Electrochemical Behavior and Interfacial Delamination of a Polymer-Coated Galvanized Steel System in Acid Media

Changfeng Fan,* Yancong Liu, Xiaoli Yin, Jianmin Shi, and Klaus Dilger

ABSTRACT: The degradation behavior of polymer coatings is essential for their protective performance under various corrosive environments. Herein, electrochemical impedance spectroscopy (EIS) is employed to study the corrosion behavior and interfacial delamination of a polymer-coated metal system exposed to 0.1, 0.5, and 1 mol/L H$_2$SO$_4$ solutions at 50 °C. The electrochemical impedance spectra are analyzed using different equivalent circuits to derive the time dependence of the parameters of the coating, delaminated area, and interfacial processes. The phase angle at 10 Hz ($\theta_{10\text{Hz}}$) is not appropriate in the case of higher delamination area ratio $\alpha$, while $\theta_{10\text{kHz}}$ provides a rapid approach to evaluate the degradation of polymer-coated metal systems. The frequency of the phase angle at $-45^\circ$ ($f_{-45}$) leads to a wrong evaluation for higher $\alpha$ and can be no longer viewed as the breakpoint frequency. The frequency $f_p$ obtained by the changing rate of phase angle (CRPA) method is proposed to monitor the coating degradation and determine the breakpoint frequency with the consideration of dispersive number $n$. The frequency $f_{\text{EIS}}$ derived from fitting EIS spectra shows a good agreement with $f_p$, which can contribute to clarify the evolution in the process of degradation.

1. INTRODUCTION

Polymer coatings have been widely used for protecting the metal substrate against corrosion.1–6 The polymer-coated metal systems usually exhibit excellent protective performance behavior in NaCl solutions, whereas the more corrosive environment such as the acid media would cause the deterioration of coatings and result in blisters.7

Electrochemical impedance spectroscopy (EIS) has been one of the main methods to evaluate the performance of polymer-coated metal systems. Electrical equivalent circuit models are established to simulate the EIS spectra.8–12 Several attempts have been made to derive the electrochemical parameters such as coating capacitance $C_c$, pore resistance $R_p$, double-layer capacitance $C_{dl}$, and charge transfer resistance $R_{ct}$, which are associated with the degradation of the system.13–17 Some rapid evaluation methods derived from the EIS spectra can contribute to understand the deterioration of the polymer-coated metal system for industrial application such as routine batch testing. The degradation of polymer-coated metal systems is associated with several parameters such as the phase angles at different frequencies, the changing rate of impedance, and breakpoint frequency $f_p$. Mahdavian and Attar compared the phase angles at 10 kHz in terms of the zinc chromate and zinc phosphate coatings and concluded that the parameter has a good agreement with other extracted parameters.18 Zuo et al. used the phase angle at 10 Hz ($\theta_{10\text{Hz}}$) and 15 kHz ($\theta_{15\text{kHz}}$) to evaluate the coating performance and found that $\theta_{10\text{Hz}}$ showed a good correlation with the degradation of polymer coatings. The phase angle at 15 kHz $\theta_{15\text{kHz}}$ indicates the state of polymer coating in the later stage of exposure.19 The changing rate of impedance, a parameter proposed by Xia et al., provides a good way to monitor the coating degradation and determine the breakpoint frequency with the consideration of dispersive number $n$. The frequency $f_{\text{EIS}}$ derived from fitting EIS spectra shows a good agreement with $f_p$, which can contribute to clarify the evolution in the process of degradation. 

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value of coating capacitance is similar to that of double-layer capacitance. The breakpoint frequency $f_{-45^\circ}$ is not available when pore resistance is high and/or the minimum of the phase angle at high-frequency range is higher than $-45^\circ$. Furthermore, the polymer coating cannot be viewed as the ideal capacitor with the penetration of the electrolyte. The dispersive number $n$ of coating capacitance deviates from 1 to much lower value during exposure. The frequency $f_{-45^\circ}$ can no longer be regarded as the breakpoint frequency. Moreover, the breakpoint frequency $f_{\text{EIS}}$ derived from fitting EIS spectra cannot be employed well onsite due to the dependence on fitting software and complicated fitting. Herein, it is essential to develop a rapid method with the consideration of the dispersive number $n$ to monitor the coating degradation and determine the breakpoint frequency at the medium and later exposure stages.

