Progress in Organic Coatings xxx (2014) xxx–xxx

Contents lists available at ScienceDirect

Progress in Organic Coatings

journal homepage: www.elsevier.com/locate/porgcoat

Analysis of the non-ideal capacitive behaviour for high impedance organic coatings

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ARTICLE INFO

Article history:
Available online xxx

Keywords:
EIS
Organic coating
Water uptake
Phase shift

ABSTRACT

High impedance organic coatings may behave differently from a pure capacitor at the beginning of immersion when studied by electrochemical impedance spectroscopy (EIS). A phase shift is then obtained in the high frequency domain of the phase Bode plot which makes water uptake estimation difficult. In some cases, the analysis of EIS spectra when considering constant phase elements (CPEs), dielectric relaxation or thickness profile is not sufficient.

In this work, we propose a model to represent high impedance thick organic coatings constituted with a dry part of the coating, in contact with the substrate and a humid part in contact with the electrolytic solution. Water is assumed to be uniformly distributed in the humid part of the coating while a resistivity decrease is considered in the dry part. Finally, a Young impedance in series with a humid film (RC) constant is obtained and compared to experimental results.

1. Introduction

The degradation of organic coatings has been widely studied using electrochemical impedance spectroscopy (EIS) since near 40 years [1–6]. Indeed, EIS is a non-destructive method that is able to characterize the organic coating and to obtain the interfacial metallic response under the coating. At the very beginning of immersion in a saline solution (e.g. NaCl 3 wt.%), the organic coating can be considered dry and the coated metallic substrate is not in ionic contact with the ageing solution. The organic coating behaves then as a pure capacitor, namely the film capacitance C_f and the system can be represented by an equivalent electrical circuit (EEC) as shown in Fig. 1a, where R_S is the solution resistance. With increasing immersion time, water and/or solution penetrate within the coating through pores and ionic pathways develop, introducing a resistance behaviour in the EIS response. This resistance, called film resistance R_f, is attributed to the solution that fills the pores and depends on the pore geometry. The corresponding EEC is then a parallel combination of C_f with R_f (Fig. 1b) in series with R_S. This ability to absorb water is a key parameter for the coating since it informs about the barrier effect of the coating which can be followed with the evolution of the film resistance and/or the film capacitance. The water ingress leads to a R_f decrease due to the development of pores and to a C_f increase since the water permittivity is higher than the coating one. Then, both the low frequency (LF) domain and the high frequency (HF) domain allow the coating performances to be evaluated. In this latter case, the film capacitance evolution allows one to evaluate the water uptake thank to the well-known Brasher and Kingsbury (B&K) relation [7] or associated derived equations [8,9].

The film capacitance can be measured by different ways: the simplest uses the imaginary part of the impedance at HF (typically between 1 and 10 kHz [10,11]) because the EIS response is mainly dominated by the capacitive behaviour. The capacitance can then be calculated as:

$$C_{HF} = -\frac{1}{2\pi f \cdot Z_{im}} \tag{1}$$

where f is the frequency and Z_{im} is the imaginary part of the impedance.

However, very often, the coating does not behave as a pure capacitance because the electrical properties of the material are not constant through the thickness along the surface (2D dispersion) or normally to the surface (3D dispersion) [12,13] or because the coating thickness is not constant [14]. Then, the measured phase angle is not equal to -90° as a pure capacitor and experimental plots present a frequency dependent phase angle in the HF domain as shown in Fig. 2 [15]. In order to account for this time–constant distribution, a constant phase element (CPE) [12] can be added in parallel to C_f in the EEC from Fig. 1b that is used to fit the experimental data but the physical meaning of this CPE remains unclear [16]. It is also possible to consider that the coating is degraded enough

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http://dx.doi.org/10.1016/j.porgcoat.2014.02.008
0300-9440/

Please cite this article in press as: G. Bouvet, et al., Analysis of the non-ideal capacitive behaviour for high impedance organic coatings, Prog. Org. Coat. (2014), http://dx.doi.org/10.1016/j.porgcoat.2014.02.008

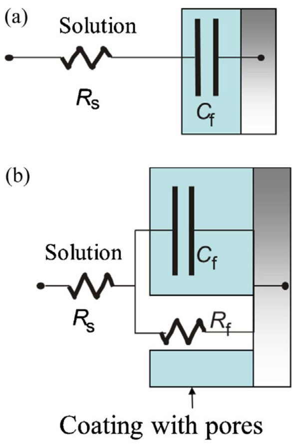

Fig. 1. Equivalent electrical circuits representing the coated metallic interface: (a) with a perfect coating; (b) with a porous coating.

to allow the presence of the aqueous solution at the metal surface and a second time constant (including usually a CPE) is added to the EEC from Fig. 1b [1,6,17,18]. In all cases, the CPE impedance is given by:

$$Z_{CPE} = \frac{1}{Y_0(j\omega)^n} \quad (2)$$

Y_0 ($\mathrm{F\,cm^{-2}\,s^{n-1}}$) and n are the CPE parameters and are independent of frequency. It is worth noting that Y_0 is not equivalent to a capacitance and should not be used in the Brasher and Kingsbury equation to calculate the water uptake. Indeed, the n exponent may vary with immersion time, leading to non-homogeneous Y_0 ratio in the B&K relation and then to erroneous water uptake results. As recently reminded by Hirschorn et al. [13], it is then necessary to use the Brug's equation [12] to calculate the effective or "true" capacitance. In the case of a pure faradic process onto a free interface, with a 2D time–constant distribution, the capacitance is given by:

