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An integrated approach in the time, frequency and time-frequency domain for the identification of corrosion using electrochemical noise

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ABSTRACT

Transients in electrochemical noise (EN) signals that are associated with localized corrosion typically contain frequency information that is quite localized in time. The study of these transients is therefore preferably performed using analysis procedures with high discrimination ability in both time and frequency simultaneously. The present work studies the combination of the Hilbert-Huang transform with the continuous wavelet transform, as data analysis methods that operate in time as well as in frequency, for the identification of localized corrosion. Additionally it incorporates fast Fourier transform as a technique to determine the distribution of power over frequency. Finally, it integrates the study of transient shape into the analysis of (time-) frequency properties. It is shown that the maxima in instantaneous frequency amplitudes of transients with otherwise different shapes can be similar. In the case of the presence of multiple transients in the EN signal, the cut-off frequency obtained from power spectral density plots is related to maxima in instantaneous frequency amplitudes of only a limited number of transients.

1. Introduction

Electrochemical noise (EN) measurements are principally intended to record charge transfer that originates from spontaneous corrosion, while keeping perturbation of the process to a minimum. Whereas measuring EN may appear straightforward, in order to obtain meaningful mechanistic information from the chemo-physical process it is essential to employ the appropriate data analysis techniques [1,2]. Amongst these, conceivably direct visual characterization of EN transients in the raw data signal is the most straightforward. However, the analysis of transient shape requires the possibility to visually locate and identify transients individually. This necessity potentially decreases the suitability of visual identification for this purpose. In the case of localized corrosion processes that occur more or less at the same time, the resulting transient overlap may impede the investigation of transient shape.

Operating in the frequency domain, for the analysis of EN signals fast Fourier transform (FFT) is most often used to determine the distribution of power over frequency, usually in the form of the power spectral density, or PSD [1]. An important limitation of FFT is the requirement for a stationary signal, which is often not met for EN signals.

The PSD shows specific characteristics that can indicate specific types of corrosion: Firstly, the overall level of the PSD is reported to be related to the intensity of the process [3,4]. Secondly, the cut-off-, roll-off- or knee frequency, which indicates the transition between the horizontal low-frequency part and the slope at higher frequencies, can be used to discriminate between different types of corrosion [4,5]. As a third parameter, the slope in the higher frequency part can be considered to differentiate between different corrosion types [3,4,6–8]. It should however be noted that in some cases the discrimination ability of the PSD can vary between the electrochemical current (ECN) or potential noise (EPN) signal, and that it may be difficult to indicate the presence of a low-frequency plateau or cut-off frequency [2].

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A more recent development is the use of data analysis procedures operating in the time-frequency domain for the investigation of EN [5,9]. As an example, corrosion studies using the Hilbert-Huang transform (HHT) have been reported to effectively identify microbiologically influenced corrosion (MIC) [10] and corrosion inhibition [11]. The HHT was first introduced by Huang et al. [12] and is based on the extraction of characteristic scales, or intrinsic mode functions from the EN signal, using a procedure called empirical mode decomposition (EMD). After EMD, instantaneous frequencies are calculated from these intrinsic oscillation modes [12]. The differentiation of those instantaneous frequencies in time allows the analysis of nonlinear and non-stationary EN signals. To a certain degree, it combines advantages of analysis procedures operating in the frequency- as well as in the time domain. A different approach is to describe the original EN signal using a linear combination of oscillations of a limited time span, called wavelets. By scaling and translation of these wavelets, these allow analysis of the signal at different timescales. The energy of each timescale can be plotted in an energy distribution plot (EDP), where the dominant process is associated with the timescale with the highest relative energy [5,7]. Aballe et al. [7] were the first to compare (discrete) wavelet transform (DWT) with FFT from the perspective of their ability to identify different corrosion mechanisms. The PSD was found to indicate the dominant timescale in the EN signal, corresponding with observations from the EDP. However, it appeared that the PSD could hardly discriminate between features in the EN signal related to processes occurring in different timescales, whereas the DWT could. The PSD is however closely related to the EDP determined by DWT [13]. Combined with the apparently superior frequency resolution as provided by continuous wavelet transform (CWT) with respect to DWT [13], it is interesting to investigate whether information obtained by CWT can be confirmed by FFT. This is therefore one of the primary objectives of the present work, together with the comparison between the use of CWT- and Hilbert spectra for the analysis of EN signals.