The aim of the present work is to compare the degradation behavior of a polymer-coated metal system in H$_2$SO$_4$ solutions with different concentrations. EIS spectra will be interpreted by appropriate equivalent circuits. The parameters derived involving $R_p$, $C_{dl}$, $R_{ct}$, $\theta_{10\, \text{kHz}}$, $\theta_{100\, \text{Hz}}$, $f_{\text{EIS}}$, $f_{-45^\circ}$, and $f_p$ will be used to monitor and analyze the coating performance. Meanwhile, the frequency $f_p$ extracted by the CRPA method with the consideration of dispersive number $n$ will be used as a coating evaluation approach for the medium and later exposure stages.

Figure 1. Optical graphs of the polymer coatings exposed to (a) 0.1 mol/L H$_2$SO$_4$ solution, (b) 0.5 mol/L H$_2$SO$_4$ solution, and (c) 1 mol/L H$_2$SO$_4$ solution for 7 days at 50 °C.

Figure 2. Cross sections of the polymer coatings exposed to (a) 0.1 mol/L H$_2$SO$_4$ solution, (b) 0.5 mol/L H$_2$SO$_4$ solution, and (c) 1 mol/L H$_2$SO$_4$ solution for 7 days at 50 °C.
stages. Delaminated area ratio $\alpha$ calculated by $f_p$ will be compared with those obtained by $f_{-45^\circ}$ and $f_{EIS}$.

2. RESULTS AND DISCUSSION

2.1. Optical Microscopic Characterization. Figure 1a,b illustrates the surface morphology under an optical microscope after exposure to 0.1 mol/L and 0.5 mol/L H$_2$SO$_4$ solutions, respectively, at 50 °C for 7 days. The exposed areas are clearly distinct from the as-received part. The polymer coating exposed to 0.5 mol/L H$_2$SO$_4$ solution presents more minor blisters and pores than that exposed to 0.1 mol/L H$_2$SO$_4$ solution. These small visual defects on the surface perform as the conductive channels resulting in the deterioration of the polymer coating. Corrosive elements can reach to the metal substrate through these pathways and result in the electrochemical reaction at the polymer/metal interface. The failure stemming from chemical degradation is usually presented in the acid electrolyte. The polymer-coated metal system exhibits visible blisters when exposed to 1 mol/L H$_2$SO$_4$ solution, Figure 1c. A large amount of defects can be observed,
which are much more than that of any other sample. These blisters are filled with electrolytes and are originated by the penetration of corrosive elements through the polymer coating.

Once ions such as H\(^+\) ions reached the polymer/metal surface, anodic reactions would occur. The metal substrate would be corroded. The accumulation of corrosion products beneath the polymer coating can be analyzed by the micrographs of cross sections shown in Figure 2. No obvious corrosion products are illustrated with regard to the case of 0.1 mol/L H\(_2\)SO\(_4\) solution. The zinc coating on the surface of steel is almost intact. However, it is noticeable that the polymer coatings exposed to 0.5 and 1 mol/L H\(_2\)SO\(_4\) solution are blistered. Corrosion products beneath polymer coatings can be observed. Soluble zinc ions and hydrogen gas will be produced, resulting from the electrochemical reaction in an acidic environment when the aggressive ions arrive on the surface of the metal substrate.\(^{26}\)

\[
\begin{align*}
\text{Zn} & \rightarrow \text{Zn}^{2+} + 2e^- \quad (1) \\
2\text{H}^+ + 2e^- & \rightarrow \text{H}_2 \quad (2)
\end{align*}
\]

2.2. EIS Measurements and Data Analysis. EIS spectra of the polymer-coated metal systems exposed to different solutions are presented in Figure 3. The impedance reduces with the increase of exposure time, revealing that the spectra are sensitive to the degradation of the system. At a very early stage, the modulus |Z| in the medium–low frequency range displayed very high values (>10\(^9\) ohm-cm\(^2\)) for all samples. Only one capacitive loop can be observed from the Bode plots, which indicates the excellent protective performance. Water and other corrosive elements penetrate into the coating and do not reach the surface of the metal. The typical equivalent circuit model A is applied to interpret the impedance spectra during this stage. The pore resistance \(R_p\) results from the ionic conducting pathways through the polymer coating.\(^{24}\)

