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# Electrochemical Evaluation Technologies of Organic Coatings

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## Abstract

Organic coatings are widely utilized to protect metals from corrosion and inevitably suffer degradation due to exposure to surroundings. Electrochemical technology is suitable for evaluating the protective performance of organic coatings since it has the advantages in rapidity and in-situ measurement. In this chapter, several electrochemical measurement technologies including open circuit potential (OCP), linear polarization resistance (LPR), electrochemical impedance spectroscopy (EIS) as well as electrochemical noise (EN) are introduced as ideal methods for acquiring mechanistic information about the failure behavior of the painted metal. The research status on measuring configurations, choosing data acquisition parameters and analytical methods are also discussed.

**Keywords:** organic coatings, open circuit potential, electrochemical impedance spectroscopy, electrochemical noise

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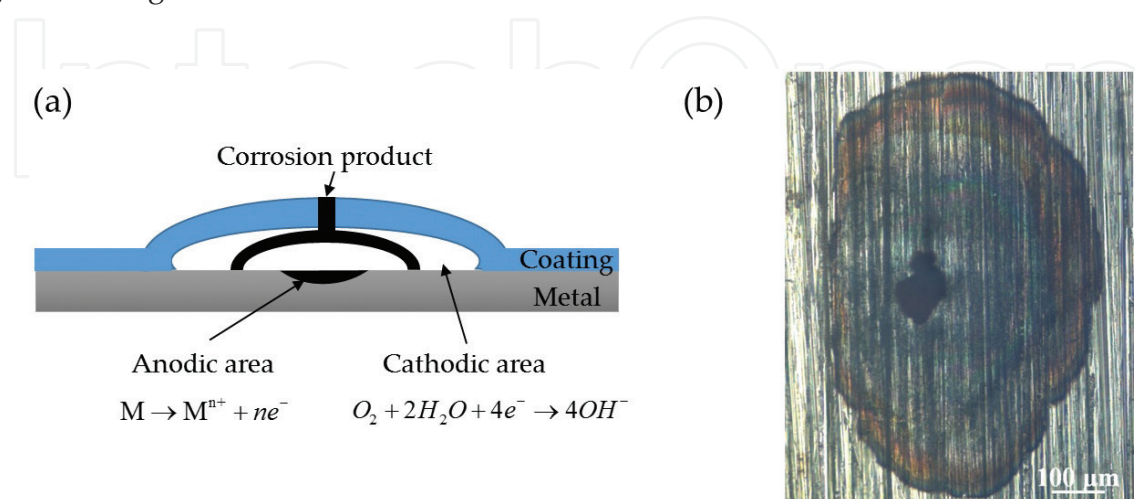
## 1. Introduction

Organic coatings mostly have dual uses of protecting the substrate and being decorative. Concerning the engineering purposes, organic coating is presumably only for the function of preventing metal corrosion, which is an effective means for the corrosion protection of marine, pipeline, bridge and so on [1]. However, coating degradation is always inevitable, due to the inherent nature and the preparation process of organic coatings. The protective function loses gradually when exposed to the corrosion environment, and it often cannot be detected in time, resulting in undetectable corrosion destruction of the metal beneath the coating. Therefore, developing an in-situ evaluation technique for the protective performance of coatings is an urgent demand presently.

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The principle of corrosion of bare metal (active dissolution) in the electrolyte aqueous solution or in the humid environment is the balancing electrochemical reactions, i.e., the anodic reaction, e.g., metal dissolution ( $M \rightarrow M^{n+} + ne^{-}$ ) and the associated cathodic reaction, e.g., oxygen reduction ( $O_2 + 2H_2O + 4e^{-} \rightarrow 4OH^{-}$ ). When it comes to the metal coated with an organic coating, the above electrochemical corrosion also occurs. Firstly, water permeates into the coating along the pores and defects of fillers/binder interface. Subsequently, the oxygen and the dissolved ions penetrate into the coating; thus, the corrosive medium solution forms on the coating/metal interface, resulting in the occurrence of electrochemical reactions [2]. The rate determining step in controlling the electrochemical reaction should be the diffusion rate of ions through the coating [3]. The locations of anode and cathode areas are separate on the surface of metal substrate, due to the inhomogeneity of transport of the corrosive medium (**Figure 1**). In conclusion, the protective performance of organic coating can be reflected by the corrosion of metal substrate. This is the reason that electrochemical measurement technologies are valid for the evaluation of the coated metals.

Compared with the routine test methods for coating evaluation, electrochemical measurement technologies have many unique advantages [4]. First, the measuring process is fast, and the instruments are relatively simple. Second, electrochemical methods achieve the quantitative or semi-quantitative evaluation for the protection level. The accurate results of the analysis are superior to other performance tests. More importantly, the in-situ examination of organic coatings makes it possible for continuous monitoring in the field. In this chapter, several electrochemical measurement technologies including open circuit potential (OCP), linear polarization resistance (LPR), electrochemical impedance spectroscopy (EIS) as well as electrochemical noise (EN), are introduced for assessing the performance and acquiring mechanistic information on the failure behavior of the painted metal. Although application of these technologies is relatively mature in the lab, lots of significant challenges still exist in the field evaluation, and the corresponding considerations are required. The aim of this review is to summarize the specific characteristics of electrochemical technologies, the data parameters and the analytical methods, which can assist the application for anti-corrosive evaluation of organic coatings.

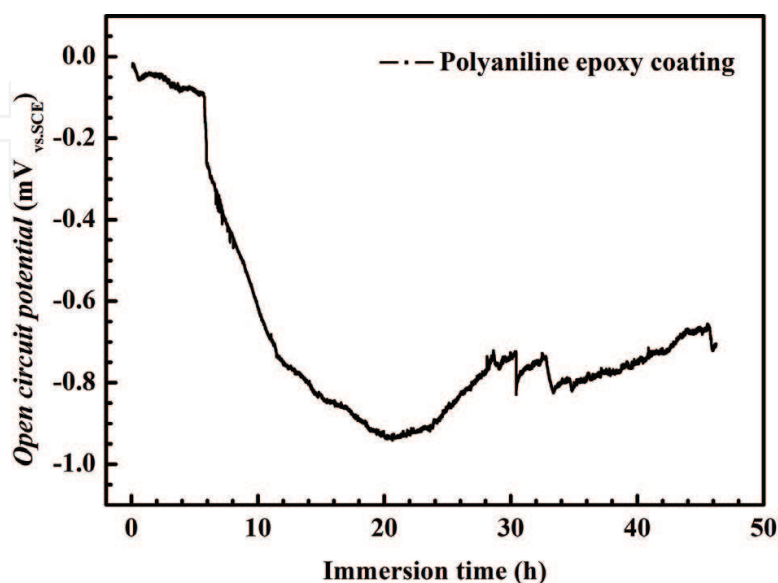


**Figure 1.** (a) Illustration diagram of electrochemical corrosion process of coating/metal system and (b) optical picture of the corrosion morphology of coated metal.

