Application of electrochemical impedance spectroscopy (EIS) for characterizing the corrosion-protective performance of organic coatings on metals

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1 Introduction

The main purpose of an organic coating is to protect the metallic substrate against a corrosive environment. The corrosive-protective properties are determined by a complex mechanism which includes the action of different factors. The behaviour of a protective system will depend on [1–12]: (a) the dielectric properties of the coating; (b) the adhesion of the coating to the substrate; (c) the water and oxygen uptake of the coating; (d) ion penetration of the coating; (e) pigments and inhibitive additives; (f) ageing of the coating; (g) mechanically weakened spots and pinholes; (h) the surface characteristics of the metal substrates; (i) surface pretreatment; (j) environmental conditions; and (k) various complicated electrochemical corrosion reactions at the metal–coating interface after permeation of water and oxygen.

Hence, the protective properties of organic coatings on metal substrates may be attributed to a barrier and an electrochemical mechanism. As organic coatings typically have a high resistance to ionic conductivity, they offer good barrier properties and retard the diffusion of chemical species to and

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from the metal surface. By adding chemically inert pigments this effect can be increased. The protective coating properties essentially are determined by the rate of water and oxygen diffusion through the insulating layer, promoted by the osmotic pressure in the pores and capillaries of the coating.

A protective coating system usually consists of primer, filler and topcoat. Thus, the primer is especially responsible for corrosion protection. Water molecules inserted at the metal–primer interface may induce adhesion losses for the coating and electrochemical underfilm corrosion may take place. In order to prevent this, typical barrier pigments are incorporated within the coating, where it is required that the interactions between pigment and binder are as water-resistant as possible. Moreover, active pigments in primers often develop further protective action in addition to the barrier effect when local destruction of the organic coating system occurs. The pigments may then protect the metal substrate electrochemically by either a galvanic or a passivating mechanism (see, for example, ref. 12).

In general, the suitability of a coating for a specific environment is tested by exposure of the coated metal plates to natural and/or accelerated weathering conditions. These tests only allow a qualitative estimation of the protective coating properties and no information is given about the degradation mechanism. Thus particular attention should be given to techniques which elucidate the deterioration mechanism and the reactions occurring at the metal–coating interface, such as corrosion and loss of adhesion.

As corrosion reactions are predominantly electrochemical reactions, the use of electrochemical methods plays an important role in the evaluation of the corrosion performance and in providing a better understanding of how a coating protects a metal substrate. Many studies of the electrical properties of protective coatings reported previously include potentiometric studies [13–18], polarization studies [19, 20], measurements of film resistance using either DC [20–26] or AC procedures [7, 12, 27–31] and a range of impedance methods such as electrical permittivity, measurements of the separate resistive and capacitive contributions of the impedance at a fixed frequency and impedance analysis over a wide frequency range [12, 13, 31–41]. Several reviews have already discussed the advantages and limitations of electrochemical test methods [15, 18, 42, 43].

Measurements of potential changes with time are the simplest of electrochemical studies. The potential/time method can provide useful information on deterioration when combined with other techniques. The decrease in potential can be taken as a measure of failure, which is to be preferred to a visual inspection of the extent of rusting. Prior to coating failure, however, not much useful information can be obtained by this method.

Polarization studies have been applied widely in the field of metallic corrosion. They have rarely been used, however, for coated metals because of experimental problems and difficulties in the interpretation of the results arising from the high resistance of the polymer coating. Results of polarization measurements of coated metals have to be interpreted carefully because the
actual flow of current under the applied potential may affect the properties of the metal–coating interface.

Irreversible changes of the system under study may be avoided by use of AC methods such as electrochemical impedance spectroscopy (EIS). EIS has provided new information previously unobtainable with conventional DC techniques. EIS has proved to be very useful because it provides a non-destructive method of determining several system parameters such as polymer capacitance and film resistance. Furthermore, information can be obtained on the charge-transfer processes occurring at the metal–coating interface.

Impedence measurements are now widely used for studies of deterioration and corrosion processes on metal–coating systems. In this paper, some of the questions as to how electrochemical data can be related to basic coating properties such as permittivity, film resistance, water uptake, adhesion and electrochemical and diffusion processes in underrusting of organic coatings on metal surfaces are dealt with.

2 Principle and technique of EIS

2.1 Basis of the method

The technique is based on the application of a continuous perturbation to a steady-state system and the subsequent analysis of the relaxation of the electrochemical system to a new steady state [44].

