



# Determination of water uptake in organic coatings deposited on 2024 aluminium alloy: Comparison between impedance measurements and gravimetry



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## ABSTRACT

Electrochemical impedance spectroscopy (EIS) and gravimetric measurements on two water-based coatings, containing either SrCrO<sub>4</sub> or a mixture of Cr(VI)-free pigments and deposited on 2024 aluminium alloy, were performed to follow the water uptake in a 0.5 M NaCl solution as a function of exposure time. To account for the observed non-ideal capacitive behaviour, the coating capacitance and dielectric constant values were extracted from the EIS data in two ways: (i) by using a complex-capacitance representation and (ii) by fitting to the EIS data a model that assumed an exponential distribution of coating resistivity. The agreement of values obtained by these independent methods served to validate the model used to account for the observed pseudo constant-phase-element (CPE) behaviour of the coatings. The water uptake calculated from dielectric constant values, employing a linear combination formula, was in good agreement with that directly measured by gravimetry, using supported-films.

## 1. Introduction

In a series of recent papers [1–5], our group has studied laboratory and industrial coatings by electrochemical impedance spectroscopy (EIS), with the objective of finding physically sound models to account for their non-ideal capacitive behaviour. Models assuming distribution of coating resistivity and uniform dielectric constants provided good account for the experimental data. Constant-phase-element (CPE) behaviour was observed for aluminium alloy/hybrid sol-gel coating samples immersed in NaCl solutions and was attributed to local resistivity distributions following a power law [1,2]. We have previously shown that a power-law resistivity profile caused CPE behaviour [6–8]; whereas, an exponential resistivity profile, discussed by Young [9,10] and by Schiller and Strunz [11], caused a continuous, though mild, variation of phase angle with frequency. The need to consider position-dependent properties of the coating materials had been previously pointed out by other authors [12–14] who, however, did not propose specific resistivity-position dependencies. Based on the observation that coatings that behaved as quasi-ideal when they were dry became

increasingly non-ideal upon immersion in electrolytes [3], we attributed the formation of resistivity profiles to inhomogeneous penetration of water and ions into the coatings. Models for the behaviour of industrial coatings, which did not correspond to a CPE, required considering exponential resistivity-position profiles extending over either the entire coating thickness or just part of it [3,4]. As power-law and exponential dependencies are only two mathematically simple cases of more general resistivity-position relationships, we have proposed the use of Voigt measurement model [15] for the identification of resistivity distributions that cause frequency dispersion in the EIS response of coatings [5].

The importance of assessing the water uptake into coatings has been acknowledged for some decades because water penetration is an initial step in the degradation process. The knowledge of the resistivity profile is insufficient to determine the water uptake in the coatings [2] because the ion concentration in the water that penetrates the film is normally unknown and probably much different from the concentration in the test electrolyte [16,17]. In principle, water uptake can be estimated from resistance data when EIS tests are performed with coatings

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exposed to pure water [18,19], although, even in this case, the resistivity of the electrolyte within the coating can be affected by ionic species initially present in the coating that become dissolved in water. Since our previous work [1–5] focused on assessing resistivity profiles, we did not discuss water uptake, and actually used the “water volume fraction” only as a formal intermediate parameter in calculations, without a direct physical meaning. In the present paper, we discuss water uptake in industrial coatings containing either strontium chromate or environmentally friendly inhibitors [4], focusing on the evolution of coating capacitance during prolonged exposure, and comparing the EIS-derived values with gravimetric measurements.

The determination of coating dielectric constant, the calculation of water uptake therefrom, and the comparison with direct gravimetric measurements have been the object of many studies. Reports in the literature include studies in which both EIS and gravimetric measurements were made on metal-supported coatings [12,16–22], where both were made on free-standing films [12,23–26], and where impedance was measured with supported coatings and mass variation with free films [27–29]. Different authors have put forward reasons for preferring free films or supported coatings. Gravimetric measurements may be more reliable when performed with free films because, in supported coatings, corrosion reactions occurring at the metal/coating interface may induce mass changes [12]. However, when corrosion is negligible, i.e., for highly adhesive and protective coatings and moderate durations of the exposure to electrolytic solutions, metal-supported coatings are more representative of practical application as compared to free films. In particular, some properties can differ due to changes in chemistry resulting from specific interactions with metal substrates, such as aluminium, during curing reaction [30,31].

