State-of-the-Art Review of Electrochemical Noise Sensors

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Introduction

There are a number of different techniques capable of being used to measure corrosion within equipment. The most simple, the use of metal coupons, usually causes the process to be shut down, is manpower intensive, and has a time delay in getting the required corrosion information. Electrical Resistance (ER) techniques are often used but their response is very sensitive to temperature and they cannot differentiate between general and localized corrosion. Electrochemical techniques, such as linear polarization resistance (LPR), electrochemical noise (EN), electrochemical impedance spectroscopy (EIS), harmonic distortion analysis (HDA), and electrochemical frequency modulation (EFM), have the capability of solving most of those drawbacks. Electrochemical probes can be mounted permanently in most equipment, give regular measurements of the intensity of corrosion, and some can detect localized corrosion.

Of all of the electrochemical techniques, EN has the most potential for being used successfully to measure general and localized corrosion rates of equipment. The EN technique was studied in the late 1970s and early 80s as a means of detecting localized (stochastic) corrosion phenomena, such as occurs with pitting, crevice and cavitation attack. EN measurements are based on fluctuations in electrochemical potential and corrosion current that occur during corrosion. Electrochemical potential is related to the driving force (thermodynamics) of the reaction, while corrosion current is related to the rate of reaction (kinetics) of the reaction. The idea is that random electrochemical events on the surface of a corroding metal will generate noise in the overall potential and current signals. Each type of corrosion (for example general corrosion, pitting corrosion, crevice corrosion, and stress corrosion cracking) will have a characteristic “fingerprint” or “signature” in the signal noise. This “fingerprint” can be used to predict the type and severity of corrosion that is occurring.

By comparison, conventional electrochemical techniques such as LPR, EIS, HDA and EFM rely on a steady-state analogy for the determination of *general* corrosion rates. Early studies were carried out using potential EN measurements, using time domain, statistical and frequency domain analyses to characterise the electrochemical response of systems undergoing localised corrosion. Current EN measurements followed quickly using zero resistance ammetry to study the current noise between two identical electrodes. For general corrosion processes, EN has been demonstrated independently by several workers to provide information similar to LPR. Noise technology has been used to study systems undergoing very low to very high rates of corrosion, for example, coatings performance, passive systems undergoing pit initiation/propagation, condensing systems, systems undergoing stress corrosion cracking, and general corrosion through to the very high corrosion rates experienced during chemical cleaning processes.

This review will describe: state of the art methods and probes used to measure EN, data acquisition requirements, theory to analyze the signal and to relate the signal to corrosion rates and types, the results of EN field trials, and laboratory results in environments similar to gas-pipelines.

EN Measurements, Methods, and Probes

Electrochemical noise sensors typically consist of three electrodes, in one of three arrangements: WE-RE-CE, WE-WE-RE, and WE-WE-WE, where WE is a working electrode (consisting of metal of the same type that is being monitored), RE is a reference electrode (an electrode that maintains a constant potential in the environment), and CE is a counter electrode (typically platinum). The WE-RE-CE arrangement is extensively used in laboratory settings for electrochemical studies under polarized conditions. In contrast, the WE-WE-RE arrangement could be used for EN measurements without potential control (i.e., freely corroding). The two WEs allow for the simultaneous measurements of current and potential noise. It is widely used in plant monitoring and surveillance situations. Special WE arrangements can be used to monitor specific types of corrosion. For example, when susceptibility to stress corrosion cracking (SCC) needs to be monitored, the two WEs could consist of one unstressed electrode and one stressed electrode. The third type uses three working electrodes. This type can be useful when reference electrodes are impractical or otherwise unsatisfactory. [Eden]

The sensor array design depends upon the application and the type of corrosion being monitored. Consideration must be given to maintain electrical isolation between the electrodes, to have materials able to withstand the environment, to have a surface appropriate to the type of corrosion being monitored, and to the conductivity of the environment. Some example sensor arrangements and considerations are:

General Corrosion: In general corrosion studies, typically in low-pressure, low-temperature aqueous systems with high conductivities, a three-finger electrode assembly is often used. The electrodes protrude into the solution through o-ring seals and are combined into one fitting through the container wall. [Eden]