## 2. Open circuit potential method

OCP is a simple but important parameter in the research of corrosion and protection, which is the potential of a working electrode (WE) when no external current is applied to the circuit [5]. As a fundamental electrochemical method for assessing the anti-corrosion performance of coating/metal system, it is generally recognized that the OCP of coated metal is more positive than that of the bare metal [6]. Gowri and Balakrishnan [7] confirmed that their greatest corrosion resistant specimen showed a more positive value in potential than other coated samples on general levels. There are several factors that affect the potential of coated metals, and the resistance of the film is the most significant one. Besides, there are corrosion products of local anode and cathode (for example, rising concentrations of  $\text{Fe}^{2+}$  and  $\text{OH}^-$  due to their slow dispersion), the cathodic protection by some active pigments, etc. Deya et al. [8] showed that the OCP of alkyd coating varied jointly with ionic resistance and changed toward less negative values in cases of coatings with high ionic resistance. Liu et al. [9] measured the OCP of aluminum alloy specimens coated with 2 wt.% polyaniline (PANI) epoxy coating over 40 h (**Figure 2**). During the initial 20 h, the potential rapidly became negative. After this period, the potential gradually increased up to 48 h. It concluded that the protection mechanism of coating changed from barrier inhibition to ionic resistance by the formation of a complete oxide layer during immersion time.

A tracking measurement of OCP can reflect the corrosion process of metal substrate. Murray [6] reported the typical epoxy coated sample potential-time data through 3000 h of exposure to the ASTM-D-1141 substitute ocean water test solution. **Figure 3** shows the OCP curve of epoxy mica coating/steel system in 3.5 wt.% NaCl solution under alternating hydrostatic pressure (AHP) condition [10]. OCP of the coating as a whole has a negative relationship with immersion time. Three stages are found in the measurement. First, there is a large fluctuation appearing in the first 24 h, the OCP decreases to the minimum point from 0.52 V (vs. Ag/AgCl) to -0.41 V (vs. Ag/AgCl), and then rebounds to about 0.2 V (vs. Ag/AgCl) rapidly.



**Figure 2.** OCP curve for 2 wt.% PANI coated aluminum in 3.5% NaCl solution for 48 h [8].

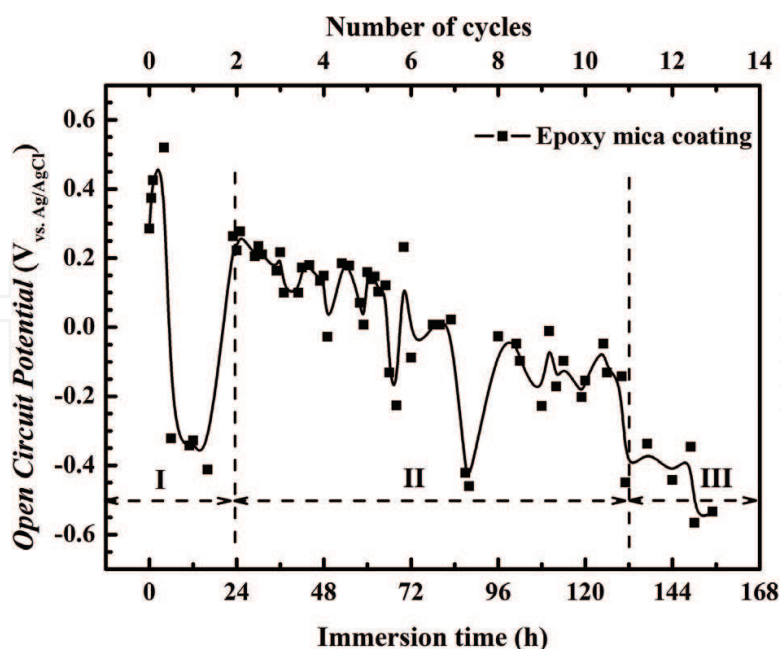


Figure 3. OCP curve for epoxy mica coating/steel system under AHP [9].

This may be attributed to the water permeation at this time, and the conductive paths for electrolyte diffusion have been created. From 25 h to about 130 h, the OCP shows decrease tendency in fluctuations. It suggested that the coating starts to deteriorate, and the substrate under coating is corroding at a low rate. However, a significant decline in the value of OCP can be obtained after 130 h, and the OCP reaches to  $-0.53$  V (vs. Ag/AgCl). This implied that the steel suffered from serious corrosion and the coating obviously degenerated. The rapid changes in OCP are much earlier than visible corrosion products on the surface of substrate.

Sometimes OCP is observed to fluctuate up and down in the initial time. This can attribute to a change in the ratio of local anodic area to cathodic area. Mayne described OCP fluctuations of coated steel by the concept of an  $iR$  drop across the coating. It suggested that an  $iR$  drop at the anodic and cathodic areas is a criterion for determination of the corrosion potential of coated specimens [5]. In general, anodic areas are quite smaller than cathodic areas at the early stage. Thus, the potential is more positive. However, with an increase in anodic sites during immersion, the corrosion potential becomes more negative. In short, OCP is an effective semi-quantitative method for coating evaluation, which is also utilized to confirm the results of EIS in many researches.

### 3. Linear polarization method

Linear polarization (LP) is one of the most commonly used electrochemical methods for the rapid test of metal corrosion rate. The characteristics of LP are sensitive and fast, which are suitable for the corrosion system in any electrolytes. The surface state of the sample would not be damaged due to a small polarization current, which is appropriate for the measurement of the anti-corrosion properties of the coated metals. The principle of LP technique is



applying current polarization on the WE, the electrode potential of WE would change near the self-corrosion potential (about  $\pm 20$  mV); thus, a linear relationship between  $\Delta E$  and  $\Delta I$  can be obtained at this point according to the Stern and Geary theory [11]. In the active corrosion system, there is a mathematical relation as follows:

$$R_p = \frac{\Delta E}{\Delta I} = \frac{b_a b_c}{2.303(b_a + b_c)} \times \frac{1}{i_c} \quad (1)$$

where  $R_p$  is the polarization resistance,  $\Delta E$  and  $\Delta I$  are the polarization potential and polarization current density, respectively;  $i_c$  is the self-corrosion current density,  $b_a$  and  $b_c$  are Tafel constants. The higher value of the resistance, the smaller corrosion rate, thus the corrosion resistance of the coating can be evaluated by  $R_p$  value. In general, the measured  $R$  values of the coating/metal system actually contain the polarization resistance, coating resistance, resistance of the lead, film resistance of the substrate and solution resistance, which are comprehensive test results. Therefore, the LP method provides comprehensive information for the evaluation of the coating/metal system, which can be used as a reference. It should be pointed out that a lot of heavy-duty corrosion protective coatings tend to reach hundreds of micrometers thick. The LP method may not work very well due to a large coating resistance (above  $10^6 \Omega \cdot \text{cm}^2$ ), but except some active pigment contained coatings, such as zinc-rich powder coatings [12]. The researches on long range change in the removal of current from the coating under cathodic protection conditions and short range currents measured after pulsing the sample also have been reported [6].

