Odd Random Phase Electrochemical Impedance Spectroscopy (ORP-EIS) as a powerful tool for corrosion studies

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Introduction

Using single sine impedance spectroscopy to study electrochemical systems is a well-known concept. Certainly for processes that are a combination of various phenomena, all occurring at a different rate, EIS is commonly used. One can find a multitude of examples in literature where EIS is applied for corrosion studies. Despite all the benefits of the EIS method, the technique has an important drawback related to the interpretation of the experimental impedance spectra. With the current state-of-the-art, a necessary prerequisite to correctly define the transfer function and to obtain a satisfactory model for an electrochemical system in general, and a corrosion process in particular, is that the system fulfills the conditions of causality, linearity and stationarity. Those last two conditions are difficult to satisfy. In practice, EIS measurements are often performed with very small amplitude excitation signals (for reason of linearity) in the stationary regime of the process (for reason of time-invariance). As a consequence, the measurements can suffer from poor signal-to-noise ratios and will not describe properly the initial, mostly rapidly evolving, stages of the corrosion process.

To check whether the conditions for reliable modelling are fulfilled, different methods are described in literature. Recently we developed a new approach in our research group. It consists of an integrated measuring and modelling methodology for EIS based on an odd random phase multisine excitation signal (ORP-EIS). With this technique, the level of disturbing noise, the level of the non-linear distortions and the level of the non-stationary behaviour can be measured and quantified. We published a number of papers on this methodology. The theoretical background can be found in [1-3]. Besides that, a new method that quantifies non-stationary behavior, corrects for it and traces the dynamics of the process by the calculation of an instantaneous impedance, was developed [4].

The advantages of the methodology and the ability to quantify model parameter values together with their confidence interval will be demonstrated on a number of practical corrosion studies.

Experimental systems

Two case studies are related to steel substrates: (1) detection of corrosion applied to hot dip galvanized steel with commercial organic coatings; (2) corrosion of different Aluminium-rich metallic coated steel products with an Al content in the coatings varying between 0.5% to 99.5% wt.
Two case are related to Aluminium substrates: (1) self healing of polycaprolactone and polyurethane coatings with Ce(NO$_3$)$_3$ as corrosion inhibitor on 2024-T3 Aluminium; (2) corrosion of ultrapure Aluminium in ethanol during deposition of n-octylphosphonic acid layers.
References