Flowing Conditions; In flowing conditions such as in oil and gas flow-lines, high-pressure spool-piece fittings can be used that replace a section of pipe. The fitting consists of three circumferential rings of WEs that are separated from each other and the pipe flanges with insulators. [Eden]

Pitting: Sensors for detecting pitting must have sufficient surface areas so that the probability of attack during monitoring is high. Eden (1998) suggests a surface area above 10 cm^2. Care must also be taken to eliminate crevices in the design since systems that are prone to pitting are also prone to crevice corrosion, and crevice corrosion may initiate prior to pitting. [Eden]

Coatings and Linings: In situations with coatings and linings, the high impedance of the coatings combined with the necessity of obtaining a representative sample area typically require electrode areas in excess of 30 cm^2. The thicker the coating, the larger the electrode surface area needs to be. One of two arrangements is typically used. In the first, an isolated WE-WE-RE array is used with the two nominally identical specimens coated as the WEs. In the second, the sensor array is beneath the coating so that it is sensitive to permeation of the coating by the corrosive environment. [Eden]

Low Conductivity: In low conductivity environments, it is important to minimize the effects of solution conductivity. This is done by reducing the spacing between electrodes and increasing the surface areas of electrodes. Care should be taken in the insulating material, especially with respect to their wetting, since it is necessary to maintain electrical isolation between the electrodes. [Eden]

Condensing Environments: In condensing environments, where the potential for corrosive condensates exist (such as acid dewpoint in flue gas), flush mounted, laminar probes have been successfully employed to detect the onset of the dewpoint condition. [Cox]

A search for EN sensor patents obtained the following five results (each followed by a very brief summary):

S. A. Reid and D. A. Eden, 2001, US 6,264,824 B1, “Assessment of Corrosion,” A method and apparatus for using EN to asses corrosion, preferably with skewness and kurtosis analysis using neural nets.

G. A. Martincheck and M. R. Yaffe, 2000, US 6,015,484, “Detection of Pitting Corrosion,” A modification of the WE-WE-RE sensor arrangement where one WE is anodically biased with respect to the other WE. It claims to allow the prediction of the on-set of pitting prior to it occurring.

D. H. Pope, Y. J. Lin, E. J. St. Martin and J. R. Frank, 1999, US 5,888,374, “In-Situ Process for the Monitoring of Localized Pitting Corrosion,” It uses a WE-WE-RE sensor arrangement for monitoring pitting corrosion in metal pipes and storage vessels using EN. Analysis transforms the EN into power spectral density (PSD) data using fast Fourier transform.

Y. Tanaka, S. Iwahashi, M. Miyazawa and K. Morita, 1996, 10019826 JP, “Apparatus for Measuring Corrosion of Metallic Material,” It describes a general process for EN measurement and data analysis.

D. H. Roarty and D. A. Eden, 1994, EP 0 607 057 A1, “Electrochemical Monitoring of Vessel Penetrations,” It is a through-vessel wall sensor array for electrochemical measurements, including EN, for monitoring SCC.

Data Acquisition System Requirements

The data acquisition system (DAS) should resolve signals in the μV range and be able to accommodate voltage offsets that result from the use of reference electrodes. At least a 16 bit analogue-to-digital converter is required. The DAS should allow simultaneous measurement of current and voltage. Very high data acquisition rates are not needed; indeed, at high rates the amplitude of the instrumental noise can approach EN levels. Therefore a minimum logging period of one second is satisfactory. [Eden]

The importance of DAS equipment has been shown by laboratory round robin testing of EN standards. In these tests, reproducible information was obtained only when there was sufficient standardization in techniques. The round robin testing resulted in recommending: 1) the use of equipment able to test in the frequency range 0.01 Hz to 10 Hz, 2) the sampling rate must be twice the highest frequency of the phenomenon being studied (however, for modern equipment this is no longer an issue), 3) the complete measuring apparatus must exhibit small amounts of background noise of less than ±100 µV or ±10 nA, 4) continuous measurements of at least 10 minutes in duration, 5) better standardization in methods used in data evaluation, and 6) greater attention to be paid to the interactions between the ways that EN measurements are made (such as sampling rate, filtering, data processing, and background noise). [Goellner]

