES

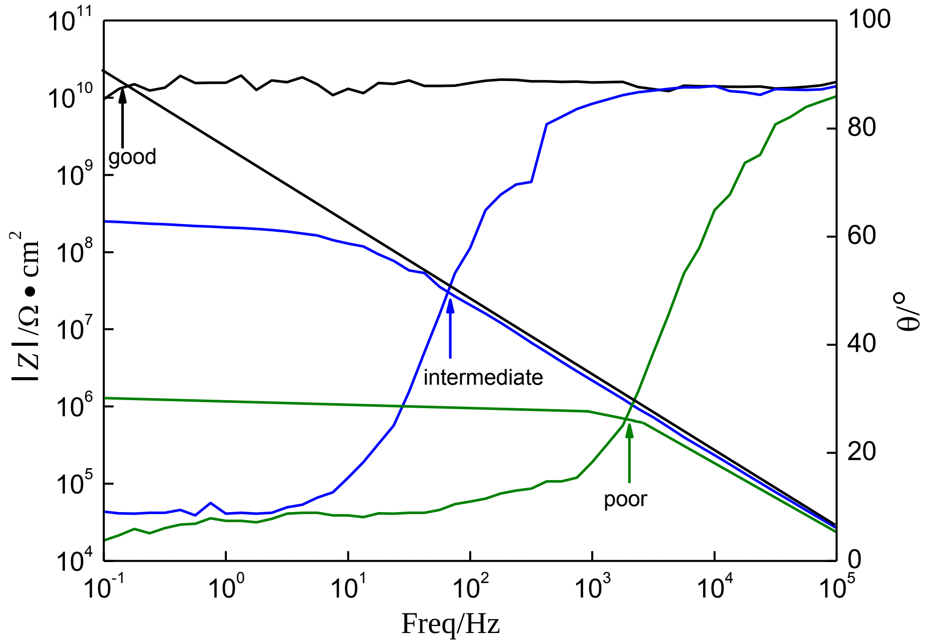

Figure 1. Typical Bode plots of good, intermediate, poor coating quality

It can be obtained typical Bode plots through analysis some electrochemical impedance spectroscopy [14, 15]. Figure 1 shows typical Bode plots when the coating performance is good, intermediate and poor, respectively. It can be seen in Fig.1 that the intersection of Bode phase plot and Bode impedance plot is in the upper left of Bode plots when the coating performance is good, the intersection is in the middle of Bode plots when the coating performance is intermediate, and the intersection is in the lower right of Bode plots when the coating performance is poor. The intersection of Bode plots (IBP) have been moved to the lower right gradually from a good performance coating to poor coating. At the same time, with the decrease of coating performance, the corresponding phase angle and impedance of IBP show similar decreasing tendencies, and the corresponding frequency shows gradually increasing tendency. Therefore, the IBP could be used as valuable references for evaluating the protective performance of coatings.

In order to find a simple and distinct analytical method, the test points of entire frequency range were numbered from 1 to n, and the first test point is 1, the next test point is 2 to n (n is the total number of test points and n is 49 in this paper). It can be found that the corresponding number of IBP reduces gradually with the decrease of coating performance. In particular, for the discreteness of EIS data, the intersection of Bode phase plot and Bode impedance plot may not be the measured points actually, and then the test point nearest the intersection could be used as IBP in this analysis.

3. EXPERIMENTAL

In order to verify the theoretical analyses above, experiments on the green organic coating, metallic paint coating and grey organic coating were carried out. All the samples used in this study were provided by the vehicle manufacturers of China， with a size of 60×60 mm. The thickness of green organic coating, metallic paint coating and grey organic coating was about 156.81um, 125.25um and 42.15 um, respectively.

EIS measurements were performed by PARSTAT 2263 electrochemical workstation and PowerSuite control software. A three-electrode cell was used which the coatings as the working electrode (WE), a saturated calomel electrode as the reference electrode (RE) and a ruthenium electrode as the counter electrode (CE). Impedance spectra were obtained at open circuit potential with a 10mV amplitude signal and the measuring frequency range was 0.1 Hz to 100 kHz. The samples were exposed to 3.5% sodium chloride solution at room temperature and examined p eriodically by EIS technique. The experimental data were analyzed by using commercial software ZSimpWin.

