Analysis of electrochemical noise measurement on an organically coated metal

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ABSTRACT

Electrochemical noise measurement (ENM) has found a credible place among the electrochemical methods applied to organic coatings, with a large number of reports in the literature of using the technique as a reliable method for the evaluation of the corrosion protection afforded by an organic coating on a metal surface. This has commonly been performed by calculating the noise resistance, R_n, or spectral noise resistance, R_{sn}, from the two main elements of electrochemical noise signal, the electrochemical current noise and potential noise. Several studies have shown that in practice R_n is a good measure of corrosion protection provided by an organic coating and affords good agreement with other measures of corrosion resistance from more established methods such as electrochemical impedance spectroscopy and DC resistance measurement. However, the theory of the electrochemical noise signal has not been fully analysed to elucidate the influence of the coating on the noise acquired. In this study a mathematical model is advanced in accordance with the equivalent electrical model in an electrochemical system consisting of a corroding metal substrate which has on it an organic coating. Experiments are also performed to evaluate the presented model in practice. Results of both theoretical and physical modelling show that potential noise is not influenced by the effect of coating while the current noise is attenuated due to the large impedance of coating.

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1. Introduction

Electrochemical Noise Measurement (ENM) is a non-destructive/non-intrusive technique capable of monitoring basic changes in an electrochemically active system. The method measures the fluctuation in the current produced by electrochemical reactions (e.g. iron dissolution ($2Fe \rightarrow 2Fe^{++} + 4e$), oxygen reduction ($2H_2O + O_2 + 4e \rightarrow 4OH^-$) as well as the effect of this fluctuation on the electrochemical potential of system. Much work has been done on bare (uncoated) metal ENM [1–5] showing that R_n is a reliable measure of corrosion resistance and that EN data may be able to determine the type of corrosion [6–8]. However when it comes to metal coated with an organic coating, although the ease with which the above electrochemical reactions go on may well control the rate with a defective organic coating, what is more commonly found is that the rate of transport of ions (e.g. sodium and chloride) through the polymer film is the rate

determining process controlling the overall rate of the corrosion reaction. The faster the transport the lower the protection afforded to the metal and vice versa. ENM may be implemented in order to acquire information about coating integrity and degradation mechanism in coated systems. The degradation process of a paint coating may be analysed by contributions from charge transfer reactions at high frequencies and mass transport reactions at low frequencies [9].

Studies have combined ENM with multi-electrode systems [10–13] as well as embedded electrodes [14] in attempt to obtain mechanistic information about corrosion process under an organic coating. Also a variety of analytical methods such as statistical functions [15,16], wavelet analysis [17–19], fractal analysis [20–22], artificial neural network [23,24], cluster and discriminant [25,26] and shot noise analyses [27] have been implemented mainly in order to acquire mechanistic information about the under-film corrosion process such as active/passive state of substrate, formation of corrosion product and the corrosion type taking place at the organic coating/metal interface. However, in coated metal systems with even a moderately protective organic coating, the current and hence the current noise is mainly controlled by transport of

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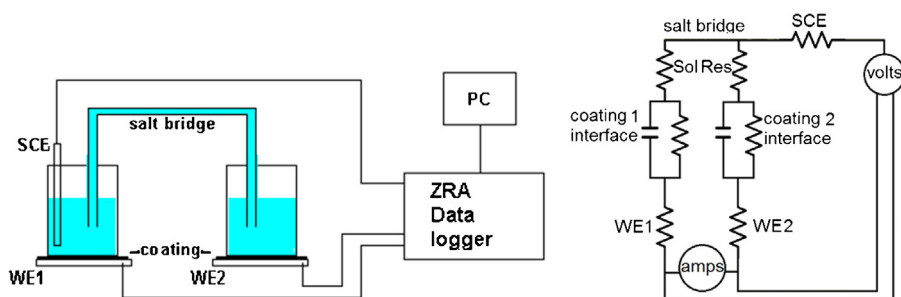
Fig. 1. Standard salt bridge arrangement (left) for electrochemical noise measurement on two organically coated metal surfaces and the associated equivalent electrical circuit (right) assuming Randles circuit modelling the coated metal. WE1 and WE2 refer to working electrodes 1 and 2 respectively. [28].

ionic species through the organic film. Despite the above empirical efforts that have been made to extract mechanistic information from ENM on an organically coated metal, little has been done to understand the origin of electrochemical noise from a coated metal and how it is altered by the coating system. This study presents a theoretical model that might hold the key to a meaningful interpretation of electrochemical noise from coated metal and hence the acquisition of mechanistic information about corrosion processes. This is tested against a physical model.

