Electrochemical Noise

A Clear Corrosion Signature

Ph.D. thesis

Axel Homborg
Cover photo: Corroded steel surface together with an electrochemical current and potential noise signal generated by metastable pitting of stainless steel

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Introduction
Chapter 1

1.1 Background

Corrosion is essentially the chemical reaction between a metal or metal alloy and its environment, where the metal returns to its condition in a chemical compound (i.e. the mineral) from which it was previously extracted [1]. In this work a corrosion process is considered as an electrochemical process consisting of both an oxidation and a reduction reaction. It occurs at the metal-solution interface where charge transfer takes place in which the metal is oxidized (anodic reaction) and species from the solution are reduced (cathodic reaction) [1, 2]. The amount of energy released by a corrosion reaction is identical to the amount that was required to extract the metal from its initial chemical state [1]. Corrosion is a complex phenomenon that cannot be captured by rate equations with simple constants. It is therefore more usual to indicate corrosion resistance by a simple scale, ranging from high to low [3]. The understanding and control of corrosion-related failure modes and their effects is generally poor [4]. Corrosion is indeed almost never reported as the major cause of accidents [1]. Therefore, however important the economic impact of corrosion might be, in certain cases underestimation of corrosion-related safety issues is probably even more important. This underestimation may come from the fact that the subject is generally considered to be quite complex [4]. Corrosion affects the structural integrity of structural systems such as ships, offshore platforms or bridges. Insight in their longer-term structural integrity therefore requires proper assessment of the (localized) corrosion processes that may occur [5].

1.2 Electrochemical monitoring

Whereas general corrosion attack can be predicted satisfactory under certain conditions, localized corrosion processes like pitting are typically very unpredictable and also hard to detect. Therefore, a clear need to monitor corrosion under real conditions emerges. Condition monitoring will aid to reduce uncertainty, improve service life [6] and, if applied using sensors providing an early corrosion indication, obviously reduce maintenance costs. Throughout the years, a large number of corrosion monitoring and evaluation methods has been developed, most of them based on electrochemistry [1, 7]. A division can be made between electrochemical methods that are potentially suitable for the characterization of localized corrosion and those that are not [8]. An example of the latter is the linear
polarization resistance method, 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) [1]. 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 [1, 2, 9, 10].

The ability to spatially resolve localized corrosion processes by electrochemical methods has found many useful applications. The use of scanning electrochemical techniques for this purpose has increased over the last 20 years [11]. For these techniques localized corrosion processes are represented as point sources. The anodic and cathodic processes take place at separate sites, generating small variations in potential that induce 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 [11]. 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) [7, 11-13]. 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 localized areas under strictly controlled experimental conditions, they might not be able to capture all details of a corrosion process involving different spatially separated reactions that occur simultaneously [14]. In addition, fixed electrode techniques are potentially 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 measuring system. A potentially interesting technique, that can provide time-resolved information about localized corrosion processes using fixed electrodes, is the method based on electrochemical noise measurements (ENM).

1.3 Electrochemical noise

The charge transfer that is involved in the oxidation of metal and reduction of species from the solution generates spontaneous fluctuations in electric current and potential. These fluctuations are detected by ENM and defined as electrochemical noise (EN). The analysis of these spontaneously occurring current and potential signatures is used in the study of
corrosion processes. Under open-circuit conditions, these provide information on the kinetics of reactions occurring at the electrochemical interface [15-17]. Throughout several decades, it has been the conviction of many researchers that spontaneous fluctuations in the electrochemical current noise (ECN) and electrochemical potential noise (EPN) contain valuable information about the underlying corrosion processes. ENM date back to the 1960s, when a relation between frequency and amplitude of the EPN signal on the one hand and the type of corrosion process of the corroding metals on the other, was noticed [18, 19]. Gradually, the focus changed from the detection of general corrosion to that of localized corrosion processes. One of the most interesting applications of ENM is the ability to identify and quantify localized corrosion processes [15, 16]. This ability largely depends on the applied signal processing technique, which is therefore the primary focus of this thesis.

Although the practical implementation of the ENM described in this work varies depending on the specific objective that is addressed, all measurements involve a conventional three-electrode configuration under open-circuit conditions. This requires two nominally identical working electrodes (both made from the material of interest) and a third electrode, which is the reference electrode with a known potential, all immersed in a conductive electrolyte. The ECN signal is measured through a zero resistance ammeter (ZRA), which connects the two working electrodes. The EPN signal is measured between the two working electrodes and the reference electrode by a potentiometer (E). Both signals are measured simultaneously and care is taken to ensure proper electromagnetic shielding. In Figure 1 this measurement setup is schematically depicted.

Figure 1 Layout of the electrochemical cell
1.4 Research objectives and outline

The objectives of this Ph.D. research are divided into a scientific and an industrial objective. The scientific objective is to determine the relation between EN and different corrosion processes. The obtained knowledge should encourage and enable practical application of ENM in corrosion prediction and monitoring, which is the industrial objective. The following research questions were addressed:

1. How does EN allow differentiation between general and localized corrosion processes?
2. To what extent can corrosion processes be identified using EN?
3. To what extent can degradation and delamination of a coating, prior to the occurrence of corrosion processes, be identified using EN?
4. To what extent are ENM complementary with EIS?
5. What are the possibilities and requirements to develop a corrosion sensor that enables (continuous in situ) corrosion measurements using EN?

The work performed to achieve the scientific objective is presented in chapters 2 to 7, whereas the industrial objective is addressed in chapter 8. Figure 2 shows a topological breakdown of this thesis.

As a starting point, chapter 2 is a critical appraisal of data analysis of EN, with an emphasis on the effectiveness of time-frequency techniques for the analysis of EN signals. In general, data analysis techniques used for the interpretation of EN signals can be divided based on their operating domain: they either operate in the time, frequency or time-frequency domain. Data analysis techniques operating essentially in the time or frequency domain have potential drawbacks that will be discussed in chapter 2. These drawbacks can largely be overcome by the time-frequency techniques, in particular the Hilbert-Huang transform (HHT). The use of this procedure for the interpretation of EN is therefore studied in chapters 3 to 7.

An important first step in the analysis of EN signals, regardless of the applied data analysis procedure, is to define and remove their direct current (DC) drift component. After this, the resultant signals can be regarded as representative for the corrosion processes under study.
Any subsequent data analysis procedure should be applied to this part of the data, or be able to discriminate between DC drift and ‘useful’ EN signal content on its own. This topic is discussed in chapter 3.

Chapter 4 introduces the Hilbert spectrum, calculated through the HHT, for the analysis of EN signals under open-circuit conditions in corrosion studies. The Hilbert spectrum provides an accurate fingerprinting capability that enables improved exploitation of the potential of ENM to identify and distinguish between different corrosion characteristics, while maintaining the unique non-disturbing nature of this technique.

Chapter 5 discusses a further optimisation of the use of Hilbert spectra for the analysis of EN. Here the identification and analysis of transients present in EN signals, generated by localized corrosion processes on stainless steel in this case, through Hilbert spectra is introduced.

The procedure of transient analysis is further developed in chapter 6, which shows the application of transient analysis through Hilbert spectra to investigate Ce-based corrosion inhibition of aluminium alloy AA2024-T3.
One of the most harmful corrosion phenomena, particularly in a maritime environment, is microbiologically influenced corrosion (MIC). Chapter 7 addresses the detection and identification of localized corrosion generated by MIC using transient analysis through Hilbert spectra of EN.

In chapter 8 the industrial objective of this research is the main focus. Here, practical applications, advantages and possible limitations of EN-based corrosion monitoring are discussed.

Finally, chapter 9 draws general conclusions from the work described in this thesis and provides answers to the research questions.
Chapter 1

1.5 References

A critical appraisal of the interpretation of electrochemical noise for corrosion studies

Abstract

In this chapter procedures and parameters that enable identification of, or discrimination between, general and localized corrosion processes through electrochemical noise are critically discussed. Their relevant similarities, differences and interdependences are indicated. In addition, the relation between different procedures and parameters with the underlying physico-chemical processes is indicated. Consistent and reliable information can be obtained from electrochemical noise data when a data analysis procedure is selected that on the one hand has a high discrimination ability and on the other hand yields a descriptive parameter that is directly associated to the underlying physico-chemical process. Procedures that meet these two requirements appear to be the Hilbert-Huang transform (Hilbert spectrum), wavelet transform (energy distribution plot) and the analysis of charge and frequency of corrosion events. In addition to the procedures that meet these two requirements, some of the descriptive parameters can be determined by different analysis procedures, which increases their reliability.

This chapter is based on:

2.1 Introduction

Corrosion processes involve charge transfer reactions that generate spontaneous fluctuations in current and potential. These fluctuations are defined as electrochemical noise (EN) and can be detected by electrochemical noise measurements (ENM). Under open-circuit conditions, these provide information on the kinetics of reactions occurring at the electrochemical interface [1-3]. Although practical considerations such as electrode area (ratio) or sampling rate are evident for correct interpretation of EN [4, 5], this work primarily considers the subsequent data analysis procedure.

The origin of ENM dates back to the 1960s, when a relation was noticed between frequency and amplitude of the electrochemical potential noise (EPN) signal on the one hand and the type of corrosion process of the corroding metals on the other hand [6, 7]. Gradually, the focus of EN research changed from the detection of general corrosion to that of localized corrosion processes. For example, Hladky et al. [8, 9] reported characteristic fluctuations in the EPN, generated by the occurrence of localized corrosion. In 1986, Eden et al. [2] reported on simultaneous monitoring of EPN and electrochemical current noise (ECN).

Fluctuations in the EN signal with a specific shape and finite duration are usually denoted as transients. Transients in the ECN signal are reported to occur simultaneously with transients in the EPN signal, indicating the occurrence of localized corrosion [10, 11]. Transients leave a specific signature, or ‘fingerprint’ in their frequency contribution. This can provide information on the nature of the related corrosion process, which is especially used by data analysis procedures operating in the time-frequency domain. The most interesting application of ENM is the ability to characterize (localized) corrosion processes, which is an important task in corrosion monitoring [3, 12-20], based on these characteristic transient features.

The present chapter critically discusses the most important data analysis methods for ENM that have been published over the last decades. The similarities, differences and interdependences between the methods are indicated and relations with the underlying physico-chemical processes are discussed.

In this work, data analysis procedures available in literature are classified based on their operating domain: time, frequency or time-frequency. Data analysis techniques operating essentially in the time domain intend to investigate specific characteristics of an EN signal, in
A critical appraisal of the interpretation of electrochemical noise for corrosion studies

order to obtain information about the corrosion process. In general, however, these data analysis procedures only provide a limited amount of information about the system under study. Moreover, many of the procedures are based on statistics, which implies a rather indirect relation with the underlying physico-chemical processes.

Calculation of the power spectral density (PSD) of a corrosion process can be performed by data analysis in the frequency domain. However, corrosion processes, as these are electrochemical in nature, are typically non-stationary and nonlinear [21]. To transform an EN signal into a stationary signal, its direct current (DC) drift component needs to be removed by a separate procedure, prior to the data analysis [1, 22-25]. This is an important first step, which is not only required for spectral analysis, but should also be considered for data analysis techniques operating in the time domain. In the present work, trend removal will therefore also be discussed.

The identification of localized corrosion processes demands the ability to distinguish between different corrosion characteristics without the precondition of stationarity or linearity. This can be achieved by applying time-frequency data analysis techniques. In particular, the Hilbert-Huang transform (HHT) can provide frequency characteristics of the physico-chemical processes while still maintaining time-resolved information (i.e. analyze in both time and frequency simultaneously). Importantly, this information is obtained without the need for subjective a-priori limitations or assumptions concerning the nature of the process under investigation.

In order to illustrate the differences between data analysis in the frequency or time-frequency domain, examples using three distinct, well-known corrosion processes are provided. The experimental details are given in section 2.2 and the results will be used throughout the chapter. These serve as comparison between fast Fourier transform (FFT) as the most widely used data analysis procedure and the two most promising procedures, HHT and discrete wavelet transform (DWT). Section 2.3 provides an overview and orders different methods and parameters in terms of their potential to identify localized corrosion. In addition, another overview classifies all methods and parameters or plots in which these are visualized based on their relation with the underlying physico-chemical processes. Section 2.4 then addresses the issue to reliably define a DC drift component. In subsequent sections the added value of each of the methods regarding the detection and identification of localized corrosion processes through EN is critically discussed. Also the relevant complementarities of the methods are considered.
Chapter 2

The major contributions of the present work are (i) the overview providing relations between all methods and corrosion process parameters operating in each of the three domains: time, frequency or time-frequency, and (ii) the overview that classifies all methods and parameters or plots based on their relation with the underlying physico-chemical processes.

2.2 Illustrative examples - experimental details

This section describes three distinct corrosion processes that will be used throughout this work as examples to indicate the difference between data analysis in the frequency or time-frequency domain. The experimental details and raw EN signals, together with visual observations through micrographs of the working electrode surfaces, will be briefly described.

The measurements were performed in a conventional three-electrode configuration under open-circuit conditions, requiring two nominally identical working electrodes. The measurement setup and electrochemical cell configuration are described in more detail in chapter 4 [26]. Three commonly used materials were tested: mild steel, stainless steel (AISI304) and an aluminium alloy (AA2024-T3).

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 0.95 cm\(^2\) (mild steel) or 0.05 cm\(^2\) (AA2024-T3 and AISI304) 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 either stored under ambient conditions at 20 °C for 24 h (AA2024-T3 and AISI304) or immediately exposed. The reference electrode used was a Radiometer analytical Red Rod type REF201 (Ag/AgCl/sat. KCl: 207 mV vs. Standard Hydrogen Electrode). The electrolytes used were aqueous NaCl solutions made from demineralized water and analytical grade reagent. The NaCl concentration was 3 wt.% (mild steel and AISI304) or 0.1 M (AA2024-T3). All solutions were open to air. The electrochemical cells were placed in a Faradaic cage to avoid electromagnetic disturbance from external sources. The ambient temperature during the measurements was controlled at 20 °C. The samples were microscopically inspected afterwards using a Reichert MEF4 M 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 (ZRA) and potentiometer, controlled by a Windows-based PC running dedicated software. The sampling frequencies used for these measurements are: 5 Hz (mild steel and AISI304) or 20 Hz (AA2024-T3). A low-pass filter of 10 Hz was applied during data recording.

The data were processed using Matlab from MathWorks. The empirical mode decomposition (EMD) and the HHT were calculated using a publicly available Matlab procedure from Rilling et al. [27, 28].

Figures 1-3 show the ECN (Figures 1a, 2a and 3a) and EPN (Figures 1b, 2b and 3b) signals for a period of 1000 s for the measurements on mild steel, AA2024-T3 and AISI304, respectively, starting immediately after exposure.

In Figure 1 no transients are visible, resulting in smooth ECN and EPN signals. Figure 2 indicates the presence of many superimposed transients that are difficult to distinguish visually, whereas the EN signals of Figure 3 only show three transients, with maximum magnitudes of over a decade smaller than the transients in Figure 2.

Figure 1 (a) ECN and (b) EPN signal of mild steel exposed to an aqueous 3 wt.% NaCl solution, starting immediately after exposure
Figure 2 (a) ECN and (b) EPN signal of AA2024-T3 exposed to an aqueous 0.1 M NaCl solution after passivation in ambient air for 24 hours, starting immediately after exposure.

Figure 3 (a) ECN and (b) EPN signal of AISI304 exposed to an aqueous 3 wt.% NaCl solution after passivation in ambient air for 24 hours, starting immediately after exposure.
Figure 4 shows typical micrographs of the working electrode surfaces after 3600 s (mild steel), 14500 s (AA2024-T3) and 1100 s (AISI304).

![Micrographs](image)

Figure 4 Example micrographs of (a) mild steel exposed to an aqueous 3 wt.% NaCl solution for 3600 s, (b) AA2024-T3 exposed to an aqueous 0.1 M NaCl solution for 14500 s after passivation in ambient air for 24 hours and (c) AISI304 exposed to an aqueous 3 wt.% NaCl solution for 1100 s after passivation in ambient air for 24 hours.

These micrographs range from a working electrode surface under general corrosion attack (dominant (oxygen) diffusion-controlled process [29], Figure 4a) to a smooth surface exhibiting only a small number of small pits due to the stable oxide film at the surface of AISI304 (a corrosion process primarily under activation control, Figure 4c) [30]. Figure 4b also indicates the presence of localized corrosion, however more severe than in Figure 4c. The observed surface features involve a combination of pitting corrosion near the intermetallic particles and corrosion attack of the aluminium matrix [31]. This corrosion process is under mixed control.

### 2.3 Overview and ordering of data analysis procedures and parameters

Figure 5 provides a concise overview of the data analysis procedures and parameters used for the analysis of EN, along with their similarities. Procedures and parameters are ordered with respect to their ability to distinguish between individual localized corrosion processes. Clusters shown at the left are based on their operation in the time, frequency or time-frequency domain. Similarities between different procedures are indicated in the figure by Roman numerals and discussed more elaborately below. The figure serves as a basis for
the discussion of these data analysis procedures in the respective sections. The terms printed in bold font in Figure 5 will be the topics that are discussed in these sections, while the terms printed in normal font are the associated parameters and those in italic font the plots in which these are visualized.

<table>
<thead>
<tr>
<th>Time-frequency</th>
<th>Frequency</th>
<th>Good Identification ability</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Hilbert-Huang transform</strong></td>
<td><strong>Discrete wavelet transform</strong></td>
<td><strong>Windowed Fourier transform</strong></td>
</tr>
<tr>
<td>Hilbert spectrum$^\text{VI}$</td>
<td>Energy distribution plot</td>
<td></td>
</tr>
<tr>
<td>Instantaneous frequencies</td>
<td>Characteristic timescales</td>
<td></td>
</tr>
<tr>
<td><strong>Fast Fourier transform</strong></td>
<td><strong>Cross correlation</strong>$^\text{V,III}$</td>
<td></td>
</tr>
<tr>
<td>Power spectral density plot</td>
<td>Autocorrelation$^\text{VI,I}$</td>
<td></td>
</tr>
<tr>
<td>Low-frequency level</td>
<td>Hurst exponent$^\text{III,I}$</td>
<td></td>
</tr>
<tr>
<td>Overall PSD$^\text{II}$</td>
<td>Cut-off frequency</td>
<td></td>
</tr>
<tr>
<td>Cut-off frequency</td>
<td>PSD exponent$^\text{I}$</td>
<td></td>
</tr>
<tr>
<td>Charge and frequency of corrosion events$^\text{V,IV}$</td>
<td>Cumulative probability of events$^\text{IV}$</td>
<td></td>
</tr>
<tr>
<td>Weibull probability plot$^\text{IV}$</td>
<td>Conditional event generation rate$^\text{IV}$</td>
<td></td>
</tr>
<tr>
<td>Visual characterization$^\text{VI,V}$</td>
<td>Statistical characteristics</td>
<td></td>
</tr>
<tr>
<td>Kurtosis$^\text{III}$</td>
<td>Skewness$^\text{V,III}$</td>
<td></td>
</tr>
<tr>
<td>Coefficient of variation of current</td>
<td>Localization index</td>
<td></td>
</tr>
</tbody>
</table>

Figure 5 Relevant data analysis procedures and parameters along with their similarities (Roman numerals), ordered according to their ability to distinguish between localized corrosion processes.
The following relations between different procedures and parameters are useful:

I. The PSD exponent $\beta$ of the EN signal provides a way to determine the validity of the data. This parameter is not only obtained directly from the slope of the PSD plot, but in addition it can be calculated by, or derived from, parameters obtained from several other methods. These operate either in the time, frequency or time-frequency domain. Such a ‘multiple method approach’ allows a comparison between the respective data analysis procedures and enhances the reliability of this parameter. The different data analysis procedures related to $\beta$ are:

- Slope of the PSD plot (as discussed in section 2.6)
- Autocorrelation (section 2.7.2)
- Hurst coefficient (section 2.7.2)
- Wavelet variance (section 2.5.2)

II. Windowed Fourier transform entails the successive calculation of the PSD for a series of segments in the EN signal. The overall PSD is an indication of the noise intensity, corresponding to the intensity of either the corrosion processes of the segment under investigation or of the total EN signal.

III. Skewness and Kurtosis provide information about the symmetry and shape of a distribution, respectively. These properties can also be related to the Hurst exponent $H$. Skewness is also related to the cross correlation between the ECN and EPN signal, since it provides information about their unidirectional nature.

IV. The charge $q$ involved in individual transients and frequency of corrosion events $f_n$ allow discrimination between localized or general corrosion processes. The plot of the cumulative probability of a parameter (e.g. $f_n$) can provide mechanistic information by indicating the ability of this parameter to discriminate between different corrosion characteristics.

In a similar way, a Weibull probability (of events) plot can be used to discriminate between different dominant stochastic processes (e.g. general corrosion, pitting corrosion or evolution of hydrogen bubbles). Additionally, the conditional event generation rate $r(t)$ is the susceptibility of a corroding system to the generation of certain events (e.g. corrosion pits), which is also described by a Weibull distribution.
The overall increase or decrease of \( r(t) \) can be compared with the average charge \( q \) in each event in order to draw reliable conclusions from this parameter regarding the (change in) nature of the corrosion process.

V. The symmetry between the two working electrodes and the nature and location of a physico-chemical process determine the cross correlation between the ECN and EPN signal, as well as the skewness of the ECN signal. This can be verified by visual characterization.

The cross correlation can be quantified by the cross correlation function. The Fourier transform of the cross correlation function results in the cross spectrum and the low-frequency limit of the cross spectral density is related to the charge involved in the transients, indicating the occurrence of localized corrosion.

VI. The identification of transients can be performed with the Hilbert spectrum. This allows characterization of transients, based on their contribution in instantaneous frequencies.

Additionally, the detection of transients can involve investigation of the autocorrelation of an EN signal, where some parts of the signal show stronger autocorrelation than other parts. In some cases, visual characterization of the EN time signals provides verification of the autocorrelation.

Combining several methods may considerably enhance the potential of EN for characterizing corrosion processes. Otherwise, in order to obtain reliable information about the corrosion process from an EN signal, a data analysis procedure must be able to discriminate between general and localized corrosion processes on its own. This can be achieved when a reasonably direct relation between the data analysis procedure and the underlying physico-chemical processes exists. Figure 6 schematically shows this relation for the various procedures and parameters or plots in which these are visualized.

Four parameters or plots have a direct relation with the underlying physico-chemical processes: Hilbert spectrum (instantaneous frequencies), energy distribution plot (EDP, characteristic timescales), PSD plot (PSD) and charge/frequency of corrosion events. These parameters or plots are based on properties of the corrosion processes that can be directly obtained from the EN signals, which allows them to discriminate between general and localized corrosion individually.
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Figure 6 Relation of parameters and data analysis procedures with the underlying physico-chemical processes

The fourth parameter, the charge and frequency of corrosion events, is generally applied for determination of a cumulative probability of events, Weibull probability plot or conditional event generation rate (as discussed in section 2.7.3). Other parameters with an even less direct relation to the process are rather based on characteristics of the EN data values, like cross correlation (section 2.7.1), autocorrelation (section 2.7.2), Hurst exponent (section 2.7.2), visual characterization (section 2.7.4) and statistical characteristics of the data (section 2.7.5).
Chapter 2

2.4 Trend removal

An important aspect considering data analysis of EN is the removal of the DC drift component [24]. Many natural processes are non-stationary and nonlinear. A non-stationary process can generate a DC drift component since its statistical parameters change over time. DC drift can also arise when the measuring time is too short for the lowest frequency components to fit the time frame. In that case a stationary process can appear as being non-stationary [24, 32]. In addition, there can be some slow alteration of the system under study during the measurement. This is the case when asymmetry occurs between working electrodes. This effect has for example been found in ECN from ENM on mild steel working electrodes [33, 34]. In this case, asymmetry between working electrodes also results in a skewed signal distribution (see section 2.7.5). A measure to determine the asymmetry between the working electrodes has been proposed by Curioni et al. [35], who propose an ENM setup without the use of a ZRA. In the presence of a protective coating, the magnitude of the DC component of the EPN represents the shielding of the substrate from the electrolyte: if the DC component is close to the corrosion potential of the substrate material, the barrier properties are poor, while higher values indicate better barrier properties.

Ideally, spontaneous fluctuations in current and potential induced by a corrosion process are considered non-stationary. Any DC drift in the signal will create new, false frequency components. It is necessary to apply some procedure to the incoming signal to eliminate the contribution of the drift. If not, this drift rather than the superimposed fluctuations dominates the data analysis.

The choice of which trend removal procedure to apply is probably one of the most difficult problems in ENM. The procedure must eliminate the low-frequency components without removing useful information or creating false frequency components. Often the linear trend removal procedure is used. There are, however, also other ways to remove DC drift, like moving average removal, polynomial fitting, high-pass filtering, wavelet transform or EMD [1, 22-24, 36]. Linear trend removal has been found to show satisfactory results in case the DC drift is approximately uniform [24, 37]. However, if this is not the case it is impossible for this technique to effectively remove the drift, which may result in large deviations between individual and nominally identical measurements.

Removal of the DC drift component gives rise to the risk of eliminating useful information [1]. In the case of the selected order of polynomial trend removal or the span of moving average
trend removal, their user-defined nature makes the compromise between eliminating useful information and leaving behind part of the DC drift quite complex. For example, an increased order of the polynomial results in more trend removal, but it is likely that this is combined with an increased loss of valuable data. Moving average trend removal has already been shown to be not appropriate for drift removal [24].

Time-frequency methods like wavelet transform and EMD both allow an investigation of amplitude and frequency as functions of time. In chapter 3, it will be shown that both analysis procedures are effective in eliminating only the drift component, without affecting useful information present in the data [36]. Furthermore, wavelet transform has also been reported to provide an effective reconstruction of the original ECN and EPN signal, prior to calculation of the (spectral) noise resistance [23]. A concise description of wavelet transform is presented in section 2.5.2. EMD enables a decomposition of a non-stationary signal representing a nonlinear process into its intrinsic modes of oscillation. The residue after this decomposition is an indication of the DC component or DC drift of the signal [32, 38]. EMD is further discussed in section 2.5.1.

The intrinsic ability of these two time-frequency techniques to define a reliable DC drift component of the EN signal is an advantage compared to other data analysis procedures. This implies that wavelet transform and HHT (which is based on EMD) do not rely on a separate technique to remove the DC drift component in advance.

### 2.5 Time-frequency domain

#### 2.5.1 Hilbert-Huang transform

The HHT was first proposed by Huang et al. [32] and is based on the assumption that any nonlinear and non-stationary signal consists of multiple characteristic scales, or intrinsic modes of oscillation, each superimposed on another. These so-called intrinsic mode functions (IMFs) are based on the local properties of the signal and can be identified empirically by their characteristic time scales through the EMD. This principle is (sometimes in a modified form) already applied in other fields of signal processing [39-43].

Unlike the wavelet transform, where the data is expanded into wavelet crystals on a basis of a pre-defined wavelet and using function orthogonality, the basis of the EMD is derived directly from the data itself, making it a flexible and adaptive procedure [32, 38, 41, 44-46].
Therefore, the information is obtained without the need for subjective a-priori limitations or assumptions concerning the nature of the process under investigation. Characteristic for each IMF is that the number of extreme values and the number of zero-crossings is equal or that the difference does not exceed the value of 1, and that the IMF is symmetric with respect to its local mean [32]. The latter ensures unbiased phase information and therefore well-defined instantaneous frequencies [32]. IMFs 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 [47]. The residue after EMD represents the DC drift component [32, 38, 41, 44].

In order to extract all instantaneous frequencies that describe the intrinsic modes of oscillation at a specific instant of time, the Hilbert transform is applied to each IMF. This results in a decomposition of the original EN signal into instantaneous frequencies and variable amplitudes, which allow the analysis of non-stationary data [21, 32, 47]. These instantaneous frequencies and variable amplitudes can be displayed in a Hilbert spectrum $H(\omega, t)$, where the amplitudes are displayed for all instantaneous frequencies at any moment in time.

In order to indicate the ability of Hilbert spectra to discriminate between different corrosion characteristics, three different corrosion processes serve as examples.

Figures 7, 8 and 9 show example Hilbert spectra of the ECN (Figures 7a, 8a and 9a) and EPN (Figures 7b, 8b and 9b) signals shown in Figures 1-3. The relative amplitudes of each original EN signal are also displayed at the back of each Hilbert spectrum. Note that the different sampling frequencies $f_s$ used for these measurements result in differences in frequency range of the Hilbert spectra (which have an upper frequency limit of $f_s/5$).

The Hilbert spectra allow identification of individual corrosion events on the time scale, but also provide information on the frequency characteristics of these events. For the ECN signals, the Hilbert spectra presented here show a shift from dominant low instantaneous frequencies, below $10^{-2}$ Hz, in Figure 7a towards dominant higher instantaneous frequencies, around $10^{1}$ Hz, in Figure 9a. The large relative magnitudes of low instantaneous frequencies in Figure 8a are indicative for the ECN signal being under mixed control.
Figure 7 Hilbert spectra of the (a) ECN and (b) EPN signal of mild steel exposed to an aqueous 3 wt.% NaCl solution, starting immediately after exposure
Figure 8 Hilbert spectra of the (a) ECN and (b) EPN signal of AA2024-T3 exposed to an aqueous 0.1 M NaCl solution after passivation in ambient air for 24 hours, starting immediately after exposure.
Figure 9 Hilbert spectra of the (a) ECN and (b) EPN signal of AISI304 exposed to an aqueous 3 wt.% NaCl solution after passivation in ambient air for 24 hours, starting immediately after exposure.

