



Application of transient analysis using Hilbert spectra of electrochemical noise to the identification of corrosion inhibition



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ABSTRACT

This study validates the ability of Hilbert spectra to investigate transients in an electrochemical noise signal for an aqueous corrosion inhibition process. The proposed analysis procedure involves the identification and analysis of transients in the electrochemical current noise signal. Their decomposition into instantaneous frequencies in a Hilbert spectrum allows detection of changes in corrosion characteristics, i.e. the evolution of corrosion inhibition with time. The effectiveness of the proposed analysis procedure is investigated for AA2024-T3 exposed to aqueous 10^{-1} M NaCl solutions with or without the addition of Ce ions at various concentrations. Examination of specific features in the electrochemical noise signals shows the presence of three characteristic regions, which represent surface activity regimes ranging from active (localized) corrosion to the inhibited state. Hilbert spectra of the electrochemical current noise signals allow identification of transients occurring in these successive regions.

The analysis procedure introduced in this work yields improved applicability of electrochemical noise measurements for the identification of an inhibition effect in corrosion processes.

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1. Introduction

Electrochemical noise (EN) consists of spontaneous fluctuations in current and potential, generated by charge transfer reactions that arise from electrochemical metal dissolution processes. It has long been the conviction of many researchers that EN contains valuable information about the underlying corrosion processes. Hladky and Dawson [1,2] reported on their investigations on characteristic fluctuations in the electrochemical potential noise (EPN), generated by the occurrence of localized corrosion. These characteristic fluctuations are defined as transients. Transients in the electrochemical current noise (ECN) signal are often accompanied by transients in the EPN signal [3,4]. Characterization of localized corrosion processes can be regarded as the most interesting application of electrochemical noise measurements (ENM), which is also important for corrosion monitoring [5–10].

For the purpose of characterization of localized corrosion processes through EN signals, many data analysis procedures exist of which the most common are fast Fourier transform and discrete wavelet transform. However, fast Fourier transform is strictly spoken not suitable for the analysis of EN, since corrosion processes are typically nonstationary, a property that is required for data analysis in the frequency domain. A separate procedure is necessary to remove its direct current (DC) drift component and to make an EN signal appear stationary. An approach to define a reliable DC drift component using empirical mode decomposition and wavelet transform is presented by the authors in an earlier work [11]. In addition, the interpretation of specific features (e.g. the roll-off slope) in the resulting power spectral density plot and its relation to the prevalent corrosion mechanism can be considered controversial [3,12–17].

Discrete wavelet transform allows investigation of the distribution of the energy present in a (nonstationary) EN signal over several timescales in an energy distribution plot. 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.

An interesting approach to distinguish local frequency characteristics of an EN signal is the application of the Hilbert-Huang

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transform as was first proposed by Huang et al. [18]. This transform is based on the assumption that any signal consists of multiple characteristic scales, or intrinsic modes of oscillation, each superposed on another. These so-called intrinsic mode functions are based on the local properties of the signal and can be identified empirically by their characteristic time scales through empirical mode decomposition. Intrinsic mode functions could be considered as a more general case of simple harmonic functions, however in close relation with the physical characteristics of the system under investigation due to the specific nature of empirical mode decomposition [19]. The basis of this technique is derived directly from the data itself, making the empirical mode decomposition flexible and adaptive [18,20–22]. A detailed description of the empirical mode decomposition and Hilbert-Huang transform procedure is reported by the authors in prior work [23], where the use of Hilbert spectra for the analysis of EN signals under open-circuit conditions has been proposed in corrosion studies. It was shown that Hilbert spectra enabled to distinguish between different corrosion characteristics [23]. Regarding the interpretation of EN signals, this ability makes the Hilbert-Huang transform a valuable data analysis technique.

The frequency contribution of individual transients yields specific signatures, or ‘fingerprints’, in the Hilbert spectrum. In earlier work, the principle of transient analysis through Hilbert spectra of EN signals has been presented for metastable pitting corrosion processes on stainless steel for which the characteristics do not change over the duration of the measurements [24]. Interestingly, analysis of the instantaneous frequencies contributing to the transients in an EN signal also enables to detect changes in corrosion characteristics. It was early recognized that the investigation of transients present in the EN signal is essential to understand the corrosion characteristics of aluminium [25]. In this work the principle of transient analysis applied to an aqueous corrosion inhibition process is therefore illustrated by the Ce-based inhibition of AA2024-T3. In order to differentiate between changing corrosion characteristics of the inhibition process, visual investigation of transient information present in these complex EN signals is not straightforward. This gives rise to the need of an adaptive analysis method that allows detection of the changes in the inhibition process. It should be noted that while the original time signatures from metastable pitting are better reported and discussed, little understanding on the signatures of other forms of localized corrosion processes such as pitting growth, crevice corrosion or galvanic corrosion has been achieved to date.

