Among a wide variety of electrochemical techniques, electrochemical impedance spectroscopy (EIS) has proven to be a suitable/powerful technique to study the protective properties and efficiency of (self-healing) coatings (containing inhibitors) on metal substrates over time. EIS can provide both qualitative and quantitative information. Qualitative in a sense that the efficiency of electrochemical systems can be monitored by comparing the magnitude of the impedance modulus at low frequencies, i.e. the polarization resistance, over time. Any decrease or increase in the polarization resistance can be related to an decrease or increase in corrosion protection, respectively. Quantitatively the system can be studied by fitting the experimental data to an equivalent electrical circuit (EEC) describing the physical phenomena occurring in the electrochemical system in such a way that the individual contributions to the global system’s performance can be studied.[1][2][3] This makes EIS a very powerful technique to study electrochemical systems.

However there are some constraints coupled to the application of this technique, the validity of the measurement and the interpretation and modelling of the experimental results. In order to perform a reliable EIS measurement, the conditions of causality, linearity and stationarity (time-invariance) need to be fulfilled. The condition of causality states that the AC output should be directly related to the AC input added with some measurement noise. The linearity conditions states that any linear transformation in the input signal results in a linear transformation of the output signal or, in case of a potentiostatic EIS measurement, that the input frequency equals the output frequency and the only difference between the applied potential and response current is a phase shift. The stationarity condition states that the system has to be time-invariant during the measurement.[4] In practice, EIS measurements are carried out by applying only a small perturbation voltage in the steady-state regime of the process to meet these requirements. Consequently, the measurements can experience a poor signal-to-noise ratio and are unable to explain the initial, rapidly evolving stages of electrochemical processes.[4] Since corrosion processes are initially de facto non-linear and non-stationary, these phenomena cannot be described adequately by means of EIS.

Odd random phase electrochemical impedance spectroscopy can present a possible solution to study these initial, rapidly evolving stages of electrochemical (corrosion) processes. Rather than exciting the system with all the frequencies subsequently, as in conventional EIS, the system is excited with a multisine signal. First of all, applying a broadband rather than a single sine signal decreases the measurement time drastically while exciting the higher frequencies even more. Secondly, through a dedicated data analysis procedure, extra information regarding the noise, non-linearities and non-stationarities present in the system under investigation can be evaluated an quantified.[5][6][7][8] Starting from the measured electrochemical impedance data, one wants to perform a reliable data interpretation and obtain reliable modelling results when fitting the experimental data to an equivalent electrical circuit (EEC). To perform an adequate data interpretation, it is important that it can be verified the correct experimental data is available. To investigate the reliability of the fitting results, a baseline needs to be present to evaluate whether the EEC model is able to describe the experimental data within the experimental error. This information is available by performing an ORP-EIS experiment. The concept of ORP-EIS has already proven to be a successful tool for a number of practical applications: as a rapid corrosion screening test of metal-coated steel, to analyze (self-healing) organic coatings, to investigate the time-varying process of self-assembling monolayers aluminum oxide, to study the mechanism of adsorption on copper and to describe the early stages of copper corrosion. [9][10][11][12][13][14][15][16]

The aerospace industry is a well-known example with an ongoing transition from chromate-containing to chromate-free corrosion inhibition technology for the various aluminum alloys used. These aluminum alloys are usually protected by organic or inorganic barrier coatings containing corrosion passivating inhibitors providing both passive and active corrosion inhibition. [17] Chromates are known to inhibit both the anodic and cathodic reactions (at least temporarily) and ideally suitable chromate-replacing pigments should do so.[18][19]

Recently, lithium-based corrosion inhibitor technology has become of particular interest to protect AA2024-T3 against (localized) corrosion. Visser et al. have proven that when dispersed in a model organic coating, lithium-carbonate and lithium-oxalate pigments can ensure fast and effective corrosion protection in an artificial damage under neutral salt spray (NSS) exposure according to ASTM B-117. These lithium-salts are able to leach from the coating matrix through a specific leaching mechanism providing active corrosion protection by rapid formation of a well-organized three-layered morphology, consisting of an inner dense layer close to the aluminum alloy metal surface, a porous middle layer and a very porous columnar outer layer. The coverage, growth process and surface chemistry of the protective layer is studied in detail with a variety of surface analysis and spectroscopic techniques. Finally, electrochemical impedance spectroscopy (EIS) has been used to study the electrochemical properties of the generated three-layered protective morphology and recently to study its formation and properties as a function of NSS exposure time. [20][21][22][23][24][25]

In this paper, ORP-EIS is applied on a lithium carbonate containing model coating on a AA2024-T3 substrate. The application of this technique is crucial to study the initial, rapidly evolving stages of inhibitor based corroding systems. In a first step, the experimental data is examined both qualitatively and quantitatively to study the influence of the additional information provided by the technique on the correctness of the data, pointing out the shortcomings of traditional EIS measurements in this case. Later on, the impact and consequences of using the additional information during fitting (to an EEC) is described, to study and improve the fitting reliability.

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