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Electrochemical Techniques for Corrosion and Tribocorrosion Monitoring: Methods for the Assessment of Corrosion Rates

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Abstract

The corrosion mechanism taking place in an aqueous phase with or without mechanical contact is electrochemical in nature. The electrochemical signal is one of the primary sources of information that relates to behavior in potential, current, and electrical charge of a corroding electrode. It arises from processes that cause corrosion and other electrochemical reactions. In a sliding contact in an ionic electrolyte medium, electrochemistry is more likely to interfere with the tribological behavior of tribocorrosion systems. In recent years, attempts by researchers have been made to control the material loss by electrochemical methods for various engineering systems. Applied online for monitoring in-situ uniform, localized, galvanic, or more forms of corrosion, such techniques are very convenient means to measure corrosion rate of materials. Such methods can also be used in different ways to evaluate their ability to protect materials (as inhibitors, protective layers, coatings). In this chapter, theoretical and experimental applications, fundamental aspects, limits of the electrochemical techniques for corrosion, and tribocorrosion monitoring are presented. Standards developed, so far, by various standardization organizations are reported. Fundamentals of traditional and advanced corrosion methods are described, focusing on their advantages, i.e. sensitivity to low corrosion rates, short experimental duration, and well-established theoretical understanding.

Keywords: corrosion methods, tribo-electrochemistry, tribocorrosion, electrochemical impedance spectroscopy, electrochemical noise analysis, linear polarization resistance, Tafel extrapolation method

1. Application of electrochemical techniques for determining corrosion rates

In the section below, practical examples are described of how a number of electrochemical techniques could be used to forecast corrosion or tribocorrosion behavior in practical case studies. The focus is on laboratory tests for rapid corrosion or tribocorrosion tests. The examples do not provide bit-by-bit procedures for screening most or all potentialities. Also, the discussion is not about how to set up and conduct electrochemical corrosion or tribocorrosion experiments. Such

information can be readily found in instruction guidelines manual or standard references [1–17]. The accent is put on the interest and validity of combination techniques to provide a better understanding of the corrosion process and more reliable predictions.

1.1 Linear polarization resistance (LPR)

The concept of “polarization resistance” has presumably been initiated by Bonhoeffer and Jena in 1951 [18]—a subsequent to Wagner and Traud’s works [19, 20]. In their study of the electrochemical behavior of iron samples of different carbon contents, they found that the slope of the polarization curve, i.e., the rate of potential change E with external current i , at the corrosion potential (or open-circuit potential of a mixed electrode), was low for some iron samples and large for others. Defining this slope as “polarization resistance,” R_P , as a result of Lange’s suggestion, it was found that there was an unambiguous correlation between the polarization resistance and the corrosion rate, whereas no correlation was found between the carbon content and the rate of corrosion.

Subsequently, Stern and Geary [21] were the first authors to theoretically establish a linear relationship between the polarization resistance and the corrosion rate based on the kinetics of electrochemical reactions (i.e., corrosion current at open-circuit conditions) and the concept of mixed potential theory, first formulated by Wagner and Traud in 1938 (i.e., parameters of the cathodic and anodic E/i relations) [19]. The advantages and limitations of their method have been discussed in a series of published articles [19, 21, 22], and the linearity of the slope of current-potential plot around the corrosion potential has been verified by experimental evidence, thereby avoiding the problem of large current densities. Their theory has been experimentally supported by other authors [19, 21, 22] for different materials and under a variety of environmental conditions. From the 1960s, plenty of publications [23, 24] reported on the use of the polarization technique, which quickly became one of the main electrochemical techniques routinely adapted to rapid corrosion rate measurements, a condition necessary to its success in industrial monitoring corrosion operations.