When a small sinusoidal voltage

\[ U(t) = U_m \sin(\omega t + \varphi_u) \]  

is applied to a system, a sinusoidal current

\[ I(t) = I_m \sin(\omega t + \varphi_i) \]  

with a phase shift \( \varphi - \varphi_u - \varphi_i \) is observed. The magnitude of the amplitudes of perturbation and response, \( U_m \) and \( I_m \), and the phase shift \( \varphi \) depend on the reactions taking place in the system under investigation [45–52].

To simplify the calculations further, the perturbation and response are transformed from a function of time into the frequency domain via a Laplace transformation [53]. The ratio of the Laplace transform of voltage to that of current \( \Delta U(s)/\Delta I(s) \) defines the frequency-dependent electrochemical impedance \( Z(s) \) by substituting \( j\omega \) for the Laplace variable \( s \), where \( \omega \) is the angular frequency \( (\omega = 2\pi f) \) and \( j \) the imaginary quantity \( \sqrt{-1} \).

2.2 Representation of impedance data

The impedance \( Z(j\omega) \) is a complex number which can be represented either in polar coordinates or in Cartesian coordinates:

\[ Z(j\omega) = \frac{U_m}{I_m} e^{j(\varphi_u - \varphi_i)} = |Z| e^{j\theta} \]  

\[ Z(j\omega) = Z' + jZ'' \]
where \(|Z|\) is the modulus of the impedance, and \(Z'\) and \(Z''\) are the real and imaginary part of the impedance, respectively. The relationships between these quantities are:

\[
|Z| = \sqrt{(Z')^2 + (jZ'')^2} \tag{5}
\]

\[
Z' = |Z| \cos \varphi; \quad Z'' = |Z| \sin \varphi \tag{6}
\]

and these can be described by means of two types of diagram. Firstly \(Z(j\omega)\) may be plotted in a complex plane at a single frequency as shown in Fig. 1. Plots of \(Z(j\omega)\) measured at different frequencies are called Nyquist plots, complex plots, impedance diagrams or impedance spectra. The second representation is the so-called Bode plot, showing the logarithm of the modulus of the impedance \(\log |Z|\) and the phase shift \(\varphi\) as a function of the logarithm of the frequency.

Analysis of impedance data is carried out over a wide range of frequencies in order to determine the coating properties and the degradation mechanism. The EIS primarily characterizes a system in terms of its electrical properties. Hence, it is convenient to describe the metal–coating system by means of an equivalent electrical circuit which converts the main processes occurring into macroscopic circuit elements such as capacitances, resistances, inductances and distributed circuit elements \((Z_{\text{diff}}, \text{CPE})\). The impedance expressions for these elements are given in Table 1.

![Fig. 1. Representation of the impedance as a complex quantity.](image)

<table>
<thead>
<tr>
<th>TABLE 1</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Impedance elements and their expression</strong></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Element</th>
<th>Symbol</th>
<th>Impedance expression</th>
</tr>
</thead>
<tbody>
<tr>
<td>Resistance</td>
<td>(R)</td>
<td>(R)</td>
</tr>
<tr>
<td>Capacitance</td>
<td>(C)</td>
<td>((j\omega C)^{-1})</td>
</tr>
<tr>
<td>Inductance</td>
<td>(L)</td>
<td>(j\omega L)</td>
</tr>
<tr>
<td>Warburg</td>
<td>(Z_{\text{diff}})</td>
<td>(K_{\text{diff}}(j\omega)^{-0.5})</td>
</tr>
<tr>
<td>Constant phase element</td>
<td>CPE</td>
<td>(K(j\omega)^{-\alpha b})</td>
</tr>
</tbody>
</table>

\(^*K_{\text{diff}} = \frac{RT}{z^2F^2c_0\sqrt{D}}\); where \(c_0\) = concentration of the diffusing species and \(D\) = diffusion coefficient.  
\(^b0.5 \leq \alpha \leq 1.0.\)
The impedance expressions for the standard elements $R$, $C$ and $L$ are given in textbooks of electrical engineering (for example ref. 44). The Warburg impedance results from a diffusion-controlled electrochemical process. The theoretical derivation of this complex impedance element has been given by Warburg [48, 49, 52, 54]. The constant phase element CPE is an impedance element with the special property that its phase angle is independent of frequency. This phenomenon was first mentioned by Fricke [55] and appears explicitly in the work of Cole and Cole [56] for dielectric systems. The understanding of this phenomenon is not complete, but generally the CPE is believed to originate from a distribution in the current density along the electrode surface as a result of surface inhomogeneities [10, 32, 39, 57–60].

This paper reviews some methods available for impedance analysis and discusses their applicability to coated metals. However, metal–coating systems are very complex systems which contain many physical phenomena which change with time. Thus impedance data have to be handled with care to avoid misleading interpretations.