#### 4. Electrochemical impedance spectroscopy method

As early as 1980s, researchers have started using EIS to investigate the protective properties and deterioration of organic coatings. EIS can get the information of coating/metal systems in different frequency bands. According to the calculation of coating capacitance and coating resistance, information of coating body can be quantitatively acquired. The double-layer capacitance and charge-transfer resistance also reflect the corrosion process of metal substrate. Therefore, EIS becomes the main method to assess coating performance among the electrochemical techniques.

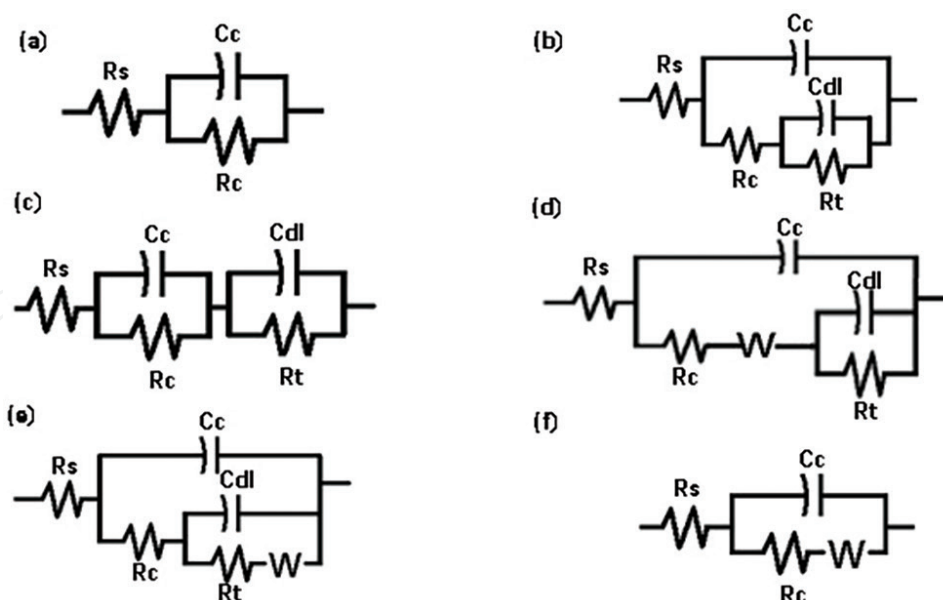
The electrochemical behavior of measured coating/metal system (i.e., the coated metal electrode) is different compared with that of bare metal. Due to a wider linear response region of coating/metal system, EIS tests were usually performed in the frequency range from 100 kHz to 10 mHz. In addition, organic coating is often a high impedance system, the impedance modulus of coating can reach  $10^{11} \Omega \cdot \text{cm}^2$ . Thus, a larger value in sinusoidal voltage is applied than that of bare metal, to avoid the errors caused by potential drift and improve the signal-noise ratio. Generally, 20 mV (rms) amplitude coupled with OCP is enough for coating system. When the coating has a higher impedance, a higher sinusoidal perturbation should be used. No more than 50 mV (rms) is accepted, otherwise the electrochemical process will be artificially changed. For the continued EIS tests, a special flat plate test cell was developed, which consists of a horizontally positioned coated-flat plate specimen, a clamped, O-ring seal and a glass tube [13]. A Faraday cage is often utilized to effectively reduce the instrumentation and ambience interferences when EIS is applied in the lab and in the field [14].

#### 4.1. Physical model of EIS and its evolution in the failure process of coating/metal system

There are two basic purposes of EIS measurement for organic coatings. One is the equivalent electrical circuit (EEC) model by fitting analysis. Furthermore, the evolution of failure process of coating/metal system can be reflected by different equivalent circuit models. Another purpose is to obtain some of the electrical parameters for evaluating on the protective performance of the coatings. The choice of physical model should follow the features of EIS plots and coating structure. Different kinds of organic coatings (involving the binder and even pigment) or the same coating in different service environments may have disparate EIS plots. Therefore, the physical models are impossible to have only a few fixed forms. Nonetheless, some typical stages in the coating failure process can be concluded by EIS analysis. It is generally accepted that the electrochemical behavior of coated metals during their exposure to aqueous solution at ambient temperature involves the penetration of water electrolyte, electrochemical reaction on the interface and further deterioration of the protectiveness (formation of under film corrosion, growth of blisters, delamination of paint film and so on), which finally culminates in the complete failure of the coatings [15]. Liu et al. [16] measured the EIS of epoxy varnish coating at different immersion time. The result indicated that there were two basic stages of coating failure, i.e., the single capacitance arc stage and double capacitance arc stage, which implied that water was absorbed into the coating after initial immersion (the single capacitance arc stage), and then electrochemical corrosion started when water arrived at the interface between the coating and the steel (double capacitance arcs stage). During the second stage, the reaction rate determining step was controlled by corrosion.

Although the EEC models of coating systems are quite different, the failure process of coating can be determined according to some typical parameters, such as the time-constant, coating capacitance and coating resistance. At the initial period of immersion, the electrolyte permeates in the coating but has not reached the coating/metal interface yet. The EEC model with only one time-constant can be used due to the great barrier properties of coating. The coating capacitance increases meanwhile the coating resistance decreases with increasing immersion time. In the medium term, water diffuses to the coating/metal interface, and then the electrochemical reactions occur, resulting in the appearance of two time-constants in the EIS plots or EEC models. There is no macroscopic corrosion product on the coating surface at this stage. When the corrosion products can be observed by naked eyes, the EEC models often return to the characteristic of one time-constant, which defines as the final stage. The coating capacitance reaches a steady value, which indicates that the water absorption of the coating gets a saturated state, and the coating losses its barrier function against electrolyte permeation [13, 17].

