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Random and systematic error as a function of sample area in electrochemical impedance spectroscopy data

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ABSTRACT

The goal of this study was the evaluation of random and systematic error sources in electrochemical impedance spectroscopy (EIS) measurements that originate from the EIS equipment and measurement protocol in contrast to errors related to the coating/metal system. By using well-defined, homogeneous, and defect-free polyvinylfluoride (Tedlar®) release films, highly reproducible EIS spectra could be obtained. Thus, it was thus possible to study data variability originating from the EIS measurement procedure while keeping the film/metal system constant. Parameters gained from EIS spectra such as film resistivity, dielectric constant and exponent n of the non-ideal capacitance were evaluated as a function of sample area and compared to reference material properties. For larger sample sizes the values obtained by EIS experiments correlated well with the reference values, validating the EIS technique for the determination of absolute values for electrical properties of coatings. However, to obtain an accurate value for film resistivity and relative dielectric constant, a sample area of at least $11.4\,cm^2$ was necessary to avoid the introduction of measurement artifacts. The implications of the findings for corrosion testing with small sample areas (e.g., as used in high-throughput corrosion testing) are discussed.

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1. Introduction

1.1. Electrochemical impedance spectroscopy

Electrochemical impedance spectroscopy (EIS) is extensively used to assess the corrosion protective properties of organic barrier coatings on various metal substrates [1–6]. In EIS measurements a small sinusoidal voltage $u(t)$ is applied to the coating–metal system at steady state and a sinusoidal current $i(t)$ is detected. The impedance Z is defined as the ratio of $u(t)$ and $i(t)$:

$$Z = \frac{u(t)}{i(t)} = \frac{\hat{u} \times \sin(\omega t + \varphi_u)}{\hat{i} \times \sin(\omega t + \varphi_i)} = \frac{\hat{u}}{\hat{i}} \times e^{j(\varphi u - \varphi i)} \qquad (1)$$

$\hat{u}$ and $\hat{i}$ are the amplitudes and φ_u and φ_i the phase angles of voltage and current respectively, ω is the angular frequency and t the time.

The magnitude of the impedance $|Z| = \hat{u}/\hat{i}$ and the phase shift between voltage and current $\varphi = \varphi_u - \varphi_i$ can be plotted as a function of the frequency in a log–log presentation (Bode plot).

Data gained from EIS experiments can help to quantify the performance of barrier coatings and to detect corrosion processes on the substrate in an early stage. Also, EIS can be used to identify coating failure modes (e.g., delamination) and monitor the water uptake of a coating over time [6].

A coating system on a metal substrate can be expressed as equivalent circuit of electronic elements such as resistors and capacitors that represent different parts of the coating–metal system [1,5,6] (Fig. 1).

The equivalent circuit in Fig. 2 is often used to represent a defect – free film exposed to an electrolyte solution. R_{El} is the uncompensated electrolyte resistance, R_P the film's resistance and C_C its capacitance. By fitting the impedance data in a non-linear least square process to an equivalent circuit model using appropriate software packages (such as Zview®), all the parameters can be obtained from the spectrum.

The coating resistance is often normalized over measurement area A and coating thickness d and is reported as the resistivity ρ (in $\Omega\,cm$):

$$\rho = \frac{R_p \times A}{d} \qquad (2)$$

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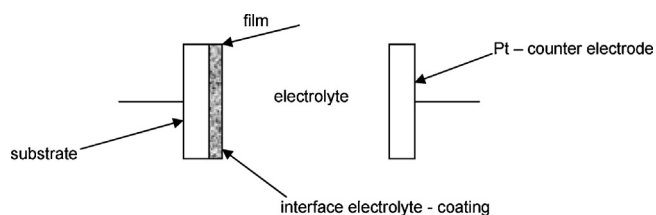
Fig. 1. Schematic depiction of a film/metal system.

The capacitance can be expressed in terms of the dimensionless relative dielectric constant ε_r of the coating:

$$\varepsilon_r = \frac{C_c \times d}{\varepsilon_0 \times A} \tag{3}$$

d is the thickness of the coating, A the measurement area and ε_0 the dielectric constant of free space (8.85×10^{-12} F/m).

A real coating system rarely behaves as an ideal capacitor. This has been attributed to substrate surface roughness [1,2,7], inhomogeneous charge distribution within the coating [7] or the interaction of polar groups [2]. In practice it has been shown that the introduction of an exponent n into the expression of the impedance of a capacitance leads to a better fit between the data and the equivalent circuit model; this non-ideal capacitance is also called a constant phase element (CPE).

The exponent n can be used to monitor the degradation of a coating. With progressing coating degradation, n decreases [1].

