

Review-Electrochemical Noise Applied in Corrosion Science: Theoretical and Mathematical Models towards Quantitative Analysis

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1	Review — Electrochemical Noise Applied in Corrosion Science:
2	Theoretical and Mathematical Models towards Quantitative Analysis 1
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¹ Dedicated to Prof. Shizhe Song on the occasion of her eightieth birthday

20 Abstract

Electrochemical noise (EN) can be used in situ to investigate corrosion processes and to detect and monitor the corrosion of metallic materials. EN data are largely influenced by the measurement mode, the surface area of the working electrodes, the electrolyte resistance, and the symmetry of the electrode system. Herein, the advantages and limitations of electrochemical kinetics, equivalent circuit, and shot noise methods for quantifying corrosion rates with EN are discussed.

29

Introduction

Since Tyagai¹⁻³ and Iverson⁴ documented the noise generated in electrochemical systems in the 1960s to 1970s, the use of electrochemical noise (EN) to detect metal dissolution has become widespread in corrosion science.⁵⁻³⁷ The development of electrochemical instrumentation,³⁸⁻⁴¹ advanced signal processing methods,^{34,42-44} and inspired experimental design⁴⁵⁻⁵⁰ in recent decades has promoted EN applications.

36 Early work used single measurements of electrochemical potential noise $(EPN)^{51-55}$ or electrochemical current noise $(ECN)^{56,57}$ to study the 37 38 nature and rate of corrosion on a single working electrode (WE). The fact 39 that the WE can be polarized at any potential under potentiostatic control 40 or at any current under galvanostatic control allows the stochastic behavior 41 of corroding electrodes to be investigated in various specific conditions, such as metastable and stable pitting corrosion,⁵⁸⁻⁶² gas evolution on 42 stressed electrodes,^{63,64} or corrosion protection by organic coatings.^{47,65-68}. 43

From the beginning of the nineties, most of the time EPN and ECN were measured synchronously on two WEs tested specifically at the corrosion potential, to get more information than single measurements of EPN or ECN, in particular to estimate the corrosion rate. Important information to be obtained prior to EN measurement includes (1) the electrode system, (2) the sensitivity limit of the measuring device, and (3) the magnitude of the solution resistance of the corrosion system. 51 Investigators employ mathematical methods and models for EN 52 analysis to determine the mechanism, rate, nucleation, and propagation of 53 corrosion over time. Mathematical methods and parameters used to 54 identify corrosion forms and corrosion rates are summarized in Table I. 55 They are classified into three groups, namely the time domain, the 56 frequency domain, and the time-frequency domain. The details of each 57 method are well-documented in the literature and will not be addressed in this paper.^{31,32,34} Several parameters in Table I (e.g. noise resistance, noise 58 59 impedance) are strongly related to the corrosion rate (see below). The most 60 attractive aspect of detecting metal corrosion by measuring the EN is the 61 absence of external excitation signal as opposed to standard 62 electrochemical techniques, such as techniques polarization or 63 electrochemical impedance spectroscopy, which average the current and 64 potential signals over time and surface area of the electrodes. This allows 65 the investigation of the early stages of corrosion processes in real time with 66 high sensitivity. However, quantitative analyses can be difficult, as EN data 67 are closely linked to the type of electrode system, the area of the electrodes, 68 and the measurement mode. The theoretical aspects of quantitative EN 69 analysis of corrosion are discussed in the following sections, including the 70 electrode systems used in EN measurements, the various sources of EN, 71 and the advantages and disadvantages of theoretical models for EN 72 analysis.

73

Electrode systems suitable for EN measurement

EN measurements require a zero-resistance ammeter (ZRA) that can measure EPN and ECN synchronously, or a potentiostat that can measure ECN at an applied potential, or a galvanostat that can measure EPN at an applied current. The electrode systems numbered #1 to #9 can be arranged as shown in Table II. The corroding WE, reference electrode (RE) and counter electrode (CE) are identified in each schematic diagram of the electrode systems.

81 The ZRA is the most frequently adopted instrument in corrosion 82 detection and monitoring, because EPN and ECN can be recorded 83 synchronously. The electrodes usually used in this mode comprise one RE 84 and two WEs, or one WE and one CE. EPN is measured between the WE 85 and the RE, and ECN (coupling current) is recorded with an ammeter 86 between the two WEs, or between the WE and the CE. In a "symmetrical" 87 electrode system, WE1 and WE2 are made of nominally identical materials 88 with the same surface area (electrode systems #1 and #2). In "asymmetrical" 89 electrode systems, WEs have different surface areas (electrode systems #3 90 and #4), or a WE and a CE are used, each made of different materials 91 (electrode system #5). Another mode of asymmetric electrode is similar to 92 #1 but a bias potential is applied between the WEs to have a single 93 corroding WE and a cathode (electrode system #6).⁷⁰

94

In the ZRA mode, an operational amplifier (Opamp) is often used to

95 measure the coupling current. The WE is directly connected to ground and 96 the other WE or CE is linked to the inverting input of the Opamp while the 97 non-inverting input is connected to ground. The current-measuring resistor 98 between the output and the inverting input of the Opamp provides a voltage 99 proportional to the coupling current at the output of the Opamp. Circuit 100 components other than the operational amplifier can be used to de-noise 101 and to increase the stability of the instrument. The current-measuring resistance of the ZRA plays a key role in the measurement of ECN.⁷¹ 102 103 Typical current-measuring resistances in most commercial electrochemical 104 instruments have values ranging from ohms to gigaohms, giving a current 105 range from picoamps to amps. Instead of using a ZRA, sometimes a resistor 106 is intentionally added between WE1 and WE2, partially decoupling the two 107 WEs. This configuration was found to decrease the instrumentation noise,⁷² 108 as simplifying the current-measuring circuit ensured that no instrumental 109 noise due to active electronic components within the ZRA were fed back 110 to the corroding electrodes. This may be important in some systems, but it 111 is only one component of the instrumentation noise appearing in the final 112 measurement, and the instrument noise associated with alternative 113 measurement methods will depend strongly on the instrument design and 114 cell properties as well as the measurement configuration.

115 Three other measurement modes are used less frequently nowadays.116 The open circuit potential (OCP) mode (electrode system #7) was the first

117 mode used to measure the fluctuations of the corrosion potential of an 118 electrode versus an RE over time, which can be regarded as EPN.⁴ Such 119 measurement enables an assessment of the transient dissolution of the 120 metallic surface with a simple voltmeter, but the information obtained is 121 purely qualitative. The last two modes concern the measurement of ECN 122 under potentiostatic control (electrode system #8) and the measurement of 123 EPN under galvanostatic control (electrode system #9). These modes were 124 widely used prior the introduction of the EN measurements in ZRA mode 125 in which the WEs are studied only at the corrosion potential (apart from 126 electrode system #6). Therefore, the potentiostatic/galvanostatic modes 127 can be used in conditions where the WEs are not at corrosion potential, 128 such as when studying (1) pitting corrosion of passive metals and allovs.^{5,20,21,45,51,53,56,58-60} (2) gas evolution on WEs,^{63,73} (3) electroplating,⁷⁴ 129 130 etc.

131

Type of electrodes used in the ZRA mode.—Symmetrical electrodes and
asymmetrical electrodes are successively considered.

Symmetrical electrodes.—Symmetrical electrodes incorporate two nominally identical WEs with the same surface area plus one true, or standard, RE, where "true" refers to its property of thermodynamic equilibrium (electrode system #1), or three identical electrodes with the same surface area (electrode system #2). In the latter case, the third electrode acts as a pseudo-RE and its noise must be considered when theEN results are analyzed.

141 Electrochemical noise can also be measured using two noisy REs 142 instead of one.⁷⁵ Such configuration allows measuring the cross-spectrum 143 of both signals issued from the REs to eliminate the noise generated by the 144 REs in the calculation of the noise impedance (this is efficient in some 145 cases, as shown in Fig. 8 of Ref. 75, in which the noise impedance is ten times lower when using two REs instead of one). However, the 146 147 measurement scheme is obviously more complicated and seldom used, 148 except in some special situations.

