



## Water uptake in protective organic coatings and its reflection in measured coating impedance

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### ABSTRACT

Water uptake in commercially available epoxy coating on mild steel using impedance spectroscopy and gravimetry was studied. The water content in the coating was determined using the Brasher-Kingsbury equation and various methods of coating capacitance calculation used in the literature. The obtained results were compared with reference gravimetric data. An overestimation of values obtained from impedance data in relation to gravimetric data was observed. It was found that the calculation of the effective coating capacitance needs to use both constant phase element (CPE) parameters. Using principal component analysis (PCA) a strong correlation between them and gravimetric data was found. The use of formula of effective capacitance in the Brasher-Kingsbury equation has allowed to obtain significant compliance with gravimetric data.

### 1. Introduction

Organic coatings tend to absorb water. This leads to a reduction of their protective properties. This phenomenon can also be observed in polymeric materials regarded as highly resistant such as epoxy resins. Water absorption by coatings is considered as the first stage of their degradation. Understanding the mechanism of water and ions ingress and transport through the coating is crucial for high performance coating selection and improving their barrier properties. Water uptake is also of fundamental importance in the determination of overall corrosion performance of a coating system on metals and a prediction of coating performance in service.

It is possible to estimate the amount of absorbed water in organic coating system on a continuous basis using electrochemical impedance spectroscopy (EIS). This is due to the fact that the dielectric constant of a typical polymeric material (usually about 3–8) is significantly different from that of water (78.5 at 25 °C). During water absorption by the coating, its effective dielectric constant increases with the resulting increase of the coating capacitance.

Changes in dielectrical properties of organic coating system during exposure to aqueous environments have been the subject of many investigations [1–14]. The most common approach to calculate the volume fraction of absorbed water  $\Phi$  was developed by Brasher and Kingsbury [15] and the obtained formula is given by:

$$\Phi = (\log(C_t/C_0))/\log(\epsilon_w), \quad (1)$$

where:  $C_t$  is the coating capacitance at time  $t$ ,

$C_0$  the capacitance of the coating at  $t = 0$  and

$\epsilon_w$  is the water dielectric constant.

From the Eq. (1) it becomes obvious that one parameter is important in defining the water uptake in the coating system, i.e. capacitance ( $C_0$ ,  $C_t$ ). In order to determine the volume fraction of absorbed water at the time  $t$ , it is necessary to know the electrical capacitance of the coating. However, the determination of the coating capacitance from impedance data is ambiguous, because the real coatings do not behave as ideal capacitor. Hence, we are forced to create so-called ‘effective capacitance’ based on the calculation at one frequency or on the parameter of the constant phase element (CPE), which is used to describe the obtained impedance data [10]. This transformation does not have general reasonable justification for three dimensional objects, like organic coatings. A similar problem exists for a real metal surface immersed in the electrolyte (two dimensional object), whose double layer capacitance, with certain exceptions (mercury/aqueous solution), cannot be described with the model of the ideal capacitor [16–18]. The reason for this behavior is heterogeneity of coating material or surface, but physical description and understanding of these phenomena are not complete [19].

The studies show, that the values derived from Brasher-Kingsbury equation, using different approaches, are overestimated in comparison to gravimetric measurements, that shall be treated as reference data. Assuming that Brasher-Kingsbury model describes aptly reality, some authors correct this formula taking into account assumptions about

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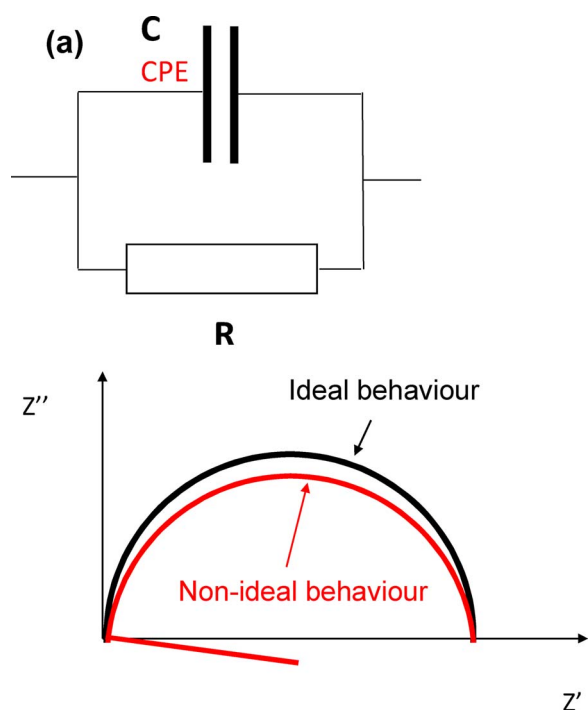


Fig. 1. Simple electrical equivalent circuit describing the coating on metal (a) and the corresponding impedance spectra in the ideal and non-ideal cases in Nyquist format (b).

model [20] or coating swelling associated with dimension changes [11].