2.3 Experimental equipment; cell design

In order to avoid artifacts, several requirements for the construction of a cell suitable for impedance measurements over a wide range of frequencies have to be considered [28, 29, 38, 61–69].

For measurements of specimens with an organic coating the electrochemical cells illustrated schematically in Fig. 2 have been used [68, 69]. Impedance data have been obtained at the open-circuit potential using an EG & G Princeton Applied Research model 388-2 AC impedance measurement system controlled by an Apple IIe computer. The frequency range analyzed was 50 kHz to 0.05 Hz. At frequencies > 50 kHz, the measurements were affected by phase shifts arising from the potentiostat. The lower frequency limit was chosen because of time limitations.

A critical problem in any impedance analysis is the validity of the experimental data [49, 70–72]. This is particularly true because of the necessity to use low amplitude excitations. In general, the amplitude of the superimposed AC signal was 20 mV. This signal was the best compromise.

Fig. 2. Cell configurations for impedance measurements on coated substrates (a) for undeformed specimens and (b) for deformed specimens. 1, Electrolyte container [glass tube (a) or sponge (b)]; 2, coated metal as working electrode; 3, Pt gauze or sheet as counter electrode; 4, reference electrode (SCE).
between the signal-to-noise requirements and the need to measure over the linearity range of voltage and current.

3 Model conceptions for the loss of protective properties during load

An organic coating ideally behaves as a dielectric, giving a capacitive impedance characterized by an $\omega^{-1}$ frequency dependence. This behaviour is electrically equivalent to the capacitance $C_0$ of the polymer layer in parallel with the resistance $R_0$ of the coating. However, most impedance spectra of coated metals immersed in an electrolyte solution with the resistance $R_E$ show deviations from this simple Debye impedance behaviour as a result of the development of ionic conductivity paths. This can be described by the general model depicted in Fig. 3 [69, 73–75], where the capacitance $C_0$ is replaced by a CPE, indicated by the CPE exponent $\alpha$ (cf. Table 1). $Z_1$ is a general impedance which occurs when an electrochemical reaction takes place at the metal–coating interface. For many systems, $Z_1$ can be characterized by a transfer resistance $R_1$ in parallel with a double-layer capacitance $C_{dl}$ (model a) or by a diffusion impedance (model b).

The dielectric properties of an organic polymer coating can be described by two frequency-dependent parameters which may define either the complex permittivity $\varepsilon(j\omega)$, the complex admittance $Y(j\omega)$ or the complex impedance $Z(j\omega)$ [32, 34]. Which of these representations is the most suitable depends on the physical nature of the system under study. For dielectrics the $\varepsilon$-representation is the most appropriate. In this case measurements are carried out in the high-frequency ($10^3$–$10^6$ Hz) and highest frequency ($10^8$–$10^{11}$ Hz) ranges [56, 76–78]. However, when considering coated metals under permanent immersion conditions, the $Y$- or $Z$-representation is commonly chosen.

An insulating coating on a metallic substrate can be characterized by the complex admittance

![Fig. 3. Equivalent circuit for the impedance of coated metals.](image-url)
\[ Y(j\omega) = \frac{1}{R_p} + j\omega C_p \]  

(7)

\[ Y' = \frac{1}{R_p}; \quad Y'' = \omega C_p \]  

(8)

(where \( R_p \) and \( C_p \) represent the parallel resistance and capacitance).

The relationships with the complex permittivity are given by

\[ B\epsilon(j\omega) = \frac{Y(j\omega)}{j\omega} = \frac{1}{j\omega R_p} + C_p \]  

(9)

\[ B\epsilon' = C_p - \frac{Y''}{\omega} \]  

(10)

\[ B\epsilon'' = \frac{1}{\omega R_p} = Y'/\omega \]  

(11)

where \( B \) is a geometric factor, which in the case of a plate-shaped capacitor in which the coating is the dielectric medium is given by the ratio of area \( A \) to thickness \( d \):

\[ B = A\epsilon_0/d \]  

(12)

(where \( \epsilon_0 \) = permittivity of free space) (cf. refs. 32 and 34).

For insulating coatings on metals, the resistance \( R_0 \) cannot be obtained due to limitations in the measuring equipment (\( \sim 10^{10} \) \( \Omega \)). Under such circumstances, the only parameter that can be determined is \( C_0 \), which is given by the expression

\[ C_0 = \frac{\epsilon_0 \epsilon A}{d} \]  

(13)

where \( C_0 \) depends on the characteristics of the coating, particularly its thickness, composition and structure. As the relative dielectric constant \( \epsilon \) of an organic coating is small (3–8) compared to that of water (\( \sim 80 \)), the value of \( C_0 \) will change with exposure time as the coating is penetrated by water.