Analogous with the observations from Figure 4, these observations correspond with a shift from dominant large timescale processes towards relatively short timescale processes.
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during the measurements. The application of EMD and HHT for the analysis of EN is explained in more detail in chapter 4 [26].
The decomposition in instantaneous frequencies visible in a Hilbert spectrum is comparable to the relative energy contribution of different time scales calculated through the DWT. DWT will be discussed in the next subsection. An important difference is that time-resolved information is preserved in Hilbert spectra (i.e. variations in instantaneous frequency information in time are visualized), while this is not the case in DWT.
Hilbert spectra also allow investigation of only the instantaneous frequency information present in the transients in the EN signal. This is described in detail by the authors in chapter 5 and 6 [30, 31]. This information can be visualized in a two-dimensional plot, which can e.g. be compared with the EDP from DWT [30]. This additional ability of transient analysis through Hilbert spectra yields increased discrimination ability between different corrosion characteristics as compared to DWT [30]. As an example, the two-dimensional representations of the Hilbert spectra from Figures 7, 8 and 9 are shown in Figures 10 and 11.
These two-dimensional representations confirm the characteristic distributions in instantaneous frequencies for the different corrosion processes, as discussed regarding the Hilbert spectra shown in Figures 7, 8 and 9. The differences between the instantaneous frequency characteristics of the two-dimensional Hilbert spectra of the EPN signals are less pronounced as compared to the differences between those of the ECN signals. This can e.g. originate from the slow process of discharge of the repassivated surface being reflected in the EPN signal of AISI304, resulting in considerable contribution of low instantaneous frequencies in the Hilbert spectrum [30]. Therefore, the Hilbert spectra of the ECN signals of the measurements described here allow improved differentiation between different corrosion characteristics as compared to those of the EPN signals.
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Figure 10 Two-dimensional representations of the Hilbert spectra of the ECN signals of (a) mild steel exposed to an aqueous 3 wt.% NaCl solution for 1000 s, (b) AA2024-T3 exposed to an aqueous 0.1 M NaCl solution for 1000 s after passivation in ambient air for 24 hours and (c) AISI304 exposed to an aqueous 3 wt.% NaCl solution for 1000 s after passivation in ambient air for 24 hours.
Figure 11 Two-dimensional representations of the Hilbert spectra of the EPN signals of (a) mild steel exposed to an aqueous 3 wt.% NaCl solution for 1000 s, (b) AA2024-T3 exposed to an aqueous 0.1 M NaCl solution for 1000 s after passivation in ambient air for 24 hours and (c) AISI304 exposed to an aqueous 3 wt.% NaCl solution for 1000 s after passivation in ambient air for 24 hours

2.5.2 Discrete wavelet transform

DWT describes the EN signal at several time scales or resolutions in so-called crystals. Different timescales of the ECN and EPN signal could be attributed to diffusion-, activation- or mixed controlled processes [11, 23, 29, 48-53]. Each crystal is therefore related to a feature of the signal of a particular time scale covering a specific frequency range [11, 16, 23, 29, 49, 50, 52, 54, 55]. An EDP visualizes the relative energy contributed by each crystal to the total EN signal [11, 23, 29, 49-52, 54, 55]. From such a plot, kinetic information about physico-chemical processes is obtained: the time scale with the maximum relative energy in the EDP corresponds to the dominant process in certain corrosion events and its change can reflect the behaviour of the dominant corrosion process [49, 50, 52, 54-57]. The number of time scales is user defined. It is experimentally determined [11, 29, 49-52, 54, 55] that for an 8-level decomposition sufficient information on corrosion characteristics is captured in
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detail crystals D1 to D8. The choice of 8 crystals (i.e. an 8-level decomposition) can therefore be considered suitable for investigating corrosion processes. In many cases the contribution of the smooth S8 crystal to the total energy is considerably high, a phenomenon that is mainly attributed to the DC drift in the original signal [11, 29, 49-52]. Table 1 provides an indication of the most essential information that DWT can provide in this respect.

Table 1 Indication of information that can be obtained from an EDP (based on [11, 23, 29, 49-52, 54, 55])

<table>
<thead>
<tr>
<th>Crystal</th>
<th>D1</th>
<th>D2---D3</th>
<th>D4---D6</th>
<th>D7---D8</th>
<th>S8</th>
</tr>
</thead>
<tbody>
<tr>
<td>Predominant</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>kinetics</td>
<td></td>
<td>Activation</td>
<td>Mixed</td>
<td>Diffusion</td>
<td>DC Drift</td>
</tr>
<tr>
<td>Corrosion</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>characteristics</td>
<td></td>
<td>Localized</td>
<td>General</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>corrosion</td>
<td>corrosion</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

As an example, Figures 12 and 13 show example EDPs of the ECN and EPN signals, respectively, from Figures 1-3.

In general, similar relative energy contributions would be expected here as compared to the shape of the two-dimensional representations of the Hilbert spectra in Figures 10 and 11. Indeed, the separation into timescales represents the same physico-chemical processes. However, DWT only takes into account the entire signal and does not differentiate in its spectra between individual transients (i.e. there is no time resolution). This possibility is provided by Hilbert spectra, as described by the authors in chapter 5 [30]. Therefore, the higher relative energy contribution of detail crystal D8 in Figure 13c could originate from an artefact resulting from the DWT, or else from the low frequency contribution in the corresponding EPN signal between \( t = 0 \) and \( t = 400 \) s, visible in the Hilbert spectrum of Figure 9b. Furthermore, analogous to the two-dimensional representations of the Hilbert spectra, the differences between the relative energy contributions of the EDPs of the EPN signals are less pronounced as compared to the differences between those of the ECN signals.
Calculation of the EDP can be an effective way to identify and discriminate between localized corrosion processes. However, the separation of frequency information into a number of scales potentially limits the ability to discriminate between small kinetic changes in the process. In addition, the user-defined number of scales necessary for the correct interpretation of information on corrosion characteristics present in EN signals is a drawback compared to the flexible and adaptive nature of the EMD as described in the previous section. Moreover, DWT does not provide time-resolved information, whereas Hilbert spectra allow momentary changes in instantaneous frequency composition of an EN signal to be detected.

The effectiveness of DWT to provide a reliable estimate of the DC drift present in EN signals through the smooth S8 crystal is reported by the authors in chapter 3 [36], as was also discussed in section 2.4.
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It is possible to determine the strength of autocorrelation (indicated by the power spectral exponent $\beta$) by means of DWT, through the wavelet variance $V_W$ [48]. Between $V_W$ and the scale of the wavelet $a$, a power-law relationship exists, with $H_W$ the wavelet variance exponent [25, 48]:

$$V_W \approx a^{H_W}$$  \hspace{1cm} (1)

In the range $-2.5 \leq \beta \leq 5$, $H_W$ is approximately equal to $\beta$. In this way $V_W$ allows determining the strength of autocorrelation [25, 48] and the value of $V_W$ can thus be applied for characterizing the corrosion process. The strength of autocorrelation can be determined by multiple different analysis procedures, as was indicated in Figure 5.

Figure 13 EDPs of the EPN signals of (a) mild steel exposed to an aqueous 3 wt.% NaCl solution for 1000 s, (b) AA2024-T3 exposed to an aqueous 0.1 M NaCl solution for 1000 s after passivation in ambient air for 24 hours and (c) AISI304 exposed to an aqueous 3 wt.% NaCl solution for 1000 s after passivation in ambient air for 24 hours.
2.5.3 Windowed Fourier transform

Windowed Fourier transform is a method that successively analyzes windows of the original EN signal, providing information about the time-dependent properties of each frequency component contributing to the signal. However, to increase detection probability of sudden transients in the signal, the segments should be made small, with a consequent loss of low frequency data [54]. Analogous, the analysis of low frequencies requires larger window lengths, resulting in lower resolution in time. Similar to the DWT, where the number of timescales is user-defined, here the user-defined nature of the choice of a proper segment size (detection probability vs. low frequency information) can be regarded as a considerable drawback.

2.6 Frequency domain

Spectral analysis using FFT is a well-known analysis technique for EN. The resulting power distribution of a signal in the frequency domain (or PSD, units of $A^2/\text{Hz}$ or $V^2/\text{Hz}$) is graphically represented by power as a function of frequency in the power spectrum. Many methods can be used to estimate a PSD, of which FFT is most common in the corrosion field [1]. In literature, some typical features of the PSD are suggested to provide information on corrosion processes. In Figure 14 the PSD from the EPN signal in Figure 3b, calculated through FFT after trend removal by EMD, is pictured with its characteristic features. The numbers in this figure correspond with the features discussed below.

The overall PSD (1), i.e. the intensity of the EN signal, corresponds with the intensity of the corrosion process [11, 52]. This parameter is related to the windowed Fourier transform, where the overall PSD is analyzed for successive segments of an EN signal. In some cases the PSD exhibits a more or less horizontal low frequency part where the PSD shows no variation with frequency (2). The level of this horizontal part typically allows discrimination between general and localized corrosion [58].

The frequency of the transition between the low frequency (constant PSD) and high frequency part (decreasing PSD) is called the cut-off or roll-off frequency (3) [49, 52, 54, 55, 59]. The value of this frequency can be an indicator of the occurrence of different types of corrosion processes [52, 55].
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Figure 14 Typical features of a PSD plot of an EPN signal of AISI304 exposed to an aqueous 3 wt.% NaCl solution for 1000 s, starting immediately after exposure: (1) overall PSD, (2) low frequency level, (3) cut-off frequency and (4) roll-off slope

Finally, the higher frequency part shows a certain slope where an exponential decay is assumed (4). This results in a straight roll-off slope on a log-log scale, which could be an indicator of the occurrence of specific corrosion processes. The magnitude of the roll-off slope is sometimes considered as a parameter to distinguish between general and localized corrosion [9, 11, 52, 54, 60], or to be related to the specific shape of ECN transients [61], which in turn is related to the corrosion characteristics. Finally, the slope can be described with the PSD exponent $\beta$, which is, for example, used to determine the autocorrelation strength of an EN signal. This parameter is discussed in the next section. Note that the possible relation between the roll-off slope and the prevalent corrosion process is controversial, since contradictory results in various different ENM are obtained. Several authors suggest that the relationship between the slope and the corrosion process is at least still under discussion [1, 10, 58, 62-65].

As an example, Figures 15 and 16 show example PSD plots of the ECN and EPN signals, respectively, from Figures 1-3. The user-defined aspect of investigation of PSD plots can be considered as its main issue. In particular for the PSD plots shown in Figures 15a and 15b and 16a and 16b, it is difficult to determine the presence and, if so, the level of the horizontal low frequency part. The same accounts for the cut-off frequency.
The roll-off slopes of the ECN PSD plots in Figure 15 do not provide a clear distinction between general (Figure 15a) and localized corrosion (Figure 15b and c), let alone between different localized processes. However, the roll-off slope of the PSD plot in Figure 16a is clearly less steep than those of the PSD plots in Figure 16b and c. It can therefore be argued that for these example processes, a distinction between general and localized corrosion can be made based on the roll-off slope of the EPN PSD plots. The slopes of the plots in Figure 16b and c are however similar, indicating that differentiation between different types of localized corrosion processes is not possible here.

It is interesting to note that the ECN signals do not differentiate between general and localized corrosion processes through their PSD plots, whereas from the perspective of the time-frequency techniques, the ECN signals do provide the ability to characterize corrosion processes. For the EPN signals on the contrary, the opposite is true.
Figure 16 PSD plots of the EPN signals of (a) mild steel exposed to an aqueous 3 wt.% NaCl solution for 1000 s, (b) AA2024-T3 exposed to an aqueous 0.1 M NaCl solution for 1000 s after passivation in ambient air for 24 hours and (c) AISI304 exposed to an aqueous 3 wt.% NaCl solution for 1000 s after passivation in ambient air for 24 hours

2.7 Time domain

2.7.1 Cross correlation

The correlation between the obtained ECN and EPN signal can vary over time. An EN signal can be either unidirectional (EPN and sometimes the ECN signal) or bidirectional (ECN signal), depending on the symmetry between the working electrodes and the nature and location of the physico-chemical processes. If only one working electrode exhibits pitting behaviour, the resulting ECN transients are expected to be unidirectional, which makes the cross correlation a valuable parameter [1, 66]. This phenomenon is also expected to become visible in the skewness of the ECN signal.
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The cross correlation can be calculated by the cross correlation function. The Fourier transform of the cross correlation function results in the cross spectrum and the low-frequency limit of the cross spectral density is related to the charge involved in the transients, which can be linked to the occurrence of localized corrosion. Note that if the sampling frequency is low compared to the frequency at which transients in the EN signals manifest, information about cross correlation can be lost [66].

The need to apply a reliable trend removal procedure is evident: any residual of the DC drift present in the EN signals can influence the calculated cross correlation. This dependence potentially weakens the cross correlation as a useful tool. Simply subtracting an estimated polynomial or moving average function from the EN signals, a procedure that is often used in this respect, may abolish or at least influence information about cross correlation.

2.7.2 Autocorrelation

After removal of any DC drift present in an EN signal, the resultant component has two main features: its statistical distribution and its autocorrelation $\beta$ (which is similar to the PSD exponent). The autocorrelation describes the correlations between values separated by varying distances (in time) within the EN signal and potentially varies from strong positive to negative and non-existent. $\beta = 1$ is the boundary value between weak and strong autocorrelation [25, 48]:

- $\beta > 1$ Strong positive autocorrelation
- $1 > \beta > 0$ Weak positive autocorrelation
- $\beta = 0$ Uncorrelated
- $\beta < 0$ Negative autocorrelation

Autocorrelation can provide information on corrosion characteristics: the value of $\beta$ is related to the occurrence of general corrosion, metastable pitting and passivity. For example, for a general corrosion process that is primarily under diffusion control, low frequencies are expected to be dominant and a smooth EN signal is expected (as visible in Figure 1). Adjacent values within such a signal are strongly correlated and a high value of $\beta$ is expected [48, 67]. A low value of $\beta$ results in a flatter (i.e. less frequency-dependent) PSD
function \( \Psi \), which can exhibit a power-law dependence on frequency in a certain part of the frequency domain [25]:

\[
\Psi(f) = \frac{1}{f^\beta}
\]  

(2)

Note that, as discussed in the previous section, the correlation between the slope of the PSD and the prevalent corrosion process is controversial. Indeed, the slope of the EPN PSD shown in Figure 16a is less steep than that of the EPN PSDs shown in Figure 16b and c. This would not be expected considering the smooth appearance of the original EPN signal shown in Figure 1b as compared to that of the EPN signals from the localized corrosion processes shown in Figures 2b and 3b.

The autocorrelation can be estimated by visual examination of the EN signal. This can be a valuable tool for detecting transients, where some parts of the signal show stronger autocorrelation than other parts. Further, the autocorrelation can be determined by spectral analysis and wavelet transform, as described in the previous sections. And finally, the autocorrelation can also be determined by the Hurst exponent \( H \). \( H \) is denoted as the ‘index of dependence’, and is the relative trend of an EN signal to either agglomerate in a specific direction, or to tend towards the mean. \( H \) can be determined by the rescaled-range (R/S) analysis. The rescaled range is calculated by dividing a range \( R_N \) of values in a subinterval \( \tau \) of an EN signal by their standard deviation \( S_N \) over the same subinterval [25]. For a large sample size \( N \) and \(-1 \leq \beta \leq 1\), the relationship between \( \beta \) and \( H \) is given as [25]:

\[
\beta = 2H - 1
\]  

(3)

Combined with the results obtained for \( \beta \), the following applies for the Hurst exponent with respect to an EN signal [25, 67]:

- \( 0.5 < H \leq 1 \) Weak positive autocorrelation (e.g. general corrosion)
- \( H = 0.5 \) Uncorrelated
- \( 0 \leq H < 0.5 \) Negative autocorrelation (e.g. pitting corrosion)
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Together with $\beta$, $H$ can thus be used to determine the autocorrelation between values in an EN signal. A general corrosion process is expected to exhibit positive autocorrelation with higher $\beta$ and $H$ values, whereas localized processes are typically associated with less correlation in the EN signal. Analogous to the calculation of the cross correlation, determination of the autocorrelation or the Hurst exponent requires initial removal of the DC drift by a separate method. This dependence can be considered as a drawback of these data analysis tools. In addition, as was indicated in Figure 6, these parameters have a rather indirect relationship to the physico-chemical process.

2.7.3 Charge and frequency of corrosion events

Corrosion processes produce pulses of charge with relatively short duration. In an EN signal, these charge pulses manifest as transients. The charge in a transient $q$ (C) and the frequency of corrosion events $f_n$ (Hz) are parameters that allow to distinguish between general and localized corrosion and, in addition, to verify the susceptibility of a corroding system for localized corrosion.

For the discrimination between general and localized corrosion, a number of assumptions should be made [1]: the cathodic processes are considered noise-free (i.e. the charge pulses are generated by the anodic processes), both working electrodes are nominally identical, the individual events generate a white noise and the electrolyte resistance is zero. The latter leads to the assumption that half of the anodic current produced by each working electrode travels to the other working electrode (through the electrical connection) and can be measured [1]. For a corrosion process with a low frequency EN PSD $\Psi_I$ and EPN PSD $\Psi_E$, the charge $q$ is calculated by [1, 66, 68, 69]:

$$q = \sqrt{\Psi_E \Psi_I} / B$$

(4)

Where $B$ (V) is the Stern-Geary coefficient. The Stern-Geary equation may not always be applicable, only in non-polarization conditions (which is always the case for open-circuit
ENM) and assuming general corrosion [70]. The frequency of corrosion events $f_n$ is calculated by [1, 10, 66, 68, 69, 71-75]:

$$f_n = \frac{B^2}{\Psi_E}$$

(5)

Since $f_n$ is proportional to the area of the working electrodes, it should be normalized for this area. A high frequency of corrosion events $f_n$ can indicate general corrosion, whereas a low frequency of corrosion events $f_n$ and a high average charge of each corrosion event $q$ is an indication of large transients and thus localized corrosion. This can also occur in combination with a drop of the noise resistance, $R_n$ [37, 66, 69]. The parameter $q$ enables discrimination between passivity (low value) and corrosion (high value, either general or localized) [1, 68, 76].

Compared to interpretation of the cross correlation, autocorrelation or the Hurst exponent, $q$ and $f_n$ have a more direct relationship to the physico-chemical process. However, the conditions for validity of the Stern-Geary coefficient $B$ yield a disadvantage to apply $q$ and $f_n$ for discrimination between general and localized corrosion, in particular compared to the time-frequency analysis procedures. In addition, identification of different localized corrosion processes is not straightforward using these parameters.

To verify the ability of a parameter to distinguish between different corrosion characteristics, its cumulative probability $F$ can be determined for different conditions [68]. For example, $F$ ($f_n$) can be used to indicate the ability of $f_n$ to discriminate between general and localized corrosion. Often, $F$ is determined by arrangement of all values of the parameter of interest in a series from small to large, and subsequent calculation of $F = n/(N+1)$, with $N$ the total number of values and $n$ the rank of the current value in the series [37, 72, 74, 77, 78]. Figure 17 shows a schematic representation of $F$ plotted against $f_n$. Here, a shift of $F$ towards the right-hand side indicates more prevalent general corrosion and to the left-hand side dominant localized corrosion. The overlap (i.e. similarity) of multiple cumulative probability plots, including their distribution width, is an indication of their discrimination ability between different corrosion processes [37, 71, 73-75, 77-81].
In order to discriminate between different dominant stochastic processes (e.g. general corrosion, pitting corrosion or evolution of hydrogen bubbles), a Weibull probability plot can also be used. Such a plot contains one or more regions with different Weibull slopes, each of them corresponding mainly to one dominant stochastic phenomenon [71, 74, 77, 79]. The Weibull distribution function for this application is defined in the time domain. Therefore the plot of the cumulative probability must be transformed from the \( f_n \) domain to the mean free time \( t_m \) (1/\( f_n \)) domain. Subsequently, the calculated cumulative probability \( F(t_m) \) is fitted to the Weibull distribution function, creating the Weibull probability plot [71, 74, 77, 79]. This plot can distinguish between general and localized corrosion [10, 71-77, 79, 80]. A schematic example is shown in Figure 18.
After the determination of different corrosion processes, the susceptibility of a corroding system to the generation of certain events can be determined by calculation of their conditional event generation rate \( r(t) \). Strictly, \( r \) reflects the probability of initiation events (e.g. pit embryos or hydrogen bubbles) for a certain period of time \( \Delta t \) ahead of time \( t \), when these events have not yet been generated. This parameter is derived from the Weibull probability plot \([71-75, 77, 79]\). A schematic example of a conditional event generation rate plot is shown in Figure 19.

When comparing different corrosion characteristics, the level of \( r \) at a given time \( t \) provides information on the generation rate of stochastic events (e.g. intensity of metastable pitting or pit initiation) for these systems relative to each other \([71, 72, 74, 75, 77, 78]\). The cumulative probability \( F \), Weibull probability plot and conditional event generation rate \( r \) all share a rather indirect relationship to the underlying physico-chemical process. They only present the behaviour of another (more physical) parameter, e.g. the frequency of events. Therefore, they can provide useful information about that parameter’s discrimination ability and the initiation probability of events.
2.7.4 Visual characterization

Visual identification of transients allows determination of different corrosion processes. Transient characteristics can be attended with certain features of the PSD [10, 11, 61]. In this subsection different reported characteristics are discussed based on a division of corrosion processes into metastable pitting, stable pitting and general corrosion attack.

Metastable pitting, the competition process of pitting initiation, local breakdown of the passive surface oxide film and repassivation, can be characterized in the ECN signal by fast fluctuations. The fluctuations consist of a rise and subsequent steep fall in the absolute value of the ECN, typically with short lifetimes (e.g. in the order of several seconds to several tens of seconds) [10, 19, 29, 48, 58, 80, 82, 83]. In the EPN signal, transients either in the same direction or in the opposite direction as their corresponding ECN transient are found during metastable pitting (also in accordance with the cross correlation and the skewness of a distribution). This bidirectional behaviour originates from the nature of ECN transients: their direction depends on which working electrode is pitting. EPN transients are
typically characterized by a relatively fast rise and slow (e.g. exponential) decay of the absolute value of the EPN signal [6, 8, 10, 11, 23, 48-50, 63, 64, 80, 84].

Stable pitting corrosion generates an ECN signal that is characterized by large transients (typically larger than for metastable pitting). These can remain at a high value for a longer time than for metastable pitting (e.g. in the order of one hundred to several hundreds of seconds) before decreasing again [48, 58, 62, 65, 82]. Just as for metastable pitting, transients in the EPN signal (with either equal or opposite character) accompany the ECN transients. In this case clearly distinguishable peaks are observed, however with less recognizable transient shapes than for metastable pitting. Analogous to the ECN transients, EPN transients can last for a period in the order of one hundred to several hundreds of seconds [48, 49, 62, 63, 65].

In the case of a general corrosion process, the dominance of a steady diffusion process causes an ECN and EPN record without noticeable transients and in many cases with a relatively large DC drift [29, 48, 58].

In the case of the example EN signals shown in Figures 1-3, the differentiation between general (Figure 1) and localized corrosion (Figures 2 and 3) can indeed be made based on the presence of transients in the EN signals of Figures 2 and 3, and the smooth appearance and lack of transients of the EN signals in Figure 1. In addition, in the case of a clear metastable pitting process as shown in Figure 3, the individual transients are well distinguishable, as are the transient shapes. However, in case multiple superimposed transients exist in the EN signals, as shown in Figure 2, visual investigation of transient characteristics is hindered. This potentially limits the effectiveness of visual investigation only to extreme cases, where individual transients are easily observable. Moreover, the strong user-defined nature of this analysis method allows it to be used merely as a means of additional verification combined with other data analysis procedures, rather than as a robust stand-alone analysis method.
2.7.5 Statistical characteristics

Statistical characteristics of an EN signal involve its kurtosis, skewness, localization index and coefficient of variation of current. Kurtosis is a measure of the shape of a distribution [85]. For an EN signal $x(n)$ ($n = 1, 2, \ldots, N$) with an average $\bar{x}$, the kurtosis is defined as [1, 33, 34, 66, 85]:

$$Kurtosis = \frac{1}{N-1} \sum_{n=1}^{N} \left( \frac{x(n) - \bar{x}}{\sqrt{x(n)^2}} \right)^4 \quad (6)$$

The kurtosis of a normal distribution equals three. This value is subtracted to get the normalized kurtosis [1]. Kurtosis allows the detection of transients (and thus localized corrosion): relatively infrequent, fast transients (either uni- or bidirectional) generate a high kurtosis. Kurtosis suffers a relatively high standard error [1].

The skewness of an EN signal is a measure for its symmetry. For an EN signal $x(n)$ ($n = 1, 2, \ldots, N$) with an average $\bar{x}$, the skewness is defined as [1, 33, 34, 66, 85]:

$$Skewness = \frac{1}{N-1} \sum_{n=1}^{N} \left( \frac{x(n) - \bar{x}}{\sqrt{x(n)^2}} \right)^3 \quad (7)$$

The skewness is normalized relative to a normal distribution and is independent of the mean and standard deviation of the EN signal. It provides information about the shape of the statistical distribution, i.e. the symmetry of the signal around the mean [66, 85]. Therefore, an EN signal containing unidirectional transients exhibits a skewed distribution, e.g. in the case of asymmetrical working electrodes. Skewness also suffers a relatively high standard error, which should be taken into consideration when applying this parameter for data analysis [1].
The coefficient of variation of current (CVC) is a normalized measure of dispersion of a probability distribution. It is proposed as a measure to identify localized corrosion, defined as [1, 66, 68]:

$$CVC = \frac{\sigma_I}{I_{corr}}$$

(8)

Where \(\sigma_I\) is the standard deviation of the ECN and \(I_{corr}\) its mean value. Note that, if both working electrodes are identical, the expected value of \(I_{corr}\) approaches zero. This may lead to a large value of the CVC regardless of the actual characteristics of the corroding system [1, 68].

The localization index (LI), or pitting index, is proposed as an alternative for the coefficient of variation, however it suffers the same drawbacks [1, 68, 85]. It is defined as [33, 66, 68, 85]:

$$LI = \frac{\sigma_I}{I_{RMS}}$$

(9)

Where \(I_{RMS}\) is the root mean square value of the ECN. A high CVC can be an indication of localized corrosion, whereas a low CVC indicates more general corrosion [62]. Note that the CVC and LI are mostly reported to be poor indicators of localized corrosion [33, 34, 37, 64, 66, 68, 69, 86, 87], however occasionally found to be informative [88]. Instead, it can be regarded as an indicator for the asymmetry between the two working electrodes [33].

All four statistical parameters discussed in this subsection suffer high standard errors, which makes them less reliable compared to the procedures operating in the time-frequency domain. Moreover, Hilbert spectra or EDPs both allow accurate discrimination between general and localized corrosion, together with a direct relation with the underlying corrosion process, without the drawbacks of the statistical methods discussed here.

In the time domain, good alternatives for the discrimination between general and localized corrosion are determination of the charge and frequency of corrosion events. In this respect, the drawback of the high standard error of the skewness can be overcome by its relation...
with the charge and frequency of corrosion events, cross correlation and visual characterization of the EN signals.

2.8 Future directions and application

ENM is a particularly interesting technique for application in corrosion monitoring. The ability to distinguish localized corrosion processes without perturbation of the corrosion process and the use of a straightforward measurement configuration make it a robust monitoring technique that is potentially suitable for continuous corrosion monitoring. The further development of this technique involves two equally important paths: first, as described in this work, a data analysis procedure should be able to indicate which information in the EN signals is representative for the occurrence of corrosion processes. Powerful (combinations of) data analysis techniques exist today and superior procedures may arise in the future. The development of a library in which typical EN signal characteristics of specific corrosion processes of interest (e.g. average instantaneous frequency information for Hilbert spectra or relative energy contribution in EDPs) are stored, can be valuable. Second, the development of EN sensors is an on-going process. Besides the question whether open-circuit, galvanostatic or potentiostatic ENM are preferred for specific applications, also accessibility of the measurement location is important here. An important development in this respect is the no connection to substrate method. This configuration uses auxiliary electrodes, providing a true non-destructive corrosion monitoring solution [89-91]. Another configuration, which is only suitable for coated substrates, applies embedded EN sensors [69, 92-94], containing inert auxiliary electrodes located permanently between the primer and the topcoat. Embedded sensors are particularly suitable for permanent application at locations that are difficult, if not impossible, to reach.

These are only a few examples of significant advancements in the field of EN sensor configurations that outline the importance of practical requirements. It is valuable to note that besides the clear need for a robust (combination of) data analysis procedure(s), ideally a future approach should carefully consider its integration with the required measurement configuration for specific applications. This will improve the overall suitability of EN for corrosion monitoring purposes.
2.9 Conclusions

Many techniques have been proposed for analysing EN data. In many cases the resulting parameters or plots in which these are visualized are reported to be valuable indicators for corrosion characterization in specific applications, but it is often unclear whether these are also generally applicable. Therefore, to guide the selection of an appropriate technique, this work discussed the available parameters and procedures. This was done by firstly showing that many interdependencies exist between the procedures, which implies that combining several methods may considerably enhance the potential for characterizing the corrosion processes. And secondly, a clear order of the available methods is provided, both in terms of identification ability and directness of the relation with the physico-chemical processes.