In this work, the combination of transient shape analysis, investigation of the PSD and time-frequency spectra obtained from CWT and HHT is investigated. Localized corrosion processes involving AISI304, carbon steel and AA2024-T3, which were already analysed in detail by introducing transient analysis through Hilbert spectra in earlier work [10,11,14], serve as case studies.

2. Experimental

All EN measurements involved a classical, open circuit configuration with two working electrodes and a reference electrode. The experimental details are identical to the ones described earlier for AISI304 [9], AA2024-T3 [11] and MIC [10].

The AISI304 and AA2024-T3 working electrode surfaces were pre-treated through wet grinding with up to 4000-grit SiC paper and rinsing with demineralized water. Subsequently, the working electrodes were kept in a dry environment at 20 °C for 1 day and analysed for imperfections prior to exposure. Each working electrode covered an area of 0.05 cm^2 and was either exposed to an aqueous 10^{-4} M HCl (AISI304) or 10^{-1} M NaCl (AA2024-T3) electrolyte. The electrolytes were produced from reagent of analytical quality, dissolved in demineralized water. The experiments were carried out under aerated conditions. A Red Rod REF201 reference electrode (Ag/AgCl/sat. KCl: 0.207 V vs. SHE), from Radiometer Analytical, served as reference electrode.

The MIC experiments involved working electrodes that were made from carbon steel, with working electrode areas of 19,6 mm^2 each. Here, a platinum mesh with an area of approximately 100 mm^2 served as reference electrode. A Postgate C solution [15] with additionally 2,5 wt.% NaCl, produced from reagent of analytical quality that was dissolved in demineralized water, was used both as electrolyte and as medium for the bacteria.

A Faradaic cage protected the measurement setup from electromagnetic distortions. The atmospheric temperature of the surrounding area was regulated at 20 °C. After each experiment, the working electrodes were analysed using an optical microscope (Reichert MEF4 M) with a maximum magnification of 1000x. Each experiment was repeated at least two times.

The ECN and EPN signals were measured using an Ivium Technologies Compactstat potentiostat. For the experiments on AISI304 a sampling rate of 5 Hz was selected and for the measurements on AA2024-T3 and MIC 20 Hz was used, all of which included the application of a low-pass filter of 10 Hz.

The CWT was computed with an analytic Morlet wavelet using the cwtft function in Matlab, which uses the discrete Fourier transform algorithm [16]. Whatever the algorithm used, a key decision when computing the CWT is the way in which the signal is extended at the beginning and at the end of the time record (known as 'padding'). This is necessary because the wavelet must overlap the ends of the time record by half its duration when computing the first and last points of the spectrum. Various padding methods can be used (see [17] for the methods available in Matlab) and the method chosen has a significant effect on the artefacts produced at the beginning and at the end of the spectrum. For this work symmetric padding was found to provide the best results. 32 Voices per octave (i.e. 32 logarithmically spaced frequencies were computed for each factor of two frequency range) were used to calculate the CWT. The Hilbert–Huang transform was calculated by the application of a Matlab program developed by Rilling et al. [18]. The analysis of transients was executed analogously to the procedure as described in [11,14]. In order to be able to calculate a reliable PSD, the DC drift of each EN signal was first identified through discrete wavelet transform and subsequently removed from the signal before application of the FFT. Further details on this trend removal procedure were published earlier in [19].

3. Results and discussion

This section starts with the analysis of single transients. Subsequently EN signals containing transients that occur over different timescales and that in some cases appear overlapped, are treated. Finally, a corrosion process that gradually changes over time is discussed.

3.1. Single transient analysis

EN signals consisting of only one transient are perhaps the most straightforward to investigate. Both transient shape and frequency characteristics are relatively easy to analyse. In the absence of multiple (different) transients which all contribute to the overall frequency spectrum, it is expected that the overall frequency characteristics visible in the PSD are similar to those determined by the HHT and CWT.

Fig. 1 shows the ECN and EPN time signal of AISI304 exposed in a 10^{-4} M HCl solution for a duration of 1000 s. Figs. 2 and 3 show the CWT- and Hilbert spectra, respectively.

One transient occurred, at approximately t = 800 s. The shape of a transient is related to local kinetics of the associated corrosion process. In the case of pitting corrosion, the characteristics of EN transients directly reflect processes occurring in the associated pits [20]. Identification of an individual transient is facilitated in cases where only one transient is present in the EN signal, or otherwise when pits do not arise simultaneously and consequently their associated transients do not overlap. For the ECN and EPN