The increase of \( C_0 \), the deviation of the coating from the \( \omega^{-1} \) dependence and the situation that a general impedance \( Z_1 \) is observed with increasing exposure time can be used as an indication of the degradation of the coating. Two situations should be considered [32, 69, 79, 80]:

1. After a given exposure time, the system undergoes changes which do not affect the continuity of the coating.
2. The system under study has defects and pores through which the electrolyte penetrates to the metal surface.

According to Schneider [79] these two situations can be described via a multilayer model (1) and a pore model (2), respectively.

3.1 Multilayer model

Figure 4 depicts Bode plots which illustrate schematically the changes occurring in an ideal coating from the start of immersion to longer time periods. Initially, the polymer coating gives a straight line plot with a slope of \(-1\), indicating that the modulus \( Z \) is inversely related to \( \omega \) and that the phase shift \( \phi \) is \(-90^\circ\) at all frequencies. The impedance behaviour is purely
Fig. 4. Theoretical Bode plots for a multilayer model over several time periods (cf. ref. 79).

Fig. 5. Theoretical Bode plots for a pore model over several time periods (cf. ref. 79).

capacitive with the upper limit \(|Z|_{\text{max}} = (\omega C_0)^{-1} = X_c\). The capacitance \(C_0\) can be determined by extrapolation of the straight line to \(\omega = 1\).

With increasing immersion time a shift of the straight line is observed depending on the water uptake into the coating, giving higher values of \(C_0\). At time \(t_2\), the lower frequency portion of the Bode plot is a straight line parallel to the log \(\omega\) axis, which intersects the log \(|Z|\) axis at the value of the layer resistance \(R_0\). In this case, the impedance is independent of frequency. The protective coating properties are essentially determined by the rate of water penetration through the insulating layer and the adhesion of the coating to the substrate. If water penetrates to the metal–coating interface, corrosion reactions can start after delamination of the coating. This can be seen at time \(t_1\).

The upper limit \(|Z|_{\text{min}}\) represents the ohmic resistance of the entirely delaminated coating saturated with electrolyte solution.

### 3.2 Pore model

Figure 5 depicts the theoretical Bode plots for a metal–coating system conforming to the pore model. As in the case of the multilayer model, the polymer coating behaves initially like a pure capacitance with an upper limit \(|Z|_{\text{max}}\). With increasing immersion time the \(R_{po}\) value attains a horizontal line. The pore resistance \(R_{po}\) can be attributed to pores and other defects filled with electrolyte solution. The value of \(R_{po}\) is mainly determined by the geometric size of these pathways and of the specific conductivity of the test solution. In general, the corrosion reaction will start at these defects, whereas the overall coating capacitance \(C_0\) does not change markedly as indicated by the constant high-frequency portion of the Bode plot. Also, in this case, the change of impedance with time is very much determined by the loss of adhesion. The lower limit \(|Z|_{\text{min}}\) characterizes the complete failure of the coating.
Both these models show that changes in the frequency dependence of the coating impedance during deterioration of the system provides significant insights into the nature of coating breakdown. Several parameters can be measured simultaneously as a function of the experimental conditions. Besides coating properties such as $C_0$ (and $\varepsilon$), $R_0$ and the degree of porosity can be obtained in relation to diffusion of electrolyte through an organic coating and the extent of corrosion occurring at the metal-coating interface. Heterogeneities inside the polymer coating cannot be detected initially because $C_0$ and $R_0$ are integral values. They only will be visible on recording the change in the coating properties during exposure as shown theoretically in Fig. 4 and 5.

However, since the behaviour of real systems frequently deviates from that expected theoretically, additional elements must therefore be taken into account. In this case, analysis of impedance only leads to reliable component values when the equivalent circuit model is known and does not become inappropriate with degradation of the coating.

Difficulties arise when overlapping between the electrical regions attributed to the dielectric coating properties and the electrochemical regions attributed to the corrosion processes occurs. To overcome these problems, deconvolution of the impedance data is often used for estimating the individual components for more complicated systems. Kendig and Mansfeld [81, 82] have illustrated how the deconvolution method can be used to determine successively the components of an equivalent circuit.

However, it should be emphasized that with deconvolution the sequence of extrapolations and subtractions tends to accumulate errors in the last-determined components [83, 84].

Recently, quantitative analysis has been carried out by complex non-linear squares impedance analysis methods which use all experimental data simultaneously to fit a predetermined model to the data [83–89]. A comparison of non-linear least squares fit (NLLSF) methods has been given by Walter et al. [89]. The NLLSF procedure may yield a more accurate description of the important steps in the degradation process. In this paper a commercially available impedance analysis program, called EQUIVCRT [85], has been used for the estimation of parameter values of metal–coating systems.