It can be concluded that consistent and reliable information can be obtained from EN data when a data analysis procedure is selected that (i) has a high discrimination ability and (ii) yields a descriptive parameter that is directly associated to the underlying physico-chemical process. Procedures that meet these two requirements appear to be the HHT (Hilbert spectrum), wavelet transform (EDP) and the analysis of charge and frequency of corrosion events. Preferably, the information is obtained without the need for subjective a-priori limitations or assumptions concerning the nature of the process under investigation. This is the case for the HHT. In addition to the procedures that meet the two requirements mentioned above, some of the descriptive parameters can be determined by different analysis procedures, which increases their reliability.

The application of the time-frequency data analysis methods, charge and frequency of corrosion events or a combination of other parameters should be verified more thoroughly experimentally. They potentially hold the key to a real added value of ENM to the understanding and monitoring of corrosion processes.
2.10 References

Chapter 2


A critical appraisal of the interpretation of electrochemical noise for corrosion studies


Chapter 2


A critical appraisal of the interpretation of electrochemical noise for corrosion studies


Chapter 2


Time-frequency methods for trend removal in electrochemical noise data

Abstract

Electrochemical current- and potential noise signals in many cases exhibit a direct current (DC) drift that should be removed prior to further data analysis. The theoretical ability of discrete wavelet transform and empirical mode decomposition to effectively remove only the DC drift component is evaluated based on their mutual performance for the first time. The correlation coefficient between individual signals after both trend removal techniques proved to be superior compared to the correlation coefficients between these and the signals after moving average, polynomial and linear trend removal. The residual power of these signals was compared and again the two time-frequency methods acknowledged their theoretical ability of removing only a well-defined part of the data.

This chapter is based on:
3.1 Introduction

One of the characteristics of many natural processes is that these are both non-stationary and nonlinear. The former may generate a direct current (DC) drift component since its statistical parameters change over time. Any DC drift in the signal will create new, false frequency components. A critical step considering the analysis of an electrochemical current (ECN) or potential (EPN) noise signal is to effectively remove this DC drift, which can have a large effect upon the outcome of the data analysis [1]. A delicate balance exists between on the one hand sufficient trend removal and on the other hand preventing loss of valuable data. How to effectively remove the DC drift and leave the valid signal is still a challenging task.

Regular trend removal methods like moving average trend removal or polynomial trend removal, suffer from the risk of eliminating useful information: for example, an increased order of the polynomial results in more trend removal, though it is likely that this is accompanied by an increased loss of valuable data. Moving average trend removal has already been shown to be not appropriate for drift removal [2]. Linear trend removal has been found to show satisfactory results in case the drift is approximately uniform [2, 3]. However, if this is not the case it is impossible for this technique to effectively remove the drift, which may result in larger deviations between individual and nominally identical measurements.

Time-frequency methods as discrete wavelet transform (DWT) and empirical mode decomposition (EMD) both allow an investigation of amplitude and frequency as functions of time. DWT has already been used as an indicator of specific corrosion mechanisms; different timescales of the ECN and EPN signal could be attributed to diffusion-, activation- or mixed controlled processes [4-12]. DWT has also been reported to provide an effective reconstruction of the original ECN and EPN signal, prior to calculation of the (spectral) noise resistance [5].

EMD enables a decomposition of a non-stationary signal representing a nonlinear process into characteristic scales, so-called intrinsic mode functions (IMFs). The residue after this decomposition is an indication of the DC component or DC drift of the signal [13, 14].

The aim of this chapter is to demonstrate that the two time-frequency techniques provide an effective trend removal solution. The original contribution of the present work is the concise evaluation of the theoretical ability of DWT and EMD to effectively remove only the DC drift.
Time-frequency methods for trend removal in electrochemical noise data

This evaluation is based on a mutual performance comparison of both methods, which has not been reported before. The correlation coefficient between a signal after subtraction of the residue calculated by on the one hand DWT and on the other hand EMD provides verification for the existence of a well-defined DC component that may be regarded as DC drift. An additional comparison of the correlation coefficients between the individual signals after all trend removal procedures (including moving average, polynomial and linear trend removal) and the two time-frequency techniques can provide information on the performance of the regular trend removal techniques with respect to these two. In addition, comparing the residual power present in the signal after the two time-frequency and the regular trend removal methods provides information on the consistency of the performance of the time-frequency procedures.

In this chapter, first the experimental set-up of the corrosion experiments is described. Then DWT and EMD procedures are discussed. Finally, the experimental results will be presented and the different trend removal methods are compared.

3.2 Experimental

In this section the practical aspects of the experiments are discussed, followed by the time-frequency trend removal procedures, DWT and EMD.

3.2.1 Practical

The electrochemical cell used in this work consists of two nominally identical panels with a self-adhesive PVC mask to ensure that only a well-defined area of the electrodes is exposed to the electrolyte. Each of the panels is attached to one end of a (electro)chemically inert PMMA tube by using a silicone glue. On top of the PMMA tube there is a hole serving two functions: to fill the cell with electrolyte and to place the reference electrode, a Radiometer analytical Red Rod type REF201 (Ag/AgCl/sat. KCl: 0,207 V vs. Standard Hydrogen Electrode). The electrolyte used is an aqueous 3 wt.% NaCl solution. The layout of the electrochemical cell is shown in Figure 1 and is identical to the set-up described for the electrochemical noise measurements (ENM) performed in [1].
The electrochemical cells were placed in a Faradaic cage to avoid electromagnetic disturbance from external sources, and connected to the measuring equipment. The wires were directly connected to the panels. The temperature of the environment was held at 21°C.

Two series of measurements were performed, all on bare carbon steel (CS): standard low carbon cold-rolled steel Q-panels from the Q-lab corporation, type S-46. Series 1 consisted of 12 identical electrochemical cells with 2 nominally identical working electrodes, both with a surface area of 10.00 cm². Each of the 12 electrochemical cells of series 1 was measured four times: two times consecutively after 1 hour of allowing it to reach steady state and again two times consecutively after 24 hours.

Series 2 consisted of 5 sets of 3 identical electrochemical cells with 2 nominally identical working electrodes, both with a surface area of 10.00, 4.91, 0.95, 0.13 or 0.03 cm². Each of the 15 electrochemical cells was measured two times: first after 24 hours and secondly after 48 hours. Both series are schematically depicted in Figure 2.

All measurements were performed with a computer-controlled Compactstat from Ivium Technologies working as zero resistance ammeter (ZRA in Figure 1) and potentiometer (E in Figure 1). The instrumental noise generated by this instrument was verified through the procedure as described by Ritter et al. [15] to ensure that the power spectral densities at different sampling rates overlapped for measurements on pure Ohmic resistances.
Data were collected using Windows-based PCs running dedicated software from Ivium Technologies and subsequently processed using Matlab from MathWorks. The data acquisition rate was 20 points per second and each measurement consisted of 8192 data points for series 1 and 2048 data points for series 2.

Regular trend removal was performed either by moving average removal with a span of 5 points, third order polynomial or linear trend removal. The results for DWT are presented after eight-level wavelet decomposition with a Daubechies 4 wavelet. The effects of a different (Daubechies 12 or 20) wavelet on the results for wavelet decomposition were verified to be not significant. For the EMD, interpolation was performed using a cubic spline and the maximum number of sifting iterations was 10. The EMD was calculated using a
publicly available Matlab procedure [16, 17]. Calculation of the power spectral density of ECN and EPN and estimation of their residual power was performed after applying a Hamming window.

3.2.2 Trend removal

In many cases an electrochemical noise (EN) signal exhibits drift. A signal may be non-stationary, the measuring time may be too short for the lowest frequency components to fit, or there may be some slow alteration of the system under study during the measurement (e.g. increasing asymmetry between working electrodes, which has been found to appear in ENM on mild steel working electrodes [18, 19]). Note that in the second case, a stationary process can appear as being non-stationary [14]. This is however not the case for spontaneous fluctuations in current and potential induced by a corrosion process, which is considered non-stationary. It is necessary to apply some procedure to the incoming signal to eliminate the contribution of the drift. If not, this drift rather than the superimposed fluctuations dominates the data analysis. The choice of which trend removal procedure to apply is probably one of the most difficult problems in ENM. The challenge is that the procedure must be robust and must effectively attenuate the low-frequency components without eliminating useful information or creating artifacts. Often the linear trend removal procedure is used. There are, however, also other ways to remove DC drift, like moving average removal, polynomial fitting, analog or digital high-pass (HP) filtering and DWT [2, 5, 20, 21]. Three of the regular methods, moving average, polynomial and linear trend removal, are applied in this chapter. DWT is subject of investigation and its effectiveness will be compared with EMD as trend removal technique.

The greatest disadvantage of many trend removal methods is the user-defined nature of influencing the extent of data elimination, e.g. the selected order for polynomial fitting. In the next subsections, either based on experimental work in literature or on the theoretical background it is shown that DWT and EMD can be considered to effectively eliminate only the drift component, without affecting useful information present in the data.

3.2.2.1 Wavelet trend removal

In this subsection first the DWT is explained and subsequently the practical calculation of
this by means of the fast wavelet transform (FWT) is treated.

**Discrete Wavelet Transform**

Consider a time record \( x(n) \) \( (n = 1, 2, \ldots, N) \), which is expressed on a Cartesian basis. The DWT expresses \( x(n) \) using a basis composed of oscillating functions with a limited span of time. These oscillating functions can be chosen in an orthogonal manner, yielding a decomposition of \( x(n) \) by means of an orthonormal basis consisting of a linear combination of basis functions of a limited time span, \( \psi_{j,n} \) and \( \phi_{j,n} \). \( x(n) \) may be expressed as \( x(t) \):

\[
x(t) = \sum_j s_{j,k} \phi_{j,k}(t) + \sum_k d_{j,k} \psi_{j,k}(t) + \sum_k d_{j-1,k} \psi_{j-1,k}(t) + \ldots
\]

\[... + \sum_k d_{1,k} \psi_{1,k}(t)\]  

(1)

This can also be expressed as:

\[
x(t) = S_j(t) + D_j(t) + D_{j-1}(t) + \ldots + D_1(t)
\]

(2)

In equation (1) \( s_{j,k}, d_{j,k}, \ldots, d_{1,k} \) are the wavelet coefficients. In equation (2) \( S_j, D_j, \ldots, D_1 \) are crystals where each crystal describes \( x(t) \) on a different scale \( j \), with \( J \) the maximum scale analyzed. By that way each crystal is related to a feature of the signal of a particular time scale covering a specific frequency range. Therefore DWT describes the signal at several timescales or resolutions [5-7, 9-11, 22-24].

The basis functions \( \psi_{j,k} \) and \( \phi_{j,k} \) are denoted as the mother wavelets and the father wavelets, respectively, through scaling and translation by the following equations [5-7, 9, 11, 22, 23]:

\[
\psi_{j,k}(t) = 2^{-j/2} \psi(2^{-j} t - k) = 2^{-j/2} \psi\left(\frac{t - 2^j k}{2^j}\right)
\]

(3)

\[
\phi_{j,k}(t) = 2^{-j/2} \phi(2^{-j} t - k) = 2^{-j/2} \phi\left(\frac{t - 2^j k}{2^j}\right)
\]

(4)
where \( k = 1, 2, \ldots, N/2 \) and \( j = 1, 2, \ldots, J \).

**Fast Wavelet Transform**

In practice, the DWT may be computed by means of the FWT algorithm, which intuitively comprises three different operations: Low-pass filtering, high-pass filtering and down sampling. Note that this down sampling procedure results in less coefficients, however the length of each signal component captured in the D and S crystals should remain equal to that of the original signal. In Figure 3 a schematic representation of this iterative process is given, the low- and high-pass filtering and down sampling operations depicted with L, H and \( \downarrow \downarrow 2 \), respectively [7, 9, 23, 24].

![Figure 3 Schematic representation of the FWT algorithm (based on [9, 23, 24])](image)

Figure 4 shows an eight-level wavelet decomposition with a Daubechies 4 wavelet of an ECN and EPN signal. The original ECN and EPN signals are displayed at the top. Note that the potentiometer already removes the DC component of the first data point from all data, resulting in a higher accuracy but also in an absolute potential value not representative for the open corrosion potential of the carbon steel.
Figure 4 Eight-level wavelet decomposition with a Daubechies 4 wavelet of an ECN (left) and EPN (right) signal

The energy contribution of each crystal to the overall signal is given by:

$$E_j^d = \frac{1}{E} \sum_{k=1}^{N/2^j} d_{j,k}^2 \quad (j = 1, 2, \ldots, J)$$  \hspace{1cm} (5)

$$E_j^s = \frac{1}{E} \sum_{k=1}^{N/2^j} s_{j,k}^2$$  \hspace{1cm} (6)

The orthogonality of the wavelets allows calculation of the overall energy by:

$$E = E_j^s + \sum_{j=1}^{J} E_j^d$$  \hspace{1cm} (7)
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For an EN signal, the relative energy contributed by each crystal may be plotted against the crystal name, resulting in an energy distribution plot (EDP) [5-11, 23, 24]. An EDP provides mechanistic information about the physico-chemical processes: the position of the maximum relative energy in the EDP corresponds to the dominant process in certain corrosion events and its change can reflect the behaviour of the dominant corrosion process [6, 7, 10, 23, 25, 26]. The number of iteration steps \( J \), schematically shown in Figure 3, is user defined. It is experimentally determined [6-11, 23, 24] that for a level \( J = 8 \) the valuable mechanistic information is captured in detail crystals D1 to D8. In Figure 5 all information from literature studies is combined to provide a compact schematic representation of the most essential information that DWT can provide in this respect.

![Figure 5: Schematic representation of the information that may be obtained from an EDP (based on [5-11, 23, 24])](image)

Short time scale crystals, typically D2 and D3, are associated with activation-controlled processes and medium time scale crystals D4-D6 represent mixed controlled processes. Medium time scales are dominant in the case of metastable pitting. Long time scale crystals D7 and D8 provide information on diffusion-controlled processes, which can e.g. be dominant for general corrosion. The choice of 8 crystals (i.e. level \( J = 8 \)) may therefore be considered suitable for investigating corrosion processes. In many cases the contribution of the smooth S8 crystal to the total energy is considerably high, a phenomenon that is mainly attributed to the DC drift in the original signal [6-11].

Rescaling the signal present in S8 back to its original timescale and subsequently subtracting the contribution of this signal from the original signal may overcome the most important drawbacks of regular trend removal methods like linear or polynomial trend removal, being the risk of insufficient trend removal or otherwise the probable loss of valuable information about the corrosion mechanisms. Dong et al. [5] determined \( R_n \) and \( R_{sn} \).
by constructing the original signal back from crystals D1-D8 and subsequently compared these with the low frequency modulus of impedance obtained by electrochemical impedance spectroscopy measurements. In this chapter, the smooth S8 crystal is subtracted from the original signal.

3.2.2.2 Empirical mode decomposition

The second time-frequency method for trend removal discussed here is the EMD. This method was proposed by Huang et al. [14] and enables a decomposition of a nonlinear and non-stationary signal into its characteristic scales, so-called IMFs. This principle is (sometimes in a modified form) already applied in other fields of signal processing [27-31]. Unlike the DWT technique, where the data are expanded into wavelet crystals on a basis of a pre-defined wavelet and using function orthogonality, here the basis is derived directly from the data itself, making the EMD flexible and adaptive [13, 14, 29, 32-34].

The basis of EMD is the assumption that any signal consists of multiple intrinsic modes of oscillation, each superimposed on another. These IMFs can be identified empirically by their characteristic time scales. An intuitive way may be to consider the part of a signal $x(t)$ between two consecutive extrema with times $t$ and $t'$ as a local high frequency part ($d(t)$, $t \leq t \leq t'$), or local detail. Besides a local maximum between these minima, this also involves a local low frequency part, or trend $m(t)$. This results in [16]:

$$x(t) = m(t) + d(t)$$

After performing this operation for all fluctuations composing the entire signal, the same procedure can be performed for the residual, composed of all local trends. This iteration allows extracting all components (or IMFs) of a signal. Summarized, the EMD algorithm may be described as shown in Figure 6.
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The different steps shown in this Figure are [13, 14, 16, 32]:

1. Identify all extrema of \( x(t) \)
2. Interpolate between extrema by interconnection of local maxima, generating the ‘upper envelope’ \( e_{\text{max}}(t) \), and local minima, resulting in the ‘lower envelope’ \( e_{\text{min}}(t) \)
3. Calculate the envelope mean \( m(t) = (e_{\text{max}}(t) + e_{\text{min}}(t))/2 \)
4. Extract the detail component \( d(t) = x(t) - m(t) \)
5. Iterate on the residual \( r(t) = x(t) - d(t) \)

Each IMF is characterized by an equal number of extreme values and zero-crossings or a difference that does not exceed the value of one, and by symmetry with respect to its local mean [14]. To meet these criteria, steps 1 to 4 are iterated \( k \) times prior to proceeding with step 5. This iteration process is designated as the sifting process. It is necessary to implement some kind of stopping criterion in this iteration, and the condition that the number of extreme values equals the number of zero-crossings seems to apply rather well [13, 14, 30, 32]. A more advanced stopping criterion could be to limit the deviation calculated between two consecutive sifting iterations to a small value [29].
The overall stopping criterion is when the residue $r_N(t)$ becomes less than a predefined threshold value of significance, or when it becomes a monotonic function, i.e. it contains no more than two extrema. In case the original signal exhibits a trend, $r_N(t)$ represents the trend. $x(t)$ may thus be defined as [13, 14, 29, 32]:

$$x(t) = \sum_{n=1}^{N} d_n(t) + r_N(t)$$  \hspace{1cm} (9)

By this way, an $N$-empirical mode decomposition with a residue $r_N(t)$ is obtained, where $r_N(t)$ represents the trend or DC component [13, 14, 29, 32].

Figure 7 shows an EMD of the same ECN and EPN signal as used for the DWT in Figure 4. The original ECN and EPN signals are displayed at the top.

Both DWT and EMD allow the extraction of the DC drift component from the data. The function orthogonality provides DWT the advantage to directly extract additional mechanistic
information from the data. However, the fact that EMD has a basis derived directly from the data itself rather than a pre-defined wavelet makes it an adaptive and more flexible technique than DWT.

3.2.3 Comparison methods

In the present chapter, two methods are applied for comparison of the performance of the trend removal procedures: the correlation coefficient between the individual signals after different trend removal procedures and calculation of their residual power.

3.2.3.1 Correlation coefficient

DWT and EMD both share the theoretical ability to effectively define the DC drift component in the data. This ability can be evaluated based on their mutual performance by determining the correlation coefficient (a measure of the similarity between two data sets) between each signal after removal of the drift component calculated by these two techniques. An additional comparison of the correlation coefficients between the individual signals after all regular trend removal procedures and the two time-frequency techniques can provide information on the performance of the regular trend removal techniques with respect to these two. The standard deviation of all sets of correlation coefficients provides information on the consistency of the performance of the trend removal methods.

It would be expected that the correlation coefficient between the signals after the two time-frequency trend removal methods is higher (0.9 or more) than of the signals after the regular methods with respect to these two. Additionally, the former case should be combined with relatively low standard deviations compared to the latter case, since the time-frequency methods are both expected to perform in a consistent way.

3.2.3.2 Residual power level

The power in the ECN or EPN signal after removal of the DC drift is representative for the physico-chemical process. A more active corrosion process generates noise signals with a higher power level. Removing a larger component that may be considered to represent the
DC drift by the respective trend removal technique from the signal will result in a lower residual power. As all the signals represent the same corrosion process, and the power of the signal is considered to indicate the overall corrosion activity, the signals after the trend removal by the two time-frequency procedures are expected to have similar power contents. Moreover, both power values are expected to show small variation for multiple nominally identical measurements. For this reason, the residual power levels after the regular trend removal procedures are also investigated as a benchmark.

3.3 Results and discussion

In this section the methods to compare the trend removal procedures are discussed. For the signals after trend removal, both the correlation coefficient and the remaining power in the signal are calculated.

3.3.1 Correlation coefficient between residual components

3.3.1.1 Series 1: Identical working electrode areas

For the measurements from series 1, all ECN and EPN noise signals have been analyzed. Figure 8a shows the correlation between on the one hand the signal after subtraction of the trend calculated by DWT (W) and on the other hand the signal after subtraction of the trend calculated by the other four techniques (empirical mode -E, moving average -M, polynomial -P and linear trend removal -L). Figure 8b provides equivalent information on the correlation between the signals after subtraction of the trend calculated by EMD and the other techniques (now W, M, P and L). Therefore, in Figure 8a the correlation coefficients between W and W and in Figure 8b those between E and E are equal to 1 (by definition). The correlation coefficients between W and E are identical in both figures. Results for the ECN and EPN signals are shown individually at the left- and right-hand side of each figure. The x-axis shows the first letters of the trend removal techniques. The colours of the individual points correspond to the colours shown in the colour bar, changing from blue (uncorrelated or even a weak negative correlation coefficient) to red (correlated). Next to the individual
The mean correlation coefficients and their standard deviation are presented in black. Each column of correlation coefficients contains 48 individual values.

Figure 8 Correlation coefficients between the signals after trend removal by (a) DWT and the other techniques and (b) EMD and the other techniques for series 1

In this figure, it is clear that, except for a few outliers, the signals after trend removal by DWT and EMD correspond well (i.e., the mean correlation coefficients are the highest), both for the ECN and EPN signals. This was also expected according to the theory behind these techniques. In the next subsection, the observed outliers are also visible for the residual power of the ECN and EPN signals. The next best mean correlation coefficients in both figures are between the signals after trend removal by DWT (8a) or EMD (8b) and on the other hand moving average trend removal for the specified span. Despite the particularly small standard deviations in Figure 8a for these correlation coefficients, the mean correlation coefficients are still lower than between the signals after trend removal by DWT and EMD. After polynomial trend removal, some EPN signals show higher correlation coefficients than after moving average trend removal, however due to a larger spread and resulting standard deviation the mean correlation coefficient is approximately equal to moving average trend removal. Linear trend removal shows the least correlation with the two time-frequency trend removal techniques.
3.3.1.2 Series 2: Different working electrode areas

In Figure 9 the same information as depicted in Figure 8 is presented for series 2.

![Figure 9](image.png)

Figure 9 Correlation coefficient between the signals after trend removal by (a) DWT and the other techniques and (b) EMD and the other techniques for series 2

Analogous to the previous series of data, the mean correlation coefficient between the ECN signals after trend removal by DWT and EMD is higher than between these two and the regular trend removal techniques. For the EPN signals this is less obvious, and in Figure 9a the mean value as well as the standard deviation of the correlation coefficients between the signals after polynomial trend removal and trend removal by DWT are comparable with those between the signals after trend removal by EMD and DWT. In addition, contrary to the previous series, the correlation coefficients between the signals after polynomial trend removal and after trend removal by DWT or EMD are now higher than after moving average trend removal and trend removal by the two time-frequency techniques. Moreover, the difference in spread (and thus standard deviation) between the correlation coefficients after moving average- and polynomial trend removal is less than in the previous series.
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Linear trend removal again provides a poor mean correlation coefficient with the two time-frequency trend removal techniques and shows the largest standard deviations. However, no negative correlation coefficients are observed for this series.

3.3.2 Residual power after trend removal

The measurements in the two series were performed on nominally identical electrodes, with the working electrode area as the only variable in series 2. Besides differences that may be attributed to the working electrode area, no large differences in residual power may therefore be expected for the signals investigated here. The signals obtained in both measurement series are investigated successively.

3.3.2.1 Series 1: Identical working electrode areas

Figures 10 and 11 show the residual power after trend removal for the ECN and EPN signals, respectively. All separate signals are shown as individual series in the plots. The letters in the legend correspond with the first letter of the respective trend removal method. The 24 measurements performed after 1 hour and 24 hours of immersion are shown at the left- and right-hand side, respectively.

Linear and polynomial trend removal result in the largest variations in the residual power between the measurements. Also, the average power level is relatively high. For the ECN signals, moving average trend removal corresponds well with the values calculated by both trend removal by DWT and EMD, but for the EPN signals the residual power after applying this technique is lower.

Trend removal by EMD and DWT both result in approximately the same residual power, although it should be noted that in the measurements performed after 24 hours, the EPN signals after trend removal by EMD show significantly larger values than after trend removal by DWT for four individual measurements. These values can also be observed in Figure 8a and b as four values of small correlation. The same holds for three ECN signals after trend removal by EMD, however less evident here due to the logarithmic scale. The reason for these few deviations in performance could not be explained.
Figure 10 Residual power of ECN signals for series 1

Figure 11 Residual power of EPN signals for series 1
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For the measurements after 24 hours, the ECN signals after trend removal by DWT, EMD and after moving average trend removal consistently show lower residual power than after 1 hour. This decrease could be due to a less homogeneous distribution of dissolution processes after 24 hours induced by the formation of magnetite, Fe$_2$O$_3$. This is an insoluble corrosion product, either sticking to the surface of the working electrodes (and decreasing the corrosion rate) or floating in the electrolyte as an insoluble particle. The vertical position of the working electrode surfaces in the electrochemical cells could not completely prevent accumulation of this corrosion product.

In addition, for five measurements after 24 hours the EPN signals show a comparable larger value of the residual power. This is clearly visible after trend removal by DWT, EMD and after moving average trend removal. This could not be attributed to a specific phenomenon.

3.3.2.2 Series 2: Different working electrode areas

Figures 12 and 13 again show the residual power after trend removal for the ECN and EPN signals. The measurements performed after 24 hours and 48 hours of immersion are shown at the left- and right-hand side, respectively. The different working electrode areas are indicated along the x-axis, where the groups of each time three identical measurement cells are visible.

Within each group the power in the signal should be similar, since the corrosion processes are comparable. In between groups differences are expected due to the variation in working electrode area.

The residual power values of the ECN signals show comparable results after trend removal by DWT and EMD. Contrary to the results in Figures 10 and 11, now the residual power of the signals after polynomial trend removal, rather than moving average trend removal, is in better agreement with that after trend removal by DWT and EMD. In Figure 9 this was visible through the higher mean correlation coefficient between ECN signals after polynomial trend removal and those after DWT and EMD trend removal.

For the residual power of the EPN signals the same applies as for series 1. After trend removal by EMD a comparable power level as after trend removal by DWT can be observed, however also here a few outliers exist. The deviations of these outliers are smaller than the deviations of the outliers in series 1, which was visible in Figure 9 by smaller deviations of the correlation coefficients.
Time-frequency methods for trend removal in electrochemical noise data

![Figure 12 Residual power of ECN signals for series 2](image1)

![Figure 13 Residual power of EPN signals for series 2](image2)
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Again the reason for these few differences is unclear. Moving average trend removal again results in structurally lower values for the specified span and linear trend removal shows the most random values (which corresponds to the largest standard deviations in Figure 9) and also a higher average value for the residual power. The relative performance of polynomial trend removal appears to be higher for this series as in the case of series 1. The residual power values of the ECN signals appear to depend on working electrode area. The difference between the two periods of immersion that is noticeable for the measurements of series 1 is not observed here. A possible reason could be that after 24 hours the corrosion products were already present at the surface of the working electrode areas. It could also be visually observed that the differences in the formation of corrosion products between 24 or 48 hours here were much less than between 1 or 24 hours in series 1. Note further that the deviations between moving average trend removal and the two time-frequency methods are small for the larger working electrode areas (which agrees with the results of series 1) and increase with decreasing working electrode area. Also note that the values of the residual power for the working electrode area of 10 cm$^2$ are in agreement with those obtained for series 1, both for the ECN and the EPN signals.

3.3.3 Summary of results

The signals after trend removal by EMD showed the highest mean correlation coefficients with those after trend removal by DWT, which acknowledged the theoretical capability of these techniques to define a reliable DC drift component in the signal. Furthermore, trend removal by DWT and EMD resulted in the most consistent measurement results regarding the residual power for the ECN and EPN signals investigated here. From the regular trend removal techniques, moving average trend removal showed the least variation in the (otherwise not particularly high) correlation coefficients with either trend removal by DWT or EMD, indicating a consistently low correspondence between the signals after these trend removal techniques. This consistency in the performance of moving average trend removal was further supported by the values of the residual power in series 1, as compared to these values after polynomial or linear trend removal. The latter two showed larger deviations in the calculated residual power and in addition a larger spread (and thus standard deviation) of the values for the correlation coefficients with the two time-frequency techniques. The reason for this correspondence in behaviour between moving average trend
removal and the two time-frequency techniques is that all three techniques operate on local oscillating behaviour of the signal. Polynomial and linear trend removal however, define a global fit (based on the entire signal) and subtract this function from the original signal.

3.4 Conclusions

The present work clearly, and for the first time, demonstrated that there is a theoretical agreement between on the one hand the signals after subtraction of the smooth S8 crystal from DWT and on the other hand the residual component from EMD. This could be verified based on the correlation coefficients between these signals and a comparison of their residual power.

