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Novel time–frequency characterization of electrochemical noise data in corrosion studies using Hilbert spectra

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ABSTRACT

Hilbert spectra, calculated with the Hilbert–Huang transform, are presented here as an analysis technique for the characterization of electrochemical noise data in corrosion studies. A highly detailed decomposition of the original current and potential data is provided in time and frequency simultaneously. Results on the decomposition of individual transients into their instantaneous frequencies at each moment in time are presented for five different corrosion processes: AISI304 in HCl solutions at different concentrations and AISI304 as well as mild steel in a 3 wt.% NaCl solution. The results demonstrate the potential of this technique to identify and distinguish different corrosion mechanisms.

1. Introduction

Throughout the years, a large number of corrosion monitoring and evaluation methods has been developed, most of them based on electrochemistry [1,2]. A division can be made between electrochemical methods that are potentially suitable for the detection of localized corrosion (or have shown, under specific conditions, suitability for detection of localized corrosion) and those that are not. A drawback of the latter category is that information of localized electrochemical corrosion processes and mechanisms at small defects is not spatially resolved [3]. An example is the Polarization Resistance Method or Linear Polarization Method (LPR), where the linear polarization resistance is determined as the slope of the polarization curve at its origin (which is inversely proportional to the corrosion rate) [2,4]. A second example is Electrochemical Impedance Spectroscopy (EIS), where the frequency resolved current response of corroding (coated) electrodes to small-amplitude alternating potential signals is analyzed [2,5,6].

The application of electrochemical methods to evaluate and spatially resolve corrosion activity has found many appearances. The application of scanning electrochemical techniques has progressively increased over the last 20 years. For these techniques it is assumed that localized corrosion, where the anodic and cathodic processes take place at separate sites, may be represented as point sources with small variations in potential generating an ionic flow within the electrolyte. The electric field generated at these point sources can be visualized by equipotential lines, which are graphically represented as a contour map [7,8]. Examples of these scanning electrochemical techniques are: Scanning Kelvin Probe (SKP), Scanning Reference Electrode Technique (SRET), Scanning Vibrating reference Electrode Technique (SVET), Local Electrochemical Impedance Spectroscopy (LEIS) and Scanning Electrochemical Microscopy (SECM) [1,7,9,10]. However it is argued that, because scanning electrode techniques in general (depending on the technique used and the surface area that can be scanned) operate in relatively specific and localized areas under strictly controlled experimental conditions, they might not be able to image the full details of an electrode process involving different reactions occurring simultaneously over distinctively separated electrode areas [9]. In addition, fixed electrode techniques might potentially be more suitable for in situ measurements of localized corrosion with corrosion sensors by the absence of moving parts, probably resulting in lower complexity and higher reliability and robustness of the corrosion sensor.

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Electrochemical noise measurements (ENM) using fixed electrodes are reported suitable as well for detecting non-localized as for localized corrosion activity. The difference depends on the applied measurement configuration and data analysis. ENM involve the measurement of self-generated potential and current fluctuations in order to study corrosion processes. This technique dates back to the 1960s, when a relation between frequency and amplitude of the electrochemical potential signal on the one hand and corrosion characteristics of the corroding metals on the other, was noticed [11,12]. Gradually, the focus changed from the detection of general to that of localized corrosion processes. Hladky et al. reported investigations on characteristic fluctuations in the electrochemical potential noise, generated by the occurrence of localized corrosion [13,14]. Nowadays, the investigation of transients occurring in electrochemical signals due to localized corrosion processes is also reported for ENM under anodic and cathodic polarization [15–19].

The fluctuations in current and potential measured with ENM in a three-electrode configuration under open-circuit conditions provide information on the kinetics of reactions occurring at the electrochemical interface. The most interesting application of ENM is the ability to identify and quantify localized corrosion processes, possibly the most challenging task regarding corrosion monitoring [20–25]. The identification of such processes demands a high distinguishing capacity in both time and frequency simultaneously without the precondition of stationarity or linearity. Until now, the wavelet transform, which is applied for the analysis of electrochemical noise for over a decade, is the only suitable analysis technique in this respect; different timescales of the current and potential signal could be attributed to diffusion-, activation- or mixed controlled processes [16,17,26–36]. The timescale (or group of timescales) with the highest relative energy corresponds to the dominant process and its change can reflect the behavior of this dominant corrosion process: a relatively fast process corresponds to smaller timescales and a relatively slow process to larger timescales [27,30–32,35]. The occurrence of metastable pitting (initiation and subsequent repassivation of pit nuclei) is a fast process with a small timescale. This is a substantially faster process than larger timescale processes, e.g. general corrosion, anodic dissolution or ion diffusion [27–32,35,37]. However, the separation of the frequency domain into so-called scales instead of real instantaneous frequencies does not result in the desired direct frequency decomposition of the data at any given moment in time. Moreover, the chosen wavelet is user-defined, as well as the number of scales. In the present work the Hilbert–Huang transform (HHT), presented by Huang et al. [38], is proposed for the analysis of electrochemical noise signals under open-circuit conditions in corrosion studies. This technique, which has also been proven to be valuable in the analysis of voltammetric data [39], provides an actual time–frequency decomposition of an electrochemical noise signal, without the aforementioned preconditions or assumptions. This ability can be interesting in corrosion monitoring by future fully automated detection of specific corrosion phenomena.