4 Impedance measurements at a constant frequency

If only a qualitative estimation of the polymer coating is of interest, the change of impedance data during the exposure in a test solution can be recorded at a constant frequency. The frequency depends on the system under study. In general, a frequency $f = 1$ kHz is preferred. The time-dependence of $C_0$ and $R_0$ corresponds qualitatively to the degradation and corrosion processes [12, 27, 29, 31, 34, 38, 69, 90]. As stated above, the resistance $R_0$ of an insulating coating cannot be measured during the first stage of exposure. Thus, over this stage, the changes in the value of the capacitance
$C_0$ are generally of greater interest. Figure 6 shows $C_p$ as a function of the time of immersion, where $C_0$ corresponds electrically with a parallel circuit element $C_p$ (cf. Fig. 3). Different time regimes may be distinguished in this figure [29, 31, 38, 90-95].

First, a linear relationship is observed between $C_p$ and $t$ (more correctly between $C_p$ and $\sqrt{t}$ [94, 95]). The increase in $C_p$ is due to the water uptake of the coating.

In the second regime the coating is saturated with water and the value of $C_p$ is constant over a longer time period. In some cases a further stepwise increase of $C_p$ may be observed over the second regime. According to Geenen et al. [94], this may be attributed to clustering of water in or under the coating. If this stepwise increase of $C_p$ coincides with changes in $U_{\text{corr}}$, this may be correlated to wet adhesion at the metal–coating interface. In this case, EIS could provide a method for the in-situ estimation of the wet adhesion properties of organic coatings. However, it appears to be difficult to provide the experimental conditions necessary for identifying this step correctly.

Finally, there is a rapid change in $C_p$ over the third regime where the coating fails completely and underfilm corrosion reactions start. For delamination and corrosion processes to occur, it is necessary that an organic coating exposed to a wet atmosphere will be penetrated by water. Hence, it is important to know the water-uptake properties of organic coatings. The degree of water uptake depends strongly on intrinsic polymer properties such as polymer structure and composition. Thus water-permeation studies may be used for the optimization of coating formulation, curing conditions and the addition of pigments or fillers. In order to study these coating properties, the percentage of water taken up by volume $X_v$ must be determined [91]. Values of $X_v$ may be derived from gravimetric measurements of free films or from capacitance measurements of coated metals. In general, capacitance measurements are to be preferred because the metallic substrate has a marked influence on the polymer properties. Thus at longer immersion times both methods give widely different results, especially in that case where water accumulates at the metal–coating interface and osmotic pressures arise.
as a result of the presence of contamination associated with the metal pretreatment or corrosion products present on the metal surface [4, 39, 40, 93, 96-98]. During the initial stage of coating exposure, the percentage of water taken up by volume $X_v$ can be calculated from a number of different relationships [94].

Of these, the most widely used is the empirical relationship of Brasher and Kingsbury [91]:

$$X_v = \frac{\log(C_{p(1)}/C_{p(0)})}{\log 80} \times 100\%$$ (14)

where $C_{p(1)}$ and $C_{p(0)}$ are the measured capacitances at times $t_1$ and $t_0$, respectively (cf. Fig. 6).

For a correct calculation of the percentage water uptake, the following assumptions and simplifications have been made [34, 38, 90, 91]:

1. The change of capacitance is entirely due to the permeation of water into the film.
2. The water uptake does not cause the coating to swell.
3. The penetrating water is distributed homogeneously in the coating.
4. The permittivity of water is constant and equal to 80.
5. No polar solvent is present in the coating.
6. The values of $C_p$ are identical to the $C_0$ value of the organic coating as expressed by equation (13) above.
7. The volume fraction penetrated by water remains relatively small.

It is obvious that such a large number of assumptions and simplifications cannot be completely fulfilled. Hence one should be careful when using $C_p$ measurements for the calculation of material constants, such as the solubility and the diffusion coefficient for water in organic coatings [75, 95]. However, in many cases, the capacitance method can be useful and give valuable information on the structure and composition of the coatings under study. This is illustrated by the results depicted in Figs. 7 and 8 [12, 31, 38, 99, 100].

Figure 7 depicts the results for several polymer coatings formed under different curing conditions. The initial values of $C_{p(0)}$ depend on the thickness of the organic coatings and the kind of polymer employed, whereas the change in $C_p$ arises mainly from the polymer structure and curing conditions (cf. Table 2). This table shows that during the initial immersion phase the change in $C_p$ is independent of the kind of metal substrate and electrolyte solution employed, respectively. For coatings formed on different substrate materials (Ag, Cu, steel) immersed in different solutions (NaCl, AgNO$_3$, CuSO$_4$), good agreement between the individual values of the water uptake was found [99].

