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The relationship between spectral and wavelet techniques for noise analysis

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ABSTRACT

Despite over 40 years of research, the optimum methods for the analysis of electrochemical noise data remain uncertain. One class of methods examine the frequency content of the noise signal. The first such method to be used was conventional spectral analysis, initially using the Fourier Transform, and subsequently the Maximum Entropy Method. Apart from questions over the relative merits of the two methods, the estimation of the power spectrum suffers from the formal requirement that the signal being analysed is stationary, since corrosion processes are frequently non-stationary. This has lead to the use of alternative analysis methods that do not require the signal to be stationary, including wavelet analysis and, more recently, the Hilbert-Huang transform. It is not always appreciated that the wavelet method was developed as an extension of the Fourier transform and that there is a close relationship between the two methods. This paper will explore this relationship and implications for the analysis of electrochemical noise.

1. Introduction

Electrochemical noise measurement is an established technique in corrosion studies, commonly measured using the conventional method whereby potential and current noise are measured simultaneously using three electrodes. The fluctuations in potential and current are typically small, and care is required to obtain reliable and valid data [1–3]. Once valid potential and current versus time data have been obtained, there remains the problem of extracting useful information. It is now reasonably well-established that average properties can be obtained using analyses that are comparable to linear polarisation resistance or electrochemical impedance spectroscopy [4]. Thus the electrochemical noise resistance, R_n, can be determined as the standard deviation of potential divided by the standard deviation of current and multiplied by the area of one working electrode to normalise for area. This can then be used to estimate corrosion rate via the Stern–Geary relationship. The estimation of electrochemical noise impedance (Z_n, also known as the spectral noise resistance) is similar, except that the power spectra of potential and current are first estimated, and the impedance amplitude is then estimated as $\sqrt{PSD_E/PSD_I}$, where PSD_E and PSD_I are the power spectral density of potential and current respectively (the estimation of power spectral density will be discussed further below). There are some limitations and constraints on these analysis methods:

- In addition to the assumptions inherent in the use of the Stern–Geary relationship, the methods require the assumptions that the two working electrodes are similar and that the noise generation process is stationary
- If the two working electrodes are similar it can be shown that the potential and current noise signals are uncorrelated.[1] This has two main consequences: the values of R_n and Z_n are inherently noisy, and it is not meaningful to compute the phase relationship between potential and current, so we can only estimate the modulus of the impedance, not the phase.
- The measurement of R_n uses an arbitrary range of frequencies and amplitudes that may not be appropriate for the valid

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[1] This results from the expectation that the two current noise sources on the two working electrodes will be uncorrelated. Then the measured current will be a function of the difference between the two uncorrelated currents, while the measured potential will be a function of the sum of the two uncorrelated currents. The sum and difference of two uncorrelated sequences are themselves uncorrelated, consequently the equivalence of R_n and R_p is a statistical expectation rather than a deterministic result.

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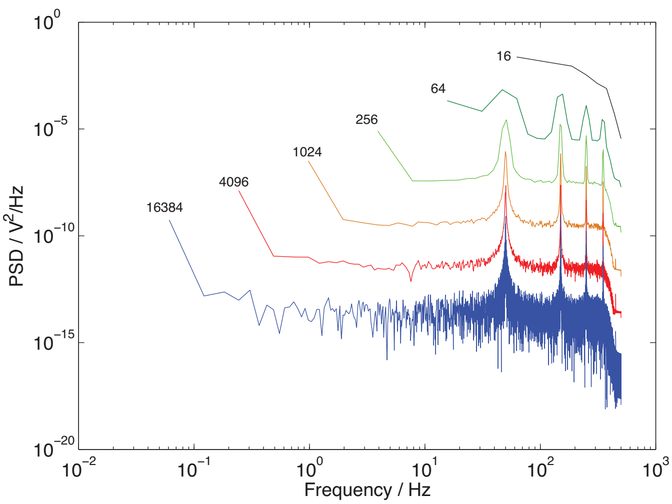

Fig. 1. Power Spectra computed using the Welch Method with a Hamming window and with a range of segment lengths; the number of points in each segment is indicated adjacent to the corresponding curve. For clarity successive curves are displace by 100 times in the y-axis.

measurement of the polarisation resistance. This can be overcome by averaging Z_n over a suitable frequency range, in much the same way that a single sine measurement can be used to obtain a measure of R_p at a specified frequency.