For a system in which electrode processes involve a slow reaction step at the electrode surface, the rate of reaction is limited by activation overvoltage; the relationship between the reaction rate, or net current density i , and the driving force for the reaction, or potential E , is given by the Butler-Volmer equation. This equation relates i , for a single electrode process, such as Eq. (1) to E by the formula (2),

$$\begin{aligned} i &= i_0 \left[\exp \left(\frac{\alpha n F \eta}{RT} \right) - \exp \left(\frac{(1 - \alpha) n F \eta}{RT} \right) \right] \\ &= i_0 \left[\exp \left(\frac{\alpha n F (E - E_{rev})}{RT} \right) - \exp \left(\frac{(1 - \alpha) n F (E - E_{rev})}{RT} \right) \right] \end{aligned} \quad (2)$$

where η is the overpotential, i_0 the exchange current density (rate of either the forward or reverse half-cell reaction) at the equilibrium potential E_{rev} , α the transfer coefficient (usually close to 0.5, but must be between 0 and 1), and n the number of electrons transferred.

The graphical representation of the Butler-Volmer equation, as shown in **Figure 1**, is called the polarization curve.

Figure 4.

(a) Schematic view of a tribocorrosion experimental setup. Potential and current are measured on a working electrode (WE_1) sliding against a counterbody ball (unidirectional reciprocating sliding, sphere-on-flat) with respect to a RE reference electrode ($Ag/AgCl$ (3 M KCl)) via a V, high-impedance voltmeter, and CE (WE_2) via a zero-resistance ammeter (ZRA), respectively. F_N , normal force; F_T , tangential force; f , sliding frequency; D , displacement amplitude. (b) Schematic view of a tribocorrosion experimental setup. Potential and current are measured on a working electrode (WE) sliding against a counterbody ball (unidirectional reciprocating sliding, sphere-on-flat) with respect to a RE reference electrode ($Ag/AgCl$ (3 M KCl)) via a V, high-impedance voltmeter, and CE micro-cathode (MC) via a zero-resistance ammeter (ZRA), respectively. F_N , normal force; F_T , tangential force; f , sliding frequency; D , displacement amplitude.

(see **Figure 4b**). This last mode of electrochemical noise analysis seems to be a promising way to obtain unambiguous estimates of the rate of chemical wear in a tribocorrosion experiment as evidenced by some recent investigations [46, 47, 51] but also to predict the corrosion rate of localized corrosion in a free corroding system [29, 31, 32, 37–45, 47–50, 56].

1.3.2 Electrochemical noise data management process

The overall approach to analyzing noise data is the assessment of mechanistic information from either time-domain analysis, frequency-domain analysis, or both, using statistical methods [44, 57, 58]. If the information in the time-domain records is evident, time-domain analysis is sufficient to distinguish different processes (e.g., different forms of corrosion).

In what follows, one assumes that all various types of noise are excluded from this description, with the exception of the thermal noise. Except for the last noise, all other noise sources can be minimized or eliminated using careful strategy within reasonable limits of materiality. Effective and convenient ways include the removal of unwanted environmental and instrumental noise from the electrochemical noise, e.g., by shielding electrical connections/wires for coupling the electrodes to the experimental apparatus, by using a Faraday cage to exclude electrostatic/electromagnetic influences, even by implementing analogue/digital filters to eliminate systematic noise at frequencies different than the frequency of interest, and so on. Guidelines for the calibration of noise measuring device can be found elsewhere [13, 59].

1.3.3 Noise resistance

The basic quantitative approach is the time-domain analysis of the noise signal. The noise resistance, R_N , is defined as the ratio of the standard deviations of potential/current noise signal time dependent, $\sigma(t)$:

$$R_N = \frac{\sigma_E(t)}{\sigma_I(t)} \quad (11)$$

Eq. (11) implies that in the case where a low-driving force noise produces a high current density noise between the two electrodes (WE_1 and WE_2), the yielding noise resistance will be low. Noise resistance, R_N , has been shown to correlate well with the polarization resistance, R_P , as determined by EIS for certain corrosion systems. This latter being directly related to the corrosion current [14, 29, 60] is using the Stern-Geary equation and Tafel slopes. Notwithstanding, much work has been devoted trying to best match R_N or the normalized R_N (per unit of exposed surface area) to the corrosion resistance or the corrosion rate [5, 14, 31, 32, 37–45, 48–50, 60]. Although signal analysis in the time domain is well established, an approach based on spectral analysis is gaining more and more importance in research laboratories. It consists of transforming the potential and current noise fluctuations recorded in the frequency domain using the Fast Fourier Transform (FFT) method [61].