As time elapsed, the electrochemical corrosion had to be taken into consideration with the arrival of water and corrosive ions at the polymer/metal interface. The modulus |Z| decreased remarkably from 10\(^9\) ohm-cm\(^2\) to less than 10\(^8\) ohm-cm\(^2\). The sample exposed to 1 mol/L H\(_2\)SO\(_4\) solution dropped to 2 \times 10\(^6\) ohm-cm\(^2\) after exposure for 2 h. The impedance spectra present one capacitive loop for the sample exposed to 0.1 mol/L H\(_2\)SO\(_4\) solution at this stage. In the Nyquist plot shown in Figure 4a, it consists of two overlapped semicircles due to the minor electrochemical reaction at polymer/metal interface. The polymer coating gradually weakened and micropores increased continuously with regard to the system, thereby model B, which indicates the homogeneous distribution of electrochemical reactions, was employed.

After a long-term exposure, a variation of the impedance spectra at the low-frequency range can be observed. The equivalent circuit model B is no longer appropriate to fit the data. The representative Nyquist plots of the polymer-coated metal systems exposed to different solutions at 50 °C after longer exposure times are shown in Figure 4. A tail is observed in the range of low frequency. This can attribute to the existence of the diffusion process. The diffusion process may become a control procedure in faradic processes.\(^{17}\) Herein, model C including diffusion parts was employed to interpret the impedance spectra. The constant phase element \(C_{\text{diff}}\) and resistance \(R_{\text{diff}}\) are derived to describe the diffusion process. The diffusion behavior is usually not ideal Warburg impedance, resulting in a deviation of the dispersive number \(n\) for \(C_{\text{diff}}\) from 0.5.\(^{17}\) Three time constants can be observed for the samples exposed to 0.5 and 1 mol/L H\(_2\)SO\(_4\) solutions. The capacitive loops at high frequency indicate the polymer coating performance, which implies its deterioration in terms of the declining diameters. The tendency can be observed according to Figure 4. The decreasing semicircle in the range of medium to low frequency indicates the electrochemical reaction at the
polymer/metal interface. Thereby, the diffusion process of ionic species at the interface emerged in Nyquist plots and shaped as a slope line or large arc at low frequency. Parameters can be further derived to elucidate the degradation process. More information on the diffusion process will not be discussed.

### 2.3. Evaluation of Polymer-Coated Metal System

Time dependence of parameters including $C_{dl}$, $R_p$, $C_{dl}$, and $R_{ct}$ for the polymer-coated metal systems during exposure to different electrolytes at 50°C is given in Figure 5. The coating capacitances tended to increase gradually and stabilized at a similar range of $10^{-10}$–$10^{-9}$ F/cm$^2$. A relationship exists between the interfacial delamination and the electrochemical parameters such as pore resistance $R_p$, double-layer capacitance $C_{dl}$ and charge transfer resistance $R_{ct}$. For the case of 0.1 mol/L, $R_p$ reduced from $10^{10}$ to $3 \times 10^5$ ohm-cm$^2$ due to the formation of pathways. More pores can be observed in Figure 1 for the sample exposed to 0.5 mol/L. $R_p$ dropped to only ca. $10^6$ ohm-cm$^2$. The sample exposed to 1 mol/L H$_2$SO$_4$ solution exhibits the lowest pore resistance and charge transfer resistance. Both of them illustrate the same tendency and decreased to about $2 \times 10^5$ ohm-cm$^2$ at the end of exposure. The decrease of $R_p$ and increase of $C_{dl}$ indicate the extension of the delaminated area beneath the polymer coating with progressive degradation, while both of them are also influenced by the electrochemical reaction involving the zinc layer, iron substrate, and corrosion products. The double-layer capacitance of the sample exposed to 0.1 mol/L H$_2$SO$_4$ solution increased from $10^{-10}$ to $10^{-9}$ F/cm$^2$ at first 24 h and stabilized till 66 h. Once the aggressive ions arrived on the surface of the metal substrate, soluble zinc ions and hydrogen gas would be produced, resulting from the electrochemical reaction expressed by eqs 1 and 2 in an acidic environment. The reaction can further take place yielding the corrosion products according to eq 3