In this paper, first the experimental set-up of the corrosion experiments is described, after which the HHT is discussed. This is followed by the presentation and discussion of the experimental results, which will illustrate the effectiveness of the Hilbert spectrum for this analysis. Electrochemical noise data are investigated for three different corrosion mechanisms involving AISI304 exposed in an aqueous HCl solution at pH 1.0, 1.9 and 3.0. In addition, the AISI304 exposed in the aqueous HCl solution at pH 1.0 is compared with mild steel exposed in an aqueous 3 wt.% NaCl solution. Finally, the AISI304 exposed in the aqueous HCl solution at pH 3.0 is discussed in relation to AISI304 exposed in an aqueous 3 wt.% NaCl solution.

2. Experimental

2.1. Materials and experimental set-up

The measurements were performed in a conventional three-electrode configuration under open-circuit conditions, requiring two nominally identical working electrodes (both either stainless steel AISI304 or mild steel). In Fig. 1 this measurement setup is schematically depicted.

The working electrodes were partly coated with an epoxy primer to prevent crevice corrosion and embedded in coupons using an epoxy resin. Only a well-defined area of 0.05 cm^2 (AISI304) or 0.95 cm^2 (mild steel) of each working electrode was exposed in the electrolyte. The working electrodes were wet ground using up to 4000-grit SiC paper. After microscopic inspection for irregularities they were either stored at 20 °C for 24 h (AISI304) or used immediately in the experiment (mild steel). The reference electrode used was a Radiometer analytical Red Rod type REF201 (Ag/AgCl/sat. KCl: 0.207 V vs. SHE). The following electrolytes were used: 1) aqueous HCl solutions at three different concentrations (0.1, 0.01 and 0.001 M, corresponding with pH 1.0, 1.9 and 3.0, respectively), 2) an aqueous 3 wt.% NaCl solution. All solutions were open to air.

The effectiveness of the use of Hilbert spectra for the investigation of electrochemical noise signals is discussed based on three different corrosion systems: AISI304 exposed in an aqueous HCl solution at pH 1.0, 1.9 and 3.0. For a comparison, additional measurements were performed on mild steel exposed in an aqueous 3 wt.% NaCl solution (series 1) and AISI304 exposed in an aqueous 3 wt.% NaCl solution (series 3).

The different measurement series with the working electrode material (m), electrolyte (e) and open circuit potential (OCP) are schematically depicted in Table 1.

The electrochemical cells were placed in a Faradaic cage to avoid electromagnetic disturbance from external sources. The ambient temperature was controlled at 20 °C. Measurements were carried out in threefold and the samples were microscopically inspected afterwards.

A low-pass filter of 10 Hz was applied during data recording. The data were processed using Matlab from MathWorks. The maximum range of the ZRA was set at 10 μA for the measurements of series 1 and 100 nA for the measurements of series 2 and 3, and the maximum range of the potentiometer was set at 100 mV. In order to maximize the resolution of the raw potential signal measurement (i.e. to be able to set the potentiometer to a small potential range), for each measurement the value of the first potential measurement was used as a fixed offset for the entire potential data range.

2.1.1. Data acquisition

Current and potential fluctuations were recorded using a Compactstat from Ivium Technologies working as zero resistance

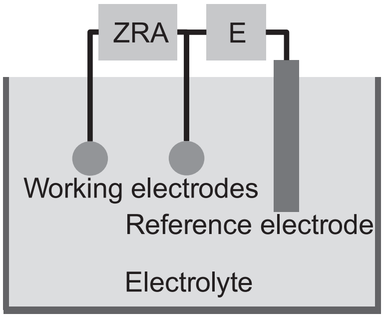

Fig. 1. Layout of the electrochemical cell.