2. Theoretical model

In order to understand the electrochemical noise generated from a complex electrochemical system such as a corroding organically coated metal coated, it is essential to break down the complex system into more understandable electrical components known as an equivalent electrical circuit (EEC). A simple Randles circuit without diffusion, i.e. no Warburg term, with an element comprising a time constant, RC, for the organic coating and a resistor for the solution impedance has been used previously [28,29] for modelling an organically coated metal that generates electrochemical noise. The capacitance simulates the capacitive characteristic of the organic coating (C_c) and the resistance corresponds to the ionic resistance of coating film (R_f). Fig. 1, reproduced from Ref. [28], illustrates the schematic cell configuration for the salt bridge electrode arrangement and the associated electrical circuit using a Randles circuit to model each coated area of metal. However, the Randles circuit assumes the coatings to be defectless and with no disbondment from the metal substrate. This does not normally hold true in "real world" scenarios where the coating may contain or evolve significant ionic pathways (sometimes known as "pores") that leads electrolyte towards the substrate surface and introduces a second time constant to the ECC associated with the double layer capacitance (C_{dl}) and charge transfer resistance (R_{ct}) at the metal surface. This time constant is considered in series with the coating resistance and in parallel with the coating capacitance. The C_{dl} and R_{ct} of this case are confined to a small area where the ionic pathway meets the metal substrate. Also in many cases significant coating disbondment occurs due to the wet interface and the corrosion domain spreading underneath the coating, in which case the impedance associated with C_{dl} and R_{ct} at the metal-solution interface, Z_{m-s}, is considered in series with the coating impedance, Z_f. Fig. 2 demonstrates an EEC for ENM in a three electrode configuration using a low noise saturated calomel electrode (SCE) as reference electrode and two metal substrates with fully disbonded coating films as working electrodes. This model is adopted from the previous work on modelling electrochemical noise measurement [30–32] for a current noise based model. Note that the solution resistance for the solution within the gap between metal and coating is not taken
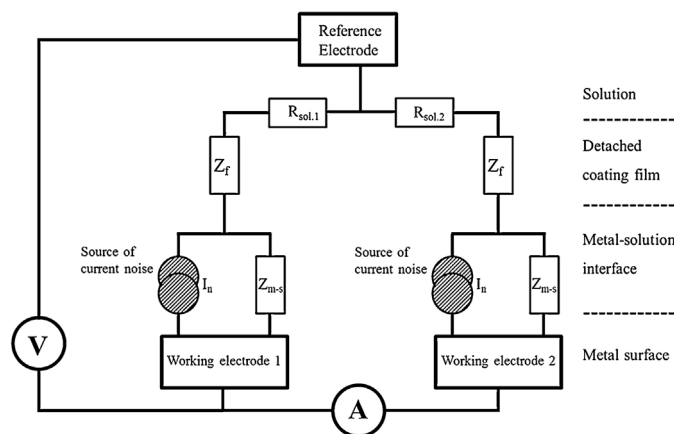
Fig. 2. Equivalent electrical circuit (EEC) simulating a three-electrode (WE1, WE2 and Ref) noise measurement configuration for a detached organic coating from a corroding metal substrate.

into account in the model as this usually is a very small gap and the solution is of high ionic activity with very low resistance.

In the EEC presented in Fig. 2, no hindrance is introduced by coating between anodic and cathodic sites underneath the disbonded coating and therefore electrochemical reactions and thus generation of electrochemical noise occur independently from the organic coating. The electrochemical noise measured via ZRA and potentiometer in a standard three electrode configuration however is altered by the coating impedance. Current noise is produced as a result of anodic and cathodic reactions underneath the coating. Potential noise is a consequence of current noise acting on the impedance of the metal-solution interface [31]. The cathodic process of oxygen reduction may be rate controlling for coatings of low oxygen permeability, but commonly the oxygen permeability is sufficient that the film does not limit oxygen transport to the metal. In the case of hydrogen evolution as the cathodic reaction, the kinetics of the electrochemical reaction is usually rate-controlling, although the transport of water could be important for low permeability coatings. Organic coatings protect metal from corrosion by providing a barrier against the flow of corrosive ions, e.g. chloride, towards the metal substrate and by introducing a large impedance between anodic and cathodic sites hence impeding the electrochemical process of corrosion. In this paper a fully detached organic coating is discussed where the coating does not isolate anodic and cathodic sites and therefore the only protective effect is by limiting the flow of ions towards and from the metal substrate. The electrolyte under the film is aerated, hence simulating a coating of high oxygen permeability. In the real case scenario of disbonded coating on a metal surface this can effectively change the electrolyte composition underneath the coating which in turn can results in