149 Electrode system #1 is used for WEs undergoing either uniform 150 corrosion or localized corrosion. Since both WEs have similar corrosion 151 reactivity, the requirement of symmetry, that is, identical electrochemical 152 impedance for both WEs, can be easily met. After long-term exposure to 153 the environment, the appearance of corrosion products may or may not 154 affect significantly the impedance of each WE. Usually, a net current 155 flowing between the WEs appears with time without changing drastically 156 the impedance of each WE. In that case, the system is still symmetric 157 despite the existence of the net current. Most EN measurements have been 158 performed on symmetric systems, even when in some cases the asymmetry between the WEs should have been considered in the quantitative 159 analysis⁷⁰. 160

161 Asymmetrical electrodes.—Asymmetrical systems include WEs of the 162 same material but different surface areas (electrode systems #3 and #4), 163 and systems with different materials in each of the WE, the CE, and the RE 164 (electrode system #5). In electrode systems #3 and #4, WE1 and WE2 have 165 different impedance values. The RE can either be a standard (true) 166 reference electrode or a pseudo-reference electrode (a corroding electrode), 167 but in the latter case, as for electrode system #2, the noise related to the 168 corrosion phenomena occurring on the pseudo RE cannot be ignored when 169 performing a quantitative analysis. In electrode system #5, the three 170 electrodes are constructed with different materials and might have different 171 surface areas and different impedance values. The CE is often made of an 172 inert material to diminish its noise level while the WE is a corroding 173 electrode studied at its corrosion potential. Moreover, the area of the CE 174 should be small enough, compared to the area of the WE, to lower the 175 galvanic current between the WE and the CE so that the WE remains at its corrosion potential.^{8,10} However, a CE of small area has a higher impedance, 176 which increases the asymmetry between the two electrodes.⁷⁶ A Pt 177 178 electrode with a small area is often used as the CE. It draws the current 179 provided by the corrosion of the WE through a reduction reaction (for 180 example, oxygen reduction in neutral solution, or hydrogen evolution in 181 acidic medium) at the corrosion potential of the WE.

182

It is important to note that the type of electrodes employed when

183 measuring EN can affect the quantitative analysis of the EN signals. 184 Attempts to provide a symmetrical electrode system where the two coupled 185 WEs have the same surface area, the same material composition, and the 186 same corrosion potential and corrosion activity are guite never completely 187 perfect, as these properties cannot be matched to perfection in different 188 electrodes, and properties change with the passage of current. Therefore, 189 the symmetry in the electrode systems listed in Table II is theoretical, even 190 if often observed in practice.

191 **The impact of electrode area on EN measurement.**—Corrosion 192 transients are assumed to be independent events; thus, the effects of 193 electrode area on ECN and EPN data can be described using a single 194 transient analysis.

195 Analysis of EPN and ECN transients.—Two important aspects are 196 considered here, the shape of ECN and EPN transients, and how these 197 transients superimpose or counteract as the WE area increases. EPN and 198 ECN transients have been observed for a long time during chemically or 199 mechanically triggered localized corrosion of various metals and alloys at 200 OCP or at an applied anodic potential in the passive domain. Multiple 201 factors influence the shape and amplitude of the transients, such as the 202 nature and preparation of the metallic material, the electrolyte composition, 203 the electrode potential, the surface area of the electrode, the measurement 204 mode, and the instrumentation limitations as resolution, sampling

frequency, and filtering. The transients are the results of the competition between the anodic process producing electrons and the cathodic process consuming these electrons, in addition with the interaction of the charge/discharge of the interfacial capacitance of the electrode.

209 Several types of ECN transients have been observed under 210 polarization control in the passive domain to study pitting corrosion of 211 various metals often in chloride-containing solutions, the most commonly 212 encountered consisting of a sudden rise followed by a slow decay (type 1) and a slow rise followed by a sudden decay (type 2).^{56,59,77-80} Type-1 213 214 transients correspond to the sudden breakdown of the passive film inducing 215 metal dissolution followed, after repassivation, by a current decay 216 corresponding to the recharge of the interfacial capacitance of the passive area by the potentiostat.56 Type-2 transients have been observed, for 217 218 example, on stainless steels on which metastable pits grow under a cover, 219 the current decaying suddenly when an opening appears in the pit cover.⁷⁸ 220 At OCP, using two identical electrodes connected through a ZRA, ECN 221 transients appear in both directions depending on which electrode supports the localized corrosion event.⁸¹⁻⁸⁴ More complicated shapes than those of 222 223 type-1 and -2 transients have also been observed, which can be attributed 224 to the influence of the cathodic processes that contribute to consume 225 rapidly the electrons produced by the anodic event. In that case, the amplitude of the measured current transient is lower than that of the anodic 226

metal dissolution current, which cannot be individually measured.^{81,82}
Other factors influence the shape of the current transients, such as the
conductivity of the solution between the WEs,⁸⁵ or the cut-off frequencies
of the filters used in the measuring instrumentation.⁸¹

231 Similar shapes have been observed for the EPN transients at OCP during metastable pitting corrosion of various metals,^{82-84,86-89} all potential 232 transients starting in the negative direction. The shape and the amplitude 233 234 of the potential transients depend as well on the kinetics of the anodic and 235 cathodic reactions. If the cathodic process is fast, as for ferric ion reduction or for a high oxygen concentration in the solution, the charge produced by 236 237 the anodic event can be consumed rapidly by the cathodic process, hence 238 giving a fast return to the original potential value, and, therefore, a potential 239 transient shape similar to that of the type-2 current transient. In contrast, 240 for a slow cathodic reaction, the charge produced by the anodic corrosion event may be temporarily stored in the interfacial capacitance of the 241 242 electrode before being consumed after repassivation by the slow cathodic 243 reaction; the shape of the potential transient is then similar to that of the 244 type-1 current transient with a slow recovery to the original potential value. This process was modelled by Pistorius who calculating the rate of change 245 of the electrode potential as:⁹⁰ 246

247
$$\frac{dE}{dt} = \frac{-1}{C_{\rm d}(A_1 + A_2)} [(A_1 + A_2)i_{\rm cath} + I_1 + I_2]$$
[1]

248 where C_d is the interface capacitance, A_1 and A_2 are the areas of WE1

and WE2, respectively, $i_{cath}(< 0)$ is the cathodic current density at the specific potential, and I_1 and I_2 (> 0) are the anodic currents on the two WEs.

252 Impact of electrode area on ECN.—As the electrode surface area 253 increases, the number of current transients increases accordingly. Pistorius suggested that the standard deviation (SD) of the current, S_{I} , could be 254 255 proportional to the area or the square root of the area depending on whether the ECN transients are separated in time or are superimposed.⁹⁰ However, 256 257 the SD is calculated on long times during which it is very rare that 258 transients superimpose exactly. Therefore, it is generally accepted that the SD of the current is proportional to the square root of the WE area, ^{13,31,90} 259 260 and such a claim is expected to be valid for both uniform corrosion and localized corrosion. Therefore, in data analyses of EN, the S_{I} should not 261 be normalized versus the electrode area. This implies that the choice of 262 263 electrode size is extremely important for EN measurements in general, and 264 the size must be kept constant in order to compare results.

Impact of electrode area on EPN.—Increasing the electrode size will decrease the SD of the EPN, S_V , because of the increase of the interfacial capacitance C_d and the area for the cathodic reaction.⁹⁰ According to Pistorius, the S_V is expected to give no area dependence for superimposed transients or an inverse proportionality with respect to $\sqrt{\text{area}}$ for temporally separated transients.⁹⁰ However, transients superimposing

exactly are rare cases in real corrosion systems, therefore the S_V is believed, in most cases, to be inversely proportional to the square root of the WE area.^{13,31} Experimental data regarding SD dependence on WE area in typical corrosion systems are limited, therefore it is unknown if this relationship works for all corrosion systems, such as passive metals or metals undergoing stress corrosion cracking or crevice corrosion.

