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Measuring electrochemical noise of a single working electrode for assessing corrosion resistance of polymer coated metals

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ABSTRACT

Electrochemical noise measurement (ENM) of the spontaneous perturbation of current and potential of coated samples immersed in electrolyte determines the resistance of the coating system. ENM offers several advantages: the measurement is relatively simple to make, it is completely non-interfering with the natural process occurring on the surface and the data are simple to interpret. The original standard arrangement for ENM using a pair of samples has limitations for practical applications because two separate and nominally identical working electrodes are needed and this requirement is very hard (if not impossible) to fulfil in on-site application. This paper describes an alternative approach for electrochemical noise measurement to measure the noise resistance (R_n) of protective coatings based on use of just one working electrode. In this so-called "Single Cell" (SC) arrangement the electrochemical noise current and electrochemical noise potential between the working electrode and a non-noisy reference electrode is measured separately and consecutively. This new approach has been tested for a range of coating resistances. Also, the coating's resistance has been measured using DC resistance and EIS (at low frequency) and the results were compared with the R_n obtained from the single cell (SC) set up.

1. Introduction

Electrochemical noise measurement comprises simultaneous measurement of potential and current fluctuations caused by spontaneous electrochemical reactions. It is accepted as a non-destructive/non-intrusive technique capable of monitoring basic changes in an electrochemically active system. The technique has been used to calculate R_n as a measure of corrosion resistance [1,2] and also statistical methods have been applied to evaluate the corrosion regime [3–5].

Since first introduced to the field of protective coatings by Skerry and Eden in 1986 [6] the electrochemical noise method (ENM) has found increasing use as an effective way of assessing the protection afforded by organic coatings on metals [7,8]. It has been shown that the noise resistance conforms with the corrosion resistance from other well-established techniques, e.g. EIS [9,10]. The usefulness and simplicity of the ENM technique plus the relatively quick measurement and inexpensive instrumentation makes the method potentially ideal for in situ corrosion assessments. It also offers the advantage of non-interfering measurement compared to DC techniques where the applied current/potential alters the system from the steady state. DC measurements may not ideally represent system characteristics in a self-corroding/uninterrupted condition and also more time will be required to reach the steady state condition [10]. ENM also provides mechanistic information about the corroding bare metals (e.g. uniformity/localization of corrosion or at a scribe in a coating) which may not be acquired by the techniques such as EIS and DC measurements. Examples of the recent breakthroughs in this field are novel methods of noise data analysis for studying localized corrosion [11], detecting the initiation of stress corrosion cracking [12] and studying nucleation of pitting corrosion [13].

The ENM technique with the original arrangement, e.g. salt bridge set-up (Fig. 1), is well established and is commonly applied for studying electrochemical behaviour of corroding systems in the laboratory. This method uses two nominally identical but separate working electrodes and works effectively for measurements on bare and coated metals. The current between the two working electrodes is measured by a zero resistance ammeter (ZRA) simultaneously with the potential of these electrodes (now in effect coupled together by the potentiostat) with respect to a noiseless standard electrode (normally a Saturated Calomel Electrode (SCE)). However, it will usually be impractical to find two nominally identical but separate working electrodes in the real on-site applications, e.g. a bridge or a ship hull. The first step towards making the

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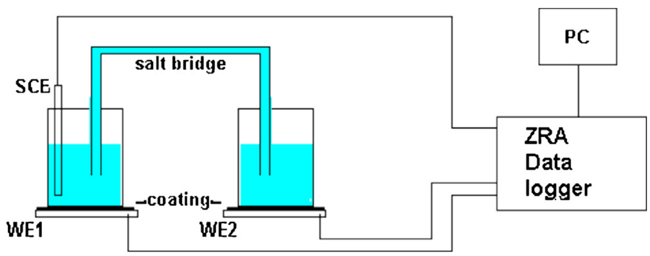

Fig. 1. Standard "Salt-Bridge" arrangement for electrochemical noise measurement.

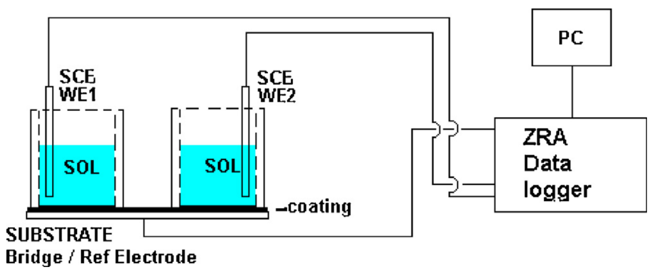

Fig. 2. Schematic laboratory set-up for ENM with Single Substrate (SS) arrangement.

technique more practically useable for organically coated metal on-site was taken by Mills and Mabbutt in 1998 [14]. The so-called "Single Substrate" (S.S.) (Fig. 2) arrangement is a re-arrangement of the original salt bridge arrangement. It replaces the working electrodes (the two substrates) by SCEs and uses the substrate as the pseudo reference. Nominally noiseless SCE's make electrolytic contact with the corroding surface and the current perturbation measured by ZRA originates from the electrochemical activity of the two coupled areas of the specimen. This arrangement was also successfully utilized for online monitoring of corrosion behaviour and degradation rate of coated substrates in long-term cyclic Prohesion exposure using embedded Pt electrodes by Bierwagen et al. [15]. There has been further work carried out on the validation of the technique, mainly by Mabbutt [16–18].

