Analysis of Constant Phase Element

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Constant phase elements (CPE) are used extensively in electrical equivalent circuits for analyzing experimental impedance data. While CPE behavior is observed experimentally, its interpretation has been controversial for many years. However, if the CPE behavior can be considered to be evidence of frequency dispersion, its origin can be due to dispersion of the resistance, of capacitance, or both. Recent work has shown that Local Electrochemical Impedance Spectroscopy (LEIS) can be used in some cases to assess the influence of local variations on the CPE behavior seen in global measurements, and a distinction between 2D and 3D distributions could be observed [1]. In this presentation, different electrochemical systems showing the CPE dependence in the high-frequency range for the global impedance are considered.

In the case of a 2D distribution, as obtained for the impedance of the Mg AZ91 alloy at the corrosion potential, a formula was proposed by Brug *et al.* [2]:

$$C = Q^{1/\alpha}\left(\frac{1}{R_e} + \frac{1}{R_t}\right)^{\frac{\alpha-1}{\alpha}} \qquad (1)$$

where R_e is the electrolyte resistance and R_t is the charge transfer resistance.

It was shown that this expression can be applied also with a good accuracy for a 2D distribution due to the geometrical effect inducing a primary current distribution [3]. Recently it was shown that for a 2D distribution, an intrinsic coupling between α and Q parameters is existing according to the Brug's formula (1) [4]. Clear correlations have been found for two different experimental conditions, anodic dissolution and scale deposit.

In the case of a 3D distribution, the impedances of coating or oxide films are considered. CPE behavior may be attributed to the distribution of physical properties in films, in direction normal to the electrode surface. A normal power-law distribution of local resistivity with a uniform dielectric constant was found to be consistent with the constant-phase element (CPE) [5]

$$\frac{\rho}{\rho_\delta} = \left(\frac{\rho_\delta}{\rho_0} + \left(1 - \frac{\rho_\delta}{\rho_0}\right)\xi^\gamma\right)^{-1} \qquad (2)$$

where ρ_0 and ρ_δ are the boundary values of the resistivity at the interfaces, δ is the film thickness, and $\xi = x/\delta$.

An analytic expression, based on the power-law resistivity distribution, was found that relates CPE parameters to the physical properties of a film:

$$Z_f(\omega) = g\frac{\delta\rho_\delta^{1/\gamma}}{\left(\rho_0^{-1} + j\omega\varepsilon\varepsilon_0\right)^{(\gamma-1)/\gamma}} \qquad (3)$$

where ε is the dielectric constant, ε_0 is the permittivity of vacuum and g is a function of γ and has a value close to 1.

This expression worked well for such diverse systems as aluminium oxides or oxides on stainless steel and on coating on aluminium alloys 2024.

The extension of the power-law model [5] to anti-corrosion coatings is shown to yield insight into the distribution of resistivity and associated water uptake [6]. Evaluation of mixing rules for conductivities and permittivities of two media (coating and electrolyte) showed that the linear combination provided results that were consistent with the observed impedance response.

References

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