According to the above analysis of coating failure, several typical equivalent circuit models for EIS results of organic coatings are summarized. As shown in **Figure 4a**, the  $R(CR)$  model is often used in the initial immersion or for an intact coating, which means that the coating can act as an isolation layer and provide a good protective performance. When the electrolyte reaches the coating/metal interface, EEC models in **Figure 4b** and **c** may be selected. The model  $R(C(R(CR)))$  in **Figure 4b** is suitable for the majority of organic coatings, because the blisters or corrosion at the coating/metal interface are often localized. Concerning the  $R(CR)$

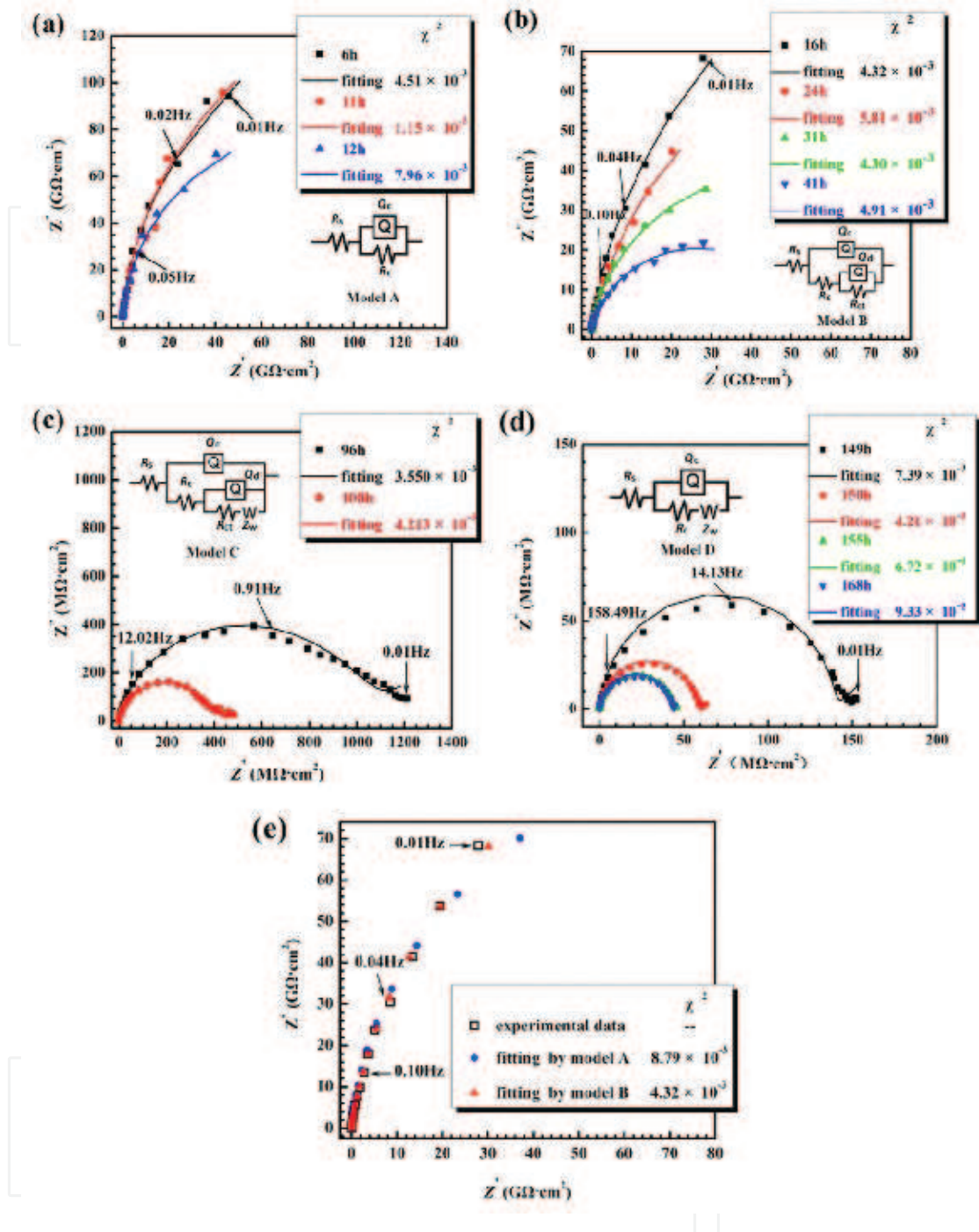


**Figure 4.** Several typical equivalent circuit models applied in the evaluation of organic coatings: (a) general model used at the first stage; (b) and (c) models with two time-constants; (d) and (e) models with two time-constants and characteristics of Warburg impedance; (f) model with Warburg impedance at the later stage of immersion.

(CR) model in **Figure 4c**, the water should uniformly permeate into the coating, such as the zinc-rich coating. Two time-constants represent the dielectric properties of polymer and the corrosion of zinc particles, respectively. Sometimes, the mass transfer of reactive particles is postponed due to the addition of pigments and fillers, resulting in diffusion characteristics of EIS, such as the Warburg impedance. Two typical EEC models with Warburg impedance are given. In **Figure 4d**, the  $R(C(RW(CR)))$  model is commonly used in the medium-term immersion, because the electrolyte diffusion occurs in the gaps among the fillers. When the diffusion region is next to the coating/metal interface, the  $R(C(R(C(RW))))$  model in **Figure 4e** is appropriate. In later stage of immersion, the  $R(C(RW))$  model in **Figure 4f** is often used, because macroscopic pores and blisters make the coating ineffective, and the diffusion process is mainly determined by the corrosion reactions of metal substrate.

When organic coating applies to a special environment, the fitting results may be different. Meng et al. [10] investigated the failure behavior of epoxy mica (EM) coating under AHP environment by EIS, which could be a typical example of organic coating with inert pigment. Four distinct stages of the coating deterioration were determined according to the evolution of EIS plots and the fitting results of EEC models (**Figure 5a–d**). At the first stage from 0 to 15 h (**Figure 5a**), the Nyquist plot reveals one capacitive characteristic, and the impedance modulus reaches  $10^{11} \Omega \cdot \text{cm}^2$  during the initial periods of immersion. It demonstrated that the coating acted as a barrier layer with a parallel connection of a high-value coating resistance and a low-value coating capacitance. The corresponding equivalent circuit A (in **Figure 5a**) was used to fit the impedance data, which included the solution resistance  $R_s$ , the coating capacitance  $C_c$  and the coating resistance  $R_c$ . The constant phase element (CPE) was used to replace the capacitance element, due to the “scattering effect” arising from the heterogeneity of the coating surface [18]. The gradually reduced capacitance arc suggested that water permeated the coating rapidly.