Current Theory in EN Analysis

Analysis of EN signals can be classified into a variety of methods: visual, sequence-independent, and sequence-independent. Visual examination of the time record trace can give indications as to the type of corrosion processes that are occurring. Statistical analysis of the noise signals indicates that the noise data generated during general corrosion has a relatively normal Gaussian distribution and will exhibit few rapid transients. In contrast, localized corrosion processes such as pitting and SCC have transients in the time record trace, and have characteristics that help distinguish between them. Localized corrosion leads to deviation from a normal distribution (Poisson distribution) as may be determined from the skewness and kurtosis of the signals. Other means of identifying localized corrosion involve the use of the Localization Index (L.I.) derived from the ratio of the standard deviation of the current to the root mean square (rms) of the current. If techniques such as LPR and HDA are also used, then independent derivation of the general corrosion current (I_{corr}) is possible. The ratio of the current noise (standard deviation of the current) to the general corrosion current may then be used as an improved indicator of localized corrosion activity.

Statistical analyses that treat the data as a set of values, without regard as to the order that the data was collected are termed “sequence-independent” and are shown below. [Eden, Cottis]

Statistic	Formula	Comment
Mean, ŷ	$\boldsymbol{\hat{y} = \frac{1}{N}\sum_{i=1}^{N} y_i}$	Mean current indicates galvanic coupling current. Mean potential verses a reference electrode indicates reaction type. Estimated error of $\sigma(1/N)^{1/2}$.
Variance, m_2	$m_2 = \frac{1}{N}\sum_{i=1}^{N}(y_i - \hat{y})^2$	Indicates the power in the noise signal.
Third moment, m_3	$m_3 = \frac{1}{N}\sum_{i=1}^{N}(y_i - \hat{y})^3$	A measure of the asymmetry of the data around the mean.
Skewness, g_1	$\boldsymbol{g_1 = \frac{m_3}{m_2^{2/3}}}$	A normal distribution will have a g_1 of zero. A distribution with more of a tail in the positive direction will have a positive g_1, and one with more of a tail in the negative direction will have a negative g_1. Estimated error of $(6/N)^{1/2}$.
Fourth moment, m_4	$\boldsymbol{m_4 = \frac{1}{N}\sum_{i=1}^{N}(y_i - \hat{y})^4}$	

Normalized Kurtosis, g_2	$\boldsymbol{g_2 = \frac{m_4}{m_2^2} - 3}$	A normal distribution will have a g_2 of zero. A positive g_2 reflects a more peaked distribution and a negative g_2 a less peaked distribution. Estimated error of $(24/N)^{1/2}$. A $g_2 \geq 2$ is typical for localized corrosion
Standard deviation, σ	$\boldsymbol{\sigma = \sqrt{m_2}}$	A measure of the spread of the data that relates to the broadband ac component of the signal. Estimated error of $\sigma(2/N)^{1/2}$.
Coefficient of variance, C of V	$\boldsymbol{C\ of\ V = \frac{\sigma}{\hat{y}}}$	Measures the distribution of the data around the mean. Similar meaning as LI.
Root mean square, rms	$rms = \sqrt{\frac{1}{N}\sum_{i=1}^{N} y_i^2}$	
Localization Index, LI (of current, i)	$\boldsymbol{LI = \frac{\sigma_i}{i_{rms}}}$	Measures the distribution of the current around the rms. LI ranges in value from 0 to 1. When LI is close to 1, localized corrosion is likely. A LI on the order of 0.001 indicates general corrosion.