$$\text{Zn}^{2+} + \text{SO}_4^{2-} \rightarrow \text{ZnSO}_4$$

The double-layer capacitance at the polymer/metal interface climbed to $10^{-7}$ F/cm$^2$ at 80 h, which is much higher than the coating capacitance. $C_{dl}$ increased gradually and reached to $2 \times 10^{-2}$ and $1 \times 10^{-5}$ F/cm$^2$ in the case of 0.5 and 1 mol/L H$_2$SO$_4$ solutions, which contain higher H$^+$ ion concentration. The corrosion products generated through the above reactions were soluble and would further fill in the blisters during the measurement.

To obtain more detailed information about the deterioration, the parameters derived from EIS spectra including $\theta_{10kHz}$ and $\theta_{10kHz}$ are employed. Figure 6 presents the time dependence of $\theta_{10kHz}$ and $\theta_{10kHz}$ during exposure to different solutions at 50°C for the polymer-coated metal system. The phase angle at 10 Hz $\theta_{10kHz}$ representing the characteristic of lower delaminated area is no longer appropriate to evaluate the degradation of the polymer-coated metal system. All of them fall into a low value around 10° at the very early stage and kept in a constant. The phase angle seems impossible to evaluate the degradation degree and ranking for other samples with higher delaminated area ratio $\alpha$. The phase angle $\theta_{10kHz}$ for 0.5 and 1 mol/L increased slightly with the exposure time prolongation, which might be explained by the formation of corrosion products. The phase angle at 10 kHz shown in Figure 6b remains high at 60° when the sample was exposed to 0.1 mol/L H$_2$SO$_4$ solution, which presents an excellent performance for protection. The variation of $\theta_{10kHz}$ indicates that the delaminated area ratio is higher due to the sensitivity to polymer coating deterioration. $\theta_{10kHz}$ reduces to only 15 and 5° with the development of degradation for the case of 0.5 and 1 mol/L H$_2$SO$_4$ solution, respectively. The tendency of the delaminated area ratio calculated by $f_{EIS}$ is consistent with that of $\theta_{10kHz}$. Herein, $\theta_{10kHz}$ can add substantially to our understanding on the degradation process at this stage, while the relationship between $\alpha$ and $\theta_{10kHz}$ for the polymer-coated metal systems is required to be further clarified. Meanwhile, the deviation of dispersive number $n$ due to the penetration of the electrolyte should be taken into consideration.

![Figure 6](https://doi.org/10.1021/acsomega.1c02270)

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The frequency $f_p$ obtained by the CRPA method is applied to shed light on the evolution of the delaminated area. Figure 7 presents the Bode plots of the changing rate of phase angle for the polymer-coated metal system exposed to various solutions at 50 °C. The smoothing curves of data points are displayed to guide the eye. The semicircles are overlapped and exhibit one capacitive loop due to the small electrochemical reaction area at the polymer/metal interface during this exposure period, which results in only one peak. The peak at the mid–low frequency region with the $f_p$ of 10 Hz at 121 min migrated to the mid–high frequency region with that of 121 Hz at 24.5 h in the case of 0.1 mol/L H$_2$SO$_4$ solution. This indicates the continuous extension of delaminated area at the polymer/metal interface. The value of $d(\theta)/d(\log f)$ is associated with the dispersive number $n$. The frequency $f_p$ derived from the Bode plot of the phase angle stabilizes at 250 Hz at the end of exposure. Only one peak can be observed as same as the circumstance of 0.5 and 1 mol/L during the initial stage; $f_p$.

Figure 7. Bode plots of the changing rate of the phase angle for the polymer-coated metal systems exposed to (a) 0.1 mol/L H$_2$SO$_4$ solution, (b) 0.5 mol/L H$_2$SO$_4$ solution, and (c) 1 mol/L H$_2$SO$_4$ solution during exposure to different solutions at 50 °C.