**Figure 5.** Nyquist plots of EM coating/steel system at different immersion time under AHP: (a) 0–15 h; (b) 16–95 h; (c) 96–150 h; (d) 151–240 h (scatter points: experimental data, solid lines: fitting results according to corresponding EEC models); (e) 16 h experimental data and fitting results of model A and B [9].

The second stage (16–95 h) was identified by the fitting results of EEC. As the immersion time increased to 16 h, the EIS data is no longer satisfactorily fitted by model A. Obvious deviation is visible in the plot (**Figure 5e**). Considering the water and oxygen molecules reached the substrate surface through micro-pores in the coating, model B (see **Figure 5b**) was applied which added the double-layer capacitance  $CPE_{dl}$  and the charge-transfer resistance  $R_{ct}$  to fit the experimental data. A better fit was obtained (**Figure 5e**), it can reveal that the

electrochemical reactions started at the coating/steel interface and developed with the water diffusion through the coating. Only one capacitive characteristic is shown in **Figure 5b**, it could be that the electrochemical reactions were quite weak during the immersion period, the order of magnitude of time-constant of the electrochemical reaction impedance is the same as that of the coating impedance [18].

After a period of immersion time under AHP, the diffusion character was added to the plot at low frequency from 96 to 150 h. The third stage shown in **Figure 5c** indicated that the corrosion behavior of the coated steel has been altered. At this moment, corrosion products were visible by the naked eyes at the surface of steel. It is probably that the corrosion of the steel substrate was accelerated at the interface area, a new diffusion field appeared around the substrate. As a result, model C (in **Figure 5c**) containing a diffusion component was applied to fit the experimental data.

At the final stage (until 240 h), a capacitive loop with a characteristic of Warburg impedance arc is observed (**Figure 5d**). Water was mainly responsible for the measured diffusion in the EIS response at the initial stage. Since water absorption approached or reached saturation, the ions or products involved in corrosion process of coating/metal interface were mainly responsible for the diffusion in the EIS response. The impedance modulus ( $|Z|$ ) has dropped to  $10^7 \Omega \cdot \text{cm}^2$ . By this time the epoxy coating cannot prevent the corrosion of metals from happening under AHP. The electrolyte has reached the surface of metal, and obvious corrosion has been observed when epoxy coating fell below  $10^6$ – $10^7 \Omega \cdot \text{cm}^2$ , which was chosen as an indicator of poor protective performance empirically.

#### 4.2. EIS analysis on water diffusion process and coating/steel interfacial reaction

As a multi-interface corrosion system, the coating/metal system often has complex failure process, due to inhomogeneous physical and chemical properties of binder/pigment and coating/metal interfaces [19]. Among several sub-processes of coating failure, there are two critical steps: the water diffusion process and the following electrochemical reactions happened at the coating/metal interface [20]. In order to investigate how electrical parameters of EIS quantitatively evaluate the protective performance of organic coating, the physical meaning of parameters and their correlation to two critical steps of coating failure behavior have been discussed in details as follow.

The process of water diffusion, i.e., the water impermeability of coatings is the key performance indicators, which is closely related to  $C_c$  and  $R_c$ . Therefore, the two important parameters can be used to indicate the anti-corrosion performance of the coatings. Tian et al. [21] compared the fitted  $R_c$  of the epoxy glass flake coating under atmospheric pressure (AP) and AHP environments (**Figure 6a**). Because the electrical resistance of electrolyte (such as 3.5 wt.% NaCl solution,  $10^1 \Omega$  order of magnitude at room temperature) is fairly smaller than that of the coatings ( $10^6$ – $10^{11} \Omega$ ), thus the variation of  $R_c$  mainly depends on water permeation [18]. The decline of  $R_c$  suggested that water permeated into coatings quickly, due to the existence of initial micro-pores in the coating. For AP, the value of  $R_c$  decreased gradually from about  $3.6 \times 10^{10}$  to  $1.4 \times 10^8 \Omega \cdot \text{cm}^2$  after being immersed for 240 h. Meanwhile, the value of  $R_c$  declined from about  $3.9 \times 10^9$  to  $3.1 \times 10^6 \Omega \cdot \text{cm}^2$  under AHP, which is smaller than that under

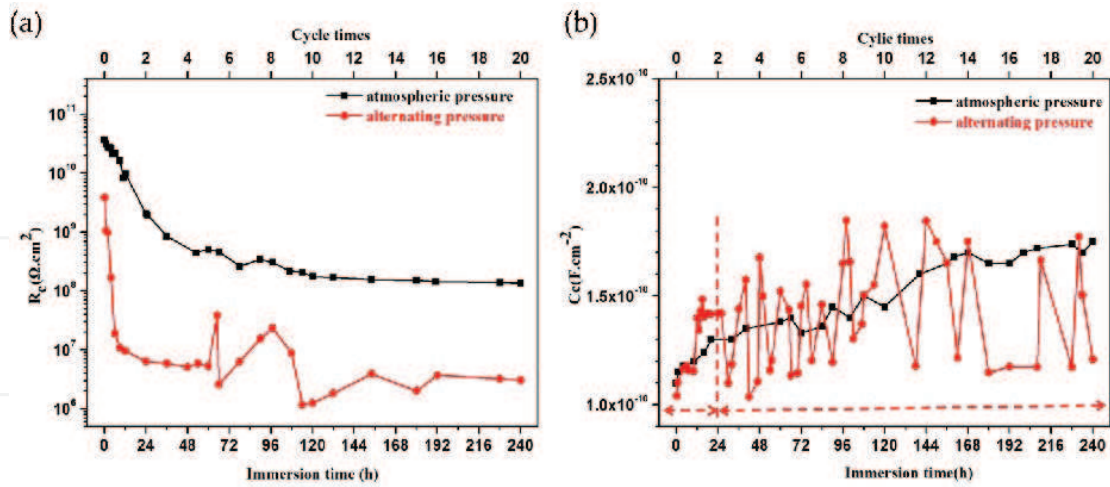


Figure 6. (a)  $R_{ct}$  and (b)  $C_c$  as a function of immersion time under AP and AHP [18].

