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## How to perform valid electrochemical noise measurements?

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From the results of the Round-Robin (RR) tests on electrochemical noise (EN) measurements with dummy cells performed by the European Cooperative Group on Corrosion Monitoring of Nuclear Materials (ECG-COMON, [www.ecg-comon.org](http://www.ecg-comon.org)) since 2006 [1-2], it can be concluded that only very few commercial potentiostats are able to perform valid EN measurements. As an example, Fig. 1a shows the power spectral densities (PSDs) of the potential fluctuations measured by the participants of the RR test in 2017 using 3 identical resistors of 100 MΩ connected in a ‘star’ arrangement and used in the conventional three electrode EN measurement setup using a zero-resistance ammeter. The aim was to measure the thermal noise of the resistors, which has a reproducible amplitude and is in the same range as for passive electrodes. This figure exhibits an extremely large scatter in the amplitude of the PSD, roughly ten decades above the thermal noise level, defined as the red line 6kTR, that is, five decades in volt! This large scatter is mainly due to the absence of anti-aliasing filters in most of the commercial potentiostats.

This paper is aimed at guiding users of the EN technique by providing the minimum knowledge for EN measurements, including the necessary validation of the signals measured at different sampling frequencies by calculation of their PSDs. Two practical works performed with a commercial potentiostat (Gamry, Ref600) are proposed. The first one is devoted to the measurement of the thermal noise of three resistors of equal value, as in the RR tests. This allows the instrumental noise of the equipment to be determined. The second practical work concerns pitting corrosion of two identical aluminum electrodes in potassium chloride to show that the noise impedance is equal to the modulus of the impedance of the electrodes (Fig. 1b). A bias voltage is then applied between the electrodes to obtain one anode and one cathode which shows the difficulty of analyzing the measured EN in asymmetric systems [3].

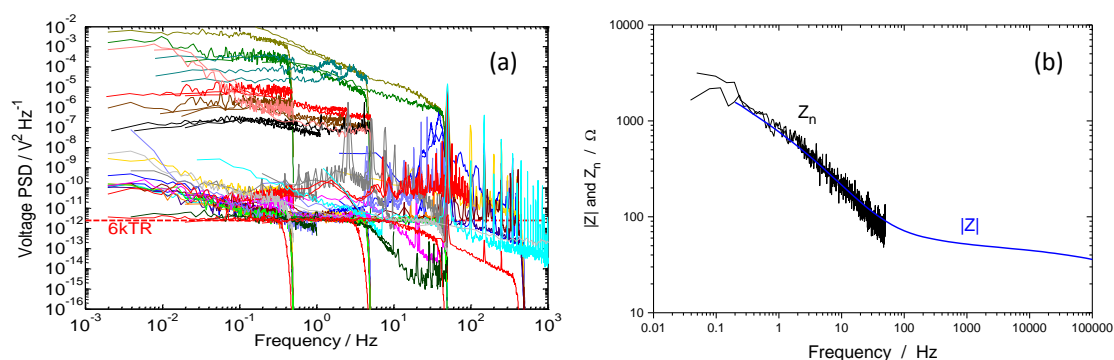


Figure 1: (a) PSD of potential fluctuations measured on dummy cells of 100 MΩ (RR-2017) and (b)  $Z_n$  and  $|Z|$  of the aluminum electrodes in potassium chloride.

1. R.-W. Bosch, R. A. Cottis, K. Csecs, T. Dorsch, L. Dunbar, A. Heyn, F. Huet, O. Hyökyvirta, Z. Kerner, A. Kobzova, J. Macak, R. Novotny, J. Öjjerholm, J. Piippo, R. Richner, S. Ritter, J.-M. Sánchez-Amaya, A. Somogyi, S. Väisänen, W. Zhang, “Reliability of electrochemical noise measurements: results of round-robin testing on electrochemical noise,” *Electrochim. Acta* 120 (2014) 379– 389.
2. F. Huet and S. Ritter, “Electrochemical noise measurements with dummy cells: Evaluation of a round-robin test series”, *Corrosion* 74 (2018) 1457–1465.
3. F. Huet, K. Ngo, “Electrochemical Noise - Guidance for Improving Measurements and Data Analysis”, *CORROSION 2018* (Houston, TX: NACE, 2018).

