Use of LEIS and the power-law model for the analysis of constant-phase-elements related to oxide layers

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Introduction

The impedance response for electrochemical systems often reflects a distribution of time constant that is commonly represented in equivalent electrical circuits as a CPE. The CPE impedance is expressed in terms of model parameters α and Q as:

$$Z_{CPE}(\omega) = \frac{1}{Q(j\omega)^{\alpha}} \tag{1}$$

When $\alpha = 1$, the parameter Q has units of capacitance; otherwise, Q has units of $\Omega^{-1}.\text{cm}^{-2}.\text{s}^{\alpha}$ or $\text{F.cm}^{-2}.\text{s}^{(\alpha-1)}$.

Origin of the CPE behavior

A CPE behavior can be attributed to a distribution of time constant either along the area of the electrode (surface distribution) or along the axis normal to the electrode surface (normal distribution) [1]. A surface distribution could arise from surface heterogeneities (grain boundaries, crystal faces on a polycrystalline electrode…), or from geometry-induced non-uniform current and potential distributions. A normal distribution may be attributed to changes in the conductivity of films or porosity.

Local electrochemical impedance spectroscopy (LEIS) measurements can be used to distinguish whether the global CPE behavior arises from a surface distribution, from a normal distribution, or from combined surface and normal distributions. Thus, if local pure capacitive behavior is evidenced, then the global CPE behavior can be explained by a surface distribution. If local impedance measurements show CPE behavior, then the global CPE behavior comes from a normal distribution. And if local CPE behavior is revealed, with CPE coefficients α and Q varying along the electrode surface, then the global CPE behavior arises from combined surface and normal distributions. Jorcin *et al.* [2] used LEIS to attribute CPE behavior seen in the global measurements to surface or normal distribution in the case of AZ91 magnesium alloy and pure aluminum.

CPE analysis in the case of oxide layers

Normal distributions of time-constants can be expected in systems such as oxide films, organic coatings, and human skin. They may be interpreted in terms of dielectric properties of the material. If the dielectric response can be associated with an effective capacitance C_{eff}, the dielectric constant ε and film thickness δ may be obtained from:

$$C_{eff} = \frac{\varepsilon\varepsilon_0}{\delta} \tag{2}$$

where ε_0 is the permittivity of vacuum ($\varepsilon_0 = 8.8542 \times 10^{-14}$ F.cm^{-1}).
The challenge is to find a correct way to extract an effective capacitance from the CPE parameters α and Q. Four methods are used in the literature: simply equating C_{eff} to Q, a formula developed by Brug *et al.* [3], a formula derived from the work of Hsu and Mansfeld [4], and the power-law model presented recently by Hirshorn *et al.* [5]. Orazem *et al.* discussed and compared these four methods in the case of metal oxides and human skin [6]. The assumption that the effective capacitance may be assigned the numerical value of Q provides poor estimates for physical properties. Use of this assumption is discouraged, even

when the CPE exponent is greater than 0.9. Brug formula was derived only for a surface time-constant distribution and does not apply to data associated with distributed properties of a film in the direction normal to the electrode surface. The effective capacitance extracted from the characteristic frequency of the impedance (Hsu and Mansfeld formula), even though this can be derived for a normal distribution, does not provide good estimates for physical properties. The power-law model for CPE behavior associated with normal distributions provides a powerful approach for interpretation of CPE parameters in terms of physical properties such as dielectric constant, film thickness and resistivity.

Power-law model [5]

A distribution of resistivity that provides bounded values was proposed to be:

$$\frac{\rho}{\rho_\delta} = \left(\frac{\rho_\delta}{\rho_0} + \left(1 - \frac{\rho_\delta}{\rho_0} \right) \xi^\gamma \right)^{-1} \tag{3}$$

where ξ is the dimensionless position $\xi = y/\delta$, ρ_0 and ρ_δ are the boundary values of resistivity at the interfaces (at $\xi = 0$ and $\xi = \delta$, respectively), and γ is a constant indicating how sharply the resistivity varies.

Under the assumption that the dielectric constant is uniform, it was shown that $\alpha = (\gamma - 1)/\gamma$, and a relationship among the CPE parameters and the physical properties of the film was found to be:

$$Q = \frac{(\varepsilon\varepsilon_0)^\alpha}{g\delta\rho_\delta^{1-\alpha}} \tag{4}$$

where g is a function of α ($g = 1+2.88(1-\alpha)^{2.375}$). The corresponding capacitance can be obtained from:

$$C_{eff} = gQ(\rho_\delta\varepsilon\varepsilon_0)^{1-\alpha} \tag{5}$$

In addition to the CPE parameters, C_{eff} depends on the dielectric constant ε and the smaller value of the resistivity ρ_δ. Unlike for Hsu and Mansfeld formula, the characteristic frequency is not invoked, and the results depend only on the high-frequency data.