Additives influence both the coating thickness and the polymer structure. Polymer layers formed under the same conditions but with different additives give different values of $C_{p(0)}$ and $C_{p(1)}$ as shown in Fig. 8 where the water-uptake properties for a coating produced by cathodic electropainting (cEP)
Fig. 7. Values of $C_p$ (measured at 1 kHz) as a function of the exposure time for different coatings. Curve 1, AH50 (alkyd varnish air-dried at 50 °C); curve 2, AH150 (alkyd varnish air-dried at 105 °C); curve 3, PC (poly(vinyl chloride) varnish air-dried at 50 °C); curve 4, PCv (poly(vinyl chloride) varnish, without oil additive, air-dried at 50 °C); curve 5, PFE (phenol-formaldehyde epoxy resin stoving varnish, 20 min at 140 °C).

Fig. 8. Values of $C_p$ (measured at 1 kHz) as a function of the exposure time for a cathodic electropaint with different additives. Curve 1, without additives; $d = 5 \mu m$, $X_v = 15.2\%$; curve 2, with 1.0 mM dodecylpyridinium bromide (DPB); $d = 25 \mu m$, $X_v = 34.1\%$; curve 3, with 1.0 mM methylmercaptobenzothiazole (MMBT); $d = 5 \mu m$, $X_v = 6.7\%$.

TABLE 2

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Thickness, $d$ (µm)</th>
<th>$C_{p1000}$ (pF cm$^{-2}$)</th>
<th>$C_{p10}$ (pF cm$^{-2}$)</th>
<th>$X_v$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>AH50</td>
<td>37±3</td>
<td>98</td>
<td>136</td>
<td>7.4</td>
</tr>
<tr>
<td>AH105</td>
<td>37±3</td>
<td>92</td>
<td>114</td>
<td>4.6</td>
</tr>
<tr>
<td>PC</td>
<td>28±3</td>
<td>117</td>
<td>134</td>
<td>3.1</td>
</tr>
<tr>
<td>PCv</td>
<td>26±3</td>
<td>102</td>
<td>105</td>
<td>0.7</td>
</tr>
<tr>
<td>PFE</td>
<td>17±2</td>
<td>176</td>
<td>187</td>
<td>1.4</td>
</tr>
</tbody>
</table>

in the presence of different additives are recorded. The steplike increase and the rapid change in $C_p$ on addition of DPB to the eEP bath may be attributed to the inhomogeneous distribution of water in the coating [12, 100].

The water permeation of organic coatings is closely related to the corrosion protection properties, other than with coatings containing active pigments. Such coatings exhibit local destruction involving another protection mechanism based on passivation, adsorption or galvanic protection (cf. refs. 12, 101–104).
This protection mechanism is still not fully understood and will not be considered further here.

In general, the lifetime expectancy of coatings under practical conditions is determined by exposure of the coated material to standard tests such as the condensation chamber test (ASTM D 2247-68), the salt spray test (ASTM B 117-73) and the Kesternich environmental chamber test (DIN 50018) \[12, 105, 106\]. To reach an objective conclusion concerning the quality of organic coatings, impedance measurements provide a useful tool. For routine analysis, the changes of the impedance data \(C_p\) and \(R_p\) at constant frequency are often recorded against time \([12, 38, 107, 108]\). Degradation and loss of adhesion is indicated by a rapid increase in \(C_p\) and a rapid decrease in \(R_p\). Assuming that there are localized areas exhibiting different behaviour, it may be possible to estimate the degree of deterioration \([34, 38, 60, 108]\).

In the presence of local defects, the entire metal–coating system may be considered as consisting of undamaged areas and conductive pathways. On the basis of such a model, the measured value of \(C_p\) at a given exposure time may be expressed as \([108]\):

\[
C_p = (1 - \Gamma)C_0 + \Gamma C_{ec}
\]

\[\text{where} \]
\[
\Gamma = A_{ec}/A_t \\
A_{ec} = \text{electrochemically activated, conducting area} \\
A_t = \text{total area} \\
C_0 = \text{capacitance of polymer layer at } t=0 \\
C_{ec} = \text{double-layer capacitance of the metallic substrate}
\]

The percentage of area damage may be estimated in the following manner:

\[
\Gamma_{1 kHz} = \frac{C_p(1 kHz) - C_0}{C_{ec}(1 kHz) - C_0} \times 100\%
\]

In general, the active area at the metal–coating interface and hence the value of \(\Gamma\) will increase with exposure time. However, estimation of the percentage of delaminated corroding area can become difficult for longer exposure times, especially if the corrosion products plug the pores as shown in Fig. 9. The cyclic behaviour observed is typical for defect coatings with a permanent change of plugged and free pores \([35, 41, 60, 108, 109]\). To overcome such complications, delamination effects are better studied using cathodic polarization methods \([60]\).