AA2024 consists of an Al matrix with second phase intermetallic particles, many of which contain Cu and are primarily involved in the localized corrosion of AA2024-T3 [26–30]. This can occur either at isolated particles or in clusters of multiple particles [29]. Two types of intermetallic particles can be distinguished, namely those containing Al-Cu(-Mg) or Al-Cu-Fe-Mn(-Si) [31–33]. The most numerous are Al_2CuMg (S-phase) particles, belonging to the first type [28,34]. Except for the S-phase particles, intermetallic particles contain elements that are more noble than the Al matrix, therefore acting as cathodic sites [30,35].

Corrosion inhibition of AA2024-T3 by the commonly used chromate-based inhibitors can be quite effective [36]. A suitable alternative to the commonly used Cr(VI) inhibitor can be e.g. to use lanthanide salts as an ecological substitute [37–43].

The process of inhibition is studied quite thoroughly by others [37–43]. The main contribution of this work is the introduction of transient analysis through Hilbert spectra of EN signals for the investigation of an aqueous corrosion inhibition process. The proposed analysis procedure involves the identification and analysis of the instantaneous frequency composition of transients in the ECN signal. The benefits of the proposed analysis method are supported by visual inspection of the EN signals in the time domain, microscopic observations and literature.

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 AA2024-T3 working electrodes. The measurement setup and electrochemical cell configuration is identical to the one described earlier [23].

The working electrodes were partly coated with an epoxy primer to prevent crevice corrosion and were embedded in coupons using an epoxy resin. Only a well-defined area of 0.05 cm^2 of each working electrode was exposed to the electrolyte. The working electrodes were wet ground using up to 4000-grit SiC paper. After rinsing with demineralized water and microscopic inspection for irregularities they were stored under ambient conditions at 20°C for 24 h. The reference electrode used was a Radiometer analytical Red Rod type REF201 (Ag/AgCl/sat. KCl: 207 mV vs. SHE). The electrolytes used were aqueous NaCl solutions made from demineralised water and analytical grade reagent. These were either used in that composition, or prepared with the addition of 10^{-2} to 10^{-5} M $\text{CeCl}_3 \cdot 7\text{H}_2\text{O}$. The applied experimental procedure is shown in Fig. 1.

All solutions were open to air. The duration of each exposure to the electrolyte was 14500 s, equal to the duration of each measurement. For each measurement containing 10^{-2} to 10^{-5} M $\text{CeCl}_3 \cdot 7\text{H}_2\text{O}$, after another 24 hours in ambient air an additional measurement of again 14500 s was performed in an electrolyte containing only 10^{-1} M NaCl.

The electrochemical cells were placed in a Faradaic cage to avoid electromagnetic disturbance from external sources. The ambient temperature was controlled at 20°C . The samples were microscopically inspected afterwards using a Reichert MEF4M optical microscope with maximum magnification of 1000x. All measurements were performed at least in triplicate.

Current and potential signals were recorded using a Compactstat from Ivium Technologies working as zero resistance ammeter and potentiometer, controlled by a Windows-based PC running dedicated software. The sampling frequency used for the measurements described in this work was 20 Hz. A low-pass filter of 10 Hz (which is the Nyquist frequency at this sampling rate) was applied during data recording. It was verified that instrumental noise generated by the measuring equipment did not affect the measurements. This is described in detail in an earlier paper by the authors [23]. The maximum range of the zero resistance ammeter was automatically determined during the measurements, depending on the dynamic range of the ECN signal locally, with a lower limit of 10 nA and an upper limit of $1\ \mu\text{A}$. The maximum range of the potentiometer was set at 1 V.

The data were processed using Matlab from MathWorks. The empirical mode decomposition and the Hilbert-Huang transform were calculated using a publicly available Matlab procedure from Rilling et al. [44,45].

2.2. Transient analysis

In order to differentiate between changing corrosion characteristics of an inhibition process, visual investigation of transient information present in the complex EN signals is not straightforward. Therefore, in order to obtain information about the localized corrosion processes, the corresponding transients in the EN signals are identified and decomposed into their instantaneous frequencies using Hilbert spectra. The process of transient analysis consists of two steps. First the areas in a Hilbert spectrum corresponding to the occurrence of individual transients are defined. Subsequently, only the amplitudes of the instantaneous frequencies present in

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