



Identification of Resistivity Distributions in Dielectric Layers by Measurement Model Analysis of Impedance Spectroscopy



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ABSTRACT

The Voigt measurement model, developed in the 1990s for identification of the error structure of impedance measurements, is shown here to have utility in identifying resistivity distributions that give rise to frequency dispersion. The analysis was validated by application to synthetic data derived from a constant–phase–element model, a power–law distribution of resistivity, and an exponential distribution corresponding to a Young impedance. The application to experimental data obtained from coated aluminum demonstrates its utility for interpretation of impedance measurements.

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1. Introduction

The origin of the constant–phase element can be attributed to the distribution of time constants along or normal to the electrode surface. The impedance response for the distribution of time constants along the electrode surface can be expressed by the model developed by Brug et al. [1] Several different models have been proposed for the impedance associated with a resistivity distribution normal to electrode surface. Young [2] assumed that the nonstoichiometry of the oxide layer resulted in an exponential variation of the resistivity. Under the assumption of a uniform dielectric constant, Hirschorn et al. [3] proposed a power–law distribution of resistivity to relate constant–phase–element parameters to film properties.

Impedance spectroscopy has been applied to the study of resistivity distributions in oxide films. Young showed that the impedance response of oxides on niobium may be explained in terms of an exponential distribution of resistivity. [2,4] Bataillon and Brunet [5] attributed dispersion in the impedance response of oxide films formed by high–temperature water oxidation of

zircaloy 4 to oxide film defects and transport. Orazem et al. [6] demonstrated the application of a power–law distribution of resistivity to extract the thickness of oxide films on 18Cr–8Ni stainless steel and X12CrNiMoV12–3 steel. They also verified the power–law distribution of resistivity for split–thickness human cadaver skin (300–400 μm thick). Not all authors have concluded that CPE behavior for oxides may be attributed to normal distribution of film properties. Mohammadi et al. [7] reported that the formula of Brug et al. [1] provided the best correlation to independently measured thicknesses of oxide films on 304 stainless steel.

Electrochemical impedance spectroscopy methods have also been used widely to assess the corrosion protection performance of coatings. Beaunier et al. [8] proposed a general model in which the ohmic resistance is in series with the parallel combination of the capacitance of the polymer coating and the electrolyte resistance in the pores; the latter is in series with the parallel combination of double layer capacity and faradaic impedance of the wet area at the metal/coating interface. This model was modified by Mansfeld [9], who replaced the faradaic impedance of the corrosion process with a polarization resistance. The faradaic impedance of Beaunier et al. [8] was treated by Hirayama and Haruyama [10] in terms of quantities that accounted for the parallel contributions of reactions at the metal/coating interface and at exposed metal

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surface by pores or coating defects. Upadhyay et al. [11] found that impedance responses of glycidyl carbamate functional coatings were closely related to structural and compositional variations. In addition, they related single-frequency impedance measurements to water uptake.

Hu et al. [12] showed that the impedance of epoxy-coated aluminum alloy LY12 in 3.5% NaCl solution was sensitive to the time-dependent uptake of water, oxygen and chloride ions. Metroke et al. [13] showed that impedance of organically modified silane thin films on 2024-T3 aluminum alloy in 0.05% NaCl or 0.5 M K_2SO_4 was sensitive to water and electrolyte uptake as well as to degradation of coating properties. Kittel et al. [14,15] used embedded electrodes to demonstrate marked variations in the impedance of organic coatings as a function of depth, concluding that accurate models for coated electrodes should integrate gradients of properties over the thickness of the coatings. However, those authors did not propose any specific resistivity or permittivity profiles.

Hinderliter et al. [16] used a two-layer representation of coating changes due to water intrusion and known effective medium theories for dielectric and resistivity changes to predict changes in impedance spectra seen in immersion or other accelerated testing of coating films. Amand et al. [17] developed a model for the impedance of coatings based on the assumptions that the coating uptakes electrolyte such that the volume fraction of the electrolyte varies along the coating thickness according to a power-law, the resistivity and permittivity profiles of the electrolyte-penetrated coating can be calculated through an effective medium theory (EMT) formula corresponding to a parallel combination of the two media (electrolyte and coating material), and some pores extend from the coating/electrolyte interface to the substrate/coating interface, providing a low resistance path. Their work showed that, of the effective medium theories proposed by Hinderliter et al. [16], linear combinations provided results that were consistent with the observed impedance response. Musiani et al. [18] demonstrated that, although resistivity profiles may be obtained using effective medium theory and linear combinations of conductivities/permittivities, the fitted water uptake values are not reliable because the real composition of the solution that penetrates the coating is unknown. [12,19] Nguyen et al. [20] suggested that a dry epoxy-polyaminoamide waterborne paint coating on a 2024 aluminium alloy showed constant-phase-element behavior that could be modeled accurately with the power-law model. However, for the same coating immersed in either a 0.5 M or a 0.05 M NaCl solution, the Young impedance model provided a better fit to the impedance data.