Statistical analyses that take into account the order in which the data were collected are termed "sequence-dependent". These methods retain more of the information in the data than the sequence-independent methods, but are much more difficult analyses to perform in terms of computational requirements and in error propagation. A description of each sequence-dependent method follows:

Autocorrelation Function: The autocorrelation function (ACF) is the expected value of the product of the time series at one time and at certain later times. For example, with Gaussian white noise (typical of general corrosion), where each reading is independent from each other and from a normal distribution, the ACF is zero. [Cottis]

Power Spectra: The estimate of the power present at various frequencies results in plots of the power spectra density (PSD) as a function of frequency. The units of PSD for potential and current are V^2/Hz and A^2/Hz, respectively. There are two primary methods used in the corrosion field: Fourier transform and maximum entropy. [Cottis]

The Fourier transform method computes the combination of sine waves needed to obtain the observed signal. The fast Fourier transform (FFT) algorithm is usually used, where the PSD is determined as the amplitude squared of the sine waves, divided by the frequency separation. To minimize artificial noise in the spectrum, trend removal and windowing are applied to the time record prior to computing the spectrum and the results from several spectra are then averaged. [Cottis]

The maximum entropy method (MEM) fits functions to the ACF and then uses a Fourier transform to obtain the PSD. This procedure acts to smooth the power spectrum. The MEM computes a number of coefficients that describe the ACF; the number of coefficients is known as the order of the MEM and is an adjustable parameter. A low-order MEM results in a very smooth PSD, while a high-order MEM results in a very noisy PSD (much like the unsmoothed FFT). [Cottis]

Higher-Order Spectra: Similar to the higher-order statistics in the sequence-independent methods, higher-order sequence-dependent methods are available. However, the results are even more difficult to interpret, and it is not yet known how to extract the relevant information contained within the spectra. [Cottis]

Other Methods: There are several other methods being examined for use in EN analysis. *Wavelet* methods use a variant of the Fourier analysis where transients with a finite duration ("wavelets") are used instead of sine waves to obtain the observed signal. The use of *chaos theory* has been attempted by several researchers, but the results are still theoretical. [Cottis]

Thus far, only parameters obtained from either the potential or current time record have been considered. However, when potential and current are measured simultaneously, combinations between the two can be used. Examples include the noise resistance, R_n, which is the ratio of the potential to current standard deviations, and the noise impedance, which is the square-root of the ratio of the potential to current PSDs (calculated at specific frequencies). [Cottis]

The above methods are used to analyze the EN from a system. Attention must also be paid to noise resulting from non-corrosion processes. These include *thermal noise* from the thermally-activated charge carrier motion (which generates a potential PSD equal to 4kTR, where k is the Boltzmann constant, T is the absolute temperature, and R is resistance), *shot noise* from the quantum nature of charge (which generates a current PSD equal to 2qI, where q is the charge on the charge carrier and I is the mean current), and *flicker noise* where the PSD is proportional to the reciprocal of the frequency. Of more interest are EN sources from corrosion processes: [Cottis]

Pitting: Metastable pit nucleation, growth, and termination all produce current transients with a duration of a few seconds. Metastable pits frequently exhibit a slow current rise followed by a sharp current fall for stainless steel and a moderate current rise followed by a slower fall for carbon steel and aluminum alloys. At high frequencies, the log (potential PSD) verses log (frequency) plot will have a characteristic "roll-off" slope, which depends on the double layer capacitance. For aluminum at low frequencies, it has been found that shot noise analysis can yield an estimate of pit dimensions. [Cottis]

Particle Impact: Particle or bubble impacts on a surface may increase or decrease the corrosion rate by removal of passive films or by shielding of the surface, respectively. The EN produced can be analyzed with essentially the same methods as in pitting. [Cottis]

Activation-Controlled Dissolution: Activation-controlled dissolution of the metal typically occurs at atomic ledges and kinks on its surface. This gives rise to a shot noise process with a charge of between 100 to 300,000 electrons (depending upon the dislocation density). This results in noise in the current PSD at about $2neI_{corr}A^2/Hz$, where n is the number of electrons involved in each burst of charge and e is the charge of an electron. [Cottis]

Crevice Corrosion: Crevice corrosion is similar to pitting and will give similar characteristics. However the onset of crevice corrosion often has a large drop in potential as the active crevice polarizes the passive non-crevice surface. If this drop is permanent, then visual inspection of the potential-time record indicates crevice corrosion. If the passive surface is unable to sustain the current needed in the active crevice, then oscillations in the potential-time record can occur as the crevice activates and passivates. [Cottis]

Stress Corrosion Cracking (SCC): Stress corrosion cracks can grow either in a continuous or discontinuous manner, and have quite different EN signatures. Discontinuous crack growth produces transient currents as new surface is exposed. It can be analyzed in a similar manner as pitting. Continuous crack growth should give lower EN levels. In either case, as the crack propagates deeper into the surface, greater shielding of EN may limit detection. [Cottis]

Corrosion Fatigue: Corrosion fatigue is expected to generate EN that is dominated by the applied load frequency. [Cottis]

The Reid and Eden patent gives the following table to identify the corrosion mechanism with skewness and Kurtosis analyses of the potential and current signals.