As noted earlier, interpretation and description of water uptake process using impedance data are not easy due to the presence of the so-called ‘frequency dispersion of capacitance’ exhibiting the behavior of the CPE type:

$$Z_{\text{CPE}}(Y, n) = 1/(Y(j 2\pi f)^n), \quad (2)$$

where:  $Z_{\text{CPE}}$  – impedance of the CPE,

$Y, n$  – parameters of the CPE,

$f$  – frequency,

$j$  – imaginary unit,  $j = \sqrt{-1}$ .

Despite the progress made last time, the CPE behavior of coatings, especially during water exposure, and a link between CPE parameters ( $Y, n$ ) and physicochemical quantities of the tested system are still not entirely clear [21–23].

In a traditional, simple approach the electrical properties of a coating on metal can be described by an equivalent circuit consisting of a parallel connection of a resistor  $R$  and a capacitor  $C$  (Fig. 1). A time constant  $\tau$  of this circuit shall be

$$\tau = RC = \rho d/S \epsilon_0 \epsilon S/d = \epsilon_0 \epsilon \rho, \quad (3)$$

where:  $\rho$  – the resistivity of the coating,

$\epsilon$  – the dielectric constant of the coating,

$\epsilon_0$  – the dielectric constant of free space,

$S$  – the coating area,

$d$  – the coating thickness.

According to the Eq. (3) the time constant depends on parameters  $\epsilon$  and  $\rho$ . If they are identical on the whole of coating we obtain on the complex impedance plain full semicircle with the centre on the horizontal axis. Otherwise, which is usually the case of real ‘dry’ coatings and/or with absorbed water, we obtain in various degrees ‘depressed’ semicircle (Fig. 1) with the centre below the horizontal axis. The point frequency of maximum imaginary part  $Z''$  is related to  $\tau$ :

$$\tau = 1/f_{\text{max}} \quad (4)$$

Because of scatter of electric and dielectric local parameters  $\rho$  and  $\epsilon$

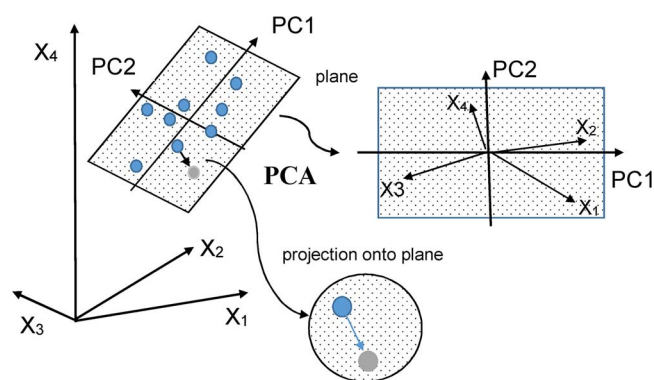


Fig. 2. A schematic representation of projections of correlated variables  $X_1, X_2, X_3$  and  $X_4$  on a plane with a lower dimensionality determined by uncorrelated variables  $PC_1$  and  $PC_2$  using PCA.

the maximum part is fuzzy in the case of real coatings. This causes difficulties in reliably assessing of water content in the coating using impedance measurements.

From the above reflection it can be assumed that for the purpose of establishing of water content in coating other electrical parameters should be incorporated. Considering gravimetric data as reference values, it was decided to study the correlation between the gravimetric data and all electrical parameters of the coating using principal component analysis (PCA).

This method is applicable to the analysis of multidimensional data in many areas of knowledge [24,25], also in the field of coatings [26–29] and corrosion studies [30].

Generally, PCA is a procedure used to reduce the number of variables when they are correlated. Its goal is to extract the maximum variance from a data set, resulting in a few orthogonal (uncorrelated) components produced as linear combinations of original variables. A small number of these combinations typically account for the majority of the variability within the set of the original variables. As a result of PCA treatment, an image of the original correlated variables in a new set of uncorrelated variables is obtained (Fig. 2). This can be explained in an intuitive way as searching for a new coordinate system in which the largest part of the information is contained in the initial dimensions, and the remaining ones can be rejected, because they contain much less information. This procedure geometrically corresponds to the projection of measurement points on an optimally chosen plane selected in such a way that it contains the maximum amount of information (Fig. 2). This analysis should indicate which electrical parameters of the coating and how they are correlated with gravimetric data.

Indirectly, this problem is related to the determination of the effective capacity of the system, which exhibits CPE behavior and is spatial, like organic coatings. Different authors use different approaches to its determination. This is caused by lack of appropriate conversion of CPE parameters into effective capacitance. These approaches were tested and critically analyzed. The final measure of the correctness of a given approach was the compliance of the calculated water content with gravimetric data.

In this work a comparison of different ways to determine the electrical capacitance of the coating for calculation of water content using the Brasher-Kingsbury equation has been made. Using the principal component analysis method (PCA), the water absorption correlation with electrical parameters of the coating has been determined. Using the conclusions obtained by the PCA, the formula for the effective electric capacity developed by Hirschorn et al. [23] has been applied in the Brasher-Kingsbury equation and the results obtained were compared with gravimetric data.

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