$$C_B = {Y_0}^{1/n}(R_S^{-1} + R_t^{-1})^{(n-1)/n} \quad (3)$$

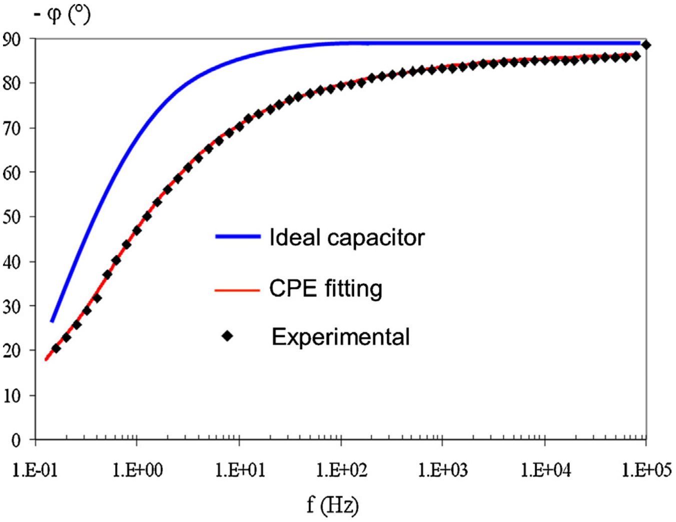

Fig. 2. Experimental and simulated phase angle in the Bode plot.

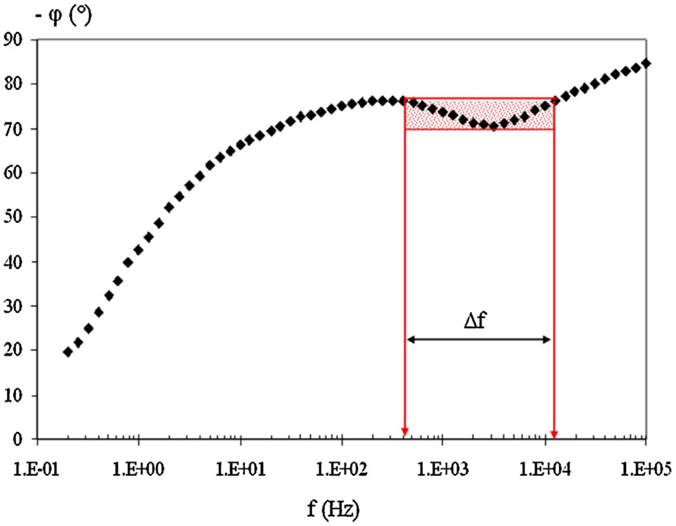

Fig. 3. Typical phase angle anomaly obtained after few minutes of immersion with thick organic coatings.

where R_t is the charge transfer resistance and C_B is related to the double layer capacitance. In the case of an organic coating with an ionic porosity, the EEC (Fig. 1b) is mathematically equivalent to that of a pure faradic process. Assuming that the coating properties are constant normal to the surface, so that only a 2D time–constant distribution is involved, R_t can then be replaced by R_f:

$$C_B = {Y_0}^{1/n}(R_S^{-1} + R_f^{-1})^{(n-1)/n} \quad (4)$$

Since the film resistance R_f is usually much higher than the solution resistance R_S, this equation finally simplifies to:

$$C_B = Y_0^{1/n} R_S^{(1-n/n)} \quad (5)$$

This relation can be used only if the electrical quantities (permittivity and resistivity) are constant along the coating thickness. Then, when calculating the water uptake with the Brasher and Kingsbury equation using capacitances obtained with Eq. (5), a good agreement was found with gravimetric results in the case of a pure, fully cured polymer coating (without fillers, pigments, additives, etc.) applied onto metallic substrates [19]. That is a rare case where gravimetry and EIS techniques agree and that can be explained by the chemical control of the coating network. Such a comparison between EIS and gravimetry has been extensively discussed in the past [20–24] and remains of interest [25,26] but it will not be discussed in the present paper.

In some cases, the non-ideal capacitive behaviour is more complex and cannot be explained by a "CPE behaviour" due to a 2D or 3D time–constant distribution. In previous studies [14,16,17,27–34], the phase angle showed anomalies in the HF domain that were explained in terms of dielectric relaxation, reference electrode artefacts, resistivity or thickness profiles, water interlayer or inhomogeneous electrolyte uptake. Of course, the capacitance values extracted from these experimental curves may lead to erroneous water uptake values. Recently [15], this non-ideal behaviour was obtained with thick organic coatings (about 250 μm with a low frequency modulus higher than $10^{10}\ \Omega\,\mathrm{cm}^2$) after only some minutes (few hours) of immersion in saline solution (Fig. 3). It must be noted that the same experimental EIS data were obtained with different EIS equipments (Gamry FAS 1 and Autolab), with different reference electrodes (Ag/AgCl or saturated calomel electrodes) that were or not short-circuited with a capacitor-Pt wire [35], with short length cables and in a double Faraday cage. It would seem reasonable that with such thick coatings, the water cannot reach the metallic interface in only few minutes so this apparent two time–constant behaviour is not related to the classical EEC for degraded organic coatings [1], where the metallic interface is considered with a

Please cite this article in press as: G. Bouvet, et al., Analysis of the non-ideal capacitive behaviour for high impedance organic coatings, Prog. Org. Coat. (2014), http://dx.doi.org/10.1016/j.porgcoat.2014.02.008