In addition the correspondence with three regular trend removal techniques was investigated, showing varying results. Provided that the effect of moving average, polynomial and linear trend removal on the information left in the data after trend removal is quite uncertain, it can be concluded that for the measurements presented here, trend removal by a time-frequency technique was the preferred technique to remove the DC drift. Based on these measurements, the best choice would be trend removal by DWT, since this method showed the most consistent values for the residual power of the (EPN) signals.

Besides well-defined experimental conditions like e.g. proper electromagnetic shielding and many other basic criteria, application of trend removal by DWT instead of moving average, polynomial or linear trend removal may contribute to an increased reliability of the data analysis of individual ENM.
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3.5 References


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

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: stainless steel 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.

This chapter is based on:

4.1 Introduction

Already in the 1980s, 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. Transient characteristics generally indicate different corrosion mechanisms. Transients in the electrochemical current noise (ECN) signal are reported to occur simultaneously with transients in the EPN signal, indicating the occurrence of localized corrosion [3, 4]. The frequency contribution of each individual transient leaves a specific signature, or 'fingerprint' that can provide information on the nature of the related corrosion process. The most interesting application of electrochemical noise measurements (ENM) is the ability to identify these localized corrosion processes based on characteristic transient features, possibly the most challenging task in corrosion monitoring [5-10].

The identification of localized corrosion processes through electrochemical noise (EN) signals preferably 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 EN for over a decade, is the only suitable analysis technique in this respect; different timescales of the ECN and EPN signal could be attributed to diffusion-, activation- or mixed controlled processes [4, 11-18]. The timescale (or group of timescales) with the highest relative energy corresponds to the dominant process and its change can reflect the behaviour of this dominant corrosion process: a relatively fast process corresponds to smaller timescales and a relatively slow process to larger timescales [13, 14, 17, 19-22]. 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 [12-14, 17]. The number of iteration steps (and therefore the number of timescales) is user defined. It is experimentally determined that an eight-level decomposition is sufficient to capture the valuable mechanistic information in these timescales [4, 13-17, 19, 20]. 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. [23], is proposed for the analysis of EN signals under open-circuit conditions in corrosion studies. This technique, which has also been proven to be valuable in the analysis of voltammetric data [24], provides an actual time-frequency decomposition of an EN 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 chapter, 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. EN data are investigated for three different corrosion mechanisms involving stainless steel AISI304 exposed to an aqueous HCl solution at pH 1.0, 1.9 and 3.0. In addition, the AISI304 exposed to the aqueous HCl solution at pH 1.0 is compared with mild steel exposed to an aqueous 3 wt.% NaCl solution. Finally, the AISI304 exposed to the aqueous HCl solution at pH 3.0 is discussed in relation to AISI304 exposed to an aqueous 3 wt.% NaCl solution.

4.2 Experimental

4.2.1 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 AISI304 or mild steel). In Figure 1 this measurement setup is schematically depicted, where ZRA represents the zero resistance ammeter and E the potentiometer.
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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 to 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. Standard Hydrogen Electrode, 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 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 using a Reichert MEF4 M optical microscope with maximum magnification of 1000x.

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

4.2.1.1 Data acquisition

Current and potential fluctuations were recorded using a Compactstat from Ivium Technologies working as ZRA and potentiometer, controlled by a Windows-based PC running dedicated software. A low-pass filter of 10 Hz was applied during data recording. 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 EPN signal measurement (i.e. to be able to set the potentiometer to a small potential range), for each measurement the value of the first EPN measurement was used as a fixed offset for the entire EPN data range.
Novel time-frequency characterization of electrochemical noise data in corrosion studies using Hilbert spectra

Table 1 Schematic representation of the measurement series together with the OCPs

<table>
<thead>
<tr>
<th>Series 1</th>
<th>General corrosion</th>
</tr>
</thead>
<tbody>
<tr>
<td>M</td>
<td>AISI304</td>
</tr>
<tr>
<td>E</td>
<td>HCl pH 1.01</td>
</tr>
<tr>
<td>OCP</td>
<td>-0.243 V vs. SHE</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Series 2</th>
<th>Localized corrosion</th>
</tr>
</thead>
<tbody>
<tr>
<td>M</td>
<td>AISI304</td>
</tr>
<tr>
<td>OCP</td>
<td>0.237 V vs. SHE</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Series 3</th>
<th>Localized corrosion</th>
</tr>
</thead>
<tbody>
<tr>
<td>M</td>
<td>AISI304</td>
</tr>
<tr>
<td>E</td>
<td>HCl pH 2.96</td>
</tr>
<tr>
<td>OCP</td>
<td>0.357 V vs. SHE</td>
</tr>
</tbody>
</table>

The instrumental noise generated by this instrument was quantified through the procedure as described by Ritter et al. [25] to ensure that this noise level is sufficiently small at different sampling rates for measurements on pure Ohmic resistances. The obtained power spectral densities (generated by a combination of instrumental noise from the device and thermal noise from the Ohmic resistances) were of the order of $10^{-20}$ A$^2$/Hz or lower for the current and $10^{-13}$ V$^2$/Hz or lower for the potential. Moreover, the power spectral densities overlapped for different sampling rates up to a sampling frequency of 20 Hz. The sampling frequency used for the measurements described in this work was 5 Hz, which is well within that region. In the next section it is shown that the highest extractable frequency in the Hilbert spectrum for this sampling frequency is 1 Hz, which can be considered as appropriate since most power of a EN signal is in frequencies below 1 Hz [26]. The instrumental noise is considered the only significant unwanted noise source between the Nyquist frequency (2.5 Hz here) and the cutoff frequency of the low-pass filter (10 Hz) that could cause aliasing and is therefore closely verified. All other noise sources are expected to be well above the cutoff frequency of the low-pass filter.

The data were processed using Matlab from MathWorks.
4.2.2 Empirical mode decomposition and Hilbert-Huang transform

The analysis methods proposed in this work, i.e. empirical mode decomposition (EMD) and subsequent HHT, operated on the raw ECN or EPN signal after application of the low-pass filter.

The HHT was first proposed by Huang et al. [23] and is based on the assumption that any nonlinear and non-stationary signal consists of multiple characteristic scales, or intrinsic modes of oscillation, each superimposed on another. These so-called intrinsic mode functions (IMFs) are based on the local properties of the signal and can be identified empirically by their characteristic time scales through the EMD. This principle is (whether or not in a modified form) already applied in other fields of signal processing [27-31].

4.2.2.1 Empirical mode decomposition

Unlike the discrete wavelet transform technique, where the data are expanded into wavelet crystals on a basis of a pre-defined wavelet and using function orthogonality, here the basis is derived directly from the data itself, making the EMD flexible and adaptive [23, 29, 32-35]. An intuitive way to understand EMD may be to consider the part of a signal $x(t)$ between two consecutive minima with times $t$ and $t'$ as a local high frequency part ($d(t)$, $t \leq t \leq t'$), or local detail. Besides a local maximum between these minima, this also involves a local low frequency part, or trend $m(t)$. This results in [36]:

$$x(t) = m(t) + d(t)$$

After performing this operation for all fluctuations composing the entire signal, the same procedure can be performed for the residual, composed of all local trends but without the local details. This iterative process allows extracting all components (or IMFs) of a signal. Summarized, the EMD algorithm may be represented by the flow diagram in Figure 2.
The different steps shown in this figure are [23, 32, 33, 36]:

1. Identify all extrema of \( x(t) \)
2. Interpolate between extrema by interconnection of local maxima, generating the ‘upper envelope’ \( e_{\text{max}}(t) \), and local minima, resulting in the ‘lower envelope’ \( e_{\text{min}}(t) \)
3. Calculate the envelope mean \( m(t) = (e_{\text{max}}(t) + e_{\text{min}}(t))/2 \)
4. Extract the detail component \( d(t) = x(t) - m(t) \); After \( K \) iterative steps an IMF \( d_n(t) \) is obtained
5. Iterate on the residual \( r(t) = x_{n-1}(t) - d_n(t) \)

Each IMF \( d_n(t) \) is characterized by an equal number of extreme values and zero-crossings or a difference that does not exceed the value of one, and by symmetry with respect to its local mean [23]. The latter ensures unbiased phase information and therefore well-defined instantaneous frequencies [23]. To meet these criteria, steps 1 to 4 are iterated \( k \) times prior to proceeding with step 5. This iteration process is called the sifting process. It is necessary to implement a stopping criterion in this iteration: the condition that the number of extreme values equals the number of zero-crossings [23, 30, 32, 33]. IMFs could be considered as a more general case of simple harmonic functions, however in close relation with the physico-
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chemical characteristics of the system under investigation due to the specific nature of EMD [37].
The overall stopping criterion is when the residue \( r_N(t) \) becomes less than a predefined
threshold value of significance, or when it becomes a monotonic function, i.e. it contains no
more than two extrema. The original signal \( x(t) \) may thus be defined as [23, 29, 32, 33]:

\[
x(t) = \sum_{n=1}^{N} d_n(t) + r_n(t)
\]

(2)

In this way, an \( N \)-empirical mode decomposition with a residue \( r_N(t) \) is obtained, where \( r_N(t) \)
represents the trend or direct current (DC) component [23, 29, 32, 33].
For the EMD, interpolation was performed using a cubic spline. The EMD and the HHT were
calculated using a publicly available Matlab procedure from Rilling et al. [36, 38].
Figures 3a, 4 and 5a show the decomposition of the original ECN (left) and EPN (right)
signals of the measurements on AISI304 exposed to an aqueous HCl solution at pH 1.0, 1.9
and 3.0 into their IMFs. Additionally, Figure 3b shows the decomposition of the original ECN
(left) and EPN (right) signal of the complementary measurement performed with mild steel
exposed to an aqueous 3 wt.% NaCl solution. Figure 5b shows the decomposition of the
original ECN (left) and EPN (right) signal of the complementary measurement performed
with AISI304 exposed to an aqueous 3 wt.% NaCl solution. Each highest curve shows the
original signal and each lowest curve represents the residual component \( (r) \), which can be
considered as the DC drift of the electrochemical ECN and EPN [23, 39]. Therefore only the
detail components \( (d) \) are taken into account in the HHT [23] and omission of the residual
can be considered as a trend removal procedure (see chapter 3 [39]).
Figure 3 (a) Top graphs: Raw ECN (left) and EPN (right) signals of the first corrosion process of series 1, AISI304 exposed to an aqueous HCl solution at pH 1.0. Below: their decomposition into IMFs, with their residual component shown in the lowest graphs.

Figure 3 (b) Top graphs: Raw ECN (left) and EPN (right) signals of the second corrosion process of series 1, mild steel exposed to an aqueous 3 wt.% NaCl solution. Below: their decomposition into IMFs, with their residual component shown in the lowest graphs.
Figure 4 Top graphs: Raw ECN (left) and EPN (right) signals of the corrosion process of series 2, AISI304 exposed to an aqueous HCl solution at pH 1.9. Below: their decomposition into IMFs, with their residual component shown in the lowest graphs.
Figure 5 (a) Top graphs: Raw ECN (left) and EPN (right) signals of the first corrosion process of series 3, AISI304 exposed to an aqueous HCl solution at pH 3.0. Below: their decomposition into IMFs, with their residual component shown in the lowest graphs.
Figure 5 (b) Top graphs: Raw ECN (left) and EPN (right) signals of the second corrosion process of series 3, AISI304 exposed to an aqueous 3 wt.% NaCl solution. Below: their decomposition into IMFs, with their residual component shown in the lowest graphs.
4.2.2.2 Hilbert-Huang transform

In order to extract all instantaneous frequencies that describe the intrinsic modes of oscillation at a specific instant of time, the Hilbert transform is applied to each IMF detail component. For each IMF detail component, or time series $X_n(t)$, its Hilbert transform is defined as [23, 32, 37]:

$$Y_n(t) = \frac{1}{\pi} \int \frac{X_n(t')}{t-t'} dt'$$

(3)

The time series $X_n(t)$ and its Hilbert transform $Y_n(t)$ are a complex conjugate pair for which the complex function $Z_n(t) = X_n(t) + jY_n(t)$ is analytical. For each IMF detail component, $Z_n(t)$ can be represented in polar form:

$$Z_n(t) = a_n(t)e^{j\theta_n(t)}$$

(4)

where $a_n(t)$ is the amplitude and $\theta_n(t)$ the phase of $Z$. These, together with the instantaneous frequency $\omega_n(t)$, can be calculated through [23, 24, 32, 37]:

$$a_n(t) = \sqrt{X_n^2(t) + Y_n^2(t)}$$

(5)

$$\theta_n(t) = \arctan(Y_n(t)/X_n(t))$$

(6)

$$\omega_n(t) = d\theta_n(t)/dt$$

(7)

Application of the Hilbert transform to all ($N$) IMF detail components results in the expression of the original signal as the real part (Re) of the complex expansion $Z(t)$ [23, 32]:

$$X(t) = \text{Re} \sum_{n=1}^{N} a_n(t)e^{j\int_{t_0}^{t} \omega_n(t) dt}$$

(8)
Unlike the constant amplitude and frequency in Fourier analysis, the variable amplitude \( a_n(t) \) and the instantaneous frequency \( \omega_n(t) \) allow the analysis of non-stationary data \([23, 24, 37]\). \( a_n(t) \) and \( \omega_n(t) \) can be displayed in a Hilbert spectrum \( H(\omega, t) \), where the amplitudes are displayed for all instantaneous frequencies at any moment in time. The time resolution has an accuracy only limited by the sampling frequency and the frequency resolution is user-defined. The highest extractable frequency is defined by \( 1/(\Delta t) \), with \( \Delta t \) the sampling interval and \( l = 5 \) the minimum number of data points to define an oscillation and to get a stable derivative (to determine \( \omega \) in equation (7)). For the Hilbert spectra presented in this work, this implies that the highest extractable frequency is 1 Hz. The lowest possible frequency is \( 1/T \), where \( T \) is the duration of the time series \([23, 37]\).

For an easier interpretation of information visible in each Hilbert spectrum, the relative amplitudes of each original EN signal as shown in the top graphs of Figures 3, 4 and 5 are also displayed at the back of each Hilbert spectrum. The colour bars displayed at the right indicate the relative amplitudes of the instantaneous frequencies in the spectra.

### 4.3 Results and discussion

The experimental results presented in this section are discussed based on the three different measurement series as depicted in Table 1, each presented and discussed in a separate subsection.

#### 4.3.1 General corrosion

General corrosion is essentially a (oxygen limited) diffusion-controlled process, mainly dominated by large timescale processes. In the ECN signal, general corrosion can be characterized by its smoothness, which is generated by the steady (oxygen limited) diffusion-controlled process \([16]\). This smoothness indicates a significantly large low-frequency contribution (i.e. presence of large timescale processes) or DC drift \([11, 16, 20]\).
4.3.1.1 Series 1: AISI 304 at pH 1.0 and mild steel in 3 wt.% NaCl

Figure 6 shows the Hilbert spectra of the ECN (a) and EPN (b) signal for the measurement on AISI304 starting immediately after exposure to an aqueous HCl solution at pH 1.0 for a period of 1000 s. The relative amplitudes of each original EN signal as shown in the top graphs of Figure 3a are also displayed at the back of each Hilbert spectrum. The actual amplitudes correspond with a dynamic range of approximately 1.2 μA (a) and 30 mV (b).

![Figure 6](image.png)

Figure 6 (a) Hilbert spectrum of the ECN signal of the measurement on AISI304 immediately after exposure to an aqueous HCl solution at pH 1.0 for a period of 1000 s

For a comparison, additional measurements were performed on a system known to exhibit general corrosion, i.e. mild steel in an aqueous 3 wt.% NaCl solution. The Hilbert spectra of the resulting ECN and EPN signal are given in Figure 7. Again the relative amplitudes of each original EN signal as shown in the top graphs of Figure 3b are also displayed at the back of each Hilbert spectrum. The actual amplitudes now correspond with a dynamic range of approximately 4 μA (a) and 5 mV (b).
Figure 6 (b) Hilbert spectrum of the EPN signal of the measurement on AISI304 immediately after exposure to an aqueous HCl solution at pH 1.0 for a period of 1000 s

Figure 7 (a) Hilbert spectrum of the ECN signal of the measurement on mild steel immediately after exposure to an aqueous 3 wt.% NaCl solution for a period of 1000 s
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Figure 7 (b) Hilbert spectrum of the EPN signal of the measurement on mild steel immediately after exposure to an aqueous 3 wt.% NaCl solution for a period of 1000 s

Although small fluctuations that were observed during the measurements are also present in the ECN and EPN signals, with the scale of the graph these are practically insignificant due to the large DC drift component present in the signals. The results are smooth ECN and EPN signals with a limited number of IMFs as compared to the EN signal obtained from localized corrosion discussed in the next section. In the case of the EPN signal for the measurement on AISI304 this effect is most apparent. The number of IMFs of this signal is smaller as compared to the EPN signal for the measurement on mild steel (see Figure 3) and the residual component describes almost the entire EPN signal. The corresponding Hilbert spectrum shown in Figure 6b shows the presence of low instantaneous frequencies (below $10^{-2}$ Hz) only in the first 200 s, after which practically all energy of the EPN signal is present in the residual component. More detailed research on the applicability of EMD to provide a reliable estimation of the DC drift present in EN data by means of the residual component is presented in chapter 3 [39].

For the duration of the experiments described here, the AISI304 exposed to the aggressive aqueous HCl solution at pH 1.0 suffers from general corrosion. This implies that this period of exposure is dominated by uniform dissolution of the oxide film on the stainless steel,
resulting in a complete breakdown of the passive layer. Gradually, the underlying metallic substrate, including some imperfections and inclusions, comes in direct contact with the electrolyte. In Figure 8a the result of this process is visible through a uniformly attacked surface and some darker spots with a diameter of up to 3 μm that are more severely attacked. These spots are shallow pits, with a maximum depth of approximately 1 μm or less (determined with an optical microscope). However, any limited pitting behaviour is not likely to be detected through the ECN signature in this case. Although the absence of the cathodic reaction may not be strictly necessary for measuring anodic ECN transients, the severely affected stability of the passive film and the resulting general corrosion behaviour involving the entire working electrode area are expected to dominate the ECN signal to a large extent [40].

The Hilbert spectra presented in Figures 6a and 7a show the presence of instantaneous frequencies only at the lowest frequency end of the spectrum, below 10^{-2} Hz, and negligible instantaneous amplitudes in the higher frequency region. This behaviour is typical for a (oxygen) diffusion-controlled process, mainly dominated by large timescale processes [16]. Therefore it could be explained that the low frequency components in the noise signal would dominate along the entire time axis.

Visual inspection of the electrode surfaces of the mild steel electrodes after the measurement confirmed a uniformly attacked surface. In Figure 8 micrographs of the AISI304 (a) and mild steel (b) electrodes are provided. On both materials, the dark and bright areas are due to light reflected by surface features with different geometries, indicating a rough uniformly attacked surface.

Figure 8 Micrographs of the working electrode surfaces after immersion for a period of 1000 s of (a) AISI304 in an aqueous HCl solution at pH 1.0 and (b) mild steel in an aqueous 3 wt.% NaCl solution
4.3.2 Localized corrosion

The susceptibility of a metal to exhibit localized corrosion and to which extent, is largely determined by the presence and properties of a passive film. These properties include its chemical composition, structure, coherence and thickness [41]. For AISI304, ECN fluctuations are related to the formation of pits initiated as a consequence of pit nucleation processes. Initiated pits exist in a short metastable phase and subsequently either continue in this metastable phase and repassivate, or become stable and grow. It is therefore likely that, since a metastable stage precedes the stable stage, the mechanism of pit initiation is identical for stable and metastable pits [42].

Pits typically nucleate at electrochemically active sites: locations where inhomogeneities (nonmetallic inclusions like manganese sulphide or complex sulphide-oxide inclusions, or second phase precipitates) are present [11, 41, 43-49]. These inhomogeneities induce imperfections in the passive oxide film, facilitating the adsorption of aggressive anions through the passive film onto the metal surface and creating the onset of pitting corrosion [41]. Nucleated pits are hardly detectable until they reach the initiation stage [11, 43-46].

Pit initiation is reflected by the initial phase of the ECN and EPN transient [50]. This event is accompanied by the release of cations and the migration of anions to microdepressions in the metal surface, where hydrolysis forms a local aggressive environment. These processes are facilitated by the imperfections in the oxide film [41]. Therefore, pit initiation requires a site that both favours nucleation and forms a depression in the metal surface, which acts as a barrier to diffusion [47, 51, 52].

The size and shape of a depression plays an important role: a relatively deep and narrow morphology acts as a diffusion barrier and supports metastable activation of the pit site, whereas a shallower and wider morphology is less able to form this barrier and is therefore less likely to be activated into the metastable phase [47, 52, 53]. However, once initiated, wider metastable pits can grow at a higher current density [47, 51]. These wider pits therefore have a higher probability of reaching stable pit growth [47]. The concentration of chloride (or other halogen anions, but chloride is considered the most important) also influences this process: sufficient chloride ions should be able to diffuse from the bulk electrolyte into the pit, otherwise repassivation will occur [41, 52]. The effect of chloride ions to prevent oxide film formation is threefold: they can form complexes with cations and
hydroxides, increase activity of hydrogen ions in the pit interior and form a salt layer at the bottom of the pit at low pH, which is considered the most important [41]. In the metastable phase, pits grow for a period of 4-32 s through a mechanism by undercutting the passive film [22, 42]. This phase is associated with the increasing intensity (negative or positive) of the ECN transient [50]. The metastable growth process is under diffusion control and is determined largely by the Ohmic resistance of the pit cover [42, 51]. This pit cover maintains the local aggressive environment inside the pit and should be sufficiently porous to allow electrolyte flow in and out and dissolution of metal ions out of the pit [42, 54]. The current inhibition through these pores generates a large Ohmic resistance and, since current density remains constant during the lifetime of a metastable pit, a drop in the potential [42, 50, 52]. If the pit cover is penetrated, the pit stops growing and repassivation takes place [42].

Repassivation of a metastable pit is reflected by the point where the current intensity reaches back to zero (i.e. the last part of the corresponding ECN transient) [50]. The repassivation process occurs fast, although the related regeneration of the passive film is a relatively slow process [42]. After repassivation of the passive film, a discharge of the interface capacity of the repassivated surface takes place. This corresponds to the last part of the EPN signal, where its intensity gradually decreases towards zero [50]. If the pit cover can sustain for a sufficiently long period, a metal salt film will precipitate on the surface and provided that this film can grow strong enough, the pit becomes stable [42, 54]. The frequency of occurrence of metastable pitting is considered to be inversely proportional to oxygen concentration. Furthermore, the number of sites available for metastable pit development is regarded to be independent of pH [52].

Figure 9 shows a schematic representation of the most important processes discussed here.
4.3.2.1 Series 2: AISI304 at pH 1.9

Figure 10 shows the Hilbert spectra for the measurement on AISI304 exposed to an aqueous HCl solution at pH 1.9 for a period of 1100 s. The corrosion process applied in this subsection generates an EN signal characterized by many transients. To emphasize the individual transients present in the data shown here, the first 100 s are used to reach a steady state for the EPN signal, after which the decomposition of the superimposed EPN fluctuations into their instantaneous frequencies can be more significant. The actual amplitudes of the original EN signals now correspond with a dynamic range of approximately 3 nA (a) and 30 mV (b). For this three-electrode configuration under open-circuit conditions, the direction of a specific ECN transient depends on which electrode undergoes the associated localized corrosion event.
Figure 10 (a) Hilbert spectrum of the ECN signal of the measurement on AISI304 exposed to an aqueous HCl solution at pH 1.9 for a period of 1100 s and started after an initial stabilization period of 100 s

Figure 10 (b) Hilbert spectrum of the EPN signal of the measurement on AISI304 exposed to an aqueous HCl solution at pH 1.9 for a period of 1100 s and started after an initial stabilization period of 100 s
The micrographs shown in Figure 11a and 11b indicate the existence of a large number of pits at the electrode surfaces after the experiment, without the irregular features of general attack as was the case for the exposure to HCl at pH 1.0 (series 1). The pit depths (determined with an optical microscope) are approximately 3-4 μm.

![Figure 11 Micrographs of the AISI304 working electrode surfaces after immersion for a period of 1100 s in an aqueous HCl solution at pH 1.9](image)

The ECN signal consists of many overlapping transients that reflect pit initiation, metastable growth and repassivation. The growth of stable pits was not observed. By increasing the pH from 1.0 (Figure 6a) to 1.9 (Figure 10a), the Hilbert spectrum of the ECN shows an increase of activity above $10^{-2}$ Hz along the entire measurement. This indicates the presence of a more stable passive oxide film [55]. As mentioned before, the susceptibility of a metal to exhibit localized corrosion and to which extent, is largely determined by the properties of the passive film. The passive film is more stable in this case as compared to the case of pH 1.0 and initiation, short metastable growth and repassivation of pits becomes visible. The relative contribution of instantaneous frequencies below $10^{-2}$ Hz (corresponding with large timescale processes) to the entire ECN signal of AISI304 has decreased in comparison to the exposure to HCl at pH 1.0, since the corrosion process becomes less diffusion-controlled [16].

Regarding a metastable pitting process, the last part of an EPN transient is characterized by relatively slow recovery of the potential after the occurrence of each transient (as visible in Figures 12a and 13a in the next subsection). It is argued that this represents discharge of the interface capacity of the repassivated surface. Repassivation of a metastable pit thus occurs prior to this and is reflected by the point where the current intensity reaches back to
zero (i.e. the last part of the corresponding ECN transient) [50]. This discharge process is rather slow and is therefore expected to generate increased low frequency components visible in the Hilbert spectrum of the EPN signal shown in Figure 10b in comparison with the Hilbert spectrum of the ECN signal shown in Figure 10a. The high number and overlapping character of the transients visible in the time domain make it difficult to determine this phenomenon visually. However, in this case the Hilbert spectrum of the EPN signal enables determination of this phenomenon.

The Hilbert spectra allow an accurate determination of the time instants at which individual corrosion events are most significant, which facilitates identification and characterization of these phenomena. Through conventional data analysis in the frequency domain, the frequency contribution of an individual corrosion event is unlikely to be detected in the 'bulk' signal. Despite the complex and highly fluctuating ECN signal, it is possible to identify individual events that might be associated with metastable pitting processes with their decomposition in instantaneous frequencies (e.g. the frequency contribution of the ECN fluctuation in Figure 10a at approximately $t = 670$ s). The Hilbert spectra thus provide an accurate resolution in time for these characteristics, instead of averaging this over the entire data set.

4.3.2.2 Series 3: AISI304 at pH 3.0 and in 3 wt.% NaCl

Figure 12 shows the Hilbert spectra for the measurement on AISI304 immediately after exposure to an aqueous HCl solution at pH 3.0 for a period of 1000 s. The actual amplitudes of the original EN signals now correspond with a dynamic range of approximately 7 nA (a) and 90 mV (b).

For comparison, additional measurements were performed on a different system exhibiting localized corrosion, i.e. AISI304 immediately after exposure to an aqueous 3 wt.% NaCl solution for a period of 1000 s. The Hilbert spectra of the resulting ECN and EPN signal are shown in Figure 13. The actual amplitudes of the original EN signals now correspond with a dynamic range of approximately 12 nA (a) and 45 mV (b).
Figure 12 (a) Hilbert spectrum of the ECN signal of the measurement on AISI304 immediately after exposure to an aqueous HCl solution at pH 3.0 for a period of 1000 s.

Figure 12 (b) Hilbert spectrum of the EPN signal of the measurement on AISI304 immediately after exposure to an aqueous HCl solution at pH 3.0 for a period of 1000 s.
Figure 13 (a) Hilbert spectrum of the ECN signal of the measurement on AISI304 immediately after exposure to an aqueous 3 wt.% NaCl solution for a period of 1000 s

Figure 13 (b) Hilbert spectrum of the EPN signal of the measurement on AISI304 immediately after exposure to an aqueous 3 wt.% NaCl solution for a period of 1000 s
In Figure 14 micrographs of the AISI304 electrodes in an aqueous HCl solution at pH 3.0 (a) and in an aqueous 3 wt.% NaCl solution (b) are presented.

In the measured ECN signals in Figures 12a and 13a, the transients can be clearly distinguished in the mostly smooth and straight signals. Their individual frequency decomposition is visible in the Hilbert spectra, with an accurate time resolution. The Hilbert spectrum in Figure 12a shows a further decrease in the relative contribution of instantaneous frequencies below $10^{-2}$ Hz during the entire measurement as compared to the Hilbert spectrum shown in Figure 10a. The reason for this can be explained as a further increase of stability of the passive oxide film at this pH. Therefore the influence of the oxygen diffusion on the corrosion process has again decreased [16]. This further increase of stability of the passive film can be derived from the decrease of the number of individual metastable pitting events as compared to the experiment at pH 1.9 and from an increase of the relative contribution of instantaneous frequencies between $10^{-2}$ and $10^{-1}$ Hz [55]. If at some time instance a larger low frequency contribution in the Hilbert spectrum of the ECN signal occurs, this can be clearly distinguished in the spectrum. This is observed for the transients visible in Figure 12a at approximately $t = 200$ s and $t = 900$ s. This could be generated by a longer phase of metastable pit growth, regarding the shape of the corresponding ECN transients, however this could not be verified [50].