1.2. Factors contributing to variability in EIS data

One major drawback of EIS is a high variability (within one sample as well as between different samples) in the data, requiring a large number of replicates to be run. Although the problem of poor data reproducibility is well known in the field, few publications (mainly by Tait) are explicitly devoted to quantify EIS data variability and identify the main error sources. In the following, an overview of factors influencing the variability of impedance data is presented.

The factors responsible for poor reproducibility of EIS data can be roughly divided into two groups: error stemming from the coating/metal system, and errors that arise due to the EIS measurement procedure and data evaluation. Error sources arising from the coating system itself include: fluctuation in film thickness, application defects and defects originating from the curing process (e.g., pinholes and craters due to evaporating solvents), inhomogeneity of the metal substrate (e.g., uneven element distribution in alloys), and surface roughness probabilistic corrosion reactions such as pitting [8–10].

The second source of data variability concerns the EIS instrument setup, electrode configuration, current and voltage distribution, measurement protocol (e.g., frequency range, open circuit potential determination etc.) and nonlinear data fitting [5,6].
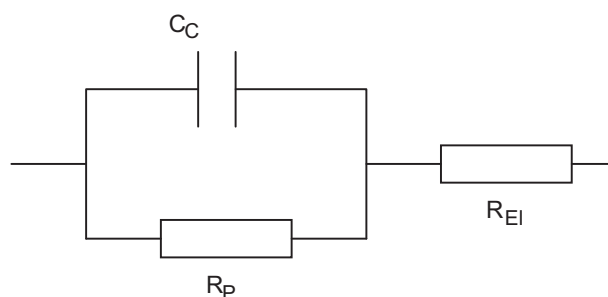

Fig. 2. Equivalent circuit (Randles circuit) for a coating–metal system.

1.2.1. Film thickness fluctuations

Tait [11] evaluated the coating thickness variations over the surface of one sample as well as between multiple samples of an epoxy coating applied to a commercial welded metal container. The film thickness on one and the same container ranged between <1 μm and up to 8 μm. The comparison of 26 containers of the same batch also showed a sample-to-sample variability of a film thickness between a mean of about 2 μm and 4 μm. As can be seen from Eqs. (2) and (3), EIS data are a function of film thickness, and unknown variations in film thickness will result in a higher uncertainty in the determination of properties derived from EIS data (e.g., coating resistance and capacitance).

The impact of coating thickness was investigated in a combinatorial study on the barrier properties, namely the diffusion coefficient [12]. The variations in diffusion coefficients are only statistically valid if the impact of coating thickness is smaller than the uncertainty measurement.

1.2.2. Defects in the coating

Defects such as scratches, pores, and pinholes facilitate the ingress of water and corrosion stimulants (ions, oxygen) into the coating and down to the substrate. As a result, the coating fails faster than it normally would. To study the effect of a defect on the EIS data, Grandle and Taylor pierced an intentional defect with a diameter of 0.1 mm into an epoxy–acrylic coating of 3.2 μm thickness on an aluminum alloy substrate [13]. The defect free coating showed the nearly purely capacitive response that is characteristic of a good coating. Already shortly after immersion of the coating into the test electrolyte, the damaged coating had a resistance that was three orders of magnitude lower than that of a defect free coating of the same thickness. Thus, random defects in the coating contribute largely to EIS data variability.

1.2.3. Stochastic corrosion events and arbitrary corrosion mechanisms

Paint samples that are nominally identical, often do not show the same corrosion rate or mechanism. Tait [10] reported cyclic polarization curves from six replicate copper samples in a high-pH test solution. Five of these samples showed active corrosion behavior leading to pits, but one sample passivated under the influence of the test solution. This demonstrates the significance of running a sufficient number of replicate samples. In addition, 100 replicate measurements were taken from an epoxy coated tinplated steel immersed in 0.4 M KCl [9,10]. The impedance spectra of the corroding samples varied by about three orders of magnitude compared to a set of 28 replicate measurements performed on non-corroding samples that showed data dispersion of only one order of magnitude. Pitting corrosion is a stochastic process and pitting sites are distributed more or less randomly over the surface of a substrate. In the case of a urea–formaldehyde modified epoxy coating, the occurrence of unevenly distributed pits contributed largely to scatter in the charge transfer resistance values determined from the impedance spectra of replicate samples of steel containers [8].

1.2.4. Open circuit potential and steady state requirement

One of the prerequisites for EIS experiments is a system at steady-state. Steady-state means that the open circuit potential of the coating–metal system is constant over time. Tait [11] measured the open circuit potential of epoxy-coated tinplated steel containers that were in contact with an acidic food. Here, it took over 50 days of exposure until the metal container reached steady-state conditions. Thus, measurements made prior to steady-state might lead to increased variability in the data. The same problem arises when the coating/metal system changes significantly in a short