**5 EIS results for coated metals prior to and during exposure in a corrosive medium**

Further analysis of the deterioration mechanism of organic coatings on metals is only possible through investigations over a broad frequency range. For practical applications such as routine analysis and quality control a simple impedance analysis is often sufficient, with only changes in the shape of the impedance diagrams being followed against time \([12, 30, 36, 38, 40, \ldots]\).
69, 110–118]. For more detailed information regarding the system under study, complete data analysis is essential.

5.1 Simple impedance analysis

Usually impedance data for organic coatings are displayed as Bode plots which depict the logarithm of the modulus of the impedance, \( \log |Z| \), and the phase angle \( \varphi \) as a function of the logarithm of the frequency, \( \log f \). The advantage of this procedure is that data for all measured frequencies are shown and a wide range of impedance values can be represented.

Employing the assumption that an organic coating can be modelled by an equivalent circuit as depicted in Fig. 3, the impedance data can also be represented as a plot of the logarithm of the equivalent parallel resistance, \( \log R_p \), or the logarithm of the equivalent parallel capacitance, \( \log C_p \), versus \( \log f \). Figure 10 illustrates the changes arising in such diagrams with changes in the exposure time [93, 119].

Prior to exposure, the organic coating shows a purely capacitive behaviour with the \( \log |Z| \) or \( \log R_p \) representation exhibiting a slope of \(-1\), indicating that the impedance is inversely related to \( f \) and that the value of \( \varphi \) is nearly \(-90^\circ\) at all frequencies. The values of \( C_p \) are independent of frequency. With progressing exposure time, however, the values of \( |Z| \) or \( R_p \) decrease and the values of \( C_p \) increase over the low-frequency range, indicating a decrease in the barrier properties of the coating. At longer exposure times,
Fig. 10. Frequency dependence of the impedance data for a specimen with an organic coating (Aqualux K electrocoat, ICI, d=20 μm) at different stages of deterioration during exposure to moisture (condensation chamber). (a) Intact coating; (b) first signs of deterioration; (c) progressive deterioration; (d) onset of corrosion.

a diffusion tail begins to appear at low frequencies. Over the middle frequency region, the log |Z| or log $R_p$ plot corresponds to a line horizontal to the $f$ axis indicating a purely resistive value of $|Z|$ and $R_p$ while the phase angle $\varphi$ tends to zero. At low frequencies the log |Z| or log $R_p$ plots curve upwards and the corresponding phase angle increases. From the definition of $Z_{diff}$
given in Table 1, a slope of $-1/2$ would be expected at low frequencies. However, this theoretical value is not achieved in most cases since the diffusion impedance also contains a resistive contribution which decreases the slope [35, 39].

The low-frequency behaviour of the coating depicted in Fig. 10(d) indicates the onset of electrochemical corrosion reaction at the metallic substrate. It should be mentioned that through the use of EIS it is possible to detect corrosion reactions long before the deterioration can be observed visually. Such simple impedance analysis is successful for optimization of different surface pretreatments [10, 40, 41, 82, 100, 118]. Due to the build-up of corrosion products at the metal–coating interface producing stresses in the coating, the pretreatment employed for a metallic substrate can have a large effect on the lifetime of a metal–coating system. The importance of proper surface pretreatment can be illustrated for the case of mild steel coated with different conversion layers before the application of cathodic electropainting. As can be seen from Fig. 11, a much more rapid change in impedance occurs if the phosphate at the cEP layer consists of (a) a Hopeit rather than (b) FeZn–phosphophyllite (Aqualux K electrocoat, ICI, $d=20$ μm) (cf. also refs. 69, 119 and 122).

Similarly, no further data analysis is required to obtain an initial insight into the degradation mechanism involved with an organic coating. Thus, in general, it is to be expected that solvent-based commercial paints usually

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**Fig. 11.** Influence of phosphating treatment on the protective properties of organic coatings produced by cathodic electropainting (Aqualux K electrocoat, ICI, $d=20$ μm) during exposure to moisture. (a) Hopeite; (b) FeZn–phosphophyllite.

**Fig. 12.** Bode plots for a solvent-based alkydamine coating ($d=45$ μm) on mild steel (plot a) and a polyamide powder coating ($d=300$ μm) on mild steel (plot b) during a continuous immersion test in a 10% NaCl solution at room temperature.
produce coatings with pores which must be considered as conductive pathways when the coating is in contact with an electrolyte solution. The pores may be present directly after application or after curing. Pores are caused by the evaporation of solvent during curing, a local low density of the polymer layer and/or the entrapment of air.