Analogous to the localized corrosion processes shown in Figure 12a, Figure 13a also shows a high relative contribution of instantaneous frequencies between $10^{-2}$ and $10^{-1}$ Hz at the occurrence of localized corrosion processes with an accurate localization in time. A
metastable behaviour of pit initiation, short growth and repassivation is visible and the metastable pitting phenomena are well distinguishable from each other. Microscopic inspection of the electrodes afterwards confirmed this: fewer pits were observed compared to the measurement of series 2 and furthermore the pit depths were in the order of 1-2 μm (determined with an optical microscope). Combined with the smoothness of the electrode surface, this is an indication of fast repassivation. In addition, there is a good agreement between the Hilbert spectra shown in Figures 12 and 13: for both measurements the dominant instantaneous frequencies are between $10^{-2}$ and $10^{-1}$ Hz. For the experiment on AISI304 in 3 wt.% NaCl, microscopic inspection of the electrodes afterwards revealed comparable electrode surfaces, however the pit depths were in the order of 3-4 μm here. This increased pitting activity is in agreement with the larger dynamic range of the ECN in this case.

In Figures 12b and 13b a relatively slow recovery of the potential after the occurrence of each transient is noted. Analogous to the arguments given in the previous subsection (however easier to detect visually in this case), this is considered to represent the discharge of the interface capacity of the repassivated surface \[50\]. This discharge process is rather slow and contributes to increased low frequency components in the EPN signals with respect to the Hilbert spectra of the ECN signals shown in Figures 12a and 13a.

Summarized, in the present work, the Hilbert spectra have provided detailed information on corrosion phenomena from EN data for different corrosion processes. This resulted in characteristic ‘fingerprints’ of instantaneous frequencies in the Hilbert spectrum at the occurrence of transients generated by localized corrosion processes. The exact determination of all aspects of this ability still demands further research.

### 4.4 Conclusions

In this chapter the Hilbert spectrum, calculated through the HHT, is introduced for the analysis of EN signals under open-circuit conditions in corrosion studies. Instead of separating the frequency spectrum in pre-determined scales, necessary in the already well-established wavelet transform, here a detailed decomposition of the original ECN and EPN data is provided in instantaneous frequencies. The contribution of these individual instantaneous frequencies can be clearly located in time, allowing a high level of accuracy in
the frequency domain at each time instant, which could not be accomplished before in the analysis of EN data. Preliminary results obtained from three different series of corrosion processes provide a detailed determination of the instantaneous frequency composition of individual corrosion phenomena observed in the EN signals at any given moment in time. This accurate fingerprinting capability enables improved exploitation of the potential of ENM to identify and distinguish between different corrosion mechanisms, while maintaining the unique non-disturbing nature of this technique.
Chapter 4

4.5 References

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


Chapter 4

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


Chapter 4

Transient analysis through Hilbert spectra of electrochemical noise signals for the identification of localized corrosion of stainless steel

Abstract

Hilbert spectra allow identification of instantaneous frequencies that are attributed to specific corrosion mechanisms in electrochemical noise (EN) data. The present work proposes to identify and analyze areas of interest in Hilbert spectra, which enables to obtain valuable frequency information from EN signals. Experiments were performed on stainless steel AISI304 exposed to aqueous HCl solutions at different pH values resulting in either distinct general or localized attack. Results indicate that application of the proposed transient analysis to Hilbert spectra provides a significantly improved determination of the frequency characteristics of the EN signals compared to time-frequency data analysis without transient analysis.

This chapter is based on:

Chapter 5

5.1 Introduction

Transients present in electrochemical noise (EN) signals usually reflect the occurrence of localized corrosion processes. To enable identification of the frequency contribution of transients, their specific signatures, or ‘fingerprints’ that can provide information on the nature of the related corrosion process should be located accurately in time. In this chapter, a procedure for the identification of transients is proposed, based on the Hilbert-Huang transform (HHT). The effectiveness of transient analysis to discriminate between different localized corrosion processes is investigated and compared with the discrimination ability of data analysis using discrete wavelet transform (DWT), without transient analysis.

As was shown in chapter 3 [1], DWT describes the EN signal at several timescales or resolutions in so-called crystals [2-10]. The relative energy contributed by each crystal can be visualized in an energy distribution plot (EDP) [3-11]. Such a plot provides mechanistic information about physico-chemical processes: the position of the maximum relative energy in the EDP indicates the dominant process in certain corrosion events and its change can reflect the behaviour of the dominant corrosion process [4, 7-10, 12, 13]. Contrary to the empirical mode decomposition (EMD), the number of iteration steps (and therefore the number of detail crystals) is user defined.

Chapter 4 discussed an interesting alternative approach: the application of the HHT, as was first proposed by Huang et al. [14], for the analysis of EN signals [15]. This transform is based on the assumption that any nonlinear and non-stationary signal consists of multiple characteristic scales, or intrinsic modes of oscillation, each superimposed on another. These so-called intrinsic mode functions (IMFs) are based on the local properties of the signal and can be identified empirically by their characteristic time scales through EMD. Unlike the wavelet transform, where wavelet crystals describe a signal on the basis of a pre-defined wavelet and using function orthogonality, here the basis is derived directly from the data itself, making the EMD flexible and adaptive [14, 16-20]. Chapter 4 showed that Hilbert spectra enable a detailed determination of the instantaneous frequency composition of individual corrosion phenomena observed in the electrochemical current noise (ECN) and electrochemical potential noise (EPN) signals at any given moment in time [15]. This accurate fingerprinting capability enabled to identify and distinguish between different corrosion mechanisms. Regarding the interpretation of EN signals, this ability makes the HHT a valuable data analysis technique.
Hilbert spectra can exhibit a significant low-frequency contribution outside the areas that are representative for transients, and therefore outside the areas that are considered to have a physico-chemical origin. Such artefacts can be considered as side effects of the sifting process. The sifting process is described in detail in chapter 4 [15]. Ideally, the sifting process must satisfy two seemingly incompatible requirements to extract the IMFs. First, an exact determination of instantaneous frequencies through the subsequent HHT requires the elimination of riding waves and a symmetrical wave profile of the IMFs. For this purpose a large number of sifting iterations is preferential [17]. On the contrary, too many sifting iterations will reduce the local variations of the fluctuations under study, thereby decreasing their physical meaning. The stopping criterion for the sifting iterations thus reflects a compromise between these two opposite requirements [17].

The present work aims to illustrate that Hilbert spectra allow the identification of only the instantaneous frequency contributions that are directly related to the occurring corrosion mechanisms. The artefacts discussed before will be shown to be largely neglected by this method. The main contribution of this work is the proposal of an advanced data analysis method examining only those areas of a Hilbert spectrum where these instantaneous frequencies are present. This yields increased discrimination ability between different corrosion mechanisms as compared to DWT. The advantages will be demonstrated using EN data from experiments of stainless steel AISI304 exposed to aqueous HCl solutions at different pH values. These experiments will generate distinctly different corrosion morphologies, ranging from general to local attack.

5.2 Experimental

5.2.1 Materials and experimental set-up

The measurements were performed in a conventional three-electrode configuration under open-circuit conditions, requiring two nominally identical stainless steel AISI304 working electrodes. The measurement setup and electrochemical cell configuration is identical to the one described in chapter 4 [15]. 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 cm² of
Chapter 5

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: 0.207 V vs. Standard Hydrogen Electrode). The electrolytes used were aqueous HCl solutions made from demineralized water and reagent, at three different concentrations: 0.1, 0.01 and 0.001 M, corresponding with pH 1.0, 1.9 and 3.0, respectively. All solutions were open to air. The duration of each exposure to the electrolyte was 1000 s, equal to the duration of each measurement. 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 MEF4 M optical microscope with maximum magnification of 1000x. At each electrolyte concentration 9 EN measurements were performed.

Current and potential signals were recorded using a Compactstat from Ivium Technologies working as zero resistance ammeter (ZRA) and potentiometer, controlled by a Windows-based PC running dedicated software. The sampling frequency used for the measurements described in this work was 5 Hz. A low-pass filter of 10 Hz was applied during data recording. Instrumental noise generated by the measuring equipment is considered the only significant unwanted noise source between the Nyquist frequency (2.5 Hz here) and the cutoff frequency of the low-pass filter (10 Hz) that could cause aliasing and was therefore closely verified. This is described in more detail in chapter 4 [15]. All other noise sources are expected to be well above the cutoff frequency of the low-pass filter. The maximum range of the ZRA was set at 10 μA for the measurements in HCl at pH 1.0 and 100 nA for the other measurements, and the maximum range of the potentiometer was set at 100 mV. In order to enhance the resolution of the measured EPN signal, the initial potential is measured and subsequently electronically adjusted to zero. From then, the cell potential is measured relative to this new reference potential. This allows a narrower potential range setting of 100 mV. The increased resolution is useful in the case of transient analysis as performed in this work, where instantaneous frequencies in the mid to high frequency range can be important for the characterization of transients [15].

The data were processed using Matlab from MathWorks. The EMD and the HHT were calculated using a publicly available Matlab procedure from Rilling et al. [21, 22].
5.2.2 Transient analysis based on Hilbert spectra

The principle of transient analysis as proposed in this work consists of two steps: identification and selection of the areas of interest in the Hilbert spectra and the subsequent analysis of the instantaneous frequencies present in these areas.

5.2.2.1 Identification and selection of areas of interest

The first step is to identify each transient in the ECN signal in order to determine its corresponding area with instantaneous frequencies in the Hilbert spectrum. To locate transient boundaries, an understanding of the different processes reflected by the transients is important. The precise definition of the boundaries may depend on the specific features of the process and the associated transient. The procedure will be demonstrated here for a typical corrosion process as investigated in this work. Figure 1 shows an actual ECN and EPN transient in grey, extracted from the EN signals of AISI304 exposed to an aqueous HCl solution at pH 3.0, together with the adopted procedure for transient identification and selection, that will be explained in more detail at the end of this subsection.

For the measurements carried out in this electrolyte, only metastable pitting processes were observed. Four phases can be distinguished in the transients depicted:

1. Pit initiation
2. Metastable growth
3. Pit repassivation
4. Regeneration of the passive film and discharge of the interfacial capacity of the repassivated surface

Note that the difference between the start and end point of the potential transient (indicated with the up-down arrow) is due to a gradual drift of the EPN signal during the measurement.
Figure 1 View of ECN (top) and EPN (bottom) transients of the EN signals of AISI304 exposed to an aqueous HCl solution at pH 3.0, with their characteristic phases and a schematic representation of the procedure of identification and selection of a transient.

Each couple of ECN and EPN transients represents all processes related to the lifetime of a specific metastable pit in stainless steel, from pit initiation to the final regeneration of the passive film and discharge of the interfacial capacity of the repassivated surface.

Pit initiation is indicated as the first phase of an ECN or EPN transient as the onset of metastable growth [23]. After initiation, metastable pits grow through a mechanism of...
undercutting the passive film [24]. Metastable growth is predominantly under diffusion control and is mainly determined by the Ohmic resistance of the perforated pit cover; i.e. its ability to withstand diffusion [24-26]. This phase is associated with the increasing magnitude of the ECN and EPN transient [23, 24, 27]. Repassivation takes place if the pit cover is penetrated and the pit stops growing [24]. This relatively fast process corresponds to the point where the magnitude of the ECN transient becomes zero again [23, 27]. Subsequently, a discharge of the interfacial capacity of the repassivated surface takes place and the potential recovers, reflected by the gradual decrease of the amplitude of the EPN transient towards zero [23, 28].

The area of the Hilbert spectrum associated to the duration of the ECN and EPN transient couple can be regarded as representative for the processes associated with the respective metastable pit. In the case of the measurements described in this work, the first step here is to define approximate transient locations as the ranges where the absolute magnitudes of the ECN as well as the EPN signal are larger than the amplitudes of these signals after application of a moving average smoothing filter with a span of 100 data points. The left side of Figure 1 represents this procedure. The ECN and EPN transients after application of the moving average smoothing filter are shown in black. This results in a set of ranges of the EN signals, equal to the number of transients present. Second, for each of these ranges the initiation and end of the associated metastable pit event is located separately. Initiation of each metastable pit event is detected as the intersection of the absolute magnitude of the ECN signal with the amplitude of the signal after application of the moving average smoothing filter. This point is defined as the starting point of the area of interest in the Hilbert spectrum. The final part of each area of interest is detected as the first location where the first derivative of 5 consecutive data points of the EPN transient crosses zero, or is equal to zero. This is schematically shown at the right-hand side of Figure 1. As such, $N$ metastable pit events generate $N$ areas of interest in a Hilbert spectrum.

In the absence of transients, e.g. in the case of a smooth ECN signal resulting from a general corrosion process, no areas of interest are defined and the entire Hilbert spectrum is analyzed in the next step.
5.2.2.2 Analysis of areas of interest

After discriminating the areas of interest in the Hilbert spectra, their decomposition in instantaneous frequencies must be analyzed in detail. To achieve this, first the amplitudes of the instantaneous frequencies present in these areas are normalized. The reason for this is that in some cases, artefacts (as explained in the introduction) are associated with (low) instantaneous frequencies with considerable high amplitudes, as compared to the amplitudes of instantaneous frequencies present within the areas of interest. The ability to discard artefacts present outside the areas of interest together with normalization of instantaneous frequencies inside these areas thus yields a good identification of only the frequency information of interest, while maintaining their amplitude proportions.

After discarding artefacts and normalization of the amplitudes in the Hilbert spectrum, the maxima present in all areas for each instantaneous frequency are averaged. The reason for averaging is that the amplitudes of instantaneous frequencies of some (large) transients dominate over those of others. The combination of normalization and averaging provides the required insensitivity for one or two dominant transients.

It is useful to note that the procedure of transient analysis as proposed in this work (without the final averaging) also allows investigation of the instantaneous frequency characteristics of one specific transient of interest. This ability can proof valuable in the case of in situ corrosion monitoring purposes, where the concern is mainly on the potential presence of a single pit with a large penetration. Application of the proposed transient analysis procedure to compare the instantaneous frequency characteristics of this single event with those of other localized processes present in the EN signals could yield an improved understanding of the mechanistic differences between individual localized corrosion events.

5.3 Results and discussion

In this section, first the characteristics of the corrosion processes will be discussed, after which an example of the application of transient analysis is provided. The experimental series involve AISI304 exhibiting general corrosion (pH 1.0) and localized corrosion (pH 1.9 and 3.0) with different corrosion behaviour in each series. Finally, the performance of the
data analysis procedures is investigated based on their ability to identify and discriminate between different corrosion mechanisms.

5.3.1 Corrosion morphology

In the case of AISI304 exposed to HCl solution at three different concentrations, for each concentration different corrosion behaviour is observed. The measurements showed good reproducibility, no significant mechanistic changes were observed after repeating the measurements multiple times.

Figure 2 shows examples of micrographs of the AISI304 working electrodes after exposure to HCl at pH 1.0 (a), 1.9 (b) and 3.0 (c) for 1000 s. In Figure 3 example ECN and EPN signals are provided for these experiments.

The example micrograph shown in Figure 2a is typical for a general corrosion process. It visually confirms a relatively uniformly attacked surface and some darker spots with a diameter of up to 3 μm that are more severely attacked. These spots are shallow pits, with a maximum depth of approximately 1 μm or less (determined with an optical microscope).

For AISI304 in the active state, transients are not expected to be significant [29]. The current record shown in Figure 3a is characterized by its smoothness, which is generated by the steady diffusion-controlled process [5]. In the absence of high-frequency transients, this smoothness indicates a significantly large low-frequency contribution (i.e. presence of large timescale processes) or direct current drift [5, 8, 28, 30].
Increasing the pH from 1.0 to 1.9 had a large effect on the corrosion characteristics of the AISI304 working electrodes, as is indicated by Figure 2b, which shows an example of this. The micrograph indicates the existence of a large number of pits at the working electrode surface after the experiment, without the irregular features of general attack as was the case in the previous series. The pit depths (determined with an optical microscope) are approximately 3-4 μm.
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Without forming stable pits within the duration of each experiment, the large number of metastable pits generated transients in the ECN and EPN signals shown in Figure 3b, many of them existing within the timeframe of others and as a result appearing partly superimposed on each other in the ECN and EPN signals.

The example micrograph provided in Figure 2c indicates a smooth working electrode surface with a smaller number of pits after 1000 s exposure to HCl solution at pH 3.0 than in the case of Figure 2b (pH 1.9). Relating the exact amount of observed pits to the amount of transients present in the ECN or EPN signal during a single measurement at pH 3.0 is hindered, because pits sometimes become difficult to observe due to the presence of their pit cap, which forms after repassivation. The pit depths were in the order of 1-2 μm (determined with an optical microscope). In the measured ECN and EPN signals, the transients can be clearly distinguished as shown in the example signals provided in Figure 3c. A metastable behaviour of pit initiation, limited growth and repassivation is visible and the metastable pitting phenomena are well distinguishable from each other.
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5.3.2 Application of transient analysis

The procedure of identification, selection and analysis of areas of interest is illustrated by using an example ECN signal after exposure of AISI304 to an aqueous HCl solution at pH 3.0 for a duration of 1000 s.

First the wavelet and empirical mode decomposition of the ECN and EPN signals is provided in Figures 4a and 4b. Figure 4a shows an eight-level wavelet decomposition of the signals based on a Daubechies 4 wavelet and Figure 4b shows their EMD. The original ECN and EPN signals are displayed at the top. Note that to enhance the resolution of the measured EPN signal, the initial potential was measured and subsequently electronically adjusted to zero. From then, the cell potential is measured relative to this new reference potential. This allows a narrower potential range setting of 100 mV.

Figure 4 (a) Decomposition of an original ECN and EPN signal of AISI304, exposed to an aqueous HCl solution at pH 3.0 for a duration of 1000 s, into their respective detail and smooth crystals.
Figure 4 (b) Decomposition of an original ECN and EPN signal of AISI304, exposed to an aqueous HCl solution at pH 3.0 for a duration of 1000 s, into their respective detail and residual components.

Figure 5 shows the Hilbert spectrum of the ECN (a) and EPN (b) signal obtained from this experiment. The original ECN and EPN signals are now displayed at the back of the Hilbert spectra with their relative amplitudes.

In the Hilbert spectra shown in Figure 5 multiple transients are visible, together with their decomposition in instantaneous frequencies, all with a clear localization in time. In Figure 5a, a large low-frequency contribution at approximately $t = 300$ s can be observed. It is clear that this low-frequency information is located outside the area that is representative for the large transient starting just before $t = 350$ s. This is considered to be an example of possible artefacts arising in Hilbert spectra as explained in the introduction.
Figure 5 (a) Hilbert spectrum of the ECN signal of AISI304 exposed to an aqueous HCl solution at pH 3.0 for a duration of 1000 s

Figure 5 (b) Hilbert spectrum of the EPN signal of AISI304 exposed to an aqueous HCl solution at pH 3.0 for a duration of 1000 s
The Hilbert spectra of the EPN signals all show similar frequency characteristics, involving a relatively large low-frequency (below $10^{-2}$ Hz) part and a rapid decrease towards the higher parts of the Hilbert spectra. According to Figure 1, the shape of an EPN transient obtained from a metastable pitting process of AISI304 is determined largely by the discharge of the interfacial capacity of the repassivated surface. This is typically a large timescale phenomenon resulting in a gradually decreasing magnitude of the EPN transient after each moment of repassivation. Whereas repassivation is well distinguishable in the Hilbert spectrum of an ECN signal through clearly detectable higher frequency components (between $10^{-2}$ and $10^{-1}$ Hz), the subsequent discharge of the interfacial capacity of the repassivated surface has a substantial influence on the Hilbert spectra of the EPN signal. The example Hilbert spectrum provided in Figure 5b visualizes this: the intrinsic frequencies above approximately $10^{-2}$ Hz are small compared to the low-frequency content. Moreover, the effect of a dominating frequency contribution of one or two transients with respect to others can be observed.

The slow process of discharge of the repassivated surface takes place within the timeframe of each transient, resulting in considerable contribution of low instantaneous frequencies in each area of interest of the Hilbert spectra, for all investigated corrosion mechanisms. It is recognized that this will prevail over any low-frequency artefacts present outside the timeframes of transients. Because of this and because Hilbert spectra of the ECN signals are not affected by the capacitive discharge processes, in this work only ECN signals are investigated. These are shown to provide a good discrimination between the different corrosion processes investigated here and to reflect the rapid metastable pitting processes properly.

In order to compare the frequency information from Hilbert spectra directly to that of EDPs as a reference, in this work a two-dimensional representation of the relative contributions of instantaneous frequencies in the spectrum is used. This may be best imagined as compacting the 3D spectrum into a 2D plot by removing the time axis, which allows presentation of frequency information from multiple Hilbert spectra in one plot in the next subsection.

For the example Hilbert spectrum of the ECN signal provided in Figure 5a the two-dimensional representations of the instantaneous frequencies, with and without transient analysis, as well as the EDP, are provided in Figure 6. In Figure 6a, for series 1 each data
point represents the average of the maxima present in all areas of interest for the respective instantaneous frequency. Series 2 shows the maxima of the instantaneous frequencies present in the entire Hilbert spectrum, including the spectrum areas between the areas of interest.

Figure 6 (a) Two-dimensional representation of the Hilbert spectrum shown in Figure 5a after transient analysis of the ECN signal (1) and without transient analysis (2)

Figure 6b shows the EDP of the entire signal. The contribution of the smooth S8 crystal is subtracted from the total signal energy.

For a measurement of AISI304 exposed to HCl solution at pH 3.0, no large low-frequency contribution to the ECN signal is expected (as will be explained in section 5.3.3). However, series 2 in Figure 6a indicates the presence of a substantial low-frequency (around $10^{-2}$ Hz and lower) contribution to the overall signal. The reason for this can be found in the presence of low-frequency artefacts in this case. This indicates the advantage of the ability to ignore artefacts in the spectrum in the case of series 1 in Figure 6a.

In addition, series 2 in Figure 6a is mainly dominated by the contribution of instantaneous frequencies of the large transient starting just before $t = 350$ s, visible in Figure 5a.
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![Bar chart showing relative energy contribution of detail crystals](chart.png)

Figure 6 (b) EDP of the ECN signal for the example measurement of AISI304 exposed to an aqueous HCl solution at pH 3.0 for a duration of 1000 s

The EDP displayed in Figure 6b also shows this effect: the relative energy contribution of detail crystals D7 and D8 is higher than expected for this measurement. In the case of a significant difference in magnitude between individual transients, the relative energy contribution of detail crystals in the EDP is indeed likely to be dominated by the largest transient(s); DWT only takes into account the entire signal and does not differentiate in its spectra between individual transients (i.e. there is no time resolution). Using wavelet transform, this problem of one or two transients dominating the spectrum is therefore difficult to solve. Using Hilbert spectra, this issue is avoided by making use of their ability to distinguish the instantaneous frequency contribution of individual transients.

Summarized, the possibility provided by a Hilbert spectrum to locate the contribution of instantaneous frequencies in time enables to differentiate between areas of the spectrum that are representative for the localized corrosion processes and areas that are not. The advantage of this ability is indicated here by the difference in low frequency contribution.
between series 1 in Figure 6a on the one hand and series 2 in Figure 6a and the EDP in Figure 6b on the other. For EMD, in Figure 4b part of the low frequency information can be regarded as artefacts from the perspective of transient analysis. Furthermore, both series 2 in Figure 6a as well as the EDP in Figure 6b are influenced largely by the transients with the highest amplitudes. Series 1 in Figure 6a indicates that if only instantaneous frequency information is taken into account that is located within areas of the Hilbert spectrum enclosed by the timeframes of the transients (and therefore can be regarded as representative for the corrosion process), this results in an improved accuracy of frequency information.

5.3.3 Frequency information

A discussion about the specific ability of Hilbert spectra to provide information on the corrosion characteristics of AISI304 exposed to an aqueous HCl solution at pH 1.0, 1.9 and 3.0 was reported in chapter 4 [15]. This subsection discusses the comparison between instantaneous frequency information provided by Hilbert spectra after transient analysis and without transient analysis, based on these three different measurement series. In addition, these findings will be compared with results from mechanistic information obtained from EDPs.

Figure 7a shows a two-dimensional representation of the instantaneous frequency information in Hilbert spectra after transient analysis, each time for the ECN signals of three measurements at pH 1.0, 1.9 and 3.0, respectively. Each data point represents the average of the maxima present in all areas of interest for the respective instantaneous frequency. Figure 7b shows two-dimensional representations of the instantaneous frequency information in Hilbert spectra of the same measurements without transient analysis. Here the data points indicate the maxima of the instantaneous frequencies present in the entire Hilbert spectra. So in that case the transients have not been discriminated. Figure 7c represents the EDPs for these signals, also each time for the entire signal. The contribution of the smooth S8 crystal is each time discounted from the total signal energy.
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Figure 7 (a) Two-dimensional representations of the Hilbert spectra after transient analysis of the ECN signals for three consecutive measurements of AISI304 exposed to an aqueous HCl solution at pH 1.0, 1.9 and 3.0 for 1000 s

Figure 7 (b) Two-dimensional representations of the Hilbert spectra without transient analysis of the ECN signals for three consecutive measurements of AISI304 exposed to an aqueous HCl solution at pH 1.0, 1.9 and 3.0 for 1000 s
For the measurements at pH 1.0, the two-dimensional representations of the Hilbert spectra show the presence of instantaneous frequencies only at the lowest frequency end of the spectrum, mainly below $10^{-2}$ Hz, and negligible instantaneous amplitudes in the higher frequency region. This behaviour is typical for a diffusion-controlled process, to a large extent dominated by large timescale processes [5]. Low frequency components in the ECN signal would therefore form the largest part of the Hilbert spectra along the entire time axis and, as a result, also dominate their two-dimensional representations. The Hilbert spectra shown in Figure 7a and 7b are identical for these three measurements, since no transients were observed in the smooth original ECN signals. For this condition (pH 1.0), there is good correspondence between the information obtained from the Hilbert spectra shown in Figures 7a and 7b and that obtained from the EDPs shown in Figure 7c. For the latter, the energy from the ECN signals is mainly located in detail crystal D8 and decreases rapidly towards shorter timescales.

By increasing the pH from 1.0 to 1.9, the Hilbert spectra of the ECN signals show an increase of activity at higher frequencies, above $10^{-2}$ Hz, which indicates the presence of a more stable passive oxide film [30]. Therefore initiation, metastable growth and repassivation of pits become visible. The relative contribution of instantaneous frequencies
below \(10^{-2}\) Hz (corresponding with large timescale processes) to the entire ECN signal of AISI304 has decreased in comparison to the exposure to HCl at pH 1.0, since the corrosion process is now less diffusion-controlled [5].

The two-dimensional representations of the instantaneous frequency information from the Hilbert spectra after transient analysis shown in Figure 7a provide well-defined frequency decompositions of the ECN signals. These decompositions correspond with the expected frequency characteristics of the corrosion processes investigated here. The large number of transients present in each EN signal yields superimposing of transients, which makes the estimation of the instantaneous frequency contribution of individual superimposed transients less accurate. However, this inaccuracy is compensated by the large total number of transients, since the superimposing (or overlap) occurs each time at different locations. In Figure 7b, a large peak can be observed around \(2 \times 10^{-1}\) Hz in the two-dimensional representation of a Hilbert spectrum indicated with the round markers (the third series). This peak is not present after transient analysis, as shown in Figure 7a, where the three two-dimensional representations of the Hilbert spectra all show similar frequency characteristics.

In the EDP shown in Figure 7c, this (third) measurement shows a larger relative energy contribution of detail crystal D6, as compared to the other two measurements presented. The reason for this difference can be explained by the averaging effect of transient analysis regarding the instantaneous frequency contribution of a transient with different frequency characteristics. Exceptional transients therefore have a limited effect on the final result. The two-dimensional representations of the Hilbert spectra without transient analysis and the EDPs do not average these differences, but are rather influenced predominantly by the largest transients. These have a significant influence on the decomposition of the signals into their characteristic timescales for EMD and on the relative energy contribution of detail crystals of the signals for DWT. This becomes visible in Figures 7b and 7c as less consistency in frequency behaviour of nominally identical measurements. In addition, this frequency behaviour is not entirely in correspondence with the expected frequency characteristics for the observed corrosion mechanisms.

The two-dimensional representations of the Hilbert spectra for the measurements at pH 3.0, provided in Figures 7a and 7b, indicate a further decrease in the relative contribution of instantaneous frequencies below \(10^{-2}\) Hz as compared to the Hilbert spectra of the ECN of the previous series. This is also visible in the large timescale crystals of the EDPs shown in Figure 7c as a decrease in the relative energy contribution of detail crystal D8. Hindered by
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an increased stability of the passive oxide film, the influence of diffusion has decreased further [5]. In addition, a clear increase of the relative contribution of instantaneous frequencies between \(10^{-2}\) and \(10^{-1}\) Hz can be observed, also indicating a more stable passive film [30]. The increased relative energy contribution of medium timescale crystals D5, D6 and, to a less extent, D3 and D4, in the EDPs shown in Figure 7c corresponds with this observation.

