Comment on "Laboratory-Scale Identification of Corrosion Mechanisms by a Novel Pattern Recognition System Based on Electrochemical Noise Measurements" [J. Electrochem. Soc. , 166, C284 (2019)]

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HAL Id: hal-02280701
https://hal.sorbonne-universite.fr/hal-02280701

Submitted on 6 Sep 2019

COMMENTS on

Laboratory-scale identification of corrosion mechanisms by a novel pattern recognition

system based on electrochemical noise measurements,

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Journal of the Electrochemical Society, 166 (12) C284-C295 (2019)

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Papers dealing with electrochemical noise measurements (ENM) published in scientific journals often propose advanced signal processing techniques, in particular to determine the corrosion mechanisms. Most of the time, this is done without first validating their measurements. However, validation is not possible by simply visualizing the time records; rather, it is necessary to measure the EN at different sampling frequencies and check the overlap of the power spectral densities (PSDs) in the common frequency ranges [1,2]. Such validation is mandatory because many commercial potentiostats do not have anti-aliasing filters before the analog-to-digital converters in the measurement channels. The aliasing of high-frequency signal components to frequencies below half of the sampling frequency corrupts the EN signal in both time and frequency domains. This explains the dramatic scatter of the PSDs of the thermal noise generated by dummy cells, as shown in the round-robin tests organized by the European Cooperative Group on Corrosion Monitoring of Nuclear Materials (ECG-COMON) [2,3].

The paper by Zhang et al. [4] presents EN results on the corrosion of 304 stainless steel (SS) in $FeCl_3$ solution. Fig. 2 of that paper shows good overlap of the PSDs of the noise measured at 3 different sampling frequencies on a dummy cell with 3 resistors of 1 MΩ in a

star arrangement, as those used in the round-robin tests mentioned above. However, the typical PSDs of the potential and current fluctuations expected to correspond to the three corrosion-related mechanisms of 304 SS (uniform corrosion, pitting corrosion and passivation) in Fig. 6 were particularly inaccurate. These PSDs were recalculated from the raw time records obtained during the review process at another journal. A simple linear detrending and a Hann window were applied on each block of 2048 points of the raw data with the software "*psd-detrend_ECG-COMON.exe*", available for free on the ECG-COMON website (www.ecg-comon.org) [1]. The results, shown in Fig. 1 below, are much more accurate than in Fig. 6 and allow a more thorough analysis of the ENM.

Even if the low-frequency parts of the PSDs could be improved by using a detrending method of order higher than 1 for the time records showing a high drift, the high-frequency parts are calculated with high precision. In the passivation case, the PSDs at frequencies above 0.1 Hz are due to the noise generated by the zero-resistance ammeter (ZRA) itself. Indeed, the amplitude of the potential PSD at 0.1 Hz is the same as for the 1 MΩ dummy cell (10^{-11} V^2 Hz^{-1}, see Fig. 2a in Zhang et al.). Moreover, the current PSD increases with frequency above 0.1 Hz and reaches a plateau of amplitude 4×10^{-21} V^2 Hz^{-1} at 1 Hz. This can only be explained by the fact that the PSD of the current noise was dominated by the regulation noise, which is equal to $\Psi_{Vreg}(f) / 4|Z|^2$ (see Fig. 7 and Eq. 18 in Ref. 5) where V_{reg} is the regulation noise (voltage fluctuations around the DC value of 0 mV applied between the two electrodes by the ZRA) of the instrument. At high frequency, $\Psi_{Vreg}(f)$ does not depend on frequency while the impedance modulus decreases with increasing frequency, hence explaining the increase of the current PSD with frequency.

As a consequence, most of the fluctuations of the potential and current time records were due to the instrumentation and not to the passivation process, so that all the moments

E_{std}, E_{skew}, E_{kurt}, I_{std}, I_{skew}, I_{kurt}, and R_n in Zhang et al. [4] cannot be attributed to the

passivation process, which should not be considered in this study.

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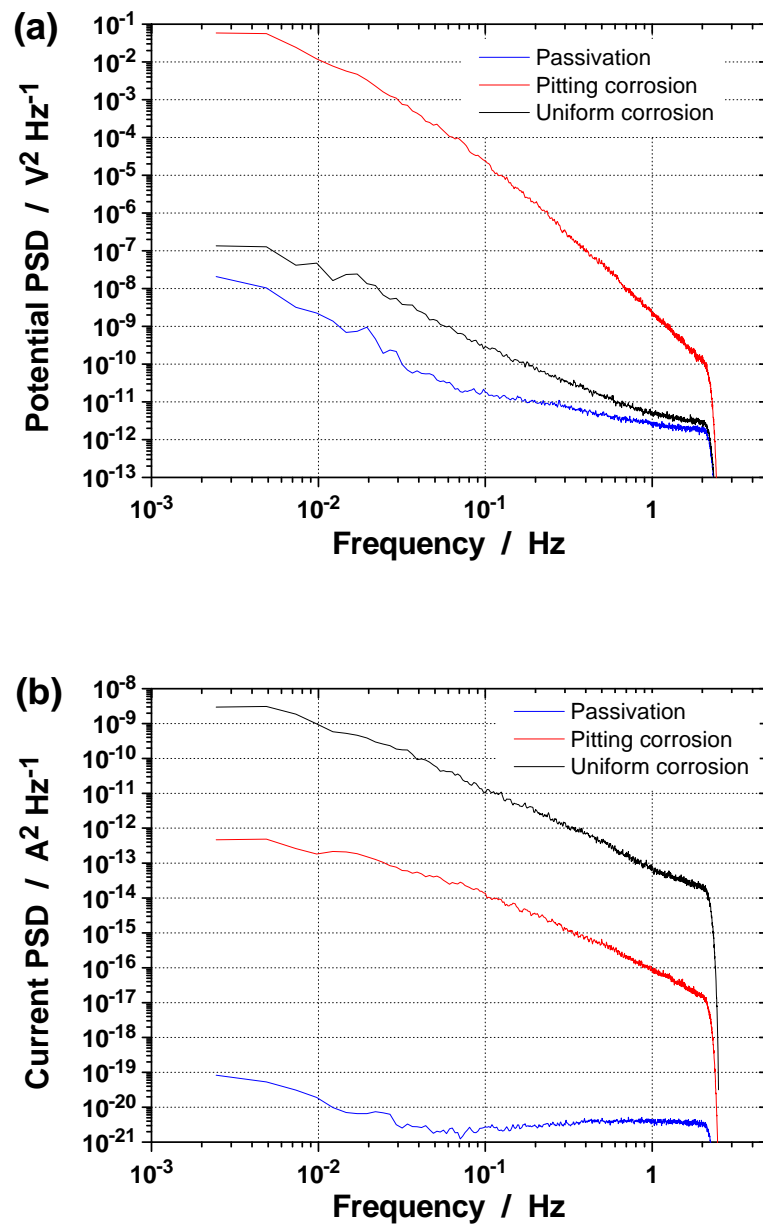[5]   U. Bertocci and F. Huet, This Journal, **144**, 2786 (1997).

Figure 1. Typical PSDs of the EN signals corresponding to the three corrosion mechanisms of 304 SS, (a) Potential PSD, (b) Current PSD.