



## Some comments on the use of the EIS phase angle to evaluate organic coating degradation

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### ABSTRACT

The impedance of a disc electrode protected by an organic coating, with a thickness profile along its radius, was considered by EIS. The local and global impedances, the ohmic resistance corrected phase angle, and raw phase angle were calculated. The thickness profile leads to a well-defined minimum in the calculated phase angle curves, which can be observed in the high frequency domain. This effect is enhanced with higher permittivity, thinner coatings and low conductivity immersion baths. From these results, it appears that the graphical treatment of experimental phase angle curves to evaluate the coating degradation may lead to erroneous conclusions.

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### 1. Introduction

Electrochemical Impedance Spectroscopy (EIS) has been used for many years to study the degradation of organic coatings [1–10]. This is because EIS is a non-destructive method that is able to characterize the organic coating and can be used to obtain the interfacial metallic response under the coating (delaminated area). Usually, the coated materials are represented by Equivalent Electric Circuits (EECs) [1] and fitting procedures allow for the extraction of useful parameters such as the film resistance and the coating capacitance, which provide some quantitative information about the barrier properties of the coatings. With a non-aged, defect-free coating (perfect coating) the EEC is composed of a resistance in series with a capacitor: the resistance represents the electrolytic solution resistance,  $R_e$ , and the capacitor stands for the polymer layer with the film capacitance,  $C_f$ . When the coating is aged in humid conditions, the aggressive medium (water, electrolytic solution) penetrates the polymer film through pores and fills in the free volume. Electrolytic paths develop within the coating and they are represented by the film resistance,  $R_f$ , which is added in parallel to the film capacitance,  $C_f$ , in the previous EEC. It must be noted that capacitors can be replaced by a Constant Phase Element (CPE) to take into account the non-homogeneity of the coating. Finally, if the water reaches the metallic substrate, an interfacial activity can develop and a faradic impedance in parallel to a double layer capacitor are

added to the above-mentioned EEC, resulting in the well-known electrical representation of a degraded paint [1]. Of course, more complex EECs can be found depending on the coating nature (e.g., zinc-rich primers), the eventual dielectric response of the polymer, or the defect presence [11–14].

Recently, some authors [15–19] proposed to use raw EIS data, particularly in the Bode format, to perform the evaluation and ranking of the coatings under investigation. In these works, the phase angle in high frequency (10 kHz) or the area under the phase angle curve were considered. These treatments are quite easy and seem to give good results. However, under some circumstances, the phase angle in high frequencies is not related only to a capacitor or a CPE. Indeed, in recent work [20], it was shown that the non-homogeneity of the system geometry could introduce some shifts in the phase angle curve. In this cited article, the case of an oxide layer with a graded thickness was studied.

In the present paper, we propose to consider this approach with an organic coating applied onto a metallic substrate and to simulate EIS phase angle plots. The coatings are assumed to be aged, meaning that an ohmic behavior developed and that a film resistance can be defined. In other words, the case of a blocking electrode, which could be the case of a perfect, non-aged organic coating, is not considered since, usually, EIS experiments are performed and analyzed for a long exposure time to follow the coating degradation. The physico-chemical properties and geometries of organic coatings are different from the work cited above but similar effects may be observed.

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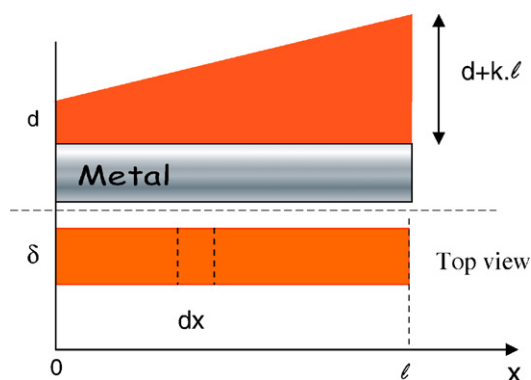


Fig. 1. Schema of a rectangular coated electrode with a thickness profile according to [20].

## 2. Theory

According to Cattarin et al. [20], in the case of a rectangular coated electrode ( $\delta$  wide,  $l$  long; Fig. 1), with an ohmic behavior and a thickness varying linearly along its length as  $d(x) = d + kx$ , the local impedance referring to a surface element of area ( $\delta dx$ ) can be written as:

$$Z_{\text{local}}(x) = \frac{1}{\delta(1 + j\omega\rho\varepsilon_0\varepsilon_r)} \left\{ \frac{R_e(1 + j\omega\rho\varepsilon_0\varepsilon_r) + \rho(d + kx)}{dx} \right\} \quad (1)$$

This corresponds to an EEC as shown in Fig. 2, where:

- $R_{e,\text{loc}}$  is the local electrolyte resistance defined as:  $R_{e,\text{loc}} = R_e/\delta dx$ , with  $R_e$  being the electrolyte resistance;
- $C_{f,\text{loc}}$  is the local film capacitance defined as:  $C_{f,\text{loc}} = \varepsilon_0\varepsilon_r\delta dx/d + kx$ , with  $\varepsilon_r$  being the coating permittivity;
- $R_{f,\text{loc}}$  is the local film resistance defined as:  $R_{f,\text{loc}} = \rho(d + kx)\delta dx$  with  $\rho$  being the finite resistivity of the film.