Although the Hilbert spectra and EDPs show similar frequency characteristics of the corrosion phenomena, the ability of the Hilbert spectra to differentiate between individual transients proves to be an important advantage. The expected frequency characteristics of the measurements investigated here are best reflected by the two-dimensional representations of the instantaneous frequency information from the Hilbert spectra after transient analysis shown in Figure 7a. By considering only the instantaneous frequency contribution that can be regarded as representative for the localized corrosion processes (i.e. applying transient identification, selection and analysis) instead of investigating the entire signal, the measurements investigated in this work could be decomposed in distinct and well-recognizable instantaneous frequencies. This yields an improved discrimination between different corrosion characteristics as compared to the EDP.

5.4 Conclusions

The advantage of Hilbert spectra to locate the instantaneous frequency contribution of individual localized corrosion phenomena in time has been demonstrated in chapter 4 [15].

The present work has shown that investigation of two-dimensional representations of the specific areas of interest in these Hilbert spectra in most cases provided an accurate and robust description of the characteristic frequency properties of localized corrosion processes occurring during the experiments investigated here.

The method as proposed here for transient identification and selection of AISI304, used to select specific areas of the Hilbert spectra that can be regarded as representative for localized corrosion processes, enables to discriminate between valuable frequency information and probable artefacts. Application of the method was shown to yield an improved definition of frequency characteristics of different corrosion mechanisms.

Experiments were performed involving three well-known corrosion processes, exposing AISI304 in aqueous HCl solutions at different pH values. The frequency characteristics
visible in two-dimensional representations of the Hilbert spectra of the ECN signals after transient analysis proved to be more consistent with the theoretically expected frequency contribution of corrosion mechanisms than information obtained from a similar analysis without transient analysis. Comparison with the information obtained from EDPs based on wavelet transform confirmed the increased accuracy of the proposed transient analysis.
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5.5 References


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

Abstract

This study validates the ability of Hilbert spectra to investigate transients in an electrochemical noise (EN) 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 aluminium alloy 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 EN 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.

This chapter is based on:

6.1 Introduction

For the purpose of characterization of localized corrosion processes through electrochemical noise (EN) signals, many data analysis procedures exist of which the most common are fast Fourier transform (FFT) and discrete wavelet transform (DWT). However, FFT is strictly spoken not suitable for the analysis of EN, since corrosion processes are typically non-stationary, a property that is required for data analysis in the frequency domain. A separate procedure is necessary to remove its direct current drift component and to make an EN signal appear stationary. 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 [1-7].

DWT allows investigation of the distribution of the energy present in a (non-stationary) 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 transform (HHT) as was first proposed by Huang et al. [8]. This transform is based on the assumption that any signal consists of multiple characteristic scales, or intrinsic modes of oscillation, each superimposed on another. These so-called intrinsic mode functions (IMFs) are based on the local properties of the signal and can be identified empirically by their characteristic time scales through empirical mode decomposition (EMD). IMFs could be considered as a more general case of simple harmonic functions, however in close relation with the physico-chemical characteristics of the system under investigation due to the specific nature of EMD [9]. The basis of this technique is derived directly from the data itself, making the EMD flexible and adaptive [8, 10-14].

Transients present in EN signals usually reflect the occurrence of localized corrosion processes. The frequency contribution of individual transients yields specific signatures, or ‘fingerprints’, in the Hilbert spectrum. In chapter 5, 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 [15]. 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 [16]. In this work the principle of transient analysis applied to an aqueous corrosion inhibition process is therefore illustrated by the Ce-based inhibition of aluminium alloy 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 [17-21]. This can occur either at isolated particles or in clusters of multiple particles [20]. Two types of intermetallic particles can be distinguished, namely those containing Al-Cu(-Mg) or Al-Cu-Fe-Mn(-Si) [22-24]. The most numerous are Al$_2$CuMg (S-phase) particles, belonging to the first type [19, 25]. Except for the S-phase particles, intermetallic particles contain elements that are more noble than the Al matrix, therefore acting as cathodic sites [21, 26]. Corrosion inhibition of AA2024-T3 by the commonly used chromate-based inhibitors can be quite effective [27]. A suitable alternative to the commonly used Cr(VI) inhibitor can be e.g. to use lanthanide salts as an ecological substitute [28-34].

The process of inhibition is studied quite thoroughly by others [28-34]. 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 electrochemical current noise (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.
6.2 Experimental

6.2.1 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 in chapter 4 [35].

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. Standard Hydrogen Electrode). The electrolytes used were aqueous NaCl solutions made from demineralized water and analytical grade reagent. These were either used in that composition, or prepared with the addition of \(10^{-2}\) to \(10^{-5}\) M CeCl\(_3\)•7H\(_2\)O. The applied experimental procedure is shown in Figure 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 CeCl\(_3\)•7H\(_2\)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 MEF4 M 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 (ZRA) 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 chapter 4 [35]. The maximum range of the ZRA 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 μA. The maximum range of the potentiometer was set at 1 V. The data were processed using Matlab from MathWorks. The EMD and the HHT were calculated using a publicly available Matlab procedure from Rilling et al. [36, 37].

6.2.2 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 these areas are averaged, in order to obtain the frequency behaviour of the corrosion processes contributing to the overall ECN signal. In this way, good discrimination between different corrosion processes can be obtained and, moreover, any instantaneous frequency information present in between the areas of interest (where no transients occur) is neglected.

An example of the procedure of transient analysis for a corrosion inhibition process is provided in the next section.
6.3 Results and discussion

6.3.1 Visual observation

Figures 2a-e show micrographs in different magnifications of a measurement of AA2024-T3 exposed to $10^{-1}$ M NaCl with $10^{-2}$ M CeCl$_3$•7H$_2$O for a duration of 14500 s, where inhibition was observed within the duration of the measurement. Figures 2f-h show micrographs of the same sample area after the second measurement, now exposed to $10^{-1}$ M NaCl without the addition of CeCl$_3$•7H$_2$O for a duration of 14500 s, in conformity with the experimental procedure shown in Figure 1. The reason for this second exposure of the same sample is explained in the next subsection.

![Micrographs](image)

Figure 2 (a)-(e) Micrographs of an example measurement of AA2024-T3 exposed to $10^{-1}$ M NaCl with $10^{-2}$ M CeCl$_3$•7H$_2$O for a duration of 14500 s (f)-(h) Micrographs of the second measurement on the same sample, exposed to $10^{-1}$ M NaCl without the addition of CeCl$_3$•7H$_2$O for a duration of 14500 s
The inhibition process of a Ce-based inhibitor is explained through the increased pH near the cathodic sites [38, 39]. It is likely that a combination of 3-valent Ce (Ce(OH)₃) and 4-valent Ce (less soluble Ce(OH)₄ or CeO₂) precipitates at cathodic particles [38-40]. This new layer forms an increased barrier for (and thus inhibits) the cathodic processes [26, 30, 38, 39, 41, 42]. In addition, further dissolution of Al and Mg from these intermetallics is reduced [26]. Due to this inhibition the deposition of Ce also decreases, which implies a self-regulating inhibition process [42].

After the first measurement, including 10⁻² M CeCl₃•7H₂O, indeed no significant corrosion attack on the surface of the working electrode areas was observed. This is visible when comparing Figure 2a and 2b with 2c and 2d, and by the further enlargement shown in Figure 2e. After the second measurement however, involving only 10⁻¹ M NaCl, at the locations of the same intermetallic particles noticeable corrosion attack is visible. This is shown in Figure 2f-h: some intermetallic particles are partly dissolved. In most cases however, the aluminium matrix around intermetallic particles was attacked.

Figure 3 shows micrographs in different magnifications of a measurement of AA2024-T3 exposed to 10⁻¹ M NaCl for a duration of 14500 s, i.e. without being exposed to a certain concentration of CeCl₃•7H₂O beforehand.

In these micrographs a clear corrosion attack is visible at or near the locations of intermetallic particles. In many cases characteristic rings were observed around intermetallic particles. The two rings visible in Figure 3b are further enlarged in Figure 3c-e. These rings of corrosion product were also observed by Glenn et al. [43]. They indicate a stable pitting process involving clusters of intermetallic particles located near their centre [20, 42, 43]. Figure 4 shows a ring of corrosion product on one of the working electrode surfaces in a SEM micrograph.
Figure 3 Micrographs of an example measurement of AA2024-T3 exposed to $10^{-1}$ M NaCl for a duration of 14500 s

Figure 4 SEM micrograph of an example measurement of AA2024-T3 exposed to $10^{-1}$ M NaCl for a duration of 14500 s
6.3.2 EN signal analysis

In this subsection, the instantaneous frequency information in the Hilbert spectra, combined with visual observations of the ECN and electrochemical potential noise (EPN) signals and literature, will be applied to analyze the Ce inhibition process of AA2024-T3. For two concentrations, $10^{-2}$ and $10^{-3}$ M CeCl$_3$$\cdot$7H$_2$O, a decrease in the number of transients, the change in instantaneous frequency behaviour (both visible in the Hilbert spectra discussed later) and the absence of corrosion attack at the working electrode surfaces after exposure indicated that inhibition occurred within the timeframe of the measurements. This was however not the case for all measurements at these concentrations, since in some cases inhibition took more time to become effective. In addition, for the measurements that did show inhibition within this timeframe, the time until inhibition became effective varied between 2500 s and 12000 s. Differences in inhibition behaviour between otherwise identical measurements can be expected. Firstly, differences in surface preparation, that are inevitably present, however small, could affect the stability of the oxide film [39]. The location of active and passive sites at the AA2024-T3 surface is also assumed to change continuously over time [44]. Furthermore, intermetallic particles other than S-phase particles can vary in composition, which serves as a basis for their classification [19, 21]. $10^{-3}$ M CeCl$_3$$\cdot$7H$_2$O is considered as the minimum concentration for effective inhibition for the measurements presented in this work. However, it should be noted that the addition of $10^{-4}$ M CeCl$_3$$\cdot$7H$_2$O to a $10^{-1}$ M [39] or a $5 \times 10^{-2}$ M [42] NaCl background solution has also been proven to provide effective inhibition. In the latter case, inhibition only occurred after longer exposure times. Therefore, in the case of $10^{-4}$ M CeCl$_3$$\cdot$7H$_2$O, inhibition could still have occurred at a later stage. The concentration of $10^{-5}$ M CeCl$_3$$\cdot$7H$_2$O is considered to be too low to act as an effective corrosion inhibitor under these conditions.

The EN signals for inhibition can be divided into three different characteristic regions. These regions represent active corrosion with the onset of inhibition (region 1), inhibition becoming effective (region 2) and the inhibited state (region 3). Their specific features depend on the concentration of CeCl$_3$$\cdot$7H$_2$O in the electrolyte and in addition on whether or not inhibition occurred within the timeframe of the measurement. Figure 5a shows an ECN and EPN signal for the same measurement (in $10^{-1}$ M NaCl with $10^{-2}$ M CeCl$_3$$\cdot$7H$_2$O) as used for the micrographs of Figure 2. Figure 5b shows an ECN and EPN signal for a measurement in $10^{-1}$ M NaCl with $10^{-3}$ M CeCl$_3$$\cdot$7H$_2$O. The three regions are also indicated in these figures.
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Figure 5 (a) ECN and EPN signal including inhibition, for AA2024-T3 exposed to $10^{-1}$ M NaCl with $10^{-2}$ M CeCl$_3$•7H$_2$O for a duration of 14500 s

As a comparison, Figure 6 shows an ECN and EPN signal for the same measurement in $10^{-1}$ M NaCl as used for the micrographs of Figure 3, i.e. without being exposed to a certain concentration of CeCl$_3$•7H$_2$O beforehand.

The EN signals for the two concentrations of CeCl$_3$•7H$_2$O are quite similar. Region 1 is characterized by large fluctuations in the EPN signal, in many cases with amplitudes exceeding 200 mV. These large fluctuations in the EPN signal were observed for all measurements for concentrations containing up to $10^{-4}$ M CeCl$_3$•7H$_2$O. For the measurements in $10^{-5}$ M CeCl$_3$•7H$_2$O and those in $10^{-1}$ M NaCl only, these large fluctuations were absent. For the cases where inhibition was observed within the timespan of the measurement, these fluctuations were visible in region 1 only, otherwise these existed throughout the entire EPN signal.
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Figure 5 (b) ECN and EPN signal including inhibition, for AA2024-T3 exposed to $10^{-1}$ M NaCl with $10^{-3}$ M CeCl$_3$•7H$_2$O for a duration of 14500 s

Figure 6 ECN and EPN signal for AA2024-T3 exposed to $10^{-1}$ M NaCl for a duration of 14500 s
In order to verify the nature of these large fluctuations, for each measurement containing $10^{-2}$ to $10^{-5}$ M CeCl$_3$$\cdot$7H$_2$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. In those cases Ce (hydr)oxide was already deposited on the surface and no Ce ions were initially present in the solution.

As an example, Figure 7 shows the ECN and EPN signal for AA2024-T3 exposed to $10^{-1}$ M NaCl for a duration of 14500 s, after an initial period of exposure to $10^{-1}$ M NaCl with $10^{-2}$ M CeCl$_3$$\cdot$7H$_2$O for a duration of 14500 s, of which the EN signals were shown in Figure 5a.

Figure 7 ECN and EPN signal for AA2024-T3 exposed to $10^{-1}$ M NaCl for a duration of 14500 s after an initial exposure to $10^{-1}$ M NaCl with $10^{-2}$ M CeCl$_3$$\cdot$7H$_2$O for a duration of 14500 s

Figure 7, without CeCl$_3$$\cdot$7H$_2$O present in the electrolyte, shows large fluctuations together with one transient exceeding 200 mV in the EPN signal within the first 1000 s of exposure to NaCl. All second measurements that were performed in electrolytes containing only $10^{-1}$ M NaCl, after measurements in $10^{-2}$ to $10^{-4}$ M CeCl$_3$$\cdot$7H$_2$O beforehand, showed large EPN fluctuations within the first 1000 s, all with one or more fluctuations exceeding 200 mV. Subsequently, analogous to the EPN signal shown in Figure 7, they returned to a similar state as observed for the measurements without Ce (hydr)oxide deposited at the working
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electrodes or the presence of Ce ions in the electrolyte (as shown in Figure 6). The observations suggest that these large transients should be attributed to the presence of a not fully intact Ce (hydr)oxide film, leading to local breakdown [24].

During inhibition, the ECN and EPN signals become smoother and the EPN signal shows a negative drift. This is reflected by region 2 in Figures 5a and 5b. The negative drift of the EPN signal can be explained through the cathodic inhibition process of Ce [28, 34, 39, 42]. The final open corrosion potential (OCP) value of around -700 mV vs. Ag/AgCl is in correspondence with that observed in the work of others [34, 42], however at an earlier stage in this case. The reason for this can be the higher concentrations of CeCl$_3$•7H$_2$O ($10^{-2}$ and $10^{-3}$ M) than compared to the concentration used by García et al. ($10^{-4}$ M), which showed inhibition after longer exposure time.

The OCP values observed for the measurements in $10^{-1}$ M NaCl (around -520 mV vs. Ag/AgCl) were also in accordance with those observed for AA2024-T3 exposed to $5 \times 10^{-2}$ M NaCl in the work of García et al. [42] during the first 4 h.

The smoothing of the ECN signal is analogous to a decrease in current density, which is reported by García et al. [39] to occur during inhibition of AA2024-T3. Transients in the ECN and EPN signals, generated by localized corrosion processes, are expected to decrease in amplitude significantly. Note that the fluctuations do not disappear completely, which is visible in Figure 5a in the magnifications of the third region, between 12000 and 13000 s. The dynamic ranges of these fluctuations are however small, in the order of 1 nA for the ECN signal and 2 mV for the EPN signal. Finally, the drift in the EPN signal disappeared and the ECN signal was close to zero, i.e. both signals indicated that the system reached an inhibited state from the perspective of localized corrosion processes.

Prior to discussion of the Hilbert spectra, an example of the procedure of transient analysis as proposed in this work will be provided. Figure 8a shows the Hilbert spectrum for the ECN signal shown in Figure 5a, between 2000 s and 4000 s. Figure 8b shows the Hilbert spectrum for the ECN signal shown in Figure 5b, in the same time interval. Figure 9 shows the Hilbert spectrum for the ECN signal shown in Figure 6, again in the same time interval. The original ECN signals are depicted at the back of the figures with their relative amplitudes. The areas corresponding to the occurrence of transients are highlighted in yellow. Only these areas are analyzed in the Hilbert spectrum.
The Hilbert spectra shown in Figures 8a, 8b and 9 will be shown to allow detection of the ECN transients based on their instantaneous frequencies. The process of identification and selection of the areas of interest in the Hilbert spectra and the subsequent analysis of the instantaneous frequencies present in these areas is reported by the authors in chapter 5 [15]. However, in the present work, the first stage of selection of areas of interest is different than proposed earlier. Transients present in the ECN signals typically contain instantaneous frequencies in the range between $10^{-1}$ Hz and 1 Hz. This is illustrated in the top graphs of Figures 8a, 8b and 9, that show the sum of all instantaneous frequency amplitudes in the Hilbert spectra within this frequency range, after removal of the standard deviation and application of a moving average smoothing filter with a specified span of 9x the sampling frequency. Each peak thus corresponds to the instantaneous frequency contribution of a single transient.
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Figure 8 (b) Hilbert spectrum of the ECN signal of AA2024-T3 exposed to $10^{-1}$ M NaCl with $10^{-3}$ M CeCl$_3$•7H$_2$O, between 2000 s and 4000 s

Transient selection is based on the timespan covered by each individual peak (i.e. its maximum duration at the time axis). This provides an accurate determination of the areas of interest in the Hilbert spectra for the ECN signals as investigated here; for each transient, within its timespan, all instantaneous frequencies are analyzed. In Figures 8a, 8b and 9, the corresponding areas of interest in each Hilbert spectrum are shown in yellow.

To facilitate interpretation of the instantaneous frequency characteristics, their two-dimensional representations are used here. This is the two-dimensional view in the X-Z plane. Any change in instantaneous frequency behaviour (e.g. due to a gradual inhibition process) can be quantified by changes in these two-dimensional representations. Combined with the time-resolved information in the original Hilbert spectra, this is the true added value of the Hilbert spectrum analysis compared to the ECN/EPN signal analysis discussed before.
Now the procedure has been illustrated, the spectra of the different experiments will be discussed.

Figures 10a and 10b show the two-dimensional representations of the Hilbert spectra of the ECN signal visible in Figure 5a and 5b, respectively. Hilbert spectra were calculated for 5 successive segments of each 2000 s duration, from \( t = 0 \) to \( t = 8000 \) s (1) to \( t = 10000 \) s (5). For each data set a trend line is shown, calculated by a moving average smoothing filter with a specified span of 9 data points.
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Figure 10 (a) Two-dimensional representations of the Hilbert spectra of the ECN signal for AA2024-T3 exposed to $10^{-1}$ M NaCl with $10^{-2}$ M CeCl$_3$•7H$_2$O. Hilbert spectra were calculated for 5 successive segments of each 2000 s duration, from $t = 0$-2000 s (1) to $t = 8000$-10000 s (5).

Figure 10 (b) Two-dimensional representations of the Hilbert spectra of the ECN signal for AA2024-T3 exposed to $10^{-1}$ M NaCl with $10^{-3}$ M CeCl$_3$•7H$_2$O. Hilbert spectra were calculated for 5 successive segments of each 2000 s duration, from $t = 0$-2000 s (1) to $t = 8000$-10000 s (5).
As a comparison, Figure 11 shows the two-dimensional representations of the Hilbert spectra of the ECN signal visible in Figure 6, i.e. a measurement without exposure to CeCl$_3$$\cdot$7H$_2$O or presence of deposited Ce (hydr)oxide.

Initially, from 0 s to 4000 s (i.e. Hilbert spectrum 1 and 2) the Hilbert spectra are characterized by a large number of transients (visible in the first part of the Hilbert spectra shown in Figures 8a and 8b, and also visible in the Hilbert spectrum shown in Figure 9), for which the decomposition in instantaneous frequencies of the two ECN signals is comparable. In this period, a gradual increase in amplitude is visible with decreasing instantaneous frequencies. Below $5 \times 10^{-2}$ Hz, the contribution of instantaneous frequencies is considerably larger.

Pitting corrosion of AA2024-T3 initiates immediately after immersion in an aqueous NaCl electrolyte [25, 26]. This process consists of several different stages, including selective dissolution, i.e. dealloying, of the active elements Al and Mg from the constituent particles, amongst others resulting in more noble Cu-rich remnants with a porous structure, and the
formation of galvanic couples between the particles and the Al matrix [19, 21, 25, 26, 45]. The local cathodic reactions generate significant amounts of OH\(^{-}\) [45]. In a stagnant electrolyte this will lead to a local alkalization near the interface between the Al matrix and an S-phase particle [45]. The Al matrix around the Cu-rich particles starts to dissolve, referred to as trenching [26, 46]. This is visible in the micrographs shown in Figures 2f-h and 3. This may develop further and especially in the presence of clusters of S-phase particles and other intermetallic particles at the alloy surface into severe (stable) pitting [20]. The surface of the clusters of particles acts as a net cathode, moving the anode into the surface along the grain boundaries [20]. Corrosion product will deposit around the cluster areas in a ring-shaped morphology [20, 42]. These features are also present at the working electrode surfaces shown in Figures 3 and 4.

Although the ECN signal of AA2024-T3 exposed to 10\(^{-1}\) M NaCl shows a small decrease in overall amplitudes over the entire measurement (visible in Figure 6), the relative contribution of instantaneous frequencies remains more or less constant throughout the entire measurement, which is visible in Figure 11. The Hilbert spectra shown in Figures 10a and 10b, however, show an increase in relative contribution of high instantaneous frequencies between 4000 s and 6000 s (spectrum 3). Combined with a considerable decrease in the number of transients, this marks the transition between the active and the inhibited state. In order to visualize this, Figure 12a shows the Hilbert spectrum of the ECN signal shown in Figure 5a between 4000 s and 6000 s. Figure 12b shows the Hilbert spectrum of the ECN signal shown in Figure 5b, in the same time interval. Figure 13 shows the Hilbert spectrum of the ECN signal shown in Figure 6, again in the same time interval. The original ECN signals are depicted at the back of the figures with their relative amplitudes.

For the Hilbert spectra shown in Figures 12a and 12b, compared to their predecessors shown in Figures 8a and 8b, in this stage fewer transients occur. In the Hilbert spectrum shown in Figure 13, this decrease in the number of transients is not observed. Compared with the observation from its two-dimensional representation shown in Figure 11, i.e. that the decomposition in instantaneous frequencies is comparable for all Hilbert spectra throughout the measurement, no significant changes in corrosion characteristics are expected for the corrosion process reflected by the EN signals shown in Figure 6.
Figure 12 (a) Hilbert spectrum of the ECN signal of AA2024-T3 exposed to $10^{-1}$ M NaCl with $10^{-3}$ M $\text{CeCl}_3 \cdot 7\text{H}_2\text{O}$, between 4000 s and 6000 s

Figure 12 (b) Hilbert spectrum of the ECN signal of AA2024-T3 exposed to $10^{-1}$ M NaCl with $10^{-3}$ M $\text{CeCl}_3 \cdot 7\text{H}_2\text{O}$, between 4000 s and 6000 s
The Hilbert spectrum visible in Figure 12b shows a relatively large transient at approximately $t = 4400$ s. By averaging the contribution in instantaneous frequencies of all transients, the domination of the amplitudes of instantaneous frequencies of some (large) transients over those of others can be prevented, which provides the required insensitivity for one or two dominant transients [15].

The high frequency range can be ascribed to spontaneous nucleation and passivation events, whereas fluctuations in the order of several seconds arise from (meta)stable pitting events [17]. Analogous to this, long fluctuations are generated by the slow diffusion processes of oxygen around these active corrosion sites [47]. The Hilbert spectrum shown in Figure 8a indicates a decreasing intensity across the entire instantaneous frequency range towards 4000 s. In the Hilbert spectra of the ECN signal shown in Figure 5b, this occurs at a later stage. This can be observed when comparing the Hilbert spectrum shown in Figure 8b with the one shown in Figure 12b, where the decrease is visible. The Hilbert spectra in Figures 12a and 12b show that the few fast transients present in this segment, with instantaneous frequencies above $5 \times 10^{-1}$ Hz, now have a higher relative contribution as compared to the reduced contribution of instantaneous frequencies below $5 \times 10^{-2}$ Hz. Still,
Chapter 6

Instantaneous frequencies below $5 \times 10^{-2}$ Hz have the largest relative amplitudes, however the absolute intensity of their related diffusion controlled processes has decreased. The reason for this can be the competition between precipitation of Ce (hydr)oxide on the one hand and its breakdown by chloride attack on the other. This gives rise to fast metastable pitting events.

During the next stage towards inhibition (spectrum 4), a decrease of the contribution of instantaneous frequencies across the entire frequency range is visible in Figures 10a and 10b. Combined with the negative drift in the EPN signal, this indicates the presence of a more robust Ce (hydr)oxide film: both fast metastable pitting events as well as slow oxygen diffusion processes become more inhibited. Subsequently, the final segment shows that when an inhibited (steady) state is reached, almost no metastable pitting events exist anymore. In addition, the final two-dimensional representations of the Hilbert spectra of the ECN signals confirm that a Ce-based inhibitor only inhibits corrosion processes related to the cathodic intermetallic particles: after inhibition, still low frequency information is present in the signal, which indicates that still a general (diffusion controlled) corrosion process is active here. Note that the absolute amplitudes of these large timescale processes have diminished, which is visible in Figures 5a and 5b by a smooth final part of the ECN signal with fluctuations in the order of 1 nA. Instantaneous frequencies above $5 \times 10^{-2}$ Hz (indicative for the competition between chloride attack and formation of the inhibiting layer) are absent here. Therefore, the Hilbert spectra show that for this final segment all instantaneous frequency contribution, however small in the original ECN signal, is in the range below $5 \times 10^{-2}$ Hz.

The combination of the range of experiments at different conditions, the associated EN measurements and the knowledge on the processes available in literature strongly support our claim that the proposed method is valuable in distinguishing different stages in a corrosion inhibition process. However, hard evidence can only be obtained when direct in-situ identification of the corrosion process is performed. This type of experiments will therefore have to be performed to further mature the method.

6.4 Conclusions

This study demonstrates the ability of Hilbert spectra to investigate transients in an EN signal for an aqueous corrosion inhibition process. Transient analysis through Hilbert spectra
enables the identification of the inhibition process of AA2024-T3 by a Ce-containing solution. Initial examination of specific features in the ECN and EPN 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 ECN signals allow identification of dominant instantaneous frequencies occurring in these successive regions. Combined with microscopic investigation, this can provide time-resolved information about the evolution of the corrosion inhibition from EN signals. Initially, the Hilbert spectra indicate a comparable decomposition in instantaneous frequencies for the AA2024-T3 exposed to a Ce-containing solution as compared to AA2024-T3 exposed to a $10^{-1}$ M NaCl solution. Then the fast competition between precipitation of Ce (hydr)oxide on the one hand and its breakdown by chloride attack on the other becomes visible as a decrease in the number of transients and an increase in relative contribution of instantaneous frequencies above $5 \times 10^{-1}$ Hz in this stage. Finally, an inhibited state is reached in which the Hilbert spectrum of the ECN signal indicates that both high and low instantaneous frequencies decrease in amplitude. Both fast metastable pitting events as well as slow oxygen diffusion processes become inhibited, probably due to the presence of a more stable Ce (hydr)oxide film at the surface.

The analysis procedure introduced in this work yields improved applicability of electrochemical noise measurements for the identification of an inhibition effect in corrosion processes. By combining transient analysis through Hilbert spectra with visual inspection of the EN signals in the time domain and microscopic observations, on the one hand the effectiveness of the inhibition process could be verified and on the other hand, supported by literature, the nature of the corrosion attack could be explained.
6.5 References

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


[38] E.A. Matter, S. Kozhukharov, M. Machkova, V. Kozhukharov, Comparison between the inhibition efficiencies of Ce(III) and Ce(IV) ammonium nitrates against corrosion of AA2024 aluminum alloy in solutions of low chloride concentration, Corros. Sci., 62 (2012) 22-33.


Detection of microbiologically influenced corrosion by electrochemical noise transients

Abstract

This work investigates the electrochemical processes involved in pitting corrosion induced by microbiologically influenced corrosion by using time-resolved instantaneous frequency information of electrochemical current noise (ECN) transients obtained from Hilbert spectra. In addition to the time-frequency analyses, also the open corrosion potential is investigated and microscopic examinations of the specimens are performed after the tests. Hilbert spectra of the ECN signals indicated the development of transients in one of the two electrochemical cells containing sulphate-reducing bacteria with a different instantaneous frequency decomposition as compared to the background ECN signal, which resulted from the anaerobic general corrosion process. After day 13, the transients in the ECN signals developed towards consistent instantaneous frequency decompositions in the Hilbert spectra that are typical for relatively fast pitting corrosion processes. Post-exposure microscopic observations confirmed the existence of pits underneath the attached biofilms at the working electrodes.

