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Recurrence plot-based dynamic analysis on electrochemical noise of the evolutive corrosion process

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ABSTRACT

The cross recurrence plot (CRP) method was applied on the simultaneous current and voltage fluctuation time records in consideration of their possible nonlinear kinetics. Sequential cross recurrence quantification analysis (CRQA), CRP pattern recognition and synchronization analysis were used to screen the paralleled running from the uncorrelated oscillations, to recognize the impedance component, and to identify the synchronization type and degree in the dynamical view point. With the aid of the proposed approach, the sulfur-induced localized corrosion of the alloy 718 in the high temperature brine was detected and evaluated during the evolutive corrosion process.

1. Introduction

Electrochemical noise (EN) has been widespread to characterize sorts of corrosion behavior due to its non-intrusive nature and sensitivity to the localized corrosion [1]. Using a common configuration of two nominally identical electrodes and a paralleled noise-free reference electrode, the electrochemical current and potential noise could be registered simultaneously. The noise resistance derived from the standard deviation of both noise time records can provide credible estimation of the polarization resistance of the electrode under certain circumstances [2].

When the asymmetric attack take place on one of the coupled electrodes as frequently occurred in practice, the noise resistance may be attributed to the less noisy electrode rather than the noisy one we are interested in [3,4]. As a consequence the behavior of the more corroded electrode would not be revealed by the noise resistance through an evolutive corrosion process.

On the other hand, the current noise has carried more attention than the potential noise in most analysis methods, by reason of its connection to the transport of charge and less sensitivity to the outside sources of distortion [5]. The instant frequency character of the current noise has been investigated by the wavelet or Hilbert spectrum method, which was correlated to individual corrosion phenomenon with different time scale [6,7]. The current noises generated from uniform corrosion, film breakdown and hydrogen evolution event etc., were characterized with the frequency of charge emission and the events generation rate based on the shot noise model [8,9]. The resulting spectral or statistical characteristic of the current noise should belong to the noisy electrode, involving possible mechanism information about the corrosion-related events. The valid characterization on the noisy current encourages us to search proper method to represent the impedance of the corroded electrode, instead of the spectral noise impedance which encounters the same problem as the noise resistance. For the electrochemical kinetics description in the equivalent circuit model, some basic impedance components named resistive, capacitive and diffusive component should be concerned [10,30].

The recurrence plot (RP)-based analysis which is adaptive to represent the complex system's dynamics, transitions or synchronization even for the short nonlinear data set, has been widely used in the dynamical systems [11–15]. The RPs and consequent recurrence quantification analysis (RQA) variables have been applied to the current noise to detect possible dynamic transition of several types of localized corrosion [16–18]. For instance, the quasi-periodic current noise was correlated to the pitting process [19], while the transition probability from metastable to stable crevice corrosion was indicated by the RQA measures [20]. The principle component model was applied on the RQA variables to monitor the carbon steel corrosion recently, but it could not distinguish the passivation and pitting status [21]. Therefore, the RQA of the current noise seems to be efficient to extract the dynamical information about the corrosion process, even though the detailed recurrence pattern was still untapped.

As an extension of the recurrence plot, the cross recurrence plot compares two simultaneously registered trajectories appropriately belonging to the same dynamical system, and subjected to different

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physical or mechanical processes [22,23]. Analogous to the determinism in the RQA, the diagonal-wise variable in the CRQA measures the dynamical similarity of the two trajectories. Suppose that the current and potential noises are simultaneously produced by the same corroding electrode, the application of cross recurrence analysis on them is suitable. The CRQA measures were used to detect stable pitting of the nickel-base alloy in our previous work, which was validated to be more credible than the RQA measures on the current noise alone [24]. The purpose of this paper is to explore the detailed dynamical information contained in the CRP and the synchronization behavior, to estimate the corrosion mechanism and degree by means of the impedance component and the synchronization index.

Dynamical synchronization phenomenon presented in the chaotic system between close coupled oscillators reveals their phase coherence, and can be measured with the aid of respective recurrence spectrum of the two trajectories [25–27]. To evaluate the synchronization type and degree, the quantitative synchronization indexes were proposed [29], and were used to estimate the corrosion degree during the evolutive localized corrosion in this study. Corrosion of the nickel-base alloy 718 exposed in the simulated sour conditions was inspected to elucidate the passivation, pitting initiation and propagation process in the frame of the proposed method, which may be instructive for either mechanism research or field monitoring in the corrosion study supported by the EN signals.