- While these analyses have good theoretical and practical justification, they provide little advantage over conventional methods. The absence of applied perturbation is often claimed to be an advantage, as is the simpler instrumentation, but both of these are rather illusory–the amplitude of the perturbation required to measure EIS need be little more than that applied by one working electrode to the other in the noise measurement, and in the absence of dedicated EN measurement systems, most EN measurements are made using the same general-purpose computerised potentiostats that are used for EIS. Disadvantages of EN methods include the inherently noisy results, the arbitrary frequency range used in determining R_n (although this can be overcome by selecting appropriate frequencies from the power spectra) and the limited frequency range of Z_n.

Thus, while the estimation of corrosion rate from EN measurements has some value, the greatest interest in the development of the EN method lies in the possibility that the method can provide information about the nature of the corrosion process. Several approaches to this problem have been tried; the method that will be examined in this paper is the analysis of the frequency content of the EN signals.

2. Spectral Estimation

Spectral estimation is the process of determining the relationship between amplitude and frequency for a signal. It is commonly assumed that the signal continues indefinitely and is stationary. Consequently it is described as an estimation process because it is assumed that the objective is to use a relatively short sample to estimate the amplitude-frequency relationship over all time, in much the same way that the standard deviation of a sample is an estimate of the standard deviation of a population.

The classical method of spectral estimation is based on the Fourier transform. In essence this uses the fact that both $\int_{-\infty}^{+\infty} \sin(xt)\sin(yt)dt$ and $\int_{-\infty}^{+\infty} \cos(xt)\cos(yt)dt$ are non-zero only when x = y. The sum of these two functions can alternatively be written in the exponential form $\int_{-\infty}^{+\infty} e^{-2\pi jyt} e^{-2\pi jxt} dt$. where j is the square root of -1. Thus we can determine the frequency content of a signal $H(t)$ by computing the integral $\int_{-\infty}^{+\infty} e^{-2\pi ft} H(t)dt$ for a range of values of the frequency f. Since the phase is often not meaningful, it is common to plot the modulus squared as a function of frequency, and since the power dissipated in a resistor is proportional to V^2 or I^2 the result per unit frequency is known as the power spectral density, PSD, with units of V^2/Hz or A^2/Hz. The PSD is essentially a frequency-discriminated form of the variance (the variance is equal to the integral of the PSD over frequency). The resultant plot of PSD against frequency, usually using log-log scaling, is known as a power spectrum or periodogram.

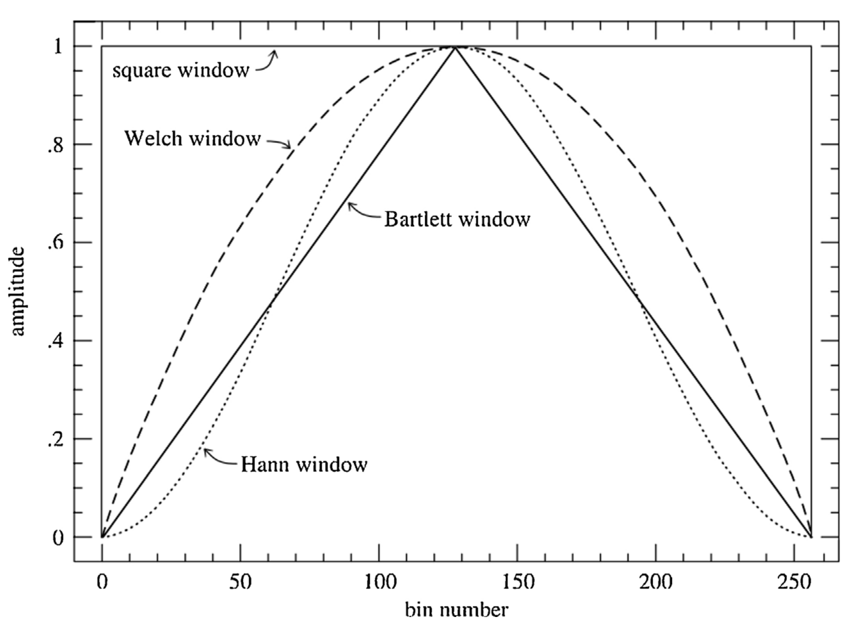

Fig. 2. Typical Window Functions (from [5]).