Mechanism	Potential		Current	
	Skewness	Kurtosis	Skewness	Kurtosis
General	< ±1	< 3	< ±1	< 3
Pitting	< -2	>> 3	> ±2	>> 3
Transgranular SCC	+4	20	-4	20
Intergranular SCC #1	-6.6	18 to 114	1.5 o 3.2	6.4 to 15.6
Intergranular SCC #2	-2 to -6	5 to 45	3 to 6	10 to 60

EN Field Experience

There is experience in using EN sensors in several field applications. A selection of these efforts are given below:

Hydrocarbon Pipelines (offshore pipeline): EN sensors with data analyses of noise resistance, R_n, and the product of the corrosion current and the localization index, $I_{corr} \cdot LI$, were used along with linear polarization to monitor corrosion in an inhibited pipeline. The low corrosion rates from the EN and linear polarization methods were in close agreement. [Ryder]

Sour Gas Processing Plant (Alberta, Canada): EN sensors were installed in several process units for two years. EN sensors identified the onset of pitting in a sulfinol contactor tower where the solvent was contaminated with air. [Teevens]

Sour Gas Field (Alberta, Canada): EN monitoring was used in field evaluation of inhibitor effectiveness and minimum effective levels in a pitting prone environment with an acid gas content of 17% H_2S and 3.5% CO_2. Corrosion inhibitors account for up to 25% of operating costs. [Barr]

Nuclear Waste Storage Tanks (Hanford, WA): EN sensors were installed in double shell underground waste tanks in both immersion and vapor-phase placements. The sensors were employed in an attempt at early detection of localized corrosion of the tanks. Early results were plagued with extraneous noise from electrostatic interference using long analog data cable and cross-talk problems. After solving these issues all channels have shown approximately 1 mpy corrosion in liquid immersion and 0 mpy in vapor-phase placement. [Edgemon and Edgemon]

Water Treatment Plant (Lost Hills, CA): Five-element probes that simultaneously performed EN and linear polarization measurements were installed at locations with historical corrosion rates of 0.5

to 450 mpy. Problems included probe fouling, data collection volume, and awkward data manipulation routines. However, the monitoring did provide useful plant operation data. [Bell]

Freshwater Cooled Heat Exchangers (Ontario, Canada): EN sensors were designed for field testing of microbiologically influenced corrosion (MIC). A reproducible electrochemical response was observed that may be a MIC EN signature. [Brennenstuhl]

EN Laboratory Studies in Gas Pipeline-Type Environments

Three laboratory studies were identified as being in environments similar to gas pipeline conditions:

A 7.5 cm diameter, 10 m long multiphase oil/water/gas flow system was examined with EN measurements with a variety of 2-phase and 3 phase slug flows. EN analysis using FFT identified uniform corrosion with full pipe flow (roll-off slopes greater than –40 dB/decade). In slug flow has characteristic frequency transients indicating pitting (roll-off slopes less than –20 dB/decade). Slugging frequencies were also identified. [Deva]

Corrosion measurements in flowing oil-electrolyte (water with 3% NaCl) mixtures was examined with EN sensors. Three distinct noise patterns were observed. The first was a low noise baseline for oil without electrolyte, for oil with small additions of electrolyte, and for oil with electrolytes but with under low-flow conditions. The second was a low noise signal but with periodic bursts of current for moderate electrolyte additions under high-flow conditions. The third pattern was a high amplitude signal for high electrolyte additions under high-flow conditions. The use of neural networks was explored in an effort to automatically analyze for the three conditions. [Malo and Malo]

The CO_2 corrosion of a carbon steel pipe was examined using EN measurements. The EN parameters of noise resistance, R_n, and noise impedance were related to corrosion activity and flow turbulence. [Krebs]

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