This chapter is based on:

Chapter 7

7.1 Introduction

Microbiologically influenced corrosion (MIC) can be described as (the acceleration and/or alteration of) corrosion processes resulting from the presence and activities of microorganisms [1], generating a biofilm at the metal surface [2, 3]. It has been documented for metals exposed to seawater, but also to e.g. groundwater and industrial waters [4-6]. MIC therefore is a process that affects systems operating in maritime environments and many other sectors of industry. The process occurs in environments where corrosion with potentially exceptionally high reaction rates would otherwise not be expected, e.g. under anaerobic or low chloride conditions [1, 4]. Therefore, MIC can lead to unexpected failure of systems. The process does not produce a unique type of corrosion, but it is usually localized, inducing e.g. pitting corrosion [1, 5]. Microorganisms can accelerate the mechanisms of the corrosion processes, for which they require water, nutrients and electron acceptors [4, 7, 8].

7.1.1 Biofilm

Bacterial biofilms are most recognized for their influence on corrosion. For example, it was observed already quite some time ago that in the presence of steel, the amount of sulphate reduced to sulphide by sulphate-reducing bacteria (SRB) increases [9]. Bacteria can either exist individually or form colonies [1]. They grow, reproduce and produce extracellular polymers forming a biofilm [1, 3]. The morphology of this biofilm depends on the surface material and roughness [10]. Bacteria either perform aerobic or anaerobic respiration [1, 4]. These processes are symbiotic in such a way that conditions for the existence of each species within the biofilm are facilitated [1, 4]. The bacterial adhesion pattern and its extent depend on many factors, including bacterial characteristics (e.g. their mobility in the electrolyte), substrate properties, available nutrients, temperature and influences of electrolyte flow (which also affects mobility of the bacteria) [1]. Moreover, the (extent of) formation of biofilms is generally not uniform and difficult to predict [1, 11]. The presence of a biofilm at a metal substrate can shift the corrosion potential in the noble direction [1, 11]. The mechanism for this ennoblement is still under discussion, however acceleration of the cathodic oxygen reduction reaction due to microbial activity is a generally accepted cause [1].
7.1.2 Corrosion mechanism

Although typical biofilm formation involves co-operation between aerobic and anaerobic bacteria, in this work the primary focus is on anaerobic bacteria (i.e. SRB). Under anaerobic conditions in a neutral electrolyte, carbon steel is expected to exhibit a very slow corrosion rate due to the relatively slow cathodic reduction reaction [4]:

$$2\text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{H}_2 + 2\text{OH}^-$$  (1)

However, in the presence of SRB, corrosion is enhanced because sulphate acts as terminal electron acceptor due to its reduction by SRB [12-17]:

$$\text{SO}_4^{2-} + 8\text{H}^+ + 8\text{e}^- \rightarrow \text{HS}^- + \text{OH}^- + 3\text{H}_2\text{O}$$  (2)

On carbon steel, the sulphide typically reacts with the iron ions made available by the anodic reaction and subsequently the anodic site acidifies by the formation of iron sulphide [1, 4, 12, 18]:

$$\text{Fe}^{2+} + \text{HS}^- \rightarrow \text{FeS} + \text{H}^+$$  (3)

The conductive iron sulphide precipitates at the metal surface, thus facilitating electron flow from the substrate to the biofilm [17, 19]. Indeed, pitting corrosion attack on carbon steel in the presence of SRB is reported to occur under the biofilm [20].

7.1.3 Investigation of MIC

To investigate MIC effectively, the phenomenon should be treated from a multidisciplinary point of view. This means that electrochemical techniques should be combined with other (surface analysis) techniques [21]. The possibility to distinguish characteristic MIC signatures using electrochemical noise measurements (ENM) is recognized [22, 23]. It was found that differences in the type of electrochemical potential noise (EPN) signal could enable differentiation between biological and non-biological corrosion [24].
the electrochemical noise (EN) time signal can provide useful information on the type of corrosion process induced by MIC [23, 25]. For example, parameters like characteristic charge and frequency of events proved valuable for this purpose [23]. Analysis of the variance of the electrochemical current noise (ECN) and EPN signal has been shown to reveal the moment of transition between general and localized corrosion [26]. In the frequency domain, application of fractional Fourier transform has been reported to give satisfactory results in distinguishing MIC mechanisms, where conventional fast Fourier transform failed [27]. In the time-frequency domain, analysis of EPN transients by using wavelet transform can reveal signal features typical for localized corrosion associated with the presence of a biofilm [22].

In the present work the application of time-frequency analysis of EN data is proposed as an innovative way to detect and characterize pitting corrosion on carbon steel induced by SRB. The identification of ECN transients generated by pitting corrosion through MIC is a difficult task. The specific signal characteristics of the transients should be separated from the background ECN generated by the anaerobic general corrosion process of the carbon steel working electrodes. But once the transients have been identified, the ability to analyze only the contribution of the individual pitting processes, and to omit any instantaneous frequency information that is associated with the anaerobic general corrosion of the carbon steel, will prove to be very useful.

The approach followed in this work is as follows. The principle of transient analysis as introduced in chapter 5 and 6 is applied to characterize the pitting corrosion process [28, 29]. To promote the metabolism of the SRB [30], the initial experimental conditions comprise a sterile, anaerobic, nutrient rich condition under elevated temperature, with a bare carbon steel substrate, initially in the absence of corrosion product. This is considered important in the investigation of MIC induced by SRB, since any corrosion product present at the metal surface acts as a diffusion layer [30]. For proper investigation of the development of EN characteristics due to the presence and activity of a bacterial biofilm, in the initial stage the working electrode surfaces should be freely accessible for species from the electrolyte.

In the next section, the experimental setup will be described in more detail, as well as the microscopic investigation and the procedure to analyze the obtained EN signal. Section 7.3 then discusses the results, where the visual and microscopic observations are related to the transients in the EN signal. Finally, in section 7.4 some conclusions are drawn.
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7.2 Experimental

7.2.1 Electrochemical cell

The four electrochemical cells consist of butyl rubber-stoppered containers with a volume of 500 ml. The measurements were performed in a conventional three-electrode configuration under open-circuit conditions, requiring two nominally identical carbon steel working electrodes and one platinum electrode, acting as reference electrode. The working electrodes consist of round bars, protruding through the butyl rubber sealing at the top to enable electrical connection while maintaining sterility. The chemical composition of the carbon steel working electrodes is provided in Table 1.

<table>
<thead>
<tr>
<th>Element</th>
<th>Carbon steel</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>≤ 0.17</td>
</tr>
<tr>
<td>Si</td>
<td>--</td>
</tr>
<tr>
<td>Mn</td>
<td>≤ 1.40</td>
</tr>
<tr>
<td>P</td>
<td>≤ 0.045</td>
</tr>
<tr>
<td>S</td>
<td>≤ 0.045</td>
</tr>
</tbody>
</table>

The working electrodes were partly coated with araldite glue, which is resistant to the dry sterilization temperature of 190 °C, and acts as a corrosion protective coating. Only a well-defined area of 19.6 mm² (corresponding with a diameter of 5 mm) of each working electrode was exposed to the electrolyte. The area of the square platinum mesh used as reference electrode was approximately 100 mm². The working electrodes were wet ground using up to 4000-grit SiC paper. The medium used was Postgate C [31], made from demineralized water and analytical grade reagent. NaCl was added to the medium to make the concentration 2.5 wt.% NaCl. After flushing the medium with N₂ for 1 hour, the medium was sterilized by autoclaving. Subsequently, the medium was allowed to cool down in a glovebox under controlled N₂ atmosphere. The electrochemical cells were mounted together and dry sterilized at 190 °C for 2 hours, to prevent the formation of corrosion product at the...
working electrodes due to autoclaving. After immediate transfer to the glovebox and cooling down, 500 ml of the medium was added to each electrochemical cell. Subsequently, 5 ml of a freshly grown culture of Desulfovibrio Indonesiensis (further denoted as SRB) was added to two of the four electrochemical cells. The other two cells served as sterile controls. The electrochemical cells were stored in an incubator at 28 °C. No additional nutrients were added during the experimental series.

During measurements, the electrochemical cells were placed in an insulating container to avoid temperature fluctuations. The cell configuration is shown in Figure 1. The numbers correspond with: (1) Working electrodes, (2) Protective coating, (3) Reference electrode, (4) Butyl rubber sealing, (5) Ring-shaped screwcap, (6) Medium, (7) Glass container.

7.2.2 Bacterial density, activity and dissolved oxygen

The bacterial density of the media containing SRB was estimated by the plate count technique. Sample media were extracted from the electrochemical cells under sterile conditions, using needles protruding the butyl rubber sealing. Dilutions were made and
bacterial counts per ml were calculated by multiplying the average (manually counted) number of colonies per plate by the reciprocal of the dilution factor used. In the sterile media, the transparency (i.e. absence of turbidity) was considered as indicative for the absence of microbial contamination. This was verified afterwards by microscopic investigation of all working electrode areas.

Bacterial activity was monitored after each ENM by measuring the amount of dissolved sulphides, according to the procedure as introduced by Cord-Ruwisch [32]. This method photometrically quantifies precipitation of CuS by adding a fixed amount of the medium to a copper reagent (consisting of 50 mM HCl and 5 mM CuSO$_4$). Furthermore, microscopic investigation of samples showed a mixture of small, single SRB with high mobility and increasingly long strings of interconnected SRB that are much less mobile. Monitoring the mobility and development of strings of SRB was performed regularly and considered as a basic additional verification of the culture’s condition. Finally, the development of ECN transients, together with ennoblement of the corresponding working electrodes and the existence of pits underneath a biofilm was considered proof of the results of this microbial activity.

To ensure that anaerobic conditions were retained throughout the measurement series, the presence of dissolved oxygen in the electrolyte was detected afterwards. This was done by immersion of oxygen indicator papers in each electrochemical cell, after opening them in a glovebox under controlled N$_2$ atmosphere. The presence of dissolved oxygen was also checked by continuous inspection of the ECN signals, as it can be associated to a low corrosion rate of the working electrodes. Additionally, visual investigation of the working electrodes afterwards was performed to check the formation of corrosion product.

### 7.2.3 Microscopic investigation

Bacteria attached to the working electrode surface and forming a biofilm were investigated using epifluorescence microscopy. After finishing the measurement series, the working electrodes were gently washed with sterile, anaerobic water (to retain only the attached biofilm) and their surface was wetted using a DNA-specific stain (SYTO® 9, $\lambda_{ex,max.}$ 485 nm, $\lambda_{emm,max.}$ 498 nm). After 5 minutes, excess stain was removed and the samples were observed under an epifluorescence microscope. When SYTO® 9 comes into contact with DNA, it shows green fluorescence caused by excitation at the specified wavelength.
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Afterwards, the biofilm was removed by rubbing and using sterile, anaerobic water and the samples were dried. Subsequently, the samples were microscopically inspected using a Reichert MEF4 M optical microscope with maximum magnification of 1000x.

7.2.4 Electrochemical noise

The electrochemical cells were placed in a Faradaic cage to avoid electromagnetic disturbance from external sources. ECN and EPN signals were recorded using a Compactstat from Ivium Technologies working as zero resistance ammeter (ZRA in Figure 1) and potentiometer (E in Figure 1), 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 chapter 4 [33]. The maximum range of the ZRA was set at 100 nA. The maximum range of the potentiometer was set at 1 V.

The data were processed using Matlab from MathWorks. The empirical mode decomposition (EMD) and the Hilbert-Huang transform (HHT) were calculated using a publicly available Matlab procedure from Rilling et al. [34, 35].

The measurement series was performed in triplicate and at least three (consecutive) measurements were performed at each SRB cell.

The analysis of EN was performed by investigation of average direct current (DC) values of the last 100 s of the EPN signals and by analysing Hilbert spectra of the ECN signals. From the DC values of the EPN signal the evolution of the open corrosion potentials (OCPs) is obtained, whereas the Hilbert spectra are used for a time-frequency analysis. Hilbert spectra are produced by the HHT as was first proposed by Huang et al. [36]. This transform is based on the assumption that any nonlinear and non-stationary signal consists of multiple characteristic scales, or intrinsic modes of oscillation, each superimposed 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 EMD. The basis of the decomposition is derived directly from the data itself, making the EMD flexible and adaptive [36-41]. A detailed description of the application of the EMD and HHT procedure for the analysis of EN signals under open-circuit conditions in corrosion studies is reported by the
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It was shown that Hilbert spectra enable a detailed determination of the instantaneous frequency composition of individual corrosion phenomena observed in the EN signal at any given moment in time.

To identify the pitting corrosion induced by SRB, the corresponding transients in the ECN signals are located and decomposed into their instantaneous frequencies using Hilbert spectra. The process of transient analysis is identical to the procedure as proposed in chapter 6 and consists of two steps [29]. First the areas in a Hilbert spectrum corresponding to the occurrence of individual transients are detected. Subsequently, only the amplitudes of the instantaneous frequencies present in these areas are averaged, in order to obtain the frequency behaviour of the pitting corrosion processes in the ECN signal. In this way, good discrimination between different corrosion processes can be obtained. Moreover, any instantaneous frequency information present outside the areas of interest (associated here with the anaerobic general corrosion of the carbon steel) is neglected.

7.3 Results and discussion

In this section, first the visual and microscopic observations are treated. After that, the ECN time signals and their decomposition in instantaneous frequencies in Hilbert spectra, together with the analysis of transients present in these ECN signals, are discussed.

7.3.1 Visual observations

Figure 2 shows the intact electrochemical cells after 16 days. The control media (Figure 2a and b) were still clear and no visual corrosion product was present at the working electrodes. The two cells containing SRB (Figure 2c and d) had become turbid and the colonies of SRB were clearly visible. Also in these cells, no visual corrosion product was present at the working electrodes. This indicates that the corrosion rate is low, which is due to the anaerobic condition during the series of experiments.
Figure 2 Electrochemical cells after 16 days: (a) Control 1, (b) Control 2, (c) SRB 1 and (d) SRB 2

7.3.2 Microscopic observations

Figure 3a shows a composite micrograph (constructed by stitching 5 separate micrographs) of a pit at the surface of working electrode 1 in cell SRB 1, with a depth of 10 µm, determined by the optical microscope. Figure 3b shows a composite epifluorescence micrograph of the same area. The presence of SRB can be observed from the epifluorescence micrograph, since they appear as green regions/stains. Figure 3b therefore shows that an area with a diameter of over 300 µm, including the pit itself, was covered with a biofilm. The thickness of the areas of biofilm observed at this working electrode varied between 1-10 µm. It should be noted here that biofilm thickness is not homogeneous. The biofilms are patchy and in many cases localized.
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Figure 3 Composite (a) micrograph and (b) epifluorescence micrograph of a pit at the surface of working electrode 1 in cell SRB 1. Arrows indicate the pit boundary.

Figure 4 shows a micrograph of the same pit at larger magnification, after removal of the biofilm.

The entire working electrode was covered with different areas of biofilm. The smallest areas of biofilm, i.e. those with a diameter in the order of 10 µm and consisting of a small number of individually identifiable strings of SRB, did not show pitting corrosion attack. Pitting attack (with pit depths between 3 and 10 µm) could be observed under larger biofilms, with diameters in the order of several hundreds µm.

At working electrode 2 of cell SRB 1, pits were less developed as compared to working electrode 1: smaller and shallower (between 1 and 6 µm) pits were observed. In Figure 5 a pit with a depth of 5 µm at the surface of this working electrode is shown.
Epifluorescence microscopy indicated that the biofilms had diameters still in the order of 10-20 \( \mu \text{m} \) and consisted of individually identifiable strings of SRB, i.e. they had not yet developed the thickness and size as was the case for biofilms at working electrode 1.
A micrograph containing small areas of attached bacteria with diameters in the order of 10-20 μm is shown in Figure 6a, together with the corresponding epifluorescence micrograph (Figure 6b).

![Micrograph and epifluorescence micrograph](image)

**Figure 6** Example (a) micrograph and (b) epifluorescence micrograph of the surface of working electrode 2 in cell SRB 1

Working electrode 1 in cell SRB 2 showed specific areas where more severe corrosion attack was concentrated, whereas outside these areas only relatively mild general corrosion attack, comparable to that visible on the working electrodes in the control cells, was observed. Figure 7 shows a micrograph of the surface of this working electrode, after removal of the biofilm. The corrosion attack within these areas was superficial, i.e. without measurable depths.

Working electrode 2 contained small pits, similar in dimensions to the ones observed at working electrode 2 in cell SRB 1, however fewer in number in this case. Both working electrodes in cell SRB 2 showed areas of attached biofilm, similar to working electrode 2 in cell SRB 1, i.e. less developed than at the surface of working electrode 1 in cell SRB 1. A micrograph of working electrode 1 in cell SRB 2 is shown in Figure 8a, together with the corresponding epifluorescence micrograph (Figure 8b).
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Figure 7 Micrograph of the surface of working electrode 1 in cell SRB 2 after removal of the biofilm, showing specific areas of corrosion attack. Arrows indicate the boundaries of these areas.

Figure 8 Example (a) micrograph and (b) epifluorescence micrograph of the surface of working electrode 1 in cell SRB 2.

The working electrodes of the two control cells showed superficial general corrosion attack, in most cases without measurable depth. A typical view on the surface of working electrode 2 of cell Control 2 is shown in Figure 9. At these working electrodes, no biofilm presence was observed using epifluorescence microscopy.
7.3.3 Bacterial densities and activity

The bacterial densities in the media of cells SRB 1 and 2 are shown in Figure 10. Measurements were performed at 5, 7, 9, 13, 14 and 15 days after starting the experiment.
Figure 11 provides the amount of dissolved sulphides in the media of cells SRB 1 and 2, which indicates the bacterial activity. The measurement of this activity was triggered by transients appearing in the ECN signals. Therefore these measurements started at day 7, and were repeated at days 9, 13, 14 and 15.

In Figure 10, the densities at the last two days were significantly lower than in the preceding period, where a steady increase in cell count was observed. A possible explanation is the formation of strings of multiple SRB, which were counted individually earlier. In addition, accumulation of SRB at the working electrodes and at the bottom of the two containers (visible in Figure 2c and d) increased in the final days. This means that counting the number of SRB in a diluted sample of the medium may no longer provide a reliable measure for the bacterial density in the container. In Figure 11, the value for cell SRB 2 at day 13 may be considered to be an outlier, possibly originating from an error during sample extraction. The amount of dissolved sulphides in the medium of a similar measurement series was about 1.5 mM at day 2. This indicates that, prior to the trigger in electrochemical activity at day 7, the SRB showed substantial increase in activity. Figure 11 shows a larger amount of dissolved sulphides for cell SRB 1 for all measurements. Analogous to the previous comment, in
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For the last days of exposure where the accumulation of SRB becomes visible, the total amount of SRB is not properly reflected by bulk cell counts anymore. Figure 11 provides information about the total activity of the SRB, which partly occurs inside the biofilm. Therefore, although the amount of SRB in the solution in cell SRB 1 is lower, it is still possible that local activity inside the biofilm is higher in cell SRB 1 than compared to cell SRB 2, resulting in a larger amount of dissolved sulphides. This corresponds with the observed pitting corrosion in cell SRB 1.

Table 2 shows the pH values of the media of all four cells at day 16. The two cells with SRB showed a higher pH than the two controls, which would be expected according to equation (2). Although the anodic sites acidify locally (under the biofilm), the overall pH of the media with SRB increases. The pH values of the two control cells are similar, which is also the case for the two SRB cells.

<table>
<thead>
<tr>
<th>Cell</th>
<th>pH</th>
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<tbody>
<tr>
<td>Control 1</td>
<td>6.00</td>
</tr>
<tr>
<td>Control 2</td>
<td>5.99</td>
</tr>
<tr>
<td>SRB 1</td>
<td>6.83</td>
</tr>
<tr>
<td>SRB 2</td>
<td>6.80</td>
</tr>
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</table>

7.3.4 Electrochemical noise analysis

In this section, the ECN signals are used for time-frequency analysis using Hilbert spectra. The EPN signals are used to investigate the development of the OCPs during the entire measurement series.

Figure 12 shows the OCPs of all measurements for the four electrochemical cells. The OCPs were determined by averaging the last 100 s of each EPN signal. The OCPs of the two control cells steadily increased during the entire measurement series. Initially, the OCPs of the cells containing SRB also increased gradually, with similar values at days 1 and 5.
Subsequently, both cells containing SRB showed an acceleration in the increase in OCP, which can be explained by the ennoblement effect generated by the acceleration of the cathodic reaction due to microbial activity [1], as was mentioned in section 7.1.1. The extent of ennoblement corresponds with the observed corrosion attack, as cell SRB 1 showed pitting corrosion at both working electrodes. From day 13 onwards, the OCPs are in a steady state. The two control cells showed an OCP of at least 100 mV lower than the cells containing SRB. Already at day 1, this difference is present. Microscopic investigation confirmed that in this case only superficial general corrosion attack was present at the working electrodes.

Figure 13 shows ECN signals of cell SRB 1 at days 5, 6, 13 and 16. Transients in the negative direction originate from localized corrosion processes occurring at the surface of working electrode 1, whereas localized corrosion activity at working electrode 2 results in transients in the opposite direction. Differences in the DC level of the ECN signals are due to the continuous anaerobic general corrosion process. This generates continuous changes in net anodic or cathodic behaviour of the two working electrodes.
An increase of the magnitude of the transients relative to their ‘base’ signal (as visible in Figure 13a, in the absence of transients) can be observed in time. The ECN signals of the two control cells were always similar to the ECN signal shown in Figure 13a. Together with
the microscopic observations of the working electrode surfaces afterwards (shown in Figure 9), this type of ECN signal is considered to originate from the slow, anaerobic general corrosion process occurring at the working electrode surfaces. In the case of cell SRB 2 this type of ECN signal was also observed throughout the entire measurement series, except for a few occasions where one or two small transients (comparable to the small transients visible in the ECN signal of Figure 13b) were present in either direction. However, the associated localized corrosion activity did not develop further within the time frame of the measurement series.

This was confirmed by the microscopic observations, showing the presence of biofilm at both working electrodes (as visible in the micrographs of Figure 8), together with concentrated areas of corrosion attack at working electrode 1 (Figure 7) and the presence of small pits at working electrode 2 (comparable to the pit visible in Figure 5). A similar series of experiments showed pitting corrosion at only one working electrode after 14 days of exposure. It is therefore difficult to predict pitting corrosion due to MIC, even under otherwise seemingly identical conditions. This indicates the value of the analysis of EN transients for the detection of MIC.

In the case of cell SRB 1, the ECN signals at days 1 and 5 are similar to the ECN signal of Figure 13a. No transients are present in the signal. From day 6 onwards, transients appeared in most of the ECN signals, as visible in Figure 13b, and developed until day 16 with an increase in amplitude by approximately one order of magnitude (see Figures 13c and 13d). From the direction of the transients present in the ECN signals it was anticipated that working electrode 1 exhibited more localized corrosion activity than working electrode 2. This was confirmed by microscopic observations afterwards, indicating the presence of biofilm and multiple small pits at the surface of working electrode 1, as well as one large pit covered with biofilm (visible in Figures 3 and 4). The surface of working electrode 2 also contained areas of attached biofilm, but only several smaller pits, as visible in Figure 5. In addition, less and smaller areas of biofilm were observed here as compared to working electrode 1. Because of the similar experimental conditions, it is considered that the only expected variable here is the heterogeneity of the working electrode surface. The presence of small imperfections and inclusions may influence the initial attachment of SRB to the electrode surface.

Figure 14a shows the Hilbert spectrum of the ECN signal of Figure 13b. The original ECN signal is displayed at the back of the figure with its relative amplitudes.
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In this Hilbert spectrum, the instantaneous frequency contribution of the relatively small transients is observable with respect to the overall instantaneous frequency decomposition of the background signal, in between the transients. The areas of the Hilbert spectrum in between the occurrence of transients represent the anaerobic general corrosion process and no noticeable dominant instantaneous frequencies are observed there. Figures 14b and 14c show the Hilbert spectra of the ECN signals of Figures 13c and 13d. The original ECN signals are again displayed at the back of the figures with their relative amplitudes.

In these Hilbert spectra the instantaneous frequency contribution of the transients is more pronounced than in the Hilbert spectrum shown in Figure 14a. The transients can now be distinguished clearly from the areas in between the transients. Moreover, since the contribution of the transients is especially in the higher frequency range, this difference confirms the increased localized corrosion activity at days 13-16 as compared to the earlier period. The biofilm has developed to a greater extent in terms of area and thickness, and increased metabolic activity induces more pronounced pitting corrosion.
Figure 14 (b) Hilbert spectrum of the example ECN signal of cell SRB 1 at day 13 as shown in Figure 13c

Figure 14 (c) Hilbert spectrum of the example ECN signal of cell SRB 1 at day 16 as shown in Figure 13d
In order to investigate the instantaneous frequency decomposition of the transients in the ECN signal in more detail, two-dimensional representations of the Hilbert spectra are used, as described in section 7.2.4. Figure 15 shows the two-dimensional representations of Hilbert spectra from four sets of four ECN signals of cell SRB 1 measured at days 13 (a), 14 (b), 15 (c) and 16 (d), respectively. At each day, the four ECN signals were measured consecutively.

The comparison of the average instantaneous frequency decomposition of the transients present in the ECN signals allows investigation of the development of the underlying localized corrosion processes. At day 13, the distribution of instantaneous frequencies varies between the four different ECN signals. Two of the spectra show a higher contribution in the frequency range below $10^{-2}$ Hz (at the right-hand side of the plot).

In the following days, the instantaneous frequency decomposition of the transients in the ECN signals gradually reaches a distribution that was also observed for metastable pitting processes on stainless steel AISI304 in chapter 5 [28]. A maximum is observed just above $10^{-1}$ Hz and the contribution tends towards zero in the frequency regions above 1 Hz and below $10^{-2}$ Hz. In the AISI304 case, pits initiated and briefly showed metastable growth, after which they repassivated again soon thereafter. Combined with the microscopic observations in the present work, it is considered that this instantaneous frequency behaviour results from pitting processes occurring underneath areas of attached biofilm, shielding the surface from the medium. Due to acidification of an anodic site underneath the biofilm, corrosion attack is induced quickly, locally and only briefly. This can potentially occur repeatedly at the same location, due to local microbial activity in the biofilm. In this way, a pit can grow relatively quickly by the occurrence of many of these individual events.

The instantaneous frequency decomposition of the transients in the ECN signals measured at day 16 shows a consistent distribution over the four different measurements, which implies that the corrosion characteristics during these four measurements were comparable.

The difference in electrochemical behaviour between the two cells containing SRB observed by transient information from the ECN signals and microscopic observations was also confirmed by the OCPs visible in Figure 12. Initially, OCPs of cell SRB 1 and 2 are similar, with biofilms developing gradually at certain spots on all four working electrodes. From day 5 onwards the OCPs of both cells increase faster, with both cells showing an onset of localized corrosion activity in their ECN signals.
Figure 15 Two-dimensional representations of Hilbert spectra from each time four ECN signals of cell SRB 1 measured at days 13 (a), 14 (b), 15 (c) and 16 (d)
Additionally, an increasing difference in OCP is observed, corresponding with increasing transient magnitudes of the ECN signal for cell SRB 1, originating from more pronounced pitting corrosion.

7.4 Conclusions

This work investigates the electrochemical processes involved in pitting corrosion induced by MIC by applying transient analysis to ECN signals. It has been demonstrated that the evolution of the localized corrosion processes can be monitored by time-resolved instantaneous frequency information of ECN transients through Hilbert spectra of the ECN signals. This was combined with investigation of the OCP and microscopic observations afterwards. The following results were obtained:

- The immediate effect of the settlement of SRB at the surface of the working electrodes was already visible at day 1 by a (approximately 100 mV) difference in OCP between the cells containing SRB and the controls. This difference further increased during the measurement series.
- From day 6, Hilbert spectra of the ECN signals indicated the occurrence of transients with noticeable different instantaneous frequency decomposition as compared to the background ECN signal. In addition, the difference in OCP between the cells containing SRB and the two controls increased, which is an indication of ennoblement of the working electrodes generated by the presence of a biofilm.
- After day 13, the transients in the ECN signals of cell SRB 1 developed towards a consistent instantaneous frequency decomposition in the Hilbert spectra that is typical for fast pitting corrosion processes. Microscopic observations confirmed the existence of pits underneath the attached biofilms at the working electrodes.

It can be concluded that the investigation of the instantaneous frequency decomposition of transients in the ECN signals, combined with monitoring of the OCP and microscopic observations, yields improved applicability of ENM for the detection and characterization of localized corrosion induced by MIC.
7.5 References


Detection of microbiologically influenced corrosion by electrochemical noise transients


Detection of microbiologically influenced corrosion by electrochemical noise transients


Novel corrosion monitoring using electrochemical noise

Abstract

For systems operating in the highly corrosive maritime environment, mitigation of the consequences of corrosion is considered important from an operational, economical and environmental perspective. Because of this, the need to monitor corrosion under real conditions emerges. This work discusses the most important characteristics of electrochemical noise measurements (ENM) as a tool for corrosion monitoring. ENM is a potentially interesting technique because of its non-intrusive nature, the robust sensor configurations, the ability to identify localized corrosion processes and ease of use. ENM can be performed through continuous monitoring using permanent electrodes or by a hand-held solution using temporary electrodes. A complicated aspect of ENM is the analysis of the electrochemical noise signals, which, however, can be fully automated if required.