4. RESULTS AND DISCUSSION

4.1 Green organic coating

The measured Bode plots of green organic coating with different immersion time are shown in Figure 2, where |Z| is impedance modulus, and θ is phase angle. It is noted that Bode plots of the green organic coating was no overall change during the whole immersion time. And the slope of the impedance against frequency was about -1 and the phase angle was almost 90° for the coating. The Bode plots containing one time-constant were observed, indicating that the coating had a good protective performance and there was no electrolyte permeation through the coating. The corresponding equivalent circuit of green organic coating can be modeled as R_s (R_c C_c) during the whole immersion time.

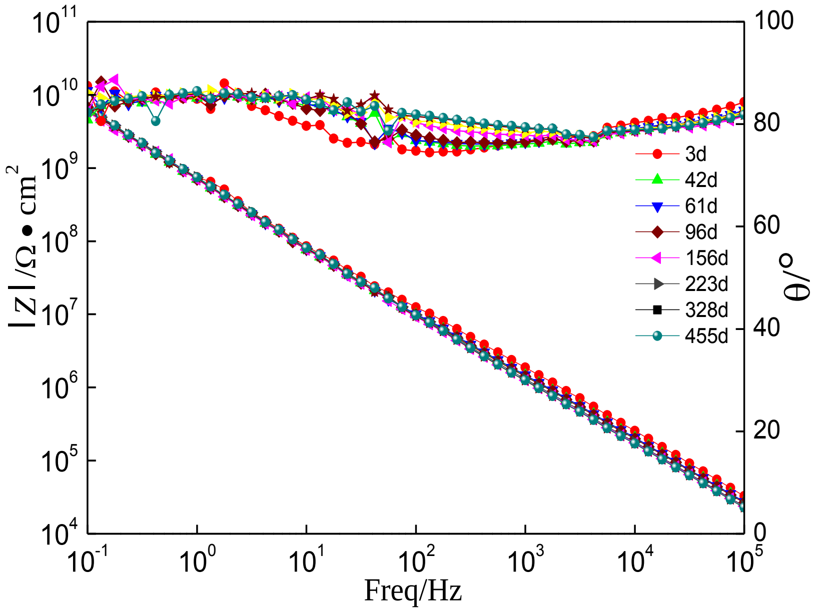

Figure 2. Bode plots of green organic coating in 3.5% sodium chloride solution

According to the measured Bode plots, the IBP was obtained for the green organic coating after processing by the theory above, as shown in Figure 3. From Fig.3 it can be seen that the IBP was in the upper left of Bode plots all the time, which proved that the green organic coating could still provide good protection after 455 d of immersion.

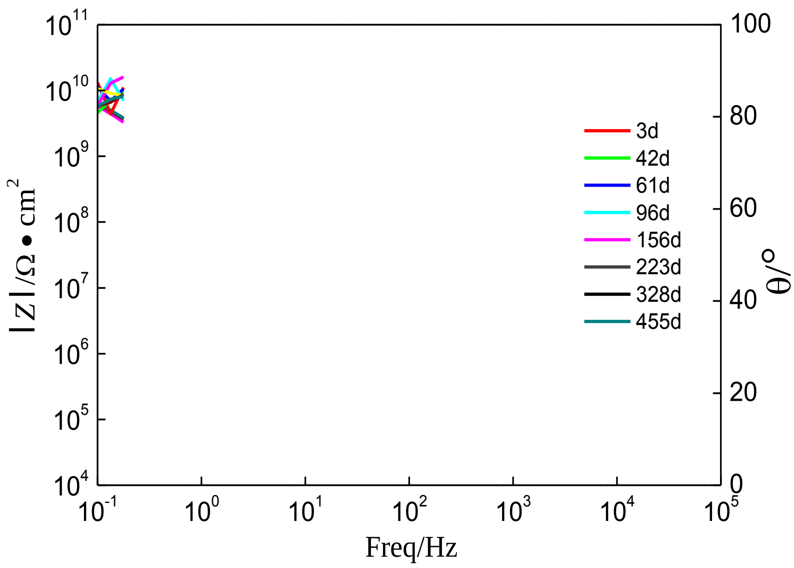

Figure 3. IBP of green organic coating with different immersion time

Figure 4 shows the change of IBP, coating resistance R_c and low frequency impedance $|Z|_{0.1Hz}$ of green organic coating with different immersion time. From Fig. 4 it can be seen that the value of R_c and $|Z|_{0.1Hz}$ was around $1.0\times10^{11}\Omega\bullet cm^2$ and $6.0\times10^{9}\Omega\bullet cm^2$, respectively, the number of IBP was 48 or 49, indicating that the coating had a good protective performance. The IBP, R_c and $|Z|_{0.1Hz}$ almost closed to a horizon linear and kept at a very high level, and the IBP showed similar tendency with R_c and $|Z|_{0.1Hz}$.