In contrast, thermosetting powder coatings or other solvent-free coatings such as synthetic resins, which are applied in practice in relatively thick layers, act as barrier-type coatings without conductive pathways. Hence, different types of degradation are to be expected during exposure according to whether the pore or multilayer model applies to the system. A selection of characteristic plot shapes for these two types of model is illustrated in Fig. 12 [69].

5.2 Detailed impedance analysis

More information on the possible mechanisms involved in degradation and corrosion, and evaluation of the system parameters, can be obtained only by a detailed computer-assisted analysis of the impedance data. The first requirement for the evaluation of impedance spectra is to have the most probable equivalent circuit for the measured impedance data. The validity of the proposed equivalent circuit can be verified by following the changes in the impedance spectra with time during deterioration of the system. An analysis of the impedance spectra reported to date shows that most metal–coating systems do not achieve a slope of \(-1\) over the frequency range studied. Hence, quantitative analysis is best carried out by fitting the data to the theoretical model proposed in Fig. 3. The data analysis procedure, based on the impedance analysis software package 'Equivalent Circuit' by Boukamp [85], is demonstrated for a powder coating by the plots depicted in Fig. 12(b). This figure shows the slope of the Bode diagrams measured after different immersion times in 10% NaCl solution. The fitted results are summarized in Table 3. The first two plots in Fig. 12(b) correspond to a quasi-ideal coating which can be described by a CPE. The CPE constant is related to the polymer layer capacitance \(C_0\) which increases with time, while the CPE exponent \(\alpha\) can be considered as a measure of the homogeneity of the coating. Only after 60 d immersion has the layer resistance \(R_0\) diminished sufficiently in magnitude to allow the data to be fitted. Bode plots for the measured and fitted data after 60 d immersion are shown in Fig.13(a).

<table>
<thead>
<tr>
<th>Exposure time</th>
<th>(C_0) (nF)</th>
<th>(\alpha)</th>
<th>(R_0) (M(\Omega))</th>
<th>(K_{\text{diff}}) ((\Omega) cm(^{-1}) s(^{-0.5}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 h</td>
<td>0.287</td>
<td>0.975</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>30 d</td>
<td>0.526</td>
<td>0.972</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>60 d</td>
<td>1.42</td>
<td>0.969</td>
<td>332</td>
<td>-</td>
</tr>
<tr>
<td>90 d</td>
<td>6.05</td>
<td>0.887</td>
<td>3.3</td>
<td>4.05 \times 10^6</td>
</tr>
</tbody>
</table>

TABLE 3

Fitted results for a powder coating (\(d = 300 \mu m\)) immersed in a 10% NaCl solution.
quality of fit can best be evaluated from a Fit Quality plot (FQ plot) in which the relative deviations $\Delta Z'$ and $\Delta Z''$ are plotted against log $\omega$ (Fig. 13(b)). The result obtained shows that quite a good fit can be achieved.

At longer immersion times, a Warburg impedance occurs at low frequencies as a result of a diffusion-controlled electrochemical corrosion process at the metal–coating interface. With increasing exposure time, an increasing number of parameters has to be taken into account. The use of a greater number of fitting parameters gives a better insight into the degradation mechanism involved, provided such parameters retain a physical meaning. One method of checking the reliability of the extended circuit model is to subtract individual elements or combinations of elements from the total dispersion curve, assuming that the remainder adopt either a series or a parallel arrangement [59, 81, 82, 89, 120–122].

The 60 d results for the powder coating are plotted in Fig. 14 as Nyquist diagrams before and after subtraction of the CPE. According to the equivalent circuit proposed, the result should lie on a straight line with a slope of 45°.
as a consequence of the diffusion impedance whose intercept with the real axis should equal $R_0$.

6 Conclusions

EIS is a powerful tool for investigating the mechanism of deterioration and corrosion of coated metals. Data analysis allows a number of important quantities to be studied successfully. The usefulness of the impedance method, however, depends on the accuracy with which the data can be determined and then related to the basic and corrosion properties of the system.

In discussing the electrical properties of an organic coating, it is convenient to describe the metal–coating system in terms of an equivalent circuit and to determine the components of this model from the measured impedance data.

It should be stressed that conclusions about the deterioration mechanism can only be drawn if the changes of the parameters with time are in accordance with results of other methods (e.g. visual inspection, corrosion potential, adhesion measurements).
The examples provided illustrate that impedance data can provide a remarkable insight into the protective properties of organic coatings, as well as of the corrosion and degradation phenomena occurring under the coating.

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