AP by two orders of magnitude. Obviously, the changes in  $R_{ct}$  reflected the water permeation differences under two environments. On the other hand, the coating capacitance  $C_c$  is also quite useful to evaluate the water uptake in organic coatings, because water diffusion can modify the dielectric constant of the polymer. When the water diffusion meets law of Fick diffusion, the diffusion coefficient can be calculated according to Eq. (2).

$$\frac{\log C_t - \log C_0}{\log C_\infty - \log C_0} = \frac{2}{l} \sqrt{\frac{D}{\pi}} \sqrt{t} \quad (2)$$

where  $C_t$ ,  $C_0$ ,  $C_\infty$  are the coating capacitance at immersion time  $t$ , before immersion, at saturation, respectively.  $D$  is the diffusion coefficient,  $l$  is the coating thickness. The dependence of the fitted coating capacitance  $C_c$  in [21] is presented in **Figure 6b**. It can be seen that  $C_c$  under AP increased from  $1.1 \times 10^{-10}$  to  $1.7 \times 10^{-10}$   $\text{F} \cdot \text{cm}^{-2}$  gradually with immersion time. For that under AHP, it shows two stages: (1) a rapid increase from  $1.04 \times 10^{-10}$  to  $1.42 \times 10^{-10}$   $\text{F} \cdot \text{cm}^{-2}$ , which showed a rapid rise and a quasi-stable stage (within 24 h); (2) a fluctuation stage (after 24 h of immersion). The rapid increase of  $C_c$  suggested that water penetrated into the coating rapidly due to increase in pressure.

After a period of immersion, the interfacial reactions between coating and steel may occur. From the EIS data fitted by EEC, the interfacial reaction is mainly electrochemical reaction, while for that under AHP [21], the interfacial reaction includes water spread at the coating/steel interface and electrochemical reaction. The charge-transfer resistance,  $R_{ct}$ , is an indicator for the electrochemical reaction at coating/steel interface. The higher value of  $R_{ct}$  implies the greater corrosion resistance and the slower development of corrosion under the coatings. The appearance of  $R_{ct}$  under AHP is faster than that under AP, suggesting the earlier appearance of electrochemical corrosion at the coating/steel interface.

## 5. Electrochemical noise method

Although EIS is a well-established method for corrosion monitoring, applying artificial disturbance to the measured system may affect the process of electrochemical reaction. Thus,

researchers are hoping to utilize a nondestructive electrochemical measurement technique in the field. EN measurement is such an appropriate technique for the coating evaluation, which is expected to be comparable to EIS [22, 23]. The spontaneous fluctuations of electrode potential and current during electrochemical reactions are known as EN. High sensitivity to high resistance system and detection of localized corrosion are additional advantages of EN. Consequently, the application of EN has gained growing attention in corrosion research [24, 25]. In recent decades, studies on EN analysis of polymer coated metals also have been reported widely [3, 26, 27]. However, two issues restrict its application in the field. First, the on-site EN configuration and its reliability remain to be identified. Second, a quick and accurate EN analysis method is needed for the in-situ coating evaluation.

### 5.1. Measuring methods and configurations for EN

Theoretically, the measuring instruments for EN are very simple. While EN configurations are complex in practical applications. Since EN research began in 1968 [28], the measuring mode and system of EN have experienced several stages of evolution. Two-electrode (working electrode and reference electrode) system was first adopted to measure potential noise under OCP or a certain constant current [28]. This simple configuration is mainly applied in the field of electro-deposition now. Then classical three-electrode system was applied so that the potential and current signals of WE can be separately measured through reference electrode (RE) and counter electrode (CE). Due to the respective measurement, however, some correlation analyses between potential and current noise cannot be made, such as noise resistance [29]. In order to overcome this, the three-electrode system was improved by researchers. Zero resistance amperometer (ZRA) was connected between two working electrodes (WE 1 and WE 2), which were made of the same material to avoid polarization [24]. Consequently, the current noise was measured as galvanic coupling current between two WEs, the potential noise between coupled WEs and RE was measured simultaneously. This electrode system has become the basic approach for EN measurement until now [30]. As for organic coatings, the EN three-electrode configuration can also be utilized to evaluate the performance of organic coatings by measuring the corrosion reactions of substrate metal [22].

Based on the principle of EN measurement above, many attempts on the improvement of EN measuring methods for in-situ monitoring have been made in recent years. Mabbutt et al. [31] firstly designed a nonstandard EN configuration. Two saturated calomel electrodes (SCEs) were utilized as the WEs, and the substrate served as the RE. Jamali et al. [32] also proposed the so-called "single cell" configuration, since the SCE served as RE and CE consecutively but not simultaneously. It is noteworthy that this configuration belongs to asymmetric electrode configuration, and further investigation on the asymmetry of electrodes is still required to clarify. In addition, some in-situ test electrode techniques, such as microelectrodes or multiple electrodes, have been used for the application of EN in coating evaluation in the field or under some specific conditions. Bierwagen et al. [33] have used the microelectrodes to study EN measurement of the coatings in a cyclic salt fog test chamber. Simpson et al. [34] made a thin sheet of gold by electron-beam-deposition, which was deposited on the painted steel and served as the microelectrode. The coating degradation was tested by the electrochemical method in an atmospheric exposure chamber. Tan [35] measured the EN of various corrosion systems by the wire beam electrode, which not only detects noise signatures and noise resistance, but also provides unprecedented spatial and temporal information on localized



corrosion. In a word, further improvement of the EN configuration is still needed, particularly in the case of asymmetric electrode and the electrode with complicated shapes, since two identical coating/metal WEs tend to impractical in the field.

In the actual measurement of EN, it is also very important to select an appropriate sampling frequency, which is directly related to the reliability of the results. An excessively high sampling frequency leads to the lower power spectral density of EN, which is close to the white noise and produces difficulty in the data analysis. If the frequency is excessively low, some useful information will be lost. The sampling frequencies at 0.5, 1 and 2 Hz are commonly used and suitable for the general corrosion system, the specific value should be determined according to the EN sources of the tested system. Regarding the coating/metal system, EN data are usually recorded with a data-sampling interval of 0.25 or 0.5 s.

For the original EN signals, data preprocessing before various theoretical analyzing is necessary. The original data is composed of the real EN signals and the direct current (DC) drift signals. The drift can significantly affect the analysis results from time domain and frequency domain [36]. Considering that the generation of EN is a stable process, thus DC drift must be removed. At present, the DC drift removal method is still being explored. Tan et al. proposed the moving average removal (MAR) method to eliminate the DC drift of EN [37]. However, improper selection of filter window will make an obvious erroneous result [38]. In 2001, Mansfield proposed the linear fitting removal method and obtained satisfactory results in some corrosion systems [39]. This method is only suitable for the condition of DC drift with a linear feature. Meanwhile, Bertocci et al. proposed the polynomial method [38], which had satisfactory results as well as a wide range of application, despite the physical meaning of choosing polynomial exponent is still not clear.