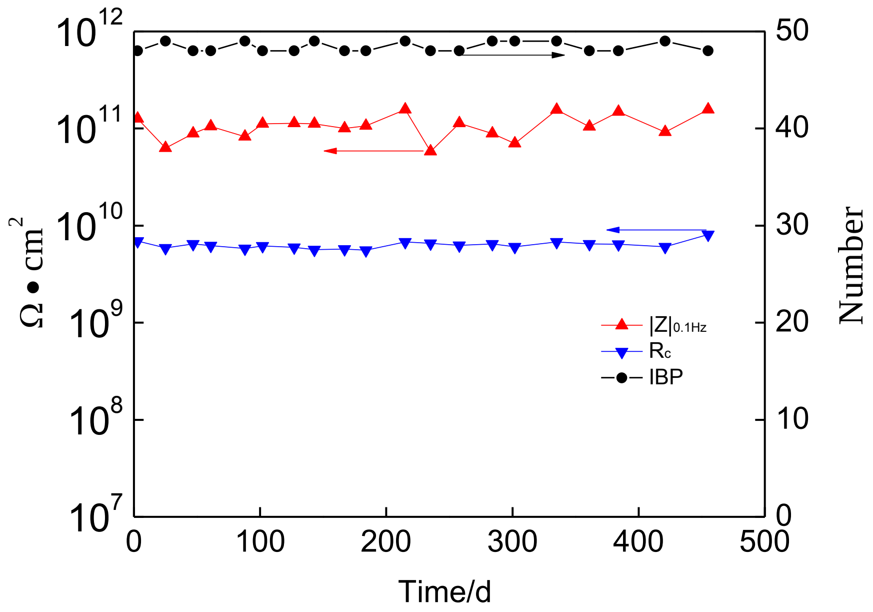

Figure 4. IBP of green organic coating compared with R_c and $|Z|_{0.1Hz}$

4.2 Metallic paint coating

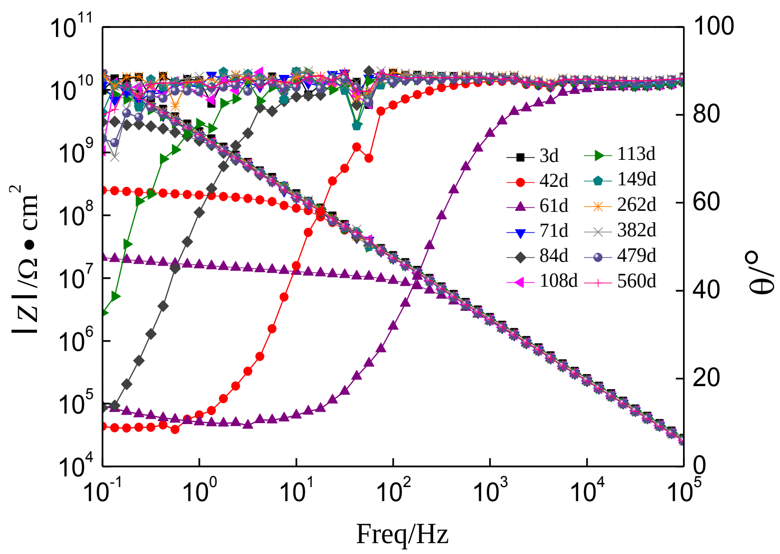

Figure 5. Bode plots of metallic paint coating in 3.5% sodium chloride solution

Figure 5 shows Bode plots of the metallic paint coating with different immersion times in 3.5% sodium chloride solution. For the first couple of days, Bode plots of the coating were composed of only one time-constant, indicating that the coating performance was good. After 42 d, the Bode plots with two time-constants were given. Two time-constants indicated that the electrolyte had permeated through the defects or pores in the metallic paint coating and double layer capacitance was formed in it. After 71 d, the Bode plots containing one time-constant were observed again. As the immersion time prolonged, the Bode plots with one or two time-constants were observed alternately, which means the coating had a good self-repairing capability. After 149 d of immersion, the Bode plots containing one time-constant were observed again and shown no overall change during the next immersion time. The corresponding equivalent circuit of metallic pain coating can be modeled as $R_s (R_c C_c)$ before 42 d, $R_s (R_c C_c)$ or $R_s (C_c (R_c Z_w))$ between 42 d and 149 d, and $R_s (R_c C_c)$ after 149 d.