This chapter is based on:
8.1 Introduction

In modern, innovative maintenance concepts, real-time information on the condition of a system is used to determine the optimal interval. Concerning corrosion, the understanding and control of corrosion-related failure modes and their effects is generally poor [1]. Corrosion affects the structural integrity of systems such as ships, offshore platforms or bridges. Insight in their longer-term structural integrity therefore requires proper assessment of the (localized) corrosion processes that may occur [2]. Awareness of the barrier properties of protective coatings and mitigation of the consequences of corrosion, especially at locations that are difficult to reach, can prevent both unnecessary maintenance and system failure and supports a reliable prediction of the operational service life of systems. However, whereas general corrosion attack can be predicted satisfactory under certain conditions, localized corrosion processes like pitting are typically very unpredictable and also hard to detect. In addition, in the presence of a protective coating, the degradation of its ability to protect the underlying metal structure (which mainly depends on its barrier- and active corrosion inhibition properties [3, 4]) is also hard to predict. Therefore, a clear need to monitor corrosion under representative conditions emerges. Condition monitoring will aid to reduce uncertainty, improve service life [5] and, if applied using sensors providing an early corrosion indication, reduce maintenance costs. The most attractive prospect of electrochemical noise (EN) based corrosion monitoring is its ability to reveal the initiation of localized corrosion well before it can be identified visually. The non-intrusive character of this technique, together with its adaptive nature and high sensitivity to changes in corrosion characteristics, make it potentially suitable for corrosion monitoring purposes. This chapter provides an overview of state-of-the-art developments regarding the technique to measure and analyze EN for application in corrosion monitoring concepts. Both the potential and limitations of (future) EN based corrosion monitoring systems will be reviewed and possible applications in naval systems will be discussed. Real measurements will be used to demonstrate the principles.

8.2 Corrosion monitoring

Many corrosion monitoring and evaluation methods are based on electrochemistry [6, 7]. A division can be made between methods that are potentially suitable for the characterization
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of localized corrosion and those that are not [8]. An example of the latter is electrochemical impedance spectroscopy (EIS), where a potential signal is applied to corroding (coated) electrodes and their frequency resolved current response is analyzed [7, 9]. Scanning electrochemical techniques, like for example scanning kelvin probe (SKP) or scanning vibrating reference electrode technique (SVET), are able to spatially resolve localized corrosion processes [6, 10-12]. Generally, these techniques only cover a small area under strictly controlled experimental conditions. Therefore their ability to capture all details of a corrosion process involving simultaneous, but spatially separated reactions can be questioned [13]. In addition, fixed electrode techniques are probably more suitable for in situ measurements of localized corrosion since they do not contain moving parts. This results in lower complexity and therefore higher reliability and robustness of the sensor. An interesting technique that can provide time-resolved information about localized corrosion processes using fixed electrodes, is the method based on electrochemical noise measurements (ENM). This method will be elaborated in this chapter.

8.3 Electrochemical noise measurements

The charge transfer that is involved in corrosion reactions generates spontaneous fluctuations in current and potential. These fluctuations are detected by ENM and defined as EN. The analysis of the associated current and potential signatures is used in the study of corrosion processes, specifically on the kinetics of the reactions involved [14-16]. One of the most interesting applications of ENM is the ability to identify and quantify localized corrosion processes [14, 15]. In addition, this technique has been proven valuable in assessing the barrier properties of protective coatings [17-21], which can contribute to reliable service life predictions [19]. The use of ENM has some significant advantages: the measurement does not influence the corrosion process and the instruments required are relatively easy to use, especially with the aid of computerized data-acquisition techniques [16, 19, 20, 22-24].

The technique can be applied in several ways, and for different purposes. Firstly, ENM can be performed under operational conditions, where either continuous monitoring using permanent sensors or periodic inspections with hand-held solutions are possible. In the latter case, the sensors are not necessarily present permanently, however the measurement location should be accessible. In the case of permanent sensors, accessibility is not an issue. This application of the technique under operational conditions enables condition
monitoring of real systems, like ships and offshore structures. However, this is only feasible when both the sensors and data analysis techniques have reached a sufficient maturity level, which is currently not the case yet.

Therefore, a second approach is to expose specimens under representative conditions first (e.g. in the case of measurements on the barrier properties of marine coatings, using separate coated panels) and subsequently perform the ENM in a laboratory setup. An advantage here is the possibility to combine real environmental conditions (e.g. natural seawater and fouling) with well-controlled measurement conditions. On the other hand, monitoring is not performed continuously in this case. And thirdly, ENM can be performed completely in a laboratory setup under controlled conditions. The advantage here is the possibility of full control of all parameters and the possibility of continuous monitoring. The latter two applications of ENM in (partly) laboratory set-ups are required to develop the concept and increase the understanding of the relation between measurements and corrosion mechanisms.

8.3.1 Measurement configurations

Depending on the monitoring requirements, different cell configurations and data analysis techniques can be applied. ENM can be performed under potentiostatic, galvanostatic or open-circuit conditions. The first two only allow the detection of either an electrochemical current (ECN) or potential noise (EPN) signal, respectively, whereas an open-circuit configuration allows the detection of both signals simultaneously. The open-circuit configuration is non-disturbing [13, 17, 18], whereas potentiostatic or galvanostatic ENM influence the corrosion processes by applying an external signal, thereby potentially risking alteration of the corrosion characteristics [13]. Nevertheless, potentiostatic or galvanostatic ENM can be useful when signal levels under open-circuit conditions appear to be very low [13]. For practical corrosion monitoring purposes this issue is however less relevant: it is important to detect and characterize (localized) corrosion processes already at the very early stages, under representative conditions.

Note that the small magnitude of a typical ECN or EPN signal (in the range of a few nA or mV, respectively) requires proper electromagnetic shielding of the measurement cell. In addition, advanced data analysis techniques, e.g. the Hilbert-Huang transform (HHT), which
will be discussed later, can enable good identification of EN signal characteristics generated by corrosion processes.

Under open-circuit conditions, ENM typically involve a three-electrode configuration. This requires two nominally identical working electrodes and a third electrode, which is a reference electrode with a known potential. All electrodes are immersed in a conductive solution, which is called the electrolyte. The ECN signal is measured through a zero resistance ammeter (ZRA), which connects the two working electrodes. The EPN signal is measured between these two electrodes and the reference electrode by the potentiometer (E). Both signals are measured simultaneously. In Figure 1 this measurement setup is schematically depicted.

![Figure 1 Layout of the electrochemical cell](image)

The measurement configuration can differ, depending on operational requirements and the kind of information that must be obtained. For example, it matters whether only the general degradation of the barrier properties of a protective coating is studied, or more details on corrosion characteristics are to be identified. Basically, the types of sensor configurations can be divided into two different groups: the first one directly measures the charge transfer involved in the actual corrosion processes on the substrate of interest by using chemically inert, conductive (e.g. graphite) auxiliary electrodes. The second option is to expose working electrodes from the same material as the substrate of interest to a representative environment. An advantage of the use of auxiliary electrodes is the possibility to monitor specific locations of interest, e.g. in the vicinity of welds or crevices, for the occurrence of (localized) corrosion. The corrosion-specific properties of these locations are otherwise difficult to imitate using representative working electrodes. On the other hand, the advantage
of using representative working electrodes is that there is no need to attach the sensor directly onto the substrate, with the associated risk of influencing the corrosion characteristics locally. However, it also implies that the corrosion process on the substrate is only indirectly monitored. In a laboratory ENM setup this is not a problem, since the corrosion characteristics of specific material-environment combinations are of interest. But for application to real structures under operational conditions a configuration with auxiliary electrodes is preferential.

An ENM configuration suitable to determine the barrier properties of protective coatings in the field without the necessity of establishing electrical contact with the substrate is the no connection to substrate (NOCS) method [16]. This configuration uses auxiliary electrodes, providing a true non-destructive corrosion monitoring solution [16, 25, 26]. The working electrode area is the part of the coated substrate that is in direct contact with the electrolyte. In Figure 2 a schematic picture of the NOCS arrangement is provided.

![Figure 2 Schematic representation of the NOCS configuration (based on [16, 25, 26])](image)

The NOCS arrangement has shown good reproducibility of results and can be regarded as being sufficiently matured for field application [25, 26]. Moreover, this configuration is interesting for hand-held monitoring using temporary sensors at locations that are relatively easy to reach, e.g. the outer hull of naval ships.

In the presence of a protective coating, the degradation of its ability to protect the underlying structure against corrosion attack can also be monitored by embedded EN sensors [27-30]. This configuration contains inert (e.g. platinum) auxiliary electrodes located permanently...
between the primer and the topcoat. The working electrode area is the part of the coated substrate that is covered by each auxiliary electrode. Figure 3 shows a schematic representation of an embedded EN sensor.

![Schematic representation of an embedded EN sensor](image)

Figure 3 Schematic representation of an embedded EN sensor (based on [27-30])

The advantage of this type of sensor is its small size and high robustness. On the other hand, it should be noted that embedded electrodes suffer from the risk of influencing the coating’s barrier properties locally, thereby decreasing the representativeness of the obtained information. This issue should be further investigated. Nevertheless, this solution is particularly interesting for corrosion monitoring at locations that are difficult to reach, e.g. inside ballast tanks, fuel tanks or between double-walled structures. The permanent sensors can be integrated in the coating system, while the ENM can be performed either continuously or with intervals.

An example of a configuration using working electrodes from the same material as the substrate of interest is the wire beam electrode (WBE) EN sensor, which simultaneously allows a high sensitivity to EN signatures and spatial localization of corrosion attack [13]. This configuration comprises a matrix of small working electrodes (providing spatial differentiation), connected to a ZRA and potentiometer through a multiplexer [13].

The choice of which monitoring configuration to apply (e.g. NOCS, embedded electrodes or representative working electrodes) not only depends on practical considerations. Their suitability for the detection of localized corrosion can also be important for certain applications. In the case of embedded electrodes, their locations have to be determined beforehand, which implies precognition about potential corrosion hotspots in the structure. The NOCS method is more flexible, since the sensor locations can be chosen just prior to each measurement. This can be an advantage in the case of microbiologically influenced
corrosion, which is very unpredictable and can occur unexpectedly, e.g. inside ballast tanks of ships. In this case, flexibility in the measurement location can be advantageous. On the other hand, the simplicity and therefore expected low cost of embedded EN sensors allows to apply an array of sensors, which increases the overall reliability of the information about the condition of a coating system and, moreover, increases the probability of detecting localized corrosion attack already in the initiation phase.

### 8.3.2 Interpretation of electrochemical noise

Whereas the measurement of EN seems straightforward, the interpretation of the resulting signals is challenging. This is not necessarily a problem, it can also be regarded as an advantage of this technique. The interpretation by the operator performing the field measurements can be facilitated to a large extent by fully automated analysis using advanced data analysis procedures. Also for other important issues, such as sensor design, working electrode area or sampling rate [31], the parameters can be determined beforehand and be implemented in the analysis procedures.

For a protective coating, the spectral noise resistance $R_{sn} (\Omega)$ provides information about its barrier properties: for an intact coating system, without defects and with good adherence, the $R_{sn}$ is high and this value typically decreases during its service life. $R_{sn}$ is calculated in the frequency domain, using fast Fourier transform, by the square root of the power spectral density (PSD) of the EPN divided by the PSD of the ECN [32, 33]. The values of the power spectral densities are determined at their low-frequency limit. Under certain conditions [15, 33-35], in the time domain the noise resistance $R_n (\Omega)$ provides comparable information [20]. $R_n$ is simply calculated by dividing the standard deviation of the EPN by that of the ECN [17, 18, 36]. As an example, Figure 4 shows the $R_n$ and $R_{sn}$ values of a coating system, as obtained from measurements on a submarine of the Royal Netherlands Navy during maintenance. The figure shows the results for different locations: inside a fuel tank (A and B) and at a location that is in direct contact with fresh seawater (C-F), each time at two adjacent locations (1 and 2). Measurements were performed using the NOCS configuration. Visually, the coating system was intact at the measurement locations. No significant differences in barrier properties between the different locations were observed.
Figure 4 $R_n$ and $R_{sn}$ values of a coating system of a submarine of the Royal Netherlands Navy during maintenance. Locations are inside a fuel tank (A and B) and in a tank that is in direct contact with seawater (C-F), each time at two adjacent locations (1 and 2) (similar to [37], however with lower $R_n$ and $R_{sn}$ values here due to modifications in data processing software).

Figure 5 shows the $R_n$ and $R_{sn}$ values of the coating system at the outside hull of a landing platform dock (LPD) of the Royal Netherlands Navy. Measurements were again performed using the NOCS configuration. In this case, the topcoat showed poor adherence, but the underlying coating system was still intact, thus providing corrosion protection. However, the values of $R_n$ and $R_{sn}$, being one or two orders of magnitude lower than the values in Figure 4, indicate that the barrier properties were poor.

The identification of the more dangerous localized corrosion processes demands the ability to distinguish between different corrosion characteristics from a single EN signal. This can be achieved by application of Hilbert spectra, allowing investigation of frequency characteristics of the corrosion processes while still maintaining time-resolved information (i.e. analyze in both time and frequency simultaneously). Importantly, this information is obtained without the need for subjective a-priori limitations or assumptions concerning the nature of the process under investigation.
Hilbert spectra are produced by the HHT, which was first proposed by Huang et al. [38] and is based on the assumption that any nonlinear and non-stationary signal consists of multiple intrinsic oscillation modes, each superimposed 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 the empirical mode decomposition [38]. A Hilbert spectrum shows instantaneous frequencies with their amplitudes varying over time. The spectrum allows identification of individual corrosion events on the time scale, but also provides information on the frequency characteristics of these events. The use of Hilbert spectra for the analysis of EN is explained in more detail in chapter 4 [39]. To illustrate the principle, Figure 6 shows the working electrode surface of stainless steel AISI304 after immersion for a period of 1000 s in an aqueous HCl solution at pH 1 (a general corrosion process) and pH 3 (a localized metastable pitting process). Figure 7 shows the Hilbert spectrum of the ECN signal corresponding to Figure 6a and Figure 8 shows the Hilbert spectrum of the ECN signal corresponding to Figure 6b. The original ECN signals are depicted at the back of the Hilbert spectra with their relative amplitudes.
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Figure 6 Micrographs of the working electrode surface of AISI304 after immersion for a period of 1000 s in an aqueous HCl solution at (a) pH 1 and (b) pH 3

In the example of Figure 6a, the AISI304 exposed to the aggressive aqueous HCl solution at pH 1 suffers from general corrosion, resulting in a complete breakdown of the passive chromium oxide layer. The Hilbert spectrum presented in Figure 7 shows the presence of instantaneous frequencies only at the lowest frequency end of the spectrum, below $10^{-2}\text{ Hz}$, and negligible instantaneous amplitudes in the higher frequency region, as described for similar experiments in chapter 4 [39].
Figure 6b shows a smooth surface with a number of pits. In the Hilbert spectrum shown in Figure 8, the initiation, growth and repassivation of these pits can be identified by the presence of transients in the ECN signal, together with their instantaneous frequency contribution in the frequency range above $10^{-2}$ Hz [39]. Moreover, for corrosion monitoring purposes it is possible to automatically identify the occurrence of transients (and therefore localized corrosion like pitting) by their instantaneous frequencies in the Hilbert spectrum [40, 41]. This is particularly interesting in the case of corrosion sensors (e.g. embedded EN sensors) at locations that are difficult to reach, where visual inspection of corrosion attack is hard, if not impossible. The automatic detection of transients by the sensors can then be used to trigger a warning signal to the maintainer of the system.

8.4 Conclusions

For systems operating in the highly corrosive maritime environment the operational, economical and environmental consequences of corrosion can be severe. Awareness of the actual corrosion processes and of the barrier properties of protective coatings, especially at
locations that are difficult to reach, can prevent both unnecessary maintenance and system failure. Moreover it supports a reliable prediction of the operational service life of systems. The most dangerous corrosion phenomena are essentially localized and very hard to predict. This motivates the use of corrosion monitoring under representative conditions. For this purpose, ENM is a potentially interesting technique because of its non-intrusive nature, the robust sensor configurations, the ability to identify localized corrosion processes and ease of use. ENM can be performed through continuous monitoring using permanent electrodes or by a hand-held solution using temporary electrodes. The most complicated aspect of ENM is the interpretation of the EN signals, for which the data analysis procedure can be fully automated if required, thereby facilitating the performance of the measurement. The most attractive prospect of EN-based corrosion monitoring is its ability to reveal the initiation of localized corrosion well before any corrosion attack is sufficiently advanced for visual identification. The identification of specific forms of corrosion already at this early stage allows preventive measures to be taken in time and prevents corrosion damage at a larger scale.
8.5 References


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General conclusions
The following conclusions are drawn based on this research:

- Removal of the direct current drift, as an important first step in electrochemical noise (EN) processing, is preferably performed by a time-frequency technique.
- Further processing of EN data requires a data analysis procedure that (i) has a high discrimination ability and (ii) yields a descriptive parameter that is directly associated to the underlying physico-chemical process.
- Procedures that meet these two requirements appear to be the Hilbert-Huang transform (HHT, Hilbert spectrum), discrete wavelet transform (energy distribution plot) and the analysis of charge and frequency of corrosion events. Moreover, the HHT lacks the need for subjective a-priori limitations or assumptions concerning the nature of the process under investigation.
- A Hilbert spectrum provides a detailed decomposition of the original electrochemical current noise (ECN) and electrochemical potential noise signal in instantaneous frequencies.
- Selection and analysis of specific areas in a Hilbert spectrum corresponding with the occurrence of transients yields an improved definition of frequency characteristics associated to different corrosion mechanisms. This enables to identify differences in corrosion characteristics more consistently than compared to a similar procedure without transient analysis.
- By combining transient analysis through Hilbert spectra with visual inspection of the EN signals in the time domain and microscopic observations, on the one hand the effectiveness of Ce-based corrosion inhibition of aluminium alloy AA2024-T3 could be verified and on the other hand, supported by literature, the nature of the corrosion attack could be explained.
- The evolution of the localized corrosion processes generated by microbiologically influenced corrosion can be detected and identified by retrieving time-resolved instantaneous frequency information from ECN transients through Hilbert spectra.
- Corrosion monitoring based on electrochemical noise measurements (ENM) is a potentially interesting technique because of its non-intrusive nature, the robust sensor configurations, the ability to identify localized corrosion processes and ease of use.
The complex aspect of data analysis of EN, which is essential for its proper interpretation, can be fully automated.

Based on these conclusions, the research questions that were addressed in the introduction could be answered:

1. **How does EN allow differentiation between general and localized corrosion processes?**
   EN allows differentiation between general and localized corrosion processes by the use of a data analysis procedure that (i) has a high discrimination ability and (ii) yields a descriptive parameter that is directly associated to the underlying physico-chemical process.

2. **To what extent can corrosion processes be identified using EN?**
   Discrimination between different corrosion processes can be performed by application of transient analysis through Hilbert spectra of EN signals. Differences in instantaneous frequency contribution of transients in ECN signals allow the identification of (changes in) specific localized corrosion characteristics.

3. **To what extent can degradation and delamination of a coating, prior to the occurrence of corrosion processes, be identified using EN?**
   The decrease of the (spectral) noise resistance can be an indication of the onset of corrosion underneath a protective coating due to loss of adhesion. The decreased barrier properties of a protective coating are also visible by changes in the open corrosion potential and the resulting increase in corrosion intensity is reflected by an increase in magnitude of the ECN fluctuations.

4. **To what extent are ENM complementary with electrochemical impedance spectroscopy (EIS)?**
   EIS does not differentiate between corrosion characteristics. EN can identify specific forms of corrosion already at their initiation stage.

5. **What are the possibilities and requirements to develop a corrosion sensor that enables (continuous in situ) corrosion measurements using EN?**
   ENM can be performed through continuous monitoring using permanent electrodes or by a hand-held solution using temporary electrodes. Its passive nature allows long-term non-destructive corrosion monitoring with minimum perturbation of the
corrosion processes. Furthermore, the low complexity of the measurement configuration is beneficial for a potentially robust sensor, which has to be miniaturized for continuous monitoring. The most complicated aspect of ENM is the interpretation of the EN signals, for which the data analysis procedure can be fully automated. Reliable identification of localized corrosion using EN requires further knowledge about the associated EN signal characteristics.
Summary

Electrochemical Noise

A Clear Corrosion Signature
Summary

The interpretation of electrochemical noise (EN) data has long been under discussion. Throughout the years, many data analysis techniques have been proposed for this purpose. As a starting point, procedures and parameters that enable identification of, or discrimination between, general and localized corrosion processes through EN are critically discussed. It is important to consider which type of information is required for a specific application. EN can be used to determine the barrier properties of a protective coating, and can therefore provide quantitative information about corrosion processes, although its most interesting ability is to provide information on corrosion characteristics.

EN signals consist of a direct current (DC) component, or trend, with superimposed fluctuations. In electrochemical potential noise (EPN), this DC component represents the open corrosion potential (OCP) of the system under study. In electrochemical current noise (ECN), the DC component can e.g. be generated by electrode asymmetry. Any DC drift should be carefully removed prior to further data analysis. A procedure is introduced to accurately define the DC drift in EN signals using either of two time-frequency data analysis techniques: discrete wavelet transform (DWT) or empirical mode decomposition (EMD).

Consistent and reliable information can be obtained from EN data when a data analysis procedure is selected that on the one hand has a high discrimination ability and on the other hand yields a descriptive parameter that is directly associated to the underlying physicochemical process. Preferably, the information is obtained without the need for subjective a-priori limitations or assumptions concerning the nature of the process under investigation. These requirements are met by the Hilbert-Huang transform, which is based on the EMD. The result is a Hilbert spectrum in which local frequency information, so-called instantaneous frequencies, of EN signals, is visualized. The use of Hilbert spectra for the characterization of EN data in corrosion studies is introduced, based on the (general and localized) corrosion characteristics of carbon steel and stainless steel AISI304. A highly detailed decomposition of the original ECN and EPN data is provided in time and frequency simultaneously. This allows distinguishing between different corrosion characteristics based on their EN signals.

Hilbert spectra also provide the possibility to analyze only transients present in the EN signals that originate from localized corrosion processes on AISI304. Initial identification of transients is based on the transient shape. Analysis of instantaneous frequency information present in these transients enables improved differentiation between corrosion
characteristics as compared to data analysis using Hilbert spectra or energy distribution plots (determined from DWT) without transient analysis.

The applicability of transient analysis through Hilbert spectra of ECN signals is further investigated for Ce-based inhibition of aluminium alloy AA2024-T3 and for detection and identification of microbiologically influenced corrosion (MIC). Transient analysis allows detection of changes in corrosion characteristics, i.e. the evolution of corrosion inhibition of AA2024-T3 by Ce-ions, with time. The initial procedure of transient detection is further developed, comprising of automatic detection of specific areas of interest in Hilbert spectra between $10^{-1}$ Hz and 1 Hz, corresponding with the occurrence of transients in the respective ECN signals. Regarding the detection of MIC, together with monitoring of the OCP and microscopic observations, the development of ECN transients generated by localized corrosion processes could be attributed to the presence and activity of sulphate-reducing bacteria. These transients are related to the existence of pits in the carbon steel surface, underneath the attached biofilm.

Finally, practical aspects and configurations for electrochemical noise measurements (ENM) are discussed. ENM can be applied in a hand-held solution, or for permanent monitoring. Analogous to the selection of the appropriate data analysis procedure to obtain the information of interest, it is important to consider the required application to select the most suitable configuration.

ENM is a potentially interesting technique because of its non-intrusive nature, the robust sensor configurations, the ability to identify localized corrosion processes and ease of use. The most complicated aspect of ENM is the interpretation of the EN signals, for which the data analysis procedure can be fully automated if required.
Samenvatting

Elektrochemische Ruis

Een Duidelijke Corrosiesignatuur
**Samenvatting**

De interpretatie van elektrochemische ruis (EN) is al lange tijd onderwerp van discussie. Door de jaren heen is hiervoor een groot aantal data-analysetechnieken voorgesteld. Als uitgangspunt voor dit onderzoek dient daarom een kritische beschouwing van verschillende procedures en parameters voor de analyse van EN die identificatie van, of onderscheid tussen, algemene en lokale corrosieprocessen mogelijk maken. Het is van belang om voor verschillende toepassingen te bepalen wat voor soort informatie benodigd is. EN kan worden gebruikt om de barrière-eigenschappen van een beschermende coating te bepalen, en kan zo kwantitatieve informatie over corrosieprocessen geven, hoewel de eigenlijke kracht van deze techniek zit in het verschaffen van informatie over het type corrosie.

EN signalen bestaan uit een direct current (DC) component, of trend, met fluctuaties daarop gesuperponeerd. In elektrochemische potentiaalruis (EPN) vertegenwoordigt de DC component de open corrosiepotentiaal (OCP) van een systeem. In elektrochemische stroomruis (ECN) kan de DC component bijvoorbeeld voortkomen uit asymmetrie tussen de werkelektroden. DC drift moet zorgvuldig worden verwijderd voordat verdere data-analyse plaatsvindt. Voor een nauwkeurige bepaling van de DC drift in EN signalen wordt een procedure geïntroduceerd die gebruikmaakt van één van de volgende twee tijd-frequentie data-analysetechnieken: discrete wavelet transformatie (DWT) of empirical mode decompositie (EMD).

Consistente en betrouwbare informatie kan worden verkregen uit EN data als een data-analyseprocedure wordt gebruikt die aan de ene kant een hoog onderscheidend vermogen heeft en aan de andere kant resulteert in een beschrijvende parameter die een directe relatie heeft met het onderliggende fysisch-chemische proces. Bij voorkeur wordt de informatie verkregen zonder noodzakelijke restricties of aannames vooraf over de aard van het proces. De Hilbert-Huang transformatie, die is gebaseerd op de EMD, voldoet aan deze vereisten. Het resultaat is een Hilbert spectrum, die lokale frequentie-informatie, zogenaamde instantane frequenties, van EN signalen weergeeft. Het gebruik van Hilbert spectra voor classificatie van EN data in corrosieonderzoek wordt geïntroduceerd, met als uitgangspunt de (algemene en lokale) corrosiekaracteristieken van koolstofstaal en roestvast staal AISI304. Dit resulteert in een zeer gedetailleerde decompositie van het originele ECN en EPN signaal, zowel in tijd als frequentie tegelijkertijd. Hierdoor kunnen verschillende typen corrosie van elkaar worden onderscheiden, gebaseerd op hun EN signalen.
Samenvatting

Hilbert spectra maken het ook mogelijk om alleen overgangsverschijnselen in de EN signalen, afkomstig van lokale corrosieprocessen van AISI304, te analyseren. Deze overgangsverschijnselen worden in eerste instantie geïdentificeerd op basis van hun vorm. Analyse van instantane frequentie-informatie die aanwezig is in de overgangsverschijnselen maakt een beter onderscheid mogelijk tussen verschillende typen corrosie dan data-analyse waarbij gebruik wordt gemaakt van Hilbert spectra of energy distribution plots (bepaald door DWT) zonder analyse van overgangsverschijnselen.

De toepasbaarheid van analyse van overgangsverschijnselen door Hilbert spectra van ECN signalen wordt verder onderzocht voor corrosie-inhibitie van aluminiumlegering AA2024-T3 door Ce-ionen en detectie en identificatie van microbiologisch beïnvloede corrosie (MIC). Analyse van overgangsverschijnselen maakt het mogelijk om veranderingen in corrosiecharacteristieken te detecteren, dat wil zeggen de ontwikkeling van corrosie-inhibitie van AA2024-T3 door Ce-ionen, in de tijd. De initiële procedure van detectie van overgangsverschijnselen wordt verder ontwikkeld door middel van automatische detectie van specifieke gebieden in Hilbert spectra tussen $10^{-1}$ Hz en 1 Hz, die overeenkomen met het optreden van overgangsverschijnselen in de ECN signalen. Bij detectie van MIC kan, met behulp van het monitoren van de OCP en microscopische waarnemingen, de ontwikkeling van overgangsverschijnselen in het ECN signaal als gevolg van lokale corrosieprocessen worden toegeschreven aan de aanwezigheid en activiteit van sulfaat reducerende bacteriën. Deze overgangsverschijnselen kunnen worden gerelateerd aan pitten in het oppervlak van het koolstofstaal onder de aanwezige biofilm.

Als laatste worden praktische aspecten en configuraties van elektrochemische ruismetingen (ENM) behandeld. ENM kunnen worden uitgevoerd in een hand-held oplossing of voor permanente monitoring. Net als bij de selectie van de juiste data-analyseprocedure om de gewenste informatie te verkrijgen, is het bij de selectie van de meest geschikte configuratie van belang om stil te staan bij de vereiste toepassing.

ENM is een erg interessante techniek door zijn passieve aard, de robuuste sensorconfiguraties, de mogelijkheid om lokale corrosieprocessen te identificeren en het gebruiksgemak. Het meest gecompliceerde aspect van ENM is de interpretatie van de EN signalen, waarvoor de data-analyseprocedure indien gewenst geheel kan worden geautomatiseerd.
Publications related to this work

Peer-reviewed articles


Publications related to this work

Conference presentations and proceedings


The paper was awarded a nomination for the Third Prize of the Sir Donald Gosling Award by the Institute of Marine Engineering, Science & Technology

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