Further development of ENM for application to coated metal has been made by Woodcock et al. in 2004 mainly to eliminate the need for electrical connection to the substrate and so make the technique more practically useable [19]. In this new, so-called "NO Connection to Substrate" (NOCS) arrangement, electrochemical noise potential is measured against a third SCE which, similar to the working electrodes, is in electrolytic contact with the specimen. The main advantages of this arrangement are elimination of wired electrical contact to the substrate and, compared with the Single Substrate arrangement and use of a highly stable reference electrode as part of the current measuring circuit. NOCS arrangement for electrochemical noise measurement is shown in Fig. 3.

An overview of the newly developed ENM arrangements and practical approach to implement these for in situ measurement

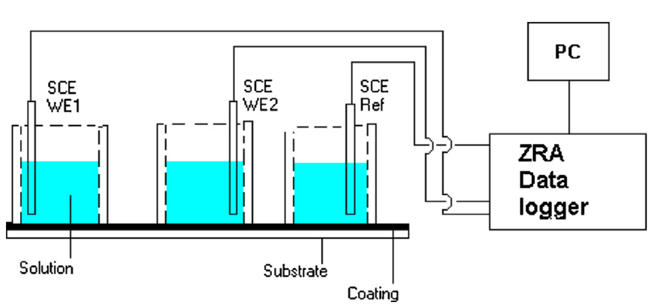

Fig. 3. Schematic laboratory set-up for ENM with NOCS arrangement.

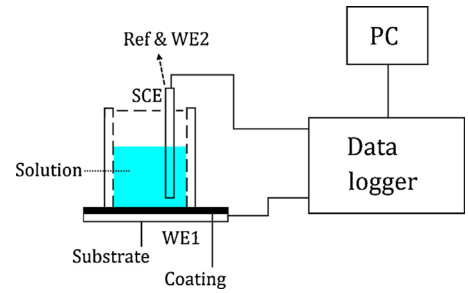

Fig. 4. Single cell (SC) arrangement for electrochemical noise measurement.

has been discussed by Mills in Ref. [20]. Despite all the efforts to make ENM a practical on-site method, field evaluation offers a significant challenge, particularly in the case of submerged structures and awkwardly shaped substrates, where providing and isolating the two or three working electrodes (respectively for SS and NOCS arrangements) may be impractical. Also in contrast with most laboratory experiments, field measurements are usually performed on random surfaces with unknown resistance values. So, practically all the proposed noise data collection arrangements introduce a significant uncertainty in regards to *which area has dominated the measured* R_n. There have been recent studies to elucidate the dominant factor(s) [21,22] but further investigations are still required to clarify the ambiguity.

In the present work a new arrangement for ENM has been introduced that makes the measurement on a single working electrode. The so-called "Single Cell" (SC) arrangement provides the capability of measuring noise resistance for immersed objects or inside storage tanks without the need for two isolated working electrodes. Also since only one area (WE) is involved in the measurement, it eliminates the uncertainty introduced by multiple working electrodes.

2. The single cell arrangement and data acquisition

The SC set-up comprises one working electrode and a noiseless reference electrode as shown in Fig. 4. Unlike previous experimental procedures, the electrochemical noise current (ENC) and electrochemical noise potential (ENP) are not (and cannot be) measured simultaneously, so it is essential to be sure that the corroding sample remains in an unchanged condition throughout the time of experiment. Since the noise data collection is relatively quick (e.g. 512 data point at 2 Hz takes about 4 min) and the process of data collection imposes no external stimulus steadiness of working electrode is a reasonable assumption. In most cases under field conditions the coated structure has been well equilibrated by the time the measurements are made.

The ENP was measured by recording the sample potential against an SCE. This was performed (similar to a conventional three-electrode ENM) under open-circuit conditions; as the SCE generates little noise (ref) only the electrochemical noise generated by the sample is measured. ENC is usually measured with the sample connected to an identical sample via a ZRA, but here ENC cannot be measured directly using a ZRA due to the potential difference between the substrate and the SCE that would generate a DC current flow. Instead, the substrate potential was determined as the mean value of electrochemical noise potential data set, then this was implemented electronically by the potentiostat acting as a constant potential source, with the SCE serving as both reference and auxiliary electrodes. This is permissible for high resistance coatings where the current is too small to perturb the reference electrode, but a separate auxiliary electrode can easily be added where necessary to give true potentiostatic control. The ENC measurement was