According to the measured Bode plots, the IBP was obtained for the metallic paint coating after processing by the theory above, as shown in Figure 6. It can be seen in Fig. 6 that the IBP was in the upper left of Bode plots in the early stage of immersion, which proved that the coating could provide good protection. The IBP changed dramatically and transferred to the middle of Bode plots after 42 d, and reached the lowest position in this study after 61 d, indicating that the coating had an intermediate protective performance. But the IBP returned to the upper left of Bode plots after 71 d of immersion. As the immersion time prolonged, the IBP transferred to the middle and then returned to the upper left of Bode plots more than once, which means the coating had a good self-repairing capability. After 149 d of immersion, the IBP returned to the upper left of Bode plots again, and showed no overall change during the next immersion time.

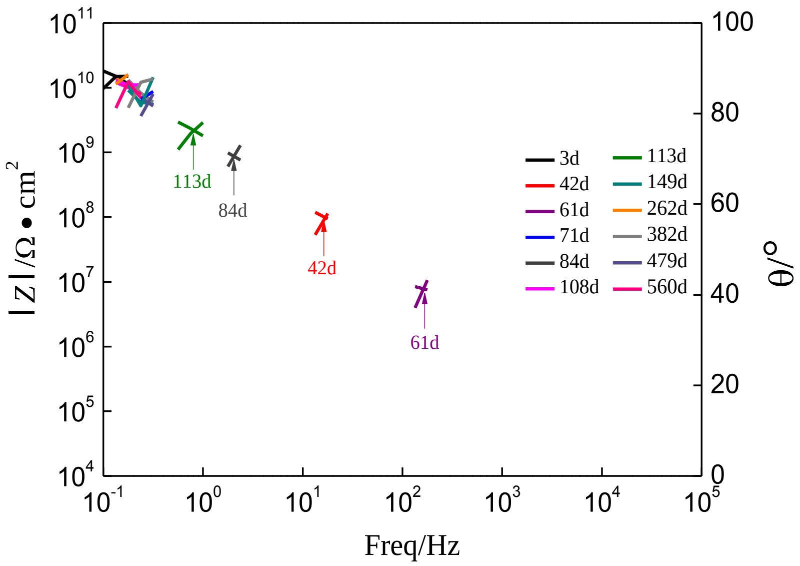

Figure 6. IBP of metallic paint coating with different immersion time

Figure 7 presented the change of IBP, coating resistance R_c and low frequency impedance $|Z|_{0.1Hz}$ of metallic paint coating during the immersing time. It can be seen that during the early 41 d, the value of R_c remained above 10^{11} Ω•cm^2, the value of $|Z|_{0.1Hz}$ remained above 10^{10} Ω•cm^2 and the number of IBP was around 47, indicating that the coating had a good protective performance. At 42 d, the value of R_c and $|Z|_{0.1Hz}$ suddenly decreased to the vicinity of 10^8 $\Omega\bullet cm^2$, while the number of IBP also quickly decreased to 31, indicating that the coating had an intermediate protective performance. The IBP, R_c and $|Z|_{0.1Hz}$ were observed a lot of fluctuations up and down between 42 d and 149d of immersion and close to a horizon linear after 149 d. The results of these parameters follow the same trend and are very close to each other.