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- 278

Noise sources during EN measurement

279 Noise sources during EN measurements include instrumentation noise, 280 aliased noise, thermal noise, and noise generated at the metal/electrolyte 281 interface. Aliasing occurs when the analog signal contains frequencies 282 higher than half the sampling frequency when it is sampled. Aliasing may 283 occur at all frequencies: for example, the frequency of 0.9 Hz is aliased at 284 0.1 Hz if the sampling frequency is 1 Hz. Aliased noise can be avoided by using an analog anti-aliasing low-pass filter and by matching the cut-off 285 286 frequency of the filter to the sampling frequency. High levels of aliased 287 noise are often present in the absence of anti-aliasing filters in the 288 equipment or because of the way the filters are used. It is, therefore, very important to use anti-aliasing filters prior to the analog-to-digital 289 conversion in EN measurements.⁹¹⁻⁹³ Electromagnetic interference may be 290 291 another noise source, but this can be reduced by using a DC power supply 292 and a Faraday cage.

293 Instrumentation noise.—Instrumentation noise cannot be avoided by 294 experimental design. Because the noise levels of some corrosion systems 295 are very low, e.g. passive metal electrodes and even sometimes electrodes undergoing uniform corrosion,^{94,95} it is critical to assess the measuring 296 297 device limit of sensitivity to noise before conducting EN measurements. 298 Instrumentation noise can be evaluated by using a dummy cell consisting 299 of several resistors to validate the EN measurement equipment and 300 determine its baseline noise performance. Measurements on dummy cells 301 performed by the European Cooperative Group on Corrosion Monitoring 302 of Nuclear Materials (www.ecg-comon.org) in the recent past have 303 demonstrated that, because of the low level of thermal noise generated by 304 resistors, few instruments are capable of measuring corrosion noises of such low level.^{92,93} 305

306

307 *Thermal noise.*—Thermal noise in an electrochemical instrument is 308 caused by the resistive elements, and, sometimes, an equivalent thermal 309 noise resistance R_e is used to represent the thermal noise level. R_e is 310 calculated from the power spectral density (PSD), $\Psi_V(f)$, of the voltage 311 noise of the measuring instrument. The PSD shows which frequencies in 312 the signal have a large amplitude and which ones have a small amplitude. 313 The R_e is calculated from the Nyquist equation:⁹⁶

314
$$R_{\rm e}(f) = \Psi_{\rm V}(f)/4kT$$
 [2]

315 where k is the Boltzmann constant and T is the temperature in Kelvin.

316 However, the above parameter is almost never used in the corrosion 317 field because it allows assessing the level of the voltage noise of the 318 measuring device, not its current noise, which is extremely dependent on 319 the value of the current-measuring resistor, as mentioned above, while the voltage noise is not.⁷¹ Therefore it is preferable to use the PSDs of the 320 321 voltage and current noises of the measuring device to quantify the 322 instrumentation noise. In EN measurements for corrosion studies in ZRA 323 mode, the instrumentation noise can be evaluated by using dummy cells 324 composed of three identical pure resistors R, which gives thermal EPN and 325 ECN with a constant PSD, 6kTR for the EPN and 2kT/R for the ECN (R is in ohms, T in Kelvin).⁹⁷ At low frequency, 1/f noise due to the 326 327 electronic components in the instrumentation may be observed. In 328 corrosion systems showing clear ECN and EPN transients, the PSD of the 329 instrumentation noise is much lower than that of the EN and, therefore, can 330 be neglected, at least at low frequencies. In other situations, especially for 331 passivation or slow uniform corrosion, the instrumentation noise may be 332 significant and EN is difficult to measure.

333

Noise generated at the metal/electrolyte interface.—Any changes in state variables at the metal/electrolyte interface will lead to fluctuations of potential and current. As detailed in several reviews,^{31,34,35,64,98,99} EN is 337 mainly generated from the following corrosion and electrochemical events: 338 Anodic dissolution during general corrosion. As the electrochemical (1)339 activity at specific points in an electrode system fluctuates over time, 340 the sites of anodic and cathodic reactions change with time during 341 uniform corrosion. ECN during general corrosion is due to bursts of 342 current of low amplitude related to the dissolution process that gives 343 changes in the surface morphology. This noise due to the discrete 344 nature of the charge carriers is called shot noise. When the charge 345 carriers move independently of each other (Poisson process), 346 according to the theory of shot noise, the mean corrosion current is 347 equal to the product of the charge of each corrosion event and the emission frequency of the event (see below).^{44,98} 348

349 (2) Fluctuations of species concentrations at the metal-electrolyte
350 interface induced by elementary fluctuations in the flux of molecules
351 or ions.¹⁰⁰ When the kinetics of the WE is controlled by mass transport,
352 the electrolyte movement due to natural or forced convection
353 enhances drastically the amplitude of EN.^{100,101}

- 354 (3) Pitting corrosion. In addition to the typical potential and current
 355 transients induced by pitting described above, the electrochemical
 356 communication between the pits is the source of complex,
 357 meandering patterns in the EN signals.¹⁰²
- 358 (4) Gas evolution. Hydrogen bubble evolution on the electrode surface

359 may occur in acidic medium and cause EPN and ECN due to the 360 fluctuations of dissolved hydrogen concentration at the interface and to the fluctuations of active surface due to bubble screening.^{64,103} 361 362 (5) Other noise sources include removal of surface layers by erosion or cavitation,¹⁰⁴⁻¹⁰⁸ crevice corrosion,^{109,110} intergranular corrosion,¹¹¹ 363 cracking,^{11,12,16,112,113} 364 corrosion microbial-induced stress corrosion,^{17,18} etc. Moreover, corrosion systems sometimes have 365 366 multiple sources of EN, leading to a complicated EN analysis.

367

368

Theoretical models for EN analysis

EN contains fundamental information about the nature and rate of metal corrosion. This information can be extracted from the EN signal using theoretical and mathematical models.

372 *Electrochemical kinetics model.*—The electrochemical kinetics model 373 of potential and current fluctuations proposed by Chen and Bogaerts is 374 based on the Butler-Volmer equation.^{8,114} The authors made three 375 assumptions supporting the theoretical analysis:

376 (1) Both anodic and cathodic reactions occurring on the WE and the CE
377 are totally under activation polarization control; therefore, the
378 electrochemical kinetics of these reactions can be described by the
379 Butler-Volmer equation.¹¹⁵

380 (2) The corrosion potential of the WE, E_{corr} , is far away from the

381 equilibrium potential of the anodic and cathodic reactions, $V_{e,a}$ and $V_{e,c}$ 382 respectively ($V_{e,c} \ll E_{corr} \ll V_{e,a}$).

383 (3) Both anodic and cathodic reactions are under steady state condition,
384 therefore, only the Faraday current is considered, the charge/discharge
385 of the interface capacitance being neglected.

386

Theoretical derivation of the noise resistance.—In the symmetrical electrode system #1, schematically shown in Fig. 1 with the anodic and cathodic currents on each WE, the coupling current measured by the ZRA at time t, I(t), flowing between WE1 and WE2 is due to a slight difference in the corrosion potentials of WE1 and WE2. The Butler-Volmer equation can be written:

393
$$I(t) = I_{a}(t) + I_{c}(t) = i_{0,a}A_{a}e^{\frac{2.303}{b_{a}}(V(t) - V_{e,a})} - i_{0,c}A_{c}e^{-\frac{2.303}{b_{c}}(V(t) - V_{e,c})}$$
394
$$= I_{corr}\left(e^{\frac{2.303}{b_{a}}(V(t) - E_{corr})} - e^{-\frac{2.303}{b_{c}}(V(t) - E_{corr})}\right) [3]$$

where V(t) is the potential of WE1, b_a and b_c the anodic and cathodic 395 396 Tafel coefficients, $i_{0,a}$ and $i_{0,c}$ the exchange current densities, A_a and $A_{\rm c}$ the anodic and cathodic areas on WE1, and $I_{\rm corr}$ the corrosion current. 397 398 The introduction of the galvanic coupling current in Ref. 114 is obscure 399 and the theoretical analysis is restricted to the case of coupling current 400 lower than the corrosion current, so a new analysis is presented that does not have such restriction. Considering that I(t) and V(t) fluctuate 401 slightly around the stable average values, I_g and V_g , the linearization of 402