Two critical aspects of the EIS/gravimetry comparison are: (i) the determination of the coating capacitance, from which dielectric constant is computed, given the sample geometry, and (ii) the calculation of water uptake from dielectric constant data. The former aspect requires special care when the coatings do not behave as ideal capacitors, and, thus, the capacitance must be computed from CPE parameters [8,32]. Although other effective medium formulas have been proposed [33], the most popular formula for the conversion of dielectric constant to water volume fraction, henceforth called the BK formula, was proposed by Brasher and Kingsbury [34]. Different authors who compared water uptake values calculated following the BK formula to gravimetric measurements reached diverging conclusions on its reliability. For example, Lindquist [20] took into account various alternative equations, finding that the BK formula gave the best results; Castela and Simões [21] found that values calculated with the BK formula were far from gravimetric values and a calculation based on a linear combination of dielectric constants provided better agreement; Sauvante-Moynot et al. [26] reported that the BK equation yielded water uptake values either in good agreement with gravimetry or not, depending on the investigated system, as was already indicated by Brasher and Kingsbury [34]. Various authors [20–23,26,27] observed a tendency of the BK formula to overestimate water uptake. A modified formula proposed by Sykes [35], who removed a possibly unjustified approximation from Brasher and Kingsbury calculation, leads to even stronger overestimations. Vosgien Lacombe et al. [36] have recently shown that the BK formula yields water uptake values in agreement with gravimetry if coating swelling is taken into account. These authors have suggested that unjustified assumption of negligible swelling probably explains reported water uptake values calculated according to the BK formula that were larger or much larger than those determined by gravimetry.

In the present work, we report on new experiments aimed at measuring the water uptake for the same coatings studied in [4] and on a deeper analysis of the EIS data reported therein. The coating capacitance and dielectric constant were determined in two independent ways: (i) the coating dielectric constant was an adjustable parameter in the fitting of EIS data using a model that assumed an exponential distribution of coating resistivity as previously described in [4], or (ii) the

coating capacitance was determined from complex-capacitance plots (Cole–Cole plots) and the dielectric constant was calculated following the equation for the capacity of a plane capacitor. Then, we used the BK formula, its Sykes variant and a linear equations for the dielectric constant–water uptake conversion. Comparison of water uptake calculated from EIS and gravimetric data provided a further test of the validity of the model [4].

## 2. Experimental

### 2.1. Coating samples

Two water-based paints were deposited by air spraying onto 2024 T3 aluminium alloy currently used in the aerospace industry. The chemical composition in weight percent of the alloy was: Cu: 4.90; Mg: 1.31; Mn: 0.56; Si: 0.08; Fe: 0.26; Zn: 0.10; Ti: 0.01 and Al to balance. The specimens consisted of 125 mm × 80 mm × 1.6 mm plates machined from a rolled plate. Before painting, the samples were degreased at 60 °C (pH = 9) for 15 min, rinsed twice with distilled water, then etched in an acid bath at 52 °C for 10 min, and rinsed again with distilled water. The liquid paints were applied by air spraying and cured at 60 °C. Both paints, manufactured by Mapaero SAS, Pamiers, France, had the same polymer matrix (based on a bisphenol A epoxy polymer and a polyaminoamide) and contained the same fillers, i.e. 12 wt.% TiO<sub>2</sub>, 11 wt.% talc and 1 wt.% SiO<sub>2</sub>, but different inhibitors. One of them (henceforth called CC) contained 16 wt.% of SrCrO<sub>4</sub>, the other was a Cr(VI)-free coating (called NCC) which contained 10 wt.% of a mixture of ZnO and a phosphosilicate. The ratio of the pigment volume concentration (PVC) to critical pigment volume concentration (CPVC) was optimized for both coatings (about 0.6). The coatings were 21 ± 2 μm and 18 ± 2 μm thick for CC and NCC, respectively.

### 2.2. Gravimetric experiments and chromate leaching

The water uptake was measured at room temperature (20 ± 2 °C) on metal-supported coatings. To minimize the mass difference between the aluminium plate and the coating, the CC and NCC water-based films were applied on 50 μm-thick aluminium foils, (purity 99.0%) (Goodfellow), without any surface preparation, and cured at 60 °C. Square samples (3 cm × 3 cm) were cut from the coated foils. Before immersion in 100 mL of 0.5 M NaCl solution, each sample was weighed on a Mettler balance with a precision of 0.1 mg. Samples were periodically removed from the NaCl solution and weighed, after carefully removing the water excess from coatings surface with filter paper. At the end of the exposure, the films were peeled piece by piece from the aluminium foil and the foil was weighed.

The sample mass before immersion, after immersion and after coating removal are denoted  $m_1$ ,  $m_2$  and  $m_0$ , respectively. Each value was obtained by averaging at least 5 measurements.

The leaching of SrCrO<sub>4</sub> from CC was measured with the procedure described in [4] and summarized briefly here. A cylindrical Plexiglas tube was fixed on top of the CC sample and filled with 100 mL of a 0.5 M NaCl solution. A 5 mL aliquot of the solution was periodically removed and replaced with 5 mL of fresh 0.5 M NaCl solution to maintain a constant volume at 100 mL. The concentrations of released chromate ions were determined by UV–vis spectroscopy using a Shimadzu UV 1800 at  $\lambda = 371$  nm. A calibration curve was built by analysing standard strontium chromate solutions. Dilution effects were taken into account. The leaching experiments showed that SrCrO<sub>4</sub> was progressively lost by CC samples during exposure to the NaCl solution. Its mass, function of immersion duration, is denoted  $m_{\text{SrCrO}_4}$ . No comparable phenomena were observed with NCC.

The mass fraction of water ( $\phi_m$ ) absorbed by the coating for each exposure time was calculated as

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