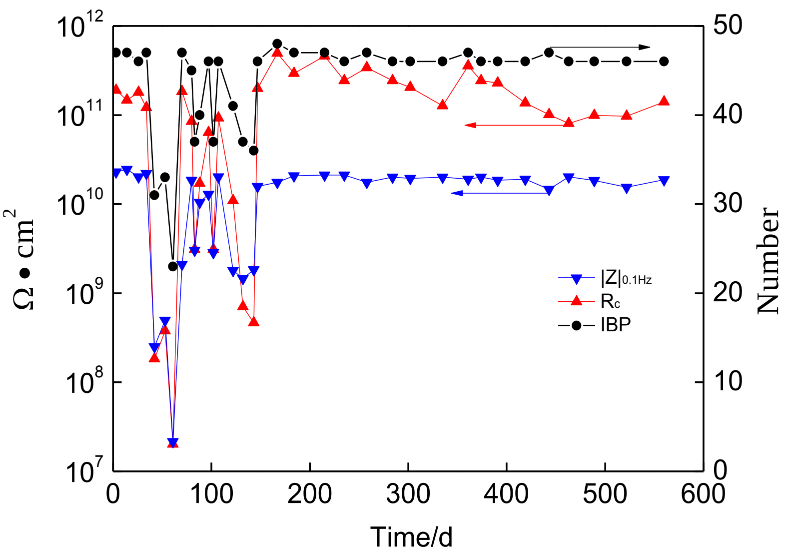

Figure 7. IBP of metallic paint coating compared with R_c and $|Z|_{0.1Hz}$

4.3 Grey organic coating

Figure 8 shows the Bode plots of grey organic coating exposed to 3.5% sodium chloride solution over a period of 63 d. During the early stage of immersion, the Bode plots showed a characteristic with one time-constant and the value of $|Z|_{0.1Hz}$ was below 10^8 $\Omega\bullet cm^2$, indicating the coating system had an intermediate performance and there was no electrolyte permeation through the coating. After 7 d, there were two time-constants in the Bode plots and the value of $|Z|_{0.1Hz}$ was below 10^7 $\Omega\bullet cm^2$, indicating the coating system had a poor performance. The time-constant at high frequency was a result of interface capacitance and surface pore resistance of organic coating; the time-constant at low frequency was caused by metal substrate double layer capacitance and charge transfer resistance, reflecting the corrosion rate of metal substrate. The corresponding equivalent circuit of grey organic coating can be modeled as $R_s (R_c C_c)$ before 7 d and $R_s (C_c (R_c (C_{dl} R_{ct})))$ after 7 d. According to the measured Bode plots, the IBP was obtained for the grey organic coating after processing by the theory above, as shown in Figure 9. It can be seen in Fig. 9 that the IBP was in the middle of Bode plots in the early stage of immersion, which proved that the coating could provide intermediate protection. With the increase of immersion time, the IBP moved to the lower right of Bode plots gradually until the coating system basically lost its protection.

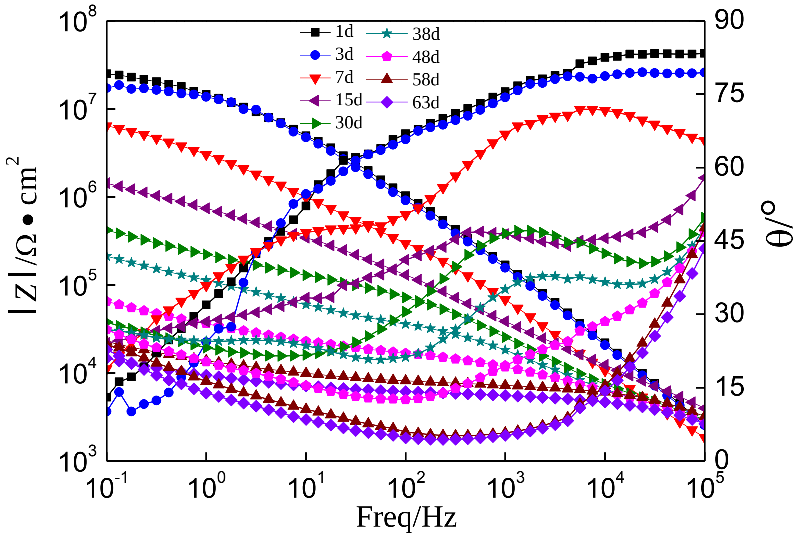

Figure 8. Bode plots of grey organic coating in 3.5% sodium chloride solution

The coating resistance R_c obtained from the electrochemical circuit above, the low frequency impedance $|Z|_{0.1Hz}$ and IBP of grey organic coating are shown in Figure 10. It was found that the number of IBP decreased from 30 to 10, both the value of R_c and $|Z|_{0.1Hz}$ decreased by 3 order of magnitude, from 10^8 Ω•cm^2 to 10^5 Ω•cm^2 and 10^7 Ω•cm^2 to 10^4 Ω•cm^2, respectively, indicating that the coating had an intermediate protective performance for the first couple of days and was corroded continuously as the immersion time prolonged. The variation of IBP with time was very close to the variation of R_c and $|Z|_{0.1Hz}$.