403 Eq. 3 gives:

404
$$I(t) = I_{\text{corr}} 2.303 \left(V(t) - E_{\text{corr}} \right) \left(\frac{1}{b_a} + \frac{1}{b_c} \right)$$
[4]

405 or, after subtracting the mean value of Eq. 4:

406
$$I(t) - I_{g} = I_{corr} 2.303 \left(V(t) - V_{g} \right) \left(\frac{1}{b_{a}} + \frac{1}{b_{c}} \right)$$
[5]

407 The SD $S_{\rm I}$ of the ECN, $I(t) - I_{\rm g}$, is then related to the SD 408 of the EPN, $V(t) - V_{\rm g}$, through the equation:

409
$$S_{\rm I} = I_{\rm corr} \ 2.303 \ S_{\rm V} \left(\frac{1}{b_{\rm a}} + \frac{1}{b_{\rm c}}\right)$$
 [6]

410 from which the noise resistance R_n , defined as the ratio S_V/S_I , can be 411 derived:

412
$$R_{\rm n} = \frac{S_{\rm V}}{S_{\rm I}} = \frac{b_{\rm a} \, b_{\rm c}}{2.303 \, I_{\rm corr} \, (b_{\rm a} + b_{\rm c})}$$
[7]

413 The last term is the expression of the polarization resistance, $R_{\rm p}$, derived by Stern and Geary.¹¹⁶ Thus, when the anodic and cathodic 414 415 reactions occurring on the WEs are under activation polarization control, 416 $R_n = R_p$. However, it should be noticed that in some cases the anodic or 417 cathodic reaction does not strictly obey a Tafel behavior so that this 418 relationship is sometimes not satisfied in practice.^{13,90,117} Besides, the calculation of R_n is slightly influenced by several factors such as the 419 sampling frequency,¹¹⁷ by the DC removal method used,^{9,118,119} by the size 420 of the WEs,¹³ or by the weak symmetry between the two WEs. All these 421 422 factors can lead to conflicting values between R_n and R_p . Although most 423 works have claimed that a frequency range of 0.01 to 10 Hz enables 424 satisfactory EN measurements of corrosion systems, the selection of 425 frequency range and, obviously, the corresponding sampling rate, depend considerably on the EN source and the intention of the measurements 426 (fundamental research, testing, monitoring).¹⁴ Also, there is no uniform 427 428 standard for the DC removal method, the most frequently used methods appearing to be polynomial detrending,¹²⁰ wavelet analysis, and empirical 429 mode decomposition.¹²¹ Finally, the theoretically symmetric electrodes 430 may become asymmetric over time, especially in cases of localized 431 432 corrosion. Therefore, the noise resistance is not an accurate quantitative 433 measure of corrosion rate for all corrosion systems. This is why, especially 434 in the field, the corrosion current can be estimated from the ratio B/R_n , where the Stern–Geary coefficient B is calibrated from weight-loss 435 436 measurements. In contrast to the SD of the current, which should not be normalized vs the electrode area, R_n can be normalized, as well as R_p , so 437 that the corrosion rate can be calculated in A cm⁻² whatever the size of the 438 439 WEs.

Electrode systems #3 to #6 in Table II are typical asymmetrical systems for which there is no derived relationship between R_n and R_p in the electrochemical kinetics model. There may be some merit for these asymmetric electrode systems when quantitative analysis is not required, but useful aspects of asymmetric electrode systems are not considered in this review.

446 Limitations of the electrochemical kinetic models.—Though kinetics

447 models can be used to understand the correlation between noise resistance448 and polarization resistance, they have some drawbacks as listed below.

449 (1) The Butler-Volmer equation assumes Tafel kinetics on both electrodes,
450 which is not the case in many corroding systems. For a single
451 corroding electrode governed by active dissolution and concentration
452 polarization, the relationship between the measured current *I* and the
453 electrode potential *V* is written as:¹²²

454
$$I(V) = \frac{e^{\frac{2.303(V-V_{e,a})}{b_a}}}{\frac{1}{A_a i_{0,a}} + \left(\frac{1}{G_a}\right)e^{\frac{2.303(V-V_{e,a})}{b_a}}} - \frac{e^{\frac{2.303(V-V_{e,c})}{b_c}}}{\frac{1}{A_c i_{0,c}} + \left(\frac{1}{G_c}\right)e^{\frac{2.303(V-V_{e,c})}{b_c}}}$$
[8]

455 where $V_{e,a}$ and $V_{e,c}$ are the equilibrium potential of the anodic and cathodic reactions, G_a and G_c are the limiting diffusion currents of 456 the anodic and cathodic reactions, $i_{0,a}$ and $i_{0,c}$ are the exchange 457 458 current densities of the anodic and cathodic reactions, and A_a and $A_{\rm c}$ are the active anodic and cathodic areas. Curioni et al. proposed a 459 numerical approach to calculate the potential and current noises.¹²³ 460 461 They modified Eq. 8 in the simplified case of a cathodic reaction only 462 under activation control, assuming that the anodic and cathodic areas, 463 $A_{a}(t)$ and $A_{c}(t)$, vary with time during corrosion:

$$464 I(V,t) = \frac{e^{\frac{2.303(V-V_{e,a})}{b_a}}}{\frac{1}{A_a(t)i_{0,a}} + \left(\frac{1}{G_a}\right)e^{\frac{2.303(V-V_{e,a})}{b_{diff}}} e^{\frac{2.303(V-V_{e,a})}{b_a}} - A_c(t)i_{0,c}e^{\frac{2.303(V-V_{e,c})}{b_c}} - C_{dl}\frac{dV(t)}{dt} [9]$$

465 where b_{diff} is an equivalent Tafel coefficient accounting for the 466 dependence of the limiting current diffusion on the potential and C_{dl} 467 is the double layer capacitance. The first two terms account for the 468 anodic and cathodic reactions, $I_a(V,t)$ and $I_c(V,t)$, and the last term 469 for the capacitive current, $I_{dl}(V,t)$, due to C_{dl} . According to the 470 authors, when WE1 and WE2, which are assumed to follow the 471 kinetics of Eq. 9, are galvanically coupled, the current $I_{1+2}(V,t)$ 472 exchanged with an external circuit can be written:

473
$$I_{1+2}(V,t) = I_1(V,t) + I_2(V,t) = I_{a,1}(V,t) - I_{c,1}(V,t) -$$

474
$$I_{dl,1}(V,t) + I_{a,2}(V,t) - I_{c,2}(V,t) - I_{dl,2}(V,t)$$
 [10]

475 with obvious notations. From a numerical point of view, the corrosion 476 potential is given by the solution of the previous equation in which 477 the first term $I_{1+2}(V,t)$ is equal to $0.^{123}$ Then, to calculate the time 478 evolution of the potential, Eq. 9 was rearranged to obtain the 479 expression of the potential time-derivative dV/dt from which the 480 potential at time $t+\Delta t$ could be approximated from its value at time *t* 481 by using Euler's method.

482
$$V(t + \Delta t) = V(t) + \Delta t \frac{\mathrm{d}V}{\mathrm{d}t}$$
[11]

For given initial values of the anodic and cathodic areas, and of the corrosion potential, the time evolution of the corrosion potential could be calculated, from which the time evolution of the current exchanged between the electrodes, the polarization resistance, and the noise resistance could be derived with the numerical model. They found that, in most cases, there was no unacceptable difference

- 489 between R_n and R_p , even for severe asymmetry between the 490 electrodes.
- 491 (2) The Butler-Volmer equation is sometimes valid for uniform corrosion,
 492 but it is not capable of interpreting localized corrosion. Although EN
 493 can be used to identify initiation and propagation stages of localized
 494 corrosion, the kinetic equations do not describe localized corrosion.
- 495 (3) For asymmetrical electrode systems, a quantitative analysis cannot be496 achieved, as mentioned above.
- 497 (4) The initially symmetric electrode systems listed in Table II may
 498 become asymmetric, especially those undergoing localized corrosion.
- 499

500 Equivalent circuit approach with fluctuating potential and current

501 sources.—In the equivalent circuit (EC) approach introduced by Huet's group,^{29,70,85,100,124-126} the elements have clear physical significance. In the 502 503 four circuits appearing in the first two rows of Table III, the EPN and ECN 504 are modelled using a single circuit element, either a current source or a 505 potential source, and it is assumed that the impedance of the electrodes 506 does not vary during corrosion. ECs for electrode systems #1 to #6 in Table II are discussed in detail below and their theoretical predictions and 507 508 experimental results are compared.