Then, the integration of  $(Z_{\text{loc}})^{-1}$  leads to the global impedance referring to the whole electrode surface ( $\delta l$ ):

$$Z_{\text{global}}^{-1} = \frac{\delta(1 + j\omega\rho\varepsilon_0\varepsilon_r)}{\rho k} \ln \left( \frac{R_e(1 + j\omega\rho\varepsilon_0\varepsilon_r) + \rho(d + kl)}{R_e(1 + j\omega\rho\varepsilon_0\varepsilon_r) + \rho d} \right) \quad (2)$$

Fig. 3 presents the raw phase angle of the impedance for the system with a thickness profile (TP) from 10 to 100 nm [20], together with the ohmic resistance corrected phase angle [20,21] and the raw phase angles that would be obtained with coated systems having a constant thickness of 10 or 100 nm. As can be seen, the TP system gives a response that is identical to the phase angle of the constant thickness systems in low frequency, while it is very different in the HF domain. This is because of the influence of the  $(d + kl)/d$  term in Eq. (2) which introduces a well-defined minimum in the ohmic resistance corrected phase angle [20].

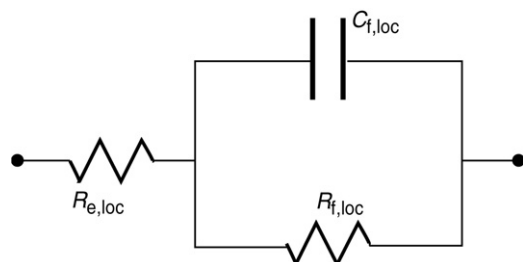


Fig. 2. Local equivalent electrical circuit for a coated electrode with ohmic behavior.

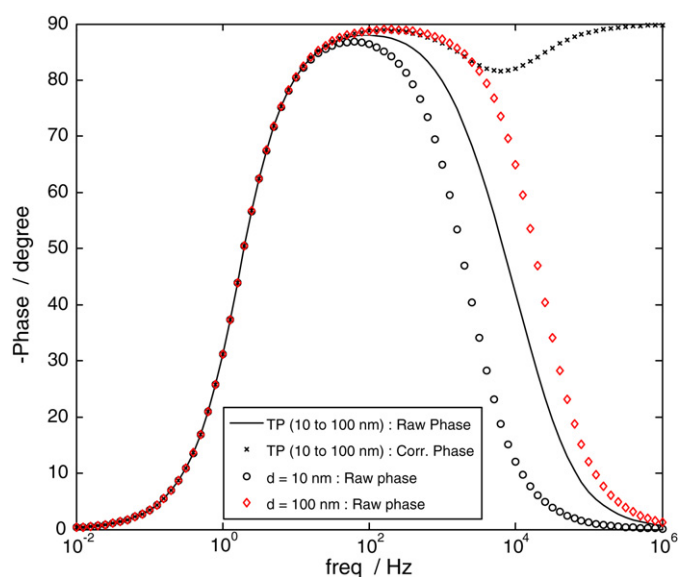


Fig. 3. Raw phase angle and ohmic resistance corrected phase angle for the rectangular system with a thickness profile (TP) from 10 to 100 nm [20], and raw phase angles obtained with a constant thickness of 10 or 100 nm with properties as:  $\delta = 3$  cm;  $l = 5$  cm;  $\varepsilon = 42$ ;  $R_e = 20 \Omega \text{ cm}^2$ ;  $k = 1.8 \times 10^{-6}$ ;  $\rho = 2.6446 \times 10^{10} \Omega \text{ cm}$ .

## 3. Simulated EIS diagrams

The above equation was considered in the case of an organic coating, with a permittivity equal to 6 since it is generally admitted that the values are between 3 and 8 [22]. The ohmic resistance corrected phase angle [21] was plotted vs.  $\log(f)$  for different organic coating thicknesses and compared to the result obtained in the case of the 10 nm oxide presented in [20]. In the four cases, the slope  $k$  is chosen to obtain a thickness increase with a factor of 10. As can be seen (Fig. 4), the phase angle curves presented a minimum in the HF domain for all organic coating thicknesses. With the same low thickness (10 nm), the minimum in the phase angle curve is shifted towards higher frequencies for lower permittivity values. This is because of the permittivity value of the polymer, which is

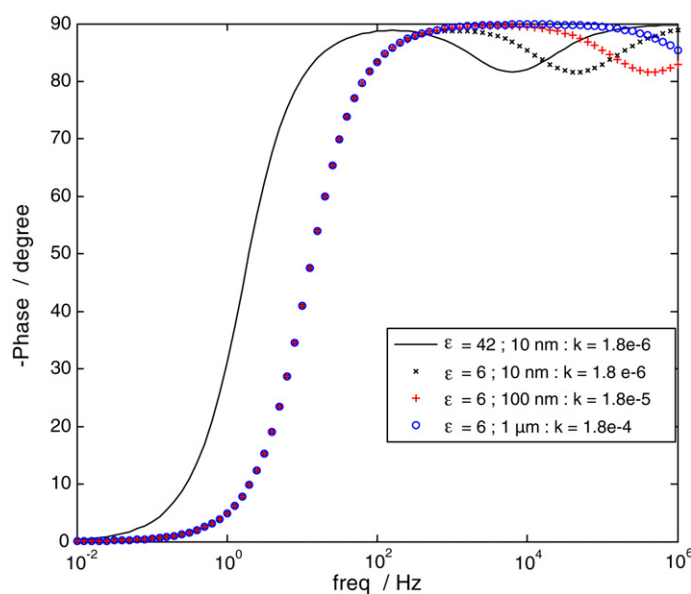


Fig. 4. Ohmic resistance corrected phase angles for an oxide layer or an organic coating with different thickness profiles in a rectangular geometry ( $\delta = 3$  cm;  $l = 5$  cm). The thickness  $d$  increases by a factor of 10 and  $R_e = 20 \Omega \text{ cm}^2$ ;  $\rho = 2.6446 \times 10^{10} \Omega \text{ cm}$ .

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