The Voigt series, used by Agarwal et al. as a measurement model to identify the error structure of impedance measurements [21–23], has been employed to identify a distribution of relaxation time constants corresponding to a given impedance spectrum. [24,25] In the present paper, a systematic method, based on the Voigt measurement model, is proposed to analyze the resistivity distribution for synthetic impedance data and for experimental data obtained for anti-corrosion coatings.

2. Theoretical Development

This section summarizes the use of the measurement model for the assessment of resistivity distribution in films, previously described by Hirschorn et al. [3] The resistivity distribution can be derived from the Voigt element parameters, τ_i and R_i . The corresponding impedance is expressed as

$$Z_{RC} = \sum_{i=1}^k \frac{R_i}{1 + j\omega\tau_i} \quad (1)$$

where each Voigt element represents the time constant and resistivity for a given differential element. The number of Voigt elements k is increased sequentially under the constraint that the 95.4 % confidence interval for each regressed parameter does not include zero. [21] Each RC -time constant is assumed to be associated with a differential layer of the film.

The differential capacitance, defined to be

$$C_i = \tau_i/R_i \quad (2)$$

is a function of dielectric constant and the thickness of the element. The corresponding thickness of each element i , d_i , is related to the local dielectric constant ε_i by

$$d_i = \frac{\varepsilon_i \varepsilon_0}{C_i} \quad (3)$$

where $\varepsilon_0 = 8.8542 \times 10^{-14}$ F/cm is the permittivity of vacuum. The local resistance can also be related to thickness of element i by

$$R_i = \rho_i d_i \quad (4)$$

Therefore, the time constant τ_i is independent of element thickness and can be expressed as

$$\tau_i = \rho_i \varepsilon_i \varepsilon_0 \quad (5)$$

Under the assumption that dielectric constant is uniform, the variability of capacitance could be the consequence of a changing element thickness. Based on equations (4) and (5), the resistivity, R_i , could also be related to the time constant by

$$\rho_i = \frac{R_i}{d_i} = \frac{\tau_i}{\varepsilon \varepsilon_0} \quad (6)$$

The elements with smallest and largest resistivity values were assumed to be located at the interfaces of the system, and the resistivity of elements in the system was assumed to increase or decrease monotonically. Thus, if the thickness of the element with the smallest resistivity value is d_1 and the element with the second smallest resistivity value is d_2 , the specific position of element with second smallest resistivity value in the system is $d_1 + d_2$. The specific position of other elements in systems can be calculated in the same manner.

3. Experimental

The coating samples and the protocol for impedance measurement were described in detail by Nguyen et al. [26] The following section summarizes the essential features.

3.1. Materials

The coating was a two-component water-based paint manufactured by Mapaero SAS, used as an anti-corrosive primer. It consisted of a polyaminoamide (Versamid type) base and a bisphenol A epoxy polymer hardener. Coatings henceforth called CC contained the following pigments: titanium oxide (12 wt.%), talc (11 wt.%), silica (1 wt.%) and strontium chromate (16 wt.%). Other coatings, henceforth called NCC, contained a mixture of zinc oxide and a phosphosilicate (10 wt.%) to replace $SrCrO_4$ as inhibitive pigment. In both cases, the ratio of the pigment volume concentration (PVC) to critical pigment volume concentration (CPVC) was 0.61. The coating preparation was that described in references [20] and [26]. Before painting, the 2024 T3 aluminium alloy samples were degreased at 60 °C (pH = 9) for 15 minutes, rinsed twice with distilled water, then etched in an acid bath at 52 °C for 10 minutes, and rinsed again with distilled water. The liquid paints were applied by air spraying. After curing at 60 °C, the coatings were 18 – 22 μm thick.

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