Figure 8. Time dependence of $\alpha$ calculated by $f_{EIS}$, $f_{-45^\circ}$, and $f_p$ for the polymer-coated metal systems during exposure to (a) 0.1 mol/L H$_2$SO$_4$ solution, (b) 0.5 mol/L H$_2$SO$_4$ solution, and (c) 1 mol/L H$_2$SO$_4$ solution during the exposure to different solutions at 50 °C.
shifted to 800 Hz at 605 min and 1000 Hz at 201 min with the degradation of the system. Two semicircles are distinguishable with the prolongation of exposure. The first peak at the high-frequency range corresponds to the component of polymer coating including coating capacitance $C_c$ and pore resistance $R_p$ in parallel. Therefore, the frequency $f_p$ in high-frequency range can be used to evaluate the delaminated area during the late stage, which reaches about $5.8 \times 10^4$ Hz at 48 h.

The variation of delaminated area ratio $\alpha$ calculated by the frequencies, which are extracted from the equivalent circuit ($f_{\text{EIS}}$) obtained at $-45^\circ$($f_{-45^\circ}$) and derived according to the CRPA method ($f_p$) for the polymer-coated metal system exposed to different solutions, is compared in Figure 8. Breakpoint frequency $f_{-45^\circ}$ cannot be obtained from Bode plot for the system with nondistinguishable time constants between the polymer coating and electrochemical reaction, which stems from the limitation of measurement. It is noteworthy that the ignorance of dispersive number $n$ would lead to the wrong estimation. The delaminated area ratio $\alpha$ calculated by $f_{\text{EIS}}$ and $f_p$ are equal to 0.45, but 0.74 according to $f_{-45^\circ}$. $\alpha$ calculated by $f_{\text{EIS}}$ for the case of 1 mol/L H$_2$SO$_4$ solution increased to 0.56 at 48 h consistent with $f_p$ which is overestimated by $f_{-45^\circ}$. After that, the breakpoint frequency is higher than 100 kHz, which is out of the measurement range and not accurate due to the limitation of the instrument. The application of $f_{-45^\circ}$ neglects the dispersive number $n$ and leads to wrong estimation, while the CRPA method involving $f_p$ can contribute to evaluate the performance and add our understanding for the interfacial delamination. The frequency $f_p$ can be viewed as a rapid approach to shed light on the degradation of the polymer-coated metal systems without complicated EIS fitting at the medium and late exposure stages. More work is underway.

3. CONCLUSIONS

This study evaluated the electrochemical behavior and interfacial delamination of a polymer-coated metal system exposed to H$_2$SO$_4$ solutions with different concentrations for 7 days at 50 °C by EIS measurement. The following conclusions can be drawn.

- Blistering and large-area delamination were observed upon exposure to H$_2$SO$_4$ solutions. Typical equivalent circuit models are employed to analyze EIS spectra and the models present a good fitting agreement with experimental data for samples measured at 50 °C. In the initial stage, the equivalent circuit only consists of the coating capacitance in parallel with the coating resistance. Following this, the electrochemical reaction occurs at the polymer/metal interface. As the exposure time elapsed, corrosion products accumulated on the surface of the metal substrate and hindered the corrosion process with mass transfer.

- Corrosion elements penetrating into the polymer coating with increase in exposure time lead to the decrease of pore resistance and increase of double-layer capacitance. Pore resistances drop from about $1 \times 10^{10}$ to $3 \times 10^4$ and $2 \times 10^9$ ohm-cm$^2$ before and after aging in 0.5 and 1 mol/L H$_2$SO$_4$ solutions at 50 °C for 7 days, respectively. The phase angle at 10 Hz $\theta_{10\text{Hz}}$ of all samples falls into a low value around 10° and is not appropriate to demonstrate the degradation in the case of higher delamination ratio $\alpha$. The tendency of $\alpha$ calculated from $f_{\text{EIS}}$ is consistent with that of $\theta_{10\text{kHz}}$ in the case of higher delaminated area.

- The frequency $f_{-45^\circ}$ can be no longer viewed as the breakpoint frequency with the deviation of dispersive number $n$. The ignorance of $n$ can lead to the wrong estimation of the delaminated area. The delaminated area ratio $\alpha$ calculated by $f_{-45^\circ}$ amount to 0.74 and 0.72 for the case of 0.5 mol/L at 160 h and 1 mol/L at 48 h, which are much higher than that obtained by $f_{\text{EIS}}$ with the values of 0.45 and 0.56, respectively. The frequency $f_p$ extracted by the CRPA method is derived from $f_{\text{EIS}}$ by fitting shows a good agreement with $f_p$. The frequency $f_p$ can be viewed as a rapid approach to shed light on the degradation of the polymer-coated metal systems at the medium and late exposure stages.