The frequency range for which the FFT is commonly performed extends from 1 mHz up to 1 Hz. The spectral noise plots are similar to those of impedance plots. The spectral noise resistance, R_{SN} , is given by the ratio of the potential and current FFTs at each frequency, and the limiting value, R_{SN}^0 , can be used as a measure of the corrosion resistance:

$$R_{SN}(f) = \left(\frac{E_{FFT}(f)}{I_{FFT}(f)} \right) \quad (12)$$

The *log-log* plot of R_{SN} versus f is similar to the impedance plot, and the spectral noise resistance limit R_{SN}^0 is given by

$$R_{SN}^0 = \lim_{f \rightarrow 0} R_{SN}(f) \quad (13)$$

Another approach would be to examine the spectral noise response in terms of power spectral densities (PSD). These latter are calculated from the FFT or using the maximum entropy method (MEM) [62]. R_{SN} is determined from the PSDs by the relation (14):

$$R_{SN}(f) = \left(\frac{E_{PSD}(f)}{I_{PSD}(f)} \right)^{1/2} \quad (14)$$

It has been shown that the use of a single data set of potential and current noise [32] would yield identical values of R_{SN} as calculated by either Eqs. (13) or (14). In some cases, R_{SN}^0 is bound to R_N or R_P as,

$$R_N = R_{SN}(0) = R_P \quad (15)$$

effective if the impedance of the two electrodes is identical and much higher than the resistance of the test solution between them [5, 32, 63]. Experiments have validated this relationship for several systems [5, 31, 63]. Nonetheless, there is no agreement on the fundamental basis for the relationship between noise resistance and corrosion rate.

1.3.4 Illustrative examples of the application of electrochemical noise in tribocorrosion systems

Investigations into electrochemical kinetics make common point research between tribocorrosion and corrosion. The study of localized phenomena of

depassivation and repassivation is essential to understand the mechanisms of corrosion-wear as well as to reduce the material loss. The possibility of using the electrochemical noise detection technique as a promising tool to study the electrochemical properties of well-controlled damaged surfaces has been widely considered due to its nondestructive nature and its potential in online corrosion monitoring applications. Time-spatially resolved measurements should provide more reliable data on the electrochemical part of tribocorrosion. The noise analysis in relation to depassivation-repassivation events randomly distributed in time and space can be traced back to Oltra et al. [64]. The power spectral density (PSD) of the noise under the impact of the jet particles was related to the Fourier transform of individual repassivation transients obeying a Poisson distribution. Later, the application of electrochemical noise analysis to tribocorrosion was reviewed. Investigations involving PSD noise analyses on various tribo-electrochemical cells for passivating materials were conducted by Ponthiaux et al. [65], by Déforge et al. [51], and in more details by Berradja et al. [46, 66]. In this latter work, the noise spectra were measured on AISI 304 L stainless steel versus corundum in a Ringer's solution in a pin-on-disk tribometer under stationary sliding-corrosion regime conditions, either at open-circuit potential or at a controlled potential. The PSD of the current noise has been interpreted as resulting from the overlap of the large number of discrete repassivation transients at the contact junctions, including the double-layer charge and the strong dependence of depassivation and repassivation kinetic rates of the oxide surface film on the sliding frequency. This was consistent with the shift in the PSD plots of the current noise fluctuations by about a decade when the sliding frequency was varied from 0.1 to 1 Hz (see **Figure 5**). Similar findings were obtained via Déforge et al. [51] by dividing open-circuit potential fluctuations to the impedance of the electrode. A $1/f$ low-frequency noise is explained by a long-term drift of the surface conditions. Only a minor influence of the applied normal load was observed on the PSD plots, recommending reaching the limit rate of the depassivation of the oxide surface film.