509

510 *Electrode systems #1, #3, #5 and #6*—The two ECs (EC1 and EC2) of

511 these electrode systems presented in the first row of Table III are 512 mathematically identical simplifications of real circuits. The circuit based 513 on current noise sources (EC1) is the Norton equivalent circuit and the 514 circuit based on potential noise sources (EC2) is the Thevenin equivalent circuit¹²⁴. In EC1 and EC2, i_1 and i_2 represent the current noise sources of 515 516 WE1 and WE2 while e_1 and e_2 represent the potential noise sources of WE1 517 and WE2. Z_1 , Z_2 , and Z_3 denote the impedances of WE1, WE2, and RE. ΔI 518 is the current fluctuation flowing from WE1 to WE2 measured by the ZRA, ΔV is the potential fluctuation of WE1, R_s is the electrolyte resistance 519 between WE1 and WE2, and x is the fraction of R_s between the RE and 520 WE1 ($0 \le x \le 1$). According to Ohm's law in the frequency domain (all 521 522 quantities, except R_s , are frequency-dependent), the expressions of $\Delta I(f)$ and $\Delta V(f)$ for these four electrode systems, are ¹²⁴: 523

524
$$\Delta I = \frac{Z_1 i_1 - Z_2 i_2}{Z_1 + Z_2 + R_s} \quad ; \qquad \Delta V = \frac{-Z_1 i_1 [Z_2 + R_s (1 - x)] - Z_2 i_2 [Z_1 + R_s x]}{Z_1 + Z_2 + R_s} \quad [12]$$

525 when using the current noise sources, and:

526
$$\Delta I = \frac{e_2 - e_1}{Z_1 + Z_2 + R_s} \quad ; \qquad \Delta V = \frac{e_1 [Z_2 + R_s (1 - x)] + e_2 [Z_1 + R_s x]}{Z_1 + Z_2 + R_s} \quad [13]$$

when using the potential noise sources. It is possible to convert one model to the other with the following expressions of the potential noise sources:¹²⁴ $e_i(f) = Z_i(f)i_i(f)$ j = 1, 2 [14]

From Eq. 12, the PSDs of the ECN and EPN can be derived as a
function of the PSDs of the current noise sources,
$$\Psi_{i_1}(f)$$
 and $\Psi_{i_2}(f)$,
which are assumed to be uncorrelated:¹²⁴

533
$$\Psi_{I}(f) = \left|\frac{Z_{1}}{Z_{1}+Z_{2}+R_{s}}\right|^{2} \Psi_{i_{1}}(f) + \left|\frac{Z_{2}}{Z_{1}+Z_{2}+R_{s}}\right|^{2} \Psi_{i_{2}}(f)$$
[15]

534
$$\Psi_{V}(f) = \left| \frac{Z_{1}[Z_{2}+R_{s}(1-x)]}{Z_{1}+Z_{2}+R_{s}} \right|^{2} \Psi_{i_{1}}(f) + \left| \frac{Z_{2}[Z_{1}+R_{s}x]}{Z_{1}+Z_{2}+R_{s}} \right|^{2} \Psi_{i_{2}}(f)$$
[16]

According to Eq. 14, the corresponding expressions of $\Psi_{\rm I}(f)$ and $\Psi_{\rm V}(f)$ as a function of the PSDs of the potential noise sources, $\Psi_{e_1}(f)$ and $\Psi_{e_2}(f)$, can be directly obtained by replacing $\Psi_{i_j}(f)$ with $\Psi_{e_j}(f)/$ $|Z_j(f)|^2$ (j = 1,2).

The noise impedance, $Z_n(f)$, initially called spectral noise resistance $R_{sn}(f)$, defined as the square root of the ratio of the PSD of EPN divided by the PSD of ECN, can be derived from Eqs. 15 and 16:^{29,70,124}

543
$$Z_{n}(f) = \sqrt{\frac{\Psi_{V}(f)}{\Psi_{I}(f)}} = \sqrt{\frac{|Z_{1}[Z_{2}+R_{s}(1-x)]|^{2}\Psi_{i_{1}}(f) + |Z_{2}(Z_{1}+R_{s}x)|^{2}\Psi_{i_{2}}(f)}{|Z_{1}|^{2}\Psi_{i_{1}}(f) + |Z_{2}|^{2}\Psi_{i_{2}}(f)}}$$
[17]

It is important to note that the noise impedance is a real number, not a complex number as a true impedance; in other words, it contains no phase information. If R_s is much lower than the impedance of the electrodes, the expression of Z_n becomes:

548
$$Z_{n}(f) = |Z_{1}Z_{2}| \sqrt{\frac{\Psi_{i_{1}}(f) + \Psi_{i_{2}}(f)}{|Z_{1}|^{2}\Psi_{i_{1}}(f) + |Z_{2}|^{2}\Psi_{i_{2}}(f)}}$$
[18]

Equation 18 indicates that, in general, $Z_n(f)$ is determined by four factors, the impedances of both electrodes and the PSDs of both current or potential noise sources. However, for electrode system #1 with identical electrodes immersed in the same electrolyte and working at the same corrosion potential, the impedances of both WEs are expected to be identical $[Z_1 = Z_2$, denoted as Z(f)]. Equation 18 then becomes:

555
$$Z_{n}(f) = |Z(f)|$$
 [19]

556 Therefore, in the common use of two identical electrodes connected 557 through a ZRA, the noise impedance is equal to the modulus of the 558 impedance of the WEs whatever the origin of the noise sources (pits, 559 bubbles, cracks...) and whatever the noise level on each electrode.

560 For electrode system #3 with WEs of the same material but different 561 surface areas, the impedance of each WE is inversely proportional to its 562 surface area while the PSD of the current noise source is proportional to 563 the surface area.^{13,31} It can then be shown from Eq. 18 that:¹²⁵

564
$$Z_{\rm n}(f) = \sqrt{|Z_1(f) Z_2(f)|}$$
 [20]

For electrode system #5 and #6, one electrode serves as the anode and the other serves as the cathode, so Z_1 is now denoted as Z_a , and Z_2 as Z_c . Using the current noise sources, Eq. 18 can be rewritten as:

568
$$Z_{n}(f) = |Z_{a}Z_{c}| \sqrt{\frac{\Psi_{i_{a}}(f) + \Psi_{i_{c}}(f)}{|Z_{a}|^{2}\Psi_{i_{a}}(f) + |Z_{c}|^{2}\Psi_{i_{c}}(f)}}$$
[21]

The expression of the noise impedance can be further discussed according to three different cases for these asymmetric electrode systems: (1) The noise level of the cathode (WE2) is significantly higher than the noise level of the anode (WE1) (for example, the cathode mainly supports hydrogen bubble evolution, whereas the anode undergoes uniform corrosion).

575
$$Z_{\rm n}(f) = |Z_{\rm a}(f)|$$
 [22]

576 The noise impedance is equal to the impedance of the anode, 577 while the EPN and ECN time records provide information on the 578 noisier electrode (cathode).⁷⁰

579 (2) The noise level on the anode is significantly higher than the noise
580 level on the cathode (for example, the cathode mainly supports
581 oxygen reduction, whereas the anode undergoes pitting corrosion).

582

$$Z_{\rm n}(f) = |Z_{\rm c}(f)|$$
[23]

583 The noise impedance is equal to the impedance of the cathode, 584 while the EPN and ECN time records provide information on the 585 noisier electrode (anode).