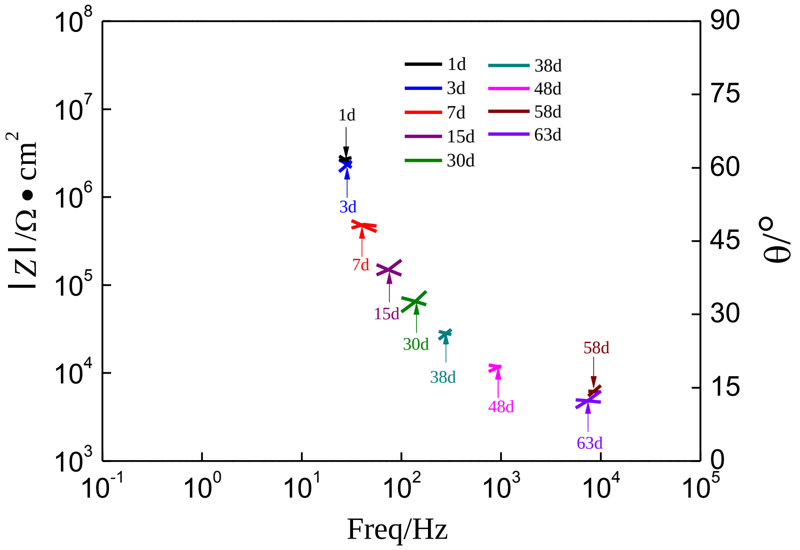

Figure 9. IBP of grey organic coating with different immersion time

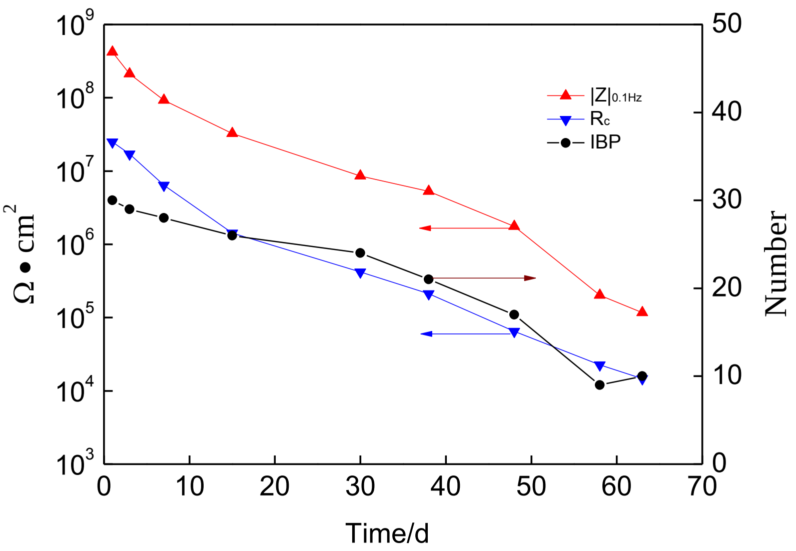

Figure 10. IBP of grey organic coating compared with R_c and $|Z|_{0.1Hz}$

As we know, abandon information related to the coating performance could be obtained by fitting electrochemical equivalent circuit models [1-7], but it is always time-taking. And other parameters such as f_b, $f_{\theta max}$ and θ_{10Hz} [10-13] could be extracted from Bode plots, but those parameters only use the information form Bode phase plot. Compared with the method mentioned above, the advantage of the parameter was that the parameter was obtained more quickly and easily, and uses the information both Bode phase plot and Bode impedance plot. From the analysis above, the IBP could be easily calculated from Bode plots. The variation of IBP also showed a good coincidence with the coating resistance R_c and low frequency impedance $|Z|_{0.1Hz}$, and can reflect the coating performance.

5. CONCLUSIONS

In this paper, a new parameter named as IBP of evaluation of the protective performance of coatings was presented. The parameter IBP extracted directly from Bode plots was presented to the discrimination indicator of coating performance. The results showed that the IBP, R_c and $|Z|_{0.1Hz}$ are in the same tendency. The method could be used as a good criterion for the evaluation of coating performance without constructing the equivalent electrical circuits. However, it still needs to be verified further by more samples.

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