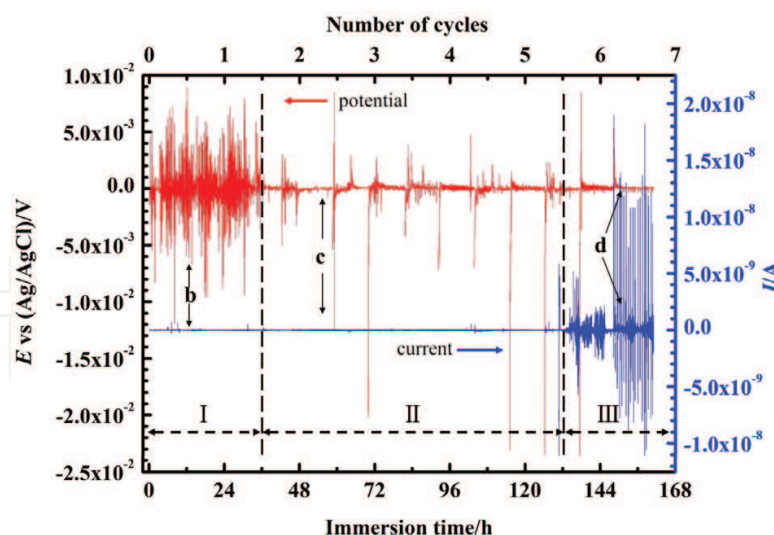
## 5.2. EN data analysis and parameter acquisition for coating/metal system

Presently, a variety of analysis methods have been developed for the processing of EN signals, which include statistical analysis [40], spectral analysis [41], wavelet analysis [42], fractal analysis [43] and so on. These methods have successfully been applied to analyze many corrosion or degradation mechanisms of coatings.

Meng et al. [44] measured EN of an epoxy coating/steel system under AHP condition. The characteristics of EN time records are related with different corrosion states of the substrate steel. Three distinct stages can be divided with different characteristics (**Figure 7**). In the first stage, the potential signal exhibited strong and stochastic fluctuations. The current signal displayed the characteristic of white noise with a narrow range of fluctuations, which always occurs in 0–36 h. In the second stage, the EN transients began to appear simultaneously in potential and current signals from about 37 to about 130 h. The transients may be caused by the localized corrosion which occurs on the surface of metal. Finally, a typical example of potential and current signals after 130 h is shown in the figure, which fluctuated in larger amplitude with quick ascending and slow recovery pattern.

Statistical analysis has several commonly used parameters [36], such as  $\bar{E}$ ,  $\bar{I}$ ,  $\sigma_E$ ,  $\sigma_I$  and noise resistance  $R_n$ . Regarding the physical meanings of these parameters, it is pointed out that the fluctuation of the average corrosion potential over the longer term may be directly related to the





**Figure 7.** Electrochemical noise records of epoxy coating in time domain after direct current trend removal [37].

changes of the corrosion process. The standard deviation can be used to describe noise intensity. It is reasonable to expect that the values of  $\sigma_E$  and  $\sigma_I$  will increase as the corrosion becomes more serious or more localized. From **Figure 8a** it could be seen that both  $\bar{E}$  and  $\sigma_E$  exhibit high amplitude fluctuations at the beginning. After about 36 h, the absolute value of  $\bar{E}$  is steady at around 0 V with a sudden decrease and a slow recovery at each moment of adding pressure or releasing pressure; the value of  $\sigma_E$  is close to zero with sudden increases during the change of pressure. On the other hand,  $\bar{I}$  is relatively stable until around 132 h; after 132 h, the value has increased suddenly. The values of  $\sigma_I$  increase gradually at a low level and then fluctuate markedly after about 126 h, as shown in **Figure 8b**. Therefore, it can be concluded that the early stage should be the water permeation period while 36–132 h should be the corrosion occurrence and development period, because the observable pits were found on the steel surface after 132 h. After 132 h, it should be the serious corrosion period.  $R_n$  is one of the most common used noise indicators, which defined as the ratio of a standard deviation of the potential to that of the current noise [45], as shown in Eq. (3). It is generally considered that  $R_n$  is inversely proportional to the corrosion current density  $i_{\text{corr}}$ .

$$R_n = \frac{\sigma_E}{\sigma_I} \quad (3)$$

Wavelet analysis is the development and continuation of Fourier analytical method. For a large number of unsteady signals, the FFT transformation is not particularly appropriate. The wavelet transform is a time-scale analytical method of signal, which has the characteristics of multi-resolution analysis, and has the ability to characterize the local characteristics of the signal in time domain and frequency domain. Therefore, People tend to use wavelet transform to extract useful information of EN. In [44], wavelet analysis was applied and energy distribution plots (EDPs) of current noise at different immersion time were provided (**Figure 9**), to figure out the correlation between corrosion states of substrate and EN results. In **Figure 9a** (0–31 h immersion), the vast majority of energy distribution (ED) is in the crystal d7, d8. The scale range of time-constants of d7 and d8 is 32–128 s, it is considered that the diffusion

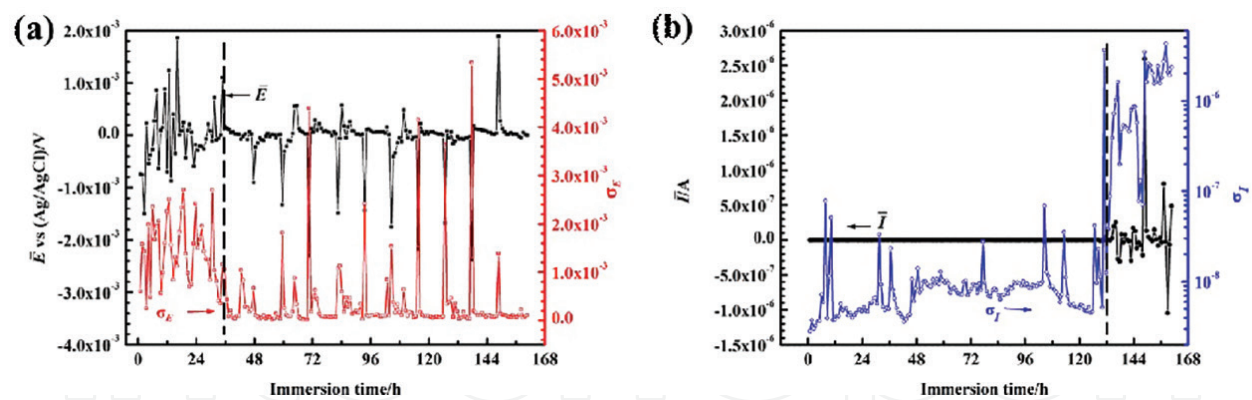


Figure 8. Variation of (a)  $E^-$  and  $\sigma_e$  as well as (b)  $I^-$  and  $\sigma_i$  of EN for epoxy coating/steel system under AHP [37].