586 (3) When the noise levels of the anode and cathode are comparable, 587 $Z_n(f)$ ranges between the impedance moduli of the electrodes 588 $|Z_a(f)|$ and $|Z_c(f)|$.⁷⁰

It is then important to underline the difficulty of the EN analysis in the case of asymmetric systems: EPN and ECN depend on four quantities (the impedance of each WE and the noise source generated by each WE) while EN measurements only give two quantities (EPN and ECN). Therefore, the EN analysis can only be performed if the impedance of each WE has been measured.^{70,76}

595 *Electrode systems #2 and #4*—Electrode systems #2 and #4 can be 596 described by equivalent circuits EC3 or EC4.¹²⁴ If a pseudo RE is used, its 597 current noise source i_3 or potential noise source e_3 has to be taken into 598 account. A new term, $Z_3 i_3$, must added to the expression of ΔV in Eq. 599 12 while the expression of ΔI is unaffected. The noise impedance can then 600 be expressed using the current noise sources of the three electrodes, which 601 are assumed to be uncorrelated, as:¹²⁴

$$602 Z_{\rm n}(f) =$$

$$603 \quad \sqrt{\frac{|Z_1[Z_2 + R_s(1-x)]|^2 \Psi_{i_1}(f) + |Z_2(Z_1 + R_s x)|^2 \Psi_{i_2}(f) + |Z_3(Z_1 + Z_2 + R_s)|^2 \Psi_{i_3}(f)}{|Z_1|^2 \Psi_{i_1}(f) + |Z_2|^2 \Psi_{i_2}(f)}}$$
[24]

In electrode system #4, the impedances of the three electrodes are not identical and, therefore, the noise impedance cannot be related to the impedance of the electrodes. In contrast, in electrode system #2 with three identical electrodes, the electrodes have equal impedance ($Z_1 = Z_2 = Z_3$, denoted as Z). Therefore, when R_s is neglected:

609
$$Z_{n}(f) = |Z(f)| \sqrt{1 + \frac{4\Psi_{i_{3}}(f)}{\Psi_{i_{1}}(f) + \Psi_{i_{2}}(f)}}$$
[25]

When the three electrodes are identically noisy, which may be a reasonable assumption in some cases but cannot be experimentally checked since the current noise sources cannot be separately measured, then:

614
$$Z_{\rm n}(f) = \sqrt{3} |Z(f)|$$
 [26]

As for the electrode system #1, it is then still possible to determine
the impedance modulus of the electrodes when using a third identical
electrode as pseudo-RE.

618 *Correlation between* R_n *and* Z_n .—For a random signal, the variance, 619 which is the square of the standard deviation, is equal to the integral of its 620 PSD, therefore, according to the definition of the noise resistance (Eq. 7):

621
$$R_{\rm n} = \sqrt{\frac{\int_0^{+\infty} \Psi_{\rm V}(f)df}{\int_0^{+\infty} \Psi_{\rm I}(f)df}} = \sqrt{\frac{\int_{f\min}^{f\max} \Psi_{\rm I}(f)Z_{\rm n}^2(f)df}{\int_{f\min}^{f\max} \Psi_{\rm I}(f)df}}$$
[27]

622 Actually, the PSD has a limited frequency bandwidth (f_{\min}, f_{\max}) . 623 The lowest frequency analyzed of the spectrum of a discrete time record sampled at frequency f_s is given by $f_{\min} = f_s / N = 1 / N \Delta t$, where N is 624 the number of samples and $\Delta t = 1/f_s$ is the sampling interval. When the 625 626 PSD is calculated using the fast Fourier transform, the frequency resolution 627 is also given by f_s/N . As an example often encountered in the literature, when $f_s = 2$ Hz and N = 2,048 points, the minimum frequency analyzed 628 629 and the frequency resolution are ~1 mHz. In practice, it is advised to 630 sample 10 times more points to obtain a sufficient accuracy of the spectrum by PSD averaging. The f_{max} being equal to one half of the sampling 631 frequency, the frequency range analyzed in the above example is (~1 mHz, 632 633 1 Hz). At higher frequencies, the noise is often due to the instrumentation.¹²⁶ 634

For electrode system #1 with identical electrodes, the noise impedance is equal to the impedance modulus of the electrodes, so Eq. 27 can be written as:

638
$$R_{\rm n} = \sqrt{\frac{\int_{f_{\rm min}}^{f_{\rm max}} \Psi_{\rm I}(f) |Z(f)|^2 df}{\int_{f_{\rm min}}^{f_{\rm max}} \Psi_{\rm I}(f) df}}$$
[28]

639 Therefore, if |Z(f)| does not depend on frequency in the range 640 (f_{\min}, f_{\max}) , that is, if |Z(f)| is equal to the polarization resistance in this range, then $R_n = R_p$ regardless of the shape of $\Psi_I(f)$. However, in the 641 frequency range (~1 mHz, 1 Hz) often analyzed in practice, |Z(f)| is 642 643 frequency dependent in real corrosion systems and R_n is in no simple way 644 related to the electrode impedance according to Eq. 28. The conditions for 645 which R_n departs significantly from R_p have been discussed in Ref 30. If f_c denotes the critical frequency above which |Z(f)| significantly 646 decreases and if the slope of the current PSD is constant in the range 647 (f_{\min}, f_{\max}) , EN measurement times for which $f_c/f_{\min} > 10$ are 648 649 sufficiently long in many cases to estimate R_p from R_n .

Table IV lists some experimental values of R_n , R_p , $Z_n(f)$, and 650 651 |Z(f)|. This table shows that R_n is equal to R_p only in some cases. Aballe et al.³⁰ claimed that the pre-condition for $R_n = R_p$ is that |Z(f)|652 is equal to R_p in the frequency bandwidth investigated, a reasonable 653 654 assumption for sufficiently low values of the maximum frequency analyzed, 655 with the notable exception of coated or stainless steel electrodes for which 656 electrochemical impedance spectroscopy (EIS) measurements should be 657 performed at extremely low frequencies (< 0.1 mHz), practically 658 inaccessible, to get the value of R_p . In addition, Table IV shows that the

values of the noise impedance and of the modulus of the electrode
impedance measured by EIS are in good accordance with the theoretical
predictions (Eqs. 19 and 26).

662 Equivalent circuit approach with fluctuating resistances.—Curioni et al.¹²⁷ proposed a new EC approach to interpret noise generation on freely 663 664 similar or dissimilar corroding electrodes. As shown in EC5 depicted in 665 Table III, it is based on the assumption that the EN results from fluctuations 666 of the electrical resistances, $R_{a,i}(t)$ and $R_{c,i}(t)$, of the surface layers 667 (oxides, hydroxides or adsorbed species) covering the anodic and cathodic areas of each electrode (i = 1,2). In their model, the effects of the double 668 669 layer capacitance of each electrode are neglected, so the analysis is limited 670 to low frequencies. Moreover, the electrode impedances are assumed to be 671 simple resistances, which limits the application of the model to corroding 672 electrodes for which the EIS Bode plot displays a low-frequency plateau 673 within practical measurement frequencies. Neglecting the solution 674 resistance in conductive solutions and according to the direction of the 675 currents in EC5, the currents flowing out of each electrode can be written 676 from Ohm's law:

677
$$I_{i}(t) = I_{a,i}(t) + I_{c,i}(t) = \frac{V(t) - E_{a,i}}{R_{a,i}(t)} + \frac{V(t) - E_{c,i}}{R_{c,i}(t)}$$
[29]

678 where V(t) is the potential of the coupled electrodes, and $E_{a,i}$, $E_{c,i}$ are 679 the equilibrium potentials for the anodic and cathodic reactions on each 680 electrode. To derive the time-varying resistances, $R_{a,i}(t)$ and $R_{c,i}(t)$, the authors used the Thevenin equivalent potential source, $V_{eq,i}(t)$, in series with the Thevenin equivalent resistance, $R_{eq,i}(t)$, for each electrode i:

683
$$V_{\text{eq},i}(t) = E_{a,i} \frac{R_{c,i}(t)}{R_{a,i}(t) + R_{c,i}(t)} + E_{c,i} \frac{R_{a,i}(t)}{R_{a,i}(t) + R_{c,i}(t)}$$
[30]

684
$$R_{eq,i}(t) = \frac{R_{a,i}(t) + R_{c,i}(t)}{R_{a,i}(t)R_{c,i}(t)}$$
[31]

from which the potential measured versus the RE can be written:

686
$$V(t) = \frac{R_{\text{eq},1}(t)}{R_{\text{eq},1}(t) + R_{\text{eq},2}(t)} V_{\text{eq},2}(t) + \frac{R_{\text{eq},2}(t)}{R_{\text{eq},1}(t) + R_{\text{eq},2}(t)} V_{\text{eq},1}(t)$$
[32]

Assuming that the potential $V_{eq,i}(t)$ of each electrode does not change significantly with time during the coupling period, Eq. 32 was rewritten by replacing $V_{eq,i}(t)$ with the value of the potential measured when the electrode is decoupled and assumed constant, $\bar{V}_{eq,i}$. The Thevenin equivalent resistances can then be estimated when the WEs are coupled from the measurement of V(t) and of the current I(t) flowing from WE1 to WE2 ($I = I_1$) with the expressions:

694
$$R_{eq,1}(t) = \frac{V(t) - \overline{V}_{eq,1}}{I(t)}$$
 and $R_{eq,2}(t) = \frac{\overline{V}_{eq,2} - V(t)}{I(t)}$ [33]

from which the resistances, $R_{a,i}(t)$ and $R_{c,i}(t)$, can be derived with Eqs. 29 and 31:

697
$$R_{a,i}(t) = R_{eq,i}(t) \frac{E_{c,i} - E_{a,i}}{E_{c,i} - V(t) + R_{eq,i}(t)I_i(t)}$$
[34]

698
$$R_{c,i}(t) = R_{eq,i}(t) \frac{E_{c,i} - E_{a,i}}{V(t) - E_{a,i} - R_{eq,i}(t)I_i(t)}$$
[35]

By using a specific arrangement allowing coupling-decoupling EN measurements on dissimilar electrodes, the authors could estimate the time evolution of the anodic and cathodic resistances for AA2024T3 and aluminum coupled electrodes in NaCl solution and validate their theoretical approach by comparing the values of these resistances with thelow-frequency limit of the impedance modulus measured by EIS.

705 Practical applications of EC for EN analysis.—Equivalent circuit 706 approaches have been successfully applied in many corrosion systems with 707 experimental results correlating well with theoretical predictions (see the results in Table IV).^{29,70,85,100,118,125,126,129} One significant advantage for EC1 708 709 to EC4 in Table III, as proposed by Huet et al., is that a single EC can 710 describe the experimental setup using two WEs connected through a ZRA. 711 Nothing is a priori assumed in the impedances Z_1 and Z_2 , which are 712 complex impedances including the double layer capacitance, and in the 713 origin of the noise sources (pits, bubbles, cracks...). In contrast, EC5 needs 714 further experiments to validate the EC design, in particular when the 715 coupling of the WEs introduces a change in their corrosion potentials. This 716 approach needs also to be extended to systems for which the impedance 717 cannot be reduced to a simple resistance.

Shot noise model.—Shot noise refers to the fluctuations in current arising from the variations in time of the number of electrical charge carriers. It was applied to corrosion systems in recognition of the fact that the current can be considered as a sum of independent bursts of charge involving 1 to 4 electrons in an elementary electrochemical reaction, or a much larger number of electrons in transients, for example due to metastable pitting.^{15,31,44,77,98,100} The shot noise model derived by Cottis et al. for two identical electrodes connected through a ZRA and a noiseless RE is based on several assumptions:^{15,31,44,98}

The WEs undergo an anodic process with relatively large bursts of
charge of short duration and independent of each other. In that case,
the current on each WE follows a Poisson process, with an average
value:

$$I_{\rm corr} = q f_{\rm n} \tag{36}$$

and a PSD:

$$\Psi_{i_1} = \Psi_{i_2} = 2qI_{\rm corr} = 2f_{\rm n}q^2$$
[37]

735 where q is the charge in each corrosion event (assumed to be the 736 same for each event), f_n is the mean emission frequency of corrosion 737 events, and I_{corr} is the corrosion current (I_{corr} and f_n are assumed 738 to be the same for each WE). As a consequence of the short duration of the events, which in practice implies working at low sampling 739 740 frequencies, the PSD is frequency independent in the measured 741 frequency range. For events of longer duration, the PSD values 742 considered in Eq. 37 are the low-frequency limit of the PSDs.

743 (2) The cathodic process on the WEs is noise-free, as for example oxygen744 reduction.



noise impedance,
$$Z_n(f)$$
, is then also equal to R_p (Eq. 19).

Under these hypotheses, the PSDs of the ECN and EPN of the coupled electrodes can be expressed as, according to Eqs. 15 and 16 when neglecting the solution resistance:

751
$$\Psi_I = qI_{\text{corr}}$$
 and $\Psi_V = |Z|^2 q I_{\text{corr}} = \Psi_I R_p^2$ [38]

The three parameters of interest in the shot noise model, I_{corr} , q, and f_n -can then be estimated from Eqs. 36, 38 and from the Stern-Geary equation:

755
$$I_{\rm corr} = \frac{B}{R_{\rm p}} = \frac{B}{Z_{\rm n}} = B \sqrt{\frac{\Psi_{\rm I}}{\Psi_{\rm V}}}$$
[39]

$$q = \frac{\sqrt{\Psi_V \Psi_I}}{B}$$
[40]

757
$$f_{\rm n} = \frac{I_{\rm corr}}{q} = \frac{B^2}{\Psi_{\rm V}}$$
[41]

758 The three parameters are directly given as a function of the PSDs $\Psi_{\rm V}$ 759 and Ψ_{I} . It has also been proposed to use the SDs of EPN and ECN, which are directly calculated in the time domain, by replacing Ψ_V with S_V^2/b 760 and $\Psi_{\rm I}$ with $S_{\rm I}^2/b$, where b is the measurement frequency bandwidth. 761 762 However, this is strictly valid under the assumption that the PSDs are 763 frequency independent in the whole frequency bandwidth. This requires 764 that the duration of each transient is short enough so that it can be 765 considered as a Dirac delta function over the frequency range considered, 766 which implies that the transient lasts for less than one period of the highest 767 frequency included in the measurement.

768 The shot noise model is based on several assumptions that may not always be valid.⁹⁸ First, the PSDs are assumed to be flat at low frequency 769 770 while the measured power spectra often show a 1/f behavior at the lowest analyzed frequencies. Second, R_n is assumed to be equal to R_n , which is 771 772 not true for some corrosion systems such as stainless steel or coated electrodes, as explained above.^{30,129}. Third, the shot noise model cannot 773 774 apply when the noise is produced by both anodic and cathodic reactions, 775 such as when bubble evolution occurs in addition to the anodic process. 776 Finally, all transients are expected to be uncorrelated and to have the same shape and amplitude, which is not observable on ECN time records 777 778 showing transients as for metastable pitting.

779

780

Conclusions and future work

The different electrode systems used in EN measurements in the corrosion field have been reviewed, most of them nowadays involving two symmetrical or asymmetrical electrodes connected through a ZRA. The impact of the electrode surface area on the ECN and EPN, which is a parameter of primary importance, has been considered. After a brief review of the various origins of the EN sources, the theoretical models used for analyzing the noise were presented.

Electrochemical kinetics models were introduced to explain thecorrelation between the noise resistance and the polarization resistance for

790 a symmetrical or asymmetrical corroding system. However, they have 791 limitations, the most important being the assumption that the anodic and 792 cathodic reactions are under activation control. Equivalent circuit 793 approaches with potential or current noise sources or with fluctuating 794 resistances have also been proposed to analyze EN data. While the latter 795 approach is limited to corroding electrodes the impedance of which are 796 reduced to simple resistance, the former approach does not presuppose 797 anything on the impedance of the electrodes and on the origin of the noise 798 sources. It is possible with this model to specify the conditions in which 799 the noise resistance is or is not equal to the polarization resistance. Finally, 800 the shot noise model was presented: under some assumptions (flat PSD at low frequency, R_n equal to R_p , single anodic noise source), the mean 801 802 occurrence frequency of corrosion events and the mean electrical charge 803 involved in the transients can be calculated to discriminate between 804 uniform corrosion and localized corrosion.

