Chapter 11
Coatings and Paints

Electrochemical impedance spectroscopy is very well suited to study paints and coatings used to prevent corrosion. There are even ISO norms developed for such tests [675] and technical notes from the equipment manufacturers [676, 681]. This topic has also been reviewed in several books [473–475].

11.1 Electrical Equivalent Models

The ideal coating is a pure capacitor (Fig. 11.1a), where R_s is the solution resistance and C_c the coating capacitance. However, real coatings in solutions rarely behave in an ideal manner; they have defects and regions of low cross linking. An electrical equivalent circuit for such coatings is displayed in Fig. 11.1b, in which the coating capacitance is in parallel with the coating resistance, R_{po}, and in series with the capacitance of the diffuse layer at the coating (containing ions [474])/metal interface, C_d° [474]. The index 0 indicates that the geometric and real surface areas are identical as the coating is adhering well to the metal surface. Because of the low dielectric constant of the coating, this value is small, approximately 0.05 μF cm^{-2}. The capacitance of the coating, C_c, is usually one to two orders of magnitude lower than C_d°.

During further exposure of the coating to solution corrosion starts under the pinholes and can spread around, but in general it is localized. This produces a double-layer capacitance of the metal/solution interface under coating, C_d, greater than that of metal/coating, $C_d > C_d^0$. The faradaic corrosion reaction is represented by the resistance, R_c (Fig. 11.1c). When disbonding of the coating continues, the solution can penetrate under the coating (Fig. 11.2). In such a case, the impedance can be modeled as a transmission line (Fig. 11.1d). When the ohmic resistance under the film, R_{si}, becomes small, the transmission line can be simplified to the model in Fig. 11.1e, where $C_D = \Sigma\, C_{di}$ and $1/R_D = \Sigma\, 1/R_{di}$.

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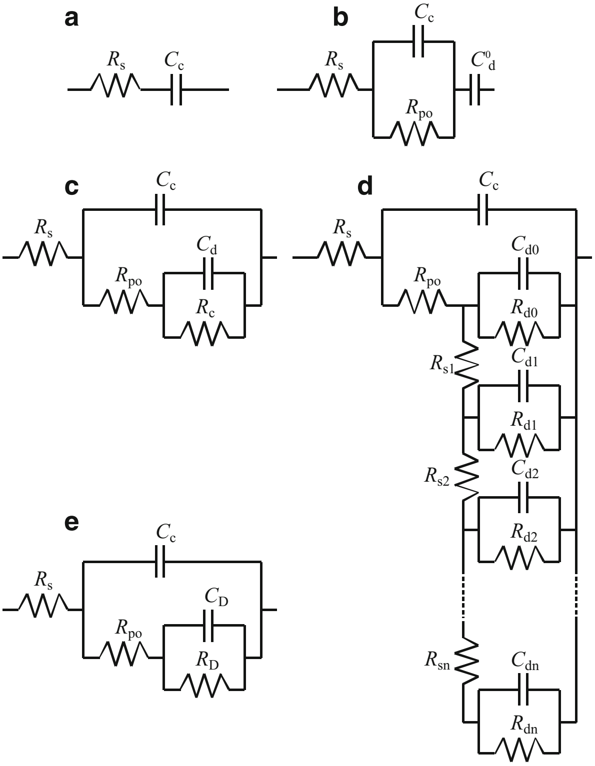

Fig. 11.1 Electrical equivalent circuits for an organic coating: (**a**) ideal coating, (**b**) real coating without corrosion, (**c**) adhering coating with the onset of corrosion in pinholes, (**d**) coating with disbonding, (**e**) coating with disbonding and small R_{si}

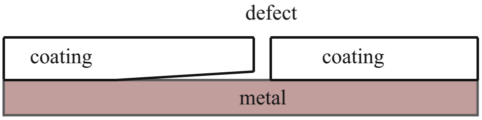

Fig. 11.2 Schematic of coating with defect and delamination under coating

11.2 Water Absorption in Organic Coating

The capacitance of a dielectric depends on its dielectric constant, ε, and thickness, d:

$$C_c = \frac{\varepsilon \varepsilon_0 A_0}{d}, \tag{11.1}$$

where ε_0 is the dielectric permittivity of vacuum and A_0 the geometric surface area. When the coating is in contact with an aqueous solution, water penetrates into the coating, changing its initial dielectric constant from 3–8 to larger values because the dielectric constant of water is $\varepsilon_W = 78.5$ at 25 °C. The most widely used model to estimate the water content in a coating was put forward by Brasher and

Kingsbury [476], who proposed the following equation for the determination of the volume fraction in a coating (see also Ref. [477]):

$$\phi = K\frac{\log[C_\mathrm{C}(t)/C_\mathrm{C}(0)]}{\log\varepsilon_\mathrm{W}}, \tag{11.2}$$

where the indices t and 0 indicate coating capacitances after time t and the initial capacitance at time zero, and K accounts for the increase in volume, and it should not exceed 1.25. Usually it is taken as $K = 1$, corresponding to a constant volume. It was found that this formula often (but not always) overestimates water content (in comparison with the gravimetric method) [476, 478]. Castela and Simões [477] proposed a different model, applicable to homogeneous coatings, that does not suffer swelling:

$$\phi = \frac{C_\mathrm{C}(t) - C_\mathrm{C}(0)}{C_\mathrm{sol} - C_\mathrm{air}}, \tag{11.3}$$

where C_sol and C_air are the capacitances of the solution and air determined using Eq. (11.1). Equation (11.3) also usually overestimates water absorption.

In practical measurements, pure capacitances are rarely observed, and the CPE should be used to approximate the experimental data. However, capacitances may be easily obtained using the theory discussed in Sect. 8.1.