Experimental

This methodology is illustrated in the following with oxide layers developed on a ferritic Fe-17Cr stainless steel. Global and local impedance measurements at different positions on the alloy surface were performed at the corrosion potential (E_{corr}) in aerated pH 4, 0.05 M NaCl + 0.005 M Na_2SO_4 solution [7]. The impedance response was also studied in the passive domain after 1 h of polarization at −0.1 V *vs* SSE in deaerated pH 4, 0.05 M Na_2SO_4 electrolyte [8]. This approach was also applied to other examples: passive layer on pure aluminum [2,8], and oxide layers developed on stainless steels (free-machining Fe-18Cr-8Ni stainless steel, also known as 303 stainless steel, and martensitic $X_{12}CrNiMoV_{12-3}$ stainless steel) [6]. The corresponding results are not shown below.

Results and Discussion

Global and local impedance diagrams obtained for the Fe-17Cr disk electrode are given in Fig. 1. The results show global and local CPE behavior with the same α and Q values ($\alpha \sim 0.85$ and $Q \sim 12\times10^{-5}$ F.cm^{-2}.s$^{-0.15}$). Therefore, the global CPE behavior arises from a normal distribution of an oxide film property, and not from a surface radial distribution of the time constant. Moreover, the high-frequency dispersion of global impedance data observed for f > 100 Hz (apparent CPE behaviour) originates from non-uniform current and potential distributions on the disk surface.

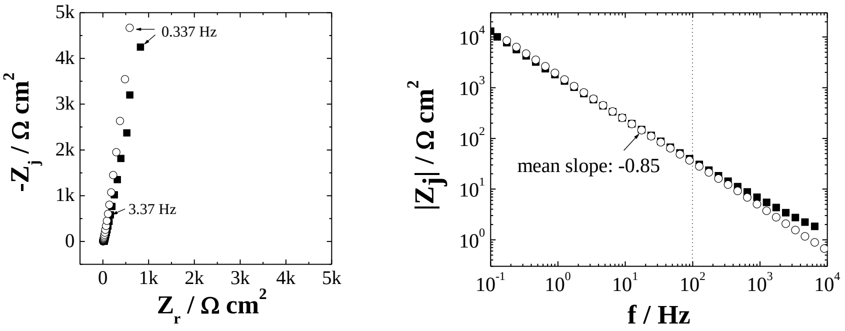

Fig. 1(a) Fig. 1(b)

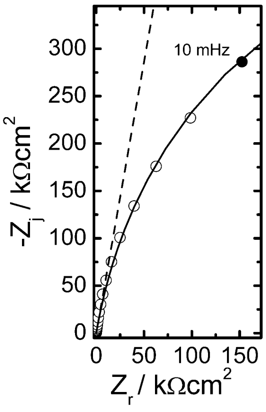

Fig. 2

Figure 1: (■) Global and (○) local impedance diagrams of Fe-17Cr disk electrode immersed at E_{corr} in aerated pH 4, 0.05 M NaCl + 0.005 M Na_2SO_4 solution. (a) Complex plane plot, and (b) imaginary part of the impedance as a function of frequency. Local impedance data were obtained at the center of the disk. Taken from [7].

Figure 2: Global impedance diagram in the complex plane of Fe-17Cr disk electrode after1 h of polarization at −0.1 V *vs* SSE in deaerated pH 4, 0.05 M Na_2SO_4 solution. Solid line: fit of the power-law model; dashed line: pure CPE impedance. Taken from [8].

From XPS analysis, Frateur *et al.* [9] showed that the passive film developed on Fe-17Cr consisted of an inner layer of Fe_2O_3 and Cr_2O_3 covered by an outer layer of $Cr(OH)_3$ and that the thickness was about 3 nm. Thus, a value of 12 was assumed for ε, corresponding to the dielectric constant for Fe_2O_3 and Cr_2O_3. Graphical analysis of the impedance presented in Fig. 2 yielded $\alpha = 0.89$ and $Q = 3.7\times10^{-5}$ F.cm^{-2}.s$^{-0.11}$. The film thickness δ being known, Eq. (4) was used to obtain $\rho_\delta = 450$ Ω.cm, which is a typical value for a semi-conductor. As shown in Fig. 2, the impedance response does not follow a straight line, but its shape suggests a finite low-frequency impedance. Introduction of $\rho_0 = 4.5\times10^{13}$ Ω.cm into Eq. (3) provided a calculated response in good agreement with the experimental results; this value of ρ_0 corresponds to an insulator.

Conclusions

A CPE behavior can be attributed to a distribution of time constant either along the area of the electrode (surface distribution) or along the axis normal to the electrode surface (normal distribution). Normal distributions can be expected in systems such as oxide films. In these cases, the CPE parameters α and Q may be interpreted in terms of physical properties such as effective capacitance, film thickness and dielectric constant. Among the methods used in the literature, the power-law model for distribution of resistivity developed recently by Hirschorn *et al.* [5,8] provides the most reliable interpretation for oxides.

References

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