The existing theoretical models and mathematical methods need to be optimized as they suffer from serious limitations, as mentioned above, for studying important topics, such as the impact of electrode area on EN data, the shape and time duration of transients in metastable pitting, or the quantification of the extent of localized corrosion (crack length, pit depth, pit number). New developments are also necessary to better interpret the shape and amplitude of the EN power spectral densities, or to analyze EN

812 data produced by simultaneous processes occurring simultaneously on the 813 electrodes, such as pitting corrosion, stress corrosion cracking, bubble 814 formation, etc. Coupling EN measurements with other techniques giving 815 access to other quantities (i.e. video recordings, microscopy images, acoustic emission) or simultaneous measurements of EN with other 816 817 (i.e. fluctuating quantities electrolyte resistance. double laver 818 capacitance...) would be of great help for improving the models.

819

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Table and figures

Table I. Mathematical methods and parameters used to identify

1152 corrosion forms and corrosion rates.^{31,32,34}

Mari	hamadia dha dh	N	Relation to	Relation to	
Mat	nematical methods	Name of parameters	corrosion rate?	corrosion form?	
		Standard deviation of the EPN or	D-l-t-l		
		ECN	Related	-	
		Skewness	-	-	
		Kurtosis	-	-	
	Statistical analysis	Pitting index	-	Related	
		Noise resistance	Strong	-	
		Weibull distribution function and		Deleted	
Time domain		pit embryo formation rate	-	Related	
analysis		Gumbel distribution	-	Related	
	Chase enclusio	Correlation dimension		Deleted	
	Chaos analysis	Largest Lyapunov exponent	-	Related	
	Recurrence quantification	Decurrence plat		Deleted	
	analysis	Recurrence plot	-	Related	
		Hausdorff exponent			
	Fractal analysis	Hurst exponent	-	Related	
		Spectral power exponents			
		Charge in each corrosion event	Strong	Related	
	Shot noise	Frequency of occurrence of	Strong	Related	
		corrosion events	Suong		
Frequency		Low frequency plateau	Related	-	
domain analysis		Plateau at high frequencies	-	-	
domain analysis		Roll-off slope	-	-	
		Knee frequency or critical	_	_	
		frequency	-	-	
		Noise impedance	Strong	-	
	Hilbert-Huang transform	Hilbert spectrum	-	Related	
Time-frequency		Wavelet entropy	-	Related	
domain	Discrete Wavelet Transform	Wavelet based fractal dimension	-	Related	
		Wavelet energy distribution - R		Related	
	Stockwell transform ³⁶	Frequency amplitude analysis	Related	Related	
	Synchrosqueezing transform ³⁷	Frequency amplitude analysis	-	Related	
	Stockwell transform -Shannon	Shannon energy levels	_	Related	
	energy ³⁶	Shamon onergy levels	-	Related	
	Synchrosqueezing transform-	Shannon energy levels	_	Related	
	Shannon energy ³⁷			Related	

Reassigned	Pseudo	Wigner-	Energy spectral densities	_	Related
Ville Transfe	orm ⁶⁹		Energy spectral defisities	-	Related



1155 Table II. Electrode systems used in EN measurement.





Table III. Equivalent circuits proposed to analyze EN in ZRA mode.

1162 Table IV. Comparison of experimental values of R_n , R_p , $Z_n(f)$, and |Z(f)|.^{a)}

Electrode	WE1	WE2	DE Electrolyte		Sampling	trend removal	Correlation among R_n , R_p ,	Daf
system No.	(surface area)	(surface area)	KE	Electrolyte	frequency me		$Z_{n}(f)$, or $ Z(f) $	Kel.
Ш1	Mild steel	Mild steel	Ag/AgCl	640 ml of 3% NaCl	211-	moving	$P \sim P$	9
#1	(3.02 cm^2)	(3.02 cm^2)	electrode	brine	2HZ	average value	$\kappa_n \approx \kappa_p$	
// 1	Contractor 1	Contractor 1	000**	0.4 M Na ₂ SO ₄	50Hz			00
#1	Carbon steel	Carbon steel	SCE**	0.1 M H ₂ SO ₄	1 kHz	-	$R_{\rm n} > R_{\rm p}$	90
							$R_{\rm n}$ is slightly higher than $R_{\rm p}$ at a	
#2	Carbon steel	Carbon steel	Carbon steel	Na ₃ PO ₄ + NaCl,	2 Hz, 8 Hz, or	Linear	sampling frequency of 32 Hz;	117
#2	(3 cm^2)	(3 cm^2)	(3 cm^2)	NaClO ₄	32 Hz	method	$R_{\rm n} > R_{\rm p}$ at low sampling	11/
							frequency (2 Hz and 8 Hz)	
				(i) in 1 M Na ₂ SO ₄ , pH				
	Fo	E		3;	0.2 Hz to 200 notwomial	$Z_{\rm n}(f) \approx Z(f) $		
#1	(0.20 sm^2)	(0.20 am^2)	SSE***	(ii) in 1 M Na ₂ SO ₄ , pH	fitting		125	
	(0.20 cm ⁻)	(0.20 cm ⁻)		4	ΠZ	ntting		
#1	Al	Al		1 M K C	0.2 Hz to 200	polynomial	$7(f) \sim 7(f) $	125
#1	(5 cm^2)	(5 cm^2)	SCE	I M KCI.	Hz	fitting	$Z_n(f) \sim Z(f) $	
#2	Al	Al	SCE**	1 M K Cl	0.2 Hz to 200	polynomial	$ Z(f) _{5\mathrm{cm}^2} < Z_{\mathrm{n}}(f)$	125
#3	(5 cm^2)	(0.2 cm^2)	SCE	I M KCI.	Hz fitting $< Z(f) _{0.2 \text{ cm}^2}$		$< Z(f) _{0.2 \text{cm}^2}$	125
				(i) in 1 M Na ₂ SO ₄ , pH				
#2	Fe	Fe	Fe	3;	0.2 Hz to 200 polynomial		$7(f) \sim 2 7(f) $	125
#2	(0.20 cm^2)	(0.20 cm^2)	(0.20 cm^2)	(ii) in 1 M Na ₂ SO ₄ , pH	Hz	fitting	$Z_{n}(J) \approx 2 Z(J) $	123
				4				

#1	Mild steel (4.5 cm ²)	Mild steel (4.5 cm ²)	SCE	0.5 M NaCl (open to air)	2 Hz	Linear method	$Z_{\rm n} \approx Z(f) $	118
#1	Pure aluminum 99.999% or 2024 T3 aluminum alloy (0.2 cm ²)	Pure aluminum 99.999% or 2024 T3 aluminum alloy (0.2 cm ²)	SCE	0.1 M Na2SO4 + 0.5 M NaCl with and without 0.01 M BTAH.	100 and 10 Hz	polynomial fitting	$Z_{\rm n} \approx Z(f) $	128
#1	X-65 mild steel (11.6 or 1 cm ²)	X-65 mild steel (11.6 or 1 cm ²)	SCE	1% NaCl electrolyte by bubbling CO ₂ , 80°C	1 Hz	polynomial fitting	$R_{\rm n} \approx R_{\rm p}$ for small WEs, $R_{\rm n} > R_{\rm p}$ for large WEs	13

1164 a) Note that an initial symmetric electrode system may become asymmetric, especially for electrodes undergoing localized corrosion. b) SCE: saturated calomel electrode. c) SSE: saturated

1165 mercury sulfate electrode.



- **Figure 1.** Schematic diagram of electrode system #1 showing the anodic,
- $I_a(t)$ and $I'_a(t)$, and cathodic, $I_c(t)$ and $I'_c(t)$, currents on each WE.