It should be kept in mind that organic coatings are characterized by low capacitances and very high resistances, demanding work at high frequencies, and it must be assured that the measuring equipment is able to measure such objects (Sects. 16.1 and 16.2 and Refs. [675–681]).

11.3 Analysis of Impedances of Organic Coatings

The parameters appearing in electrical equivalent models depend on the surface area [473, 474, 479–481]. There are two principal parameters: A_0, the geometric surface area of the sample, and A_d, the disbonded surface area under the coating. Initially, only pinhole pores perpendicular to the electrode surface are formed without delamination (Fig. 11.1b), C_c is as defined in Eq. (11.1), and

$$R_\mathrm{po} = R_\mathrm{po}^0/A_\mathrm{d} = \rho d/A_\mathrm{d}, \tag{11.4}$$

where ρ is the specific resistivity of the pinhole, and $C_\mathrm{d}{}^0$ is calculated with respect to the geometric surface area. At this stage, $A_\mathrm{d} \ll A_0$. With the increasing delamination of the coating, the parameters must be recalculated with respect to the real surface areas:

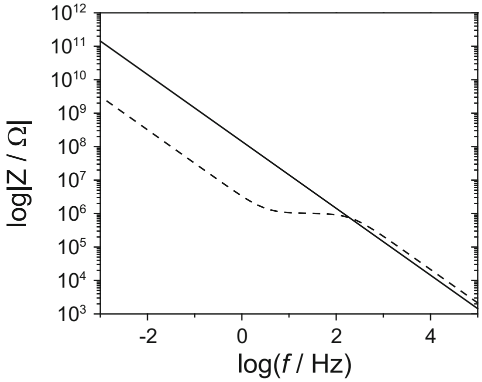

Fig. 11.3 Bode magnitude plots resulting from capacitive behavior of coatings corresponding to circuits in Fig. 11.1 a – *continuous line*, b – *dashed line*. Parameters: $R_s = 100\ \Omega$, $C_d{}^0 = 5 \times 10^{-8}$ F, $C_c = 1.1 \times 10^{-10}$ F, $R_{po} = 10^6\ \Omega$

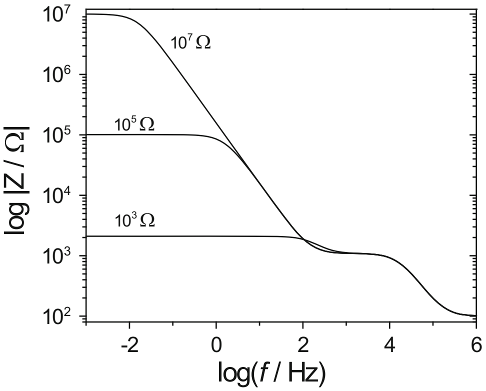

Fig. 11.4 Bode magnitude plots corresponding to disbonding coating (Fig. 11.1e). Parameters: $R_s = 100\ \Omega$, $C_c = 10^{-8}$ F, $R_{po} = 10^3\ \Omega$, $C_D = 10^{-6}$ F; R_D is indicated in graph

$$\begin{aligned} R_c &= R_c^0 / A_d, \\ C_d &= C_d^0 A_d, \\ C_c &= C_c^0 (A_0 - A_d), \end{aligned} \tag{11.5}$$

where $R_c{}^0$ is the specific corrosion resistance of the metal and the value of R_{po} decreases as damage to the coating increases, leading to the solution penetration.

The complex plane plots of the circuits in Fig. 11.1a, b are as those in Figs. 2.32 and 2.35, respectively. In the analysis of coating, usually Bode plots are studied. Bode magnitude plots for circuits in Fig. 11.1a, b are displayed in Fig. 11.3.

The complex plane plots corresponding to the circuits in Fig. 11.1c–e display two semicircles, as in Fig. 2.39. The corresponding Bode plots are shown in Fig. 11.4.

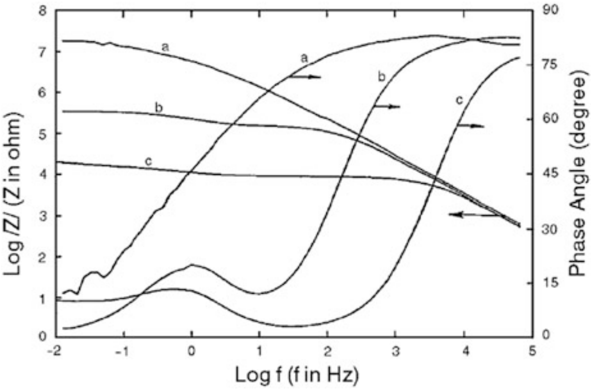

Fig. 11.5 Bode plots of steel coated with alkyd enamel after exposure to 0.5 M NaCl for (**a**) 43 days, (**b**) 90 days, and (**c**) 162 days (Reproduced with permission from NACE International, Houston, TX. All rights reserved; from Ref. [481] © NACE International 1993)

With a decrease in the corrosion resistance, low-frequency impedance decreases, displaying poorer coating protection. A practical example of the accelerated corrosion of coated steel following exposure to concentrated NaCl solution is displayed in Fig. 11.5, where a decrease in the low-frequency resistance from over 10^7 to 10^4 Ω is observed after 162 days.

11.4 Conclusions

EIS has proven to be highly successful in studies of the quality of organic coatings, leading to publication of ISO norms. The alternative electrochemical methods based on corrosion current measurements are not sensitive enough, and methods based on peeling off the coating and inspection of the corrosion are destructive and cannot be applied to the initial stages of degradation. However, care must be taken to assure that the measurements are carried out correctly and the measuring equipment is able to measure very high resistances and low capacitances. Specialized equipment, such as the Solartron 1296 Dielectric Interface, is available commercially.