2. Methodology

2.1. Cross recurrence plot

The cross recurrence plot establishment on two simultaneous number series is analogue to that of the normal RP described elsewhere [11]. The first step is to reconstruct the phase space according to the delay coordinate embedding method. The false nearest neighboring and average mutual information method are commonly applied in selecting the embedding dimension (m) and the time delay (τ). If the embedding parameters of two systems are not equal then the higher embedding dimension should be chosen [22]. Whilst the smaller time delay was recommended in this work, because the high frequency information contained in the current noise may lose if larger τ was used. Next, the distances matrix between the two trajectories is calculated using a specified norm, resulting in the cross recurrence matrix CR_{ij} by comparing the distance matrix with the threshold ε

$$\mathrm{CR}_{ij}(\varepsilon) = \Theta(\varepsilon - \|\vec{x_i} - \vec{y_j}\|) \ , i = 1, \ \ldots, \ N, \ j = 1, \ \ldots, \ M \tag{1}$$

where Θ is the Heaviside function. The number series are usually normalized before cross recurrence analysis by subtracting the mean value and dividing by their standard deviation. The primary distinction between the RP and CRP lies in the symmetry or asymmetry with respect to the main diagonal. The line of identity (LOI) for the former is replaced by the line of synchronization (LOS) for the latter, which is defined as the line to align the paralleled running trajectories with different time scales through the non-parametric rescaling function [28].

2.2. Cross recurrence quantification analysis

There are three types of CRQA measures extracting point-wise, diagonal-wise and laminar-wise statistics, defined as recurrence rate (R), determinism (D) and laminarity (L) respectively. Considering the position of the recurrence point with distance τ to the main diagonal, the τ-recurrence rate, τ-determinism etc. have been introduced [22]

$$R_\tau = \frac{1}{N-\tau}\sum_{i=1}^{N-\tau} R_{i,i+\tau} = \frac{1}{N-\tau}\sum_{l=1}^{N-\tau} lP_\tau(l) \tag{2}$$

$$D_\tau = \frac{\sum_{l=l_{min}}^{N} lP_\tau(l)}{\sum_{l=1}^{N} lP_\tau(l)} \tag{3}$$

where P_τ (l) is the distribution histogram of diagonal lines of length l,

$$P_\tau(l) = \sum_{i=1}^{N-\tau}(1 - \mathrm{R}_{i-1,i+\tau-1})(1 - \mathrm{R}_{i+l,i+\tau+l})\prod_{k=0}^{l-1}\mathrm{R}_{i+k,i+\tau+k} \tag{4}$$

The laminarity L is analogously defined by the vertical or horizontal lines in the CRP to represent the invariant recurrence of one trajectory to the other. The CRQA measures are accessible automatically with sliding window to detect possible dynamical coupling period from the uncorrelated random noises [37].

2.3. RP-based synchronization analysis

The types of synchronization considered in this work include phase synchronization, representing a situation where the phases and frequencies of chaotic oscillators being locked and their amplitude remain uncorrelated; and the generalized synchronization, defining a transformation $y = \psi(x)$ which maps asymptotically the trajectories of one system to the other attractor with not only phase coherence but also amplitude related [25].

The RP-based synchronization analysis compares the respective recurrence spectrum (recurrence rate distribution upon τ) of two processes. According to the probability $P^\varepsilon(\tau)$ that the system returns to the neighborhood of a former point x_i of the trajectory after τ time steps, the criterion named correlation of probability of recurrence (C_{index}) was introduced to detect and quantify phase synchronization [29]

$$C_{\mathrm{index}} = <\bar{P}^{\vec{x}}(\tau)\bar{P}^{\vec{y}}(\tau)> \tag{5}$$

where $\bar{P}^{\vec{x}}(\tau)$ and $\bar{P}^{\vec{y}}(\tau)$ are the probabilities $P^\varepsilon(\tau)$ normalized to zero mean and standard deviation of one. $P^\varepsilon(\tau)$ can be estimated directly from the RP by using the τ-recurrence rate R_τ according to Eq. (2). If both trajectories are in phase synchronization, the probability of recurrence is maximal at the same time interval τ and $C_{\mathrm{index}} \approx 1$.

Considering the respective probability of recurrence not only phase coherent but also amplitude related, the generalized synchronization shall be measured by the index called the similarity of probability of recurrence (S_{index})

$$S_{\mathrm{index}} = 1 - \frac{<(\bar{P}^{\vec{x}}(\tau) - \bar{P}^{\vec{y}}(\tau))^2>}{\sigma_x\sigma_y} \tag{6}$$

where σ is the standard deviation of $P^\varepsilon(\tau)$. The degree of generalized synchronization is increasing with S_{index} up to 1, which is robust in the noisy and non-stationary conditions [29].

2.4. Numerical simulation

According to the kinetics described in the Butler-Volmer equation, the compound exponential function connecting the current and voltage defines the resistive or diffusive impedance, together with the capacitive impedance in the differential form arising from the interfacial capacitance [30,31]. EN signals, which are sensitive to the early stage of the localized attack, record the transients corresponding to the film breakdown event usually [32]. One of the typical current transient with sudden rise and exponential decay was simulated to represent the metastable pitting event [33]. The cross recurrence analysis was carried out on these transient-included signals, in comparison with the randomly generated noises, giving us a preliminary impression on the CRP pattern of the coupled and irrelevant oscillations.

To illustrate the recurrence feature of the random oscillations, the Gausian white noise and $1/f$ random noise were generated in the Matlab software. Both of their RP present uniform distribution as