4. EXPERIMENTAL SECTION

4.1. EIS Measurements. A commercial epoxy coating on the galvanized steel substrate with the coating thickness of about 196.9 ± 22.5 μm was provided by a company. The plate with the substrate thickness of 3 mm was cut into the size of 80 mm × 80 mm and kept in air for 24 h according to ISO 16773-2: 2016 (E) before measurements. An electrochemical workstation (VersaSTAT 4, AMETEK) was used for all of the electrochemical measurements. The electrochemical cell was modified from a flat cell K235. The EIS spectra were measured at 50 °C in situ with a two-electrode setup using a platinum grid counter electrode and the sample with an exposed area of 10 cm$^2$ as working electrode. The cell was filled with H$_2$SO$_4$ solutions with different concentrations. The degradation process is fast and requires rapid scanning during the very early stage. Herein, the frequency range was 10$^{-3}$—1 Hz to obtain more data in a short time. As the time elapsed, the applied frequency range was 10$^3$—10$^{-2}$ Hz with a signal amplitude of 50 mV. Analysis of electrochemical impedance spectra was conducted by the software Zview (Version 3.5, Scribner Associates, Inc.).

Model A shown in Figure 9a is proposed to interpret the EIS spectra in the stage without the electrochemical process. Constant phase elements (CPE) are introduced to obtain more accurate fitting results considering the nonideal capacitance behavior for $C_c$ and $C_{dl}$ in the system, which is expressed as

$$Z(\omega) = (Y_0)^{-1}(\omega)^n$$

where $Y_0$ is the CPE constant with the units of F·cm$^{-2}$, $\omega$ is the angular frequency, and $n$ is a value indicating the deviation from purely capacitive behavior ($0 \leq n \leq 1$). Capacitance is nearly equal to $Y_0$ of the CPE with $n \approx 1$. Along with the exposure time, the polymer coating gradually weakened and pores increased continuously, and the distribution of electrochemical reactions is roughly homogeneous. Model B presented in Figure 9b is used to describe the
electrochemical reaction. Herein, the electrochemical component is illustrated as a capacitance (double-layer capacitance \( C_{dl} \)) in parallel with a resistance (charge transfer resistance \( R_{ct} \)). At the medium and last stages of exposure, the presence of corrosion products can give rise to the diffusion process, which might be a control procedure in the electrochemical reaction. Model C including the diffusion capacitance \( C_{dl} \) and diffusion resistance \( R_{dl} \) is established to fit the spectra.\(^{9}\)

Coating capacitance \( C_{c} \) and pore resistance \( R_{p} \) derived from equivalent circuits can be used to calculate the breakpoint frequency \( f_{b} \) which exhibits a good correlation with the delaminated area.\(^{31}\) Herein, the breakpoint frequency \( f_{b} \) extracted from equivalent circuit is defined as \( f_{EIS} \). The higher the \( f_{EIS} \), the larger the delaminated area at the coating/metal interface.\(^{32}\) The extent of delamination can be determined experimentally from the breakpoint frequency \( f_{EIS} \), which is given by

\[
f_{EIS} = \frac{1}{2\pi R_{p} C_{c}} = \frac{A_{d}/A}{2\pi R_{p} C_{c}^0 (1 - A_{d}/A)} = \frac{K}{\alpha - 1}
\]

\(\alpha = A_{d}/A\) is the delaminated area ratio. \( A_{d} \) and \( A \) represent the equivalent delaminated area and whole exposure area, respectively. The constant \( K \) depends only on the coating parameters \( \rho \) and \( \epsilon \). It is independent of coating thickness

\[
K = 1/(2\pi \epsilon_{\text{eq}} \epsilon_{0} \epsilon_{\rho})
\]

\(\epsilon_{\text{eq}} = 4\) and \(\rho = 6.27 \times 10^6\) ohm-cm according to the literature.\(^{33,34}\) \( K \) can be approximately regarded as a constant according to the parameters above.\(^{32,33}\)