process often occurs during this period. Therefore, the first stage should be the water permeation period, which is in agreement with the other analysis results. In the second stage (Figure 9b), ED of d8 decreased and ED of d1, d3 increased obviously. The crystal d1, d3 (scale range 0.25–0.5 s and 1–2 s) represent fast corrosion process, which could be attributed to

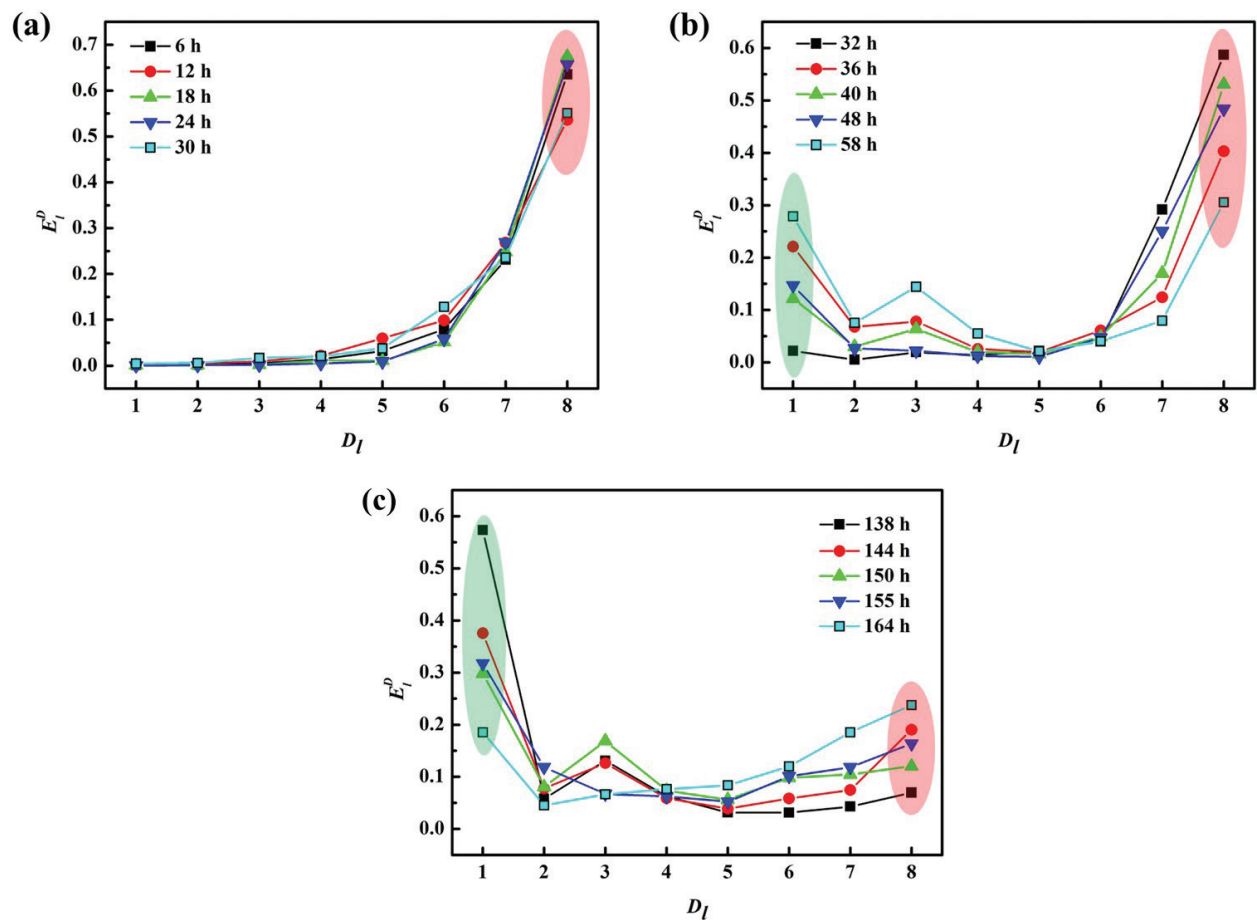


Figure 9. EDPs of current noise of coating/steel system at different immersion time: (a) ED in the first stage; (b) ED in the second stage and (c) ED in the later stage [37].

pitting nucleation and metastable pitting process [46]. It indicated that the corrosion of metal occurred at this time, the failure behavior was dominated by the mixed mechanisms of water transport and charge-transfer reaction. In the third stage, the energy was stored predominantly in the crystal d1 and d3 (**Figure 9c**), which might indicate the fast corrosion process in this period, and the charge-transfer mechanism was the dominant process. It could be found that the EDPs were not only in accordance with, but also reflect more information about the corrosion mechanisms.

To enable the rapid and automatic monitoring of the coatings by EN, the combination with artificial intelligence method and theory of nonlinear mathematics should be explored. For example, pattern recognition (PR) is an important method of information science that focuses on the recognition of regularities in data and the data classification [47]. EN signals show different distribution characteristics in different stages of corrosion, thus the similarity and the difference of EN waveform features could be categorized by PR. A close correlation is expected to be established between the classification results and the corrosion states. Huang et al. [48] applied some PR procedures for identifying different pitting states for Q235 carbon steel in  $\text{NaHCO}_3 + \text{NaCl}$  solutions. Meng et al. [44] applied PR method to the establishment of an evaluation model for EN statistical parameters. For the painted steel system, different failure stages can be conveniently identified. The unique role of new analytical method will be more pronounced in the future.

## 6. Conclusion

Since water penetrates to the coating/steel interface, the delamination of coating from steel and the corrosion of steel substrate lead to obvious changes in electrochemical signals. Therefore, for the state of coating/steel interface, electrochemical evaluation technique can get the first-hand information. In addition, defects in the coating body, such as pores and cracks of pigment/binder interfaces, are gradually increasing by the erosion environment. Enlarged conductive paths for electrolyte cause a decrease in permeability resistance of coating, which can be detected by electrochemical methods consequently. In short, coating adhesion and compactness are two critical parts in failure process of organic coating, which can be used to achieve in-situ evaluation by electrochemical measurement methods. As to the further investigation of electrochemical evaluation, the application of artificial intelligence analysis [49, 50] may be an essential trend.

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## Conflict of interest

The authors declare no conflict of interest.

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