**4.2. Frequency \( f_{p} \) from the Changing Rate of Phase Angle.** The dispersive number \( n \) of coating capacitance deviates from 1 to much lower value during the late exposure due to the water uptake behavior and interfacial reactions, which should be taken into consideration for the calculation of \( f_{b} \). In this case, the frequency corresponding to \(-45^\circ\) \((\phi_{-45})\) cannot be ignored as a breakpoint frequency.\(^{25}\) Herein, the frequency corresponding to the first peak at high-frequency range \((f_{p})\) obtained by the changing rate of the phase angle (CRPA) method is derived to monitor the coating degradation and determine the breakpoint frequency. The pore resistance \( R_{p} \) is usually much higher than the electrolyte resistance \( R_{e} \). Herein, the electrochemical equivalent circuit for the polymer coating can be represented as a resistance \( R \) in parallel with coating capacitance \( C \). The real part \( Y' \) and imaginary part \( Y'' \) of admittance about coating capacitance can be expressed by

\[
Y'_{c} = Y_{d} \rho^\omega \cos \frac{n\pi}{2}
\]

\[
Y''_{c} = Y_{d} \rho^\omega \sin \frac{n\pi}{2}
\]

Therefore, the admittance \( Y \) of the polymer coating component

\[
Y = Y_{R} + Y_{c} = \frac{1}{R} + Y_{d} \rho^\omega \cos \left( \frac{n\pi}{2} \right) + jY_{d} \rho^\omega \sin \left( \frac{n\pi}{2} \right)
\]

And the impedance \( Z \) of polymer coating component

\[
Z = \frac{1}{Y} = \left( \frac{1}{R} \right) + \left( \frac{1}{Y_{d} \rho^\omega} \right) \cos \left( \frac{n\pi}{2} \right) + \left( Y_{d} \rho^\omega \right)^2
\]

The real part \( Z_{re} \) and imaginary part \( Z_{im} \) of impedance are demonstrated by eqs 11 and 12, respectively.

\[
Z_{re} = \left( \frac{1}{Y_{d} \rho^\omega} \right) \cos \left( \frac{n\pi}{2} \right) + \left( Y_{d} \rho^\omega \right)^2
\]

\[
Z_{im} = \left( \frac{1}{Y_{d} \rho^\omega} \right) \sin \left( \frac{n\pi}{2} \right)
\]

Hence, the phase angle can be expressed by

\[
\theta = \tan^{-1} \left( \frac{Z_{im}}{Z_{re}} \right) = \tan^{-1} \left( \frac{RY_{d} \rho^\omega \sin \left( \frac{n\pi}{2} \right)}{1 + Y_{d} \rho^\omega \cos \left( \frac{n\pi}{2} \right)} \right)
\]

The changing rate of the phase angle \( q \) satisfying eq 14 is sensitive to reflect the variation of the phase angle, especially in the range of high frequency with less interference from interfacial reaction.

\[
q = \frac{d(\theta)}{d(\log_{10} f)} = \frac{a n y_{o} \ln(10)}{a^2 f^2 + (1 + b y_{o}^n)^2}
\]

where \( a \) and \( b \) represent \( R Y_{c} (2\pi)^n \sin(n\pi/2) \) and \( R Y_{c} (2\pi)^n \cos(n\pi/2) \), respectively. The frequency at the first peak \( f_{p} \) in the range of high frequency can be calculated when the derivative of \( q \) versus \( \log_{10} f \) equals to zero, as shown in eqs 15 and 16

\[
f_{p} = \frac{1}{2\pi} \left( \frac{1}{\sqrt{RY_{0}}} \right)
\]

At this time, the changing rate of the phase angle \( q \) can be calculated by

\[
q = \frac{n \sin \left( \frac{n\pi}{2} \right) \ln(10)}{2 + 2 \cos \left( \frac{n\pi}{2} \right)}
\]
The data analysis for extracting $f_n$ is simple with the help of the function in Microsoft Excel. The frequency $f_n$ indicates the characteristic of polymer coating and can be viewed as a parameter to evaluate the delamination area with the consideration of dispersive number $n$. The changing rate of phase angle $q$ at the frequency $f_n$ can also be used to estimate the value of $n$ when the time constants of the polymer coating and electrochemical process are distinguishable.

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**Notes**

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