# Reliability of electrochemical impedance spectroscopy measurements: Results of round-robin testing

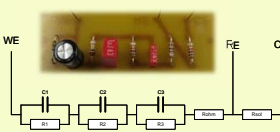
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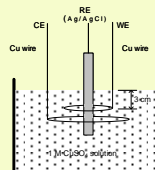
## Introduction

In order to verify the reproducibility of electrochemical impedance spectroscopy (EIS) measurements, nineteen laboratories around the world performed a series of three Round-Robin testing on EIS measurements. A total of twenty-three measurement systems, including mainly general-purpose potentiostats and frequency response analyzers from different manufacturers were used to perform EIS measurements using three testing systems: a dummy cell, a low-impedance electrochemical system and a high-impedance electrochemical system. This paper summarizes the results of these round-robin testing and discusses about measurement issues for the three electrochemical systems.

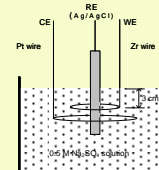
## EIS measurement equipments and testing systems



**System 1: Dummy cell and electrical scheme**  
5.1 MΩ // 100 μF + 100 kΩ // 1 μF + 1 kΩ // 100 nF + 100 Ω (Rsol = 1 kΩ)

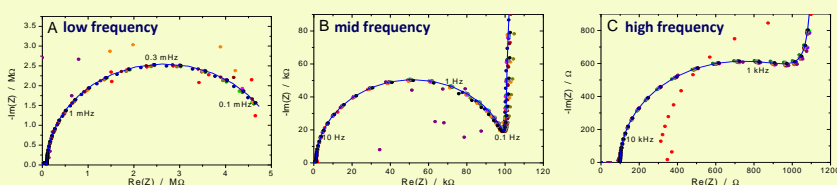


**System 2: Low-impedance electrochemical system (Cu-wire in 1M CuSO<sub>4</sub> solution)**



**System 3: High-impedance electrochemical system (Zr-wire in 0.5M Na<sub>2</sub>SO<sub>4</sub> solution)**

## EIS data for the first system: dummy cell

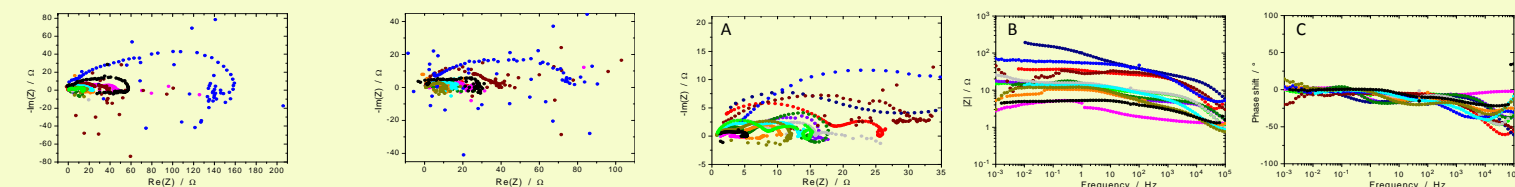


Nyquist diagrams of EIS data for the dummy cell in 0.1 mHz – 1 MHz range, no Faraday cage, ΔV = 10 mV<sub>rms</sub>. The blue full lines correspond to the impedance simulated with the fitted parameters (see Table)

Component	R <sub>1</sub> (MΩ)	R <sub>2</sub> (kΩ)	R <sub>3</sub> (Ω)	R <sub>ohm</sub> (Ω)	R <sub>sol</sub> (Ω)	C <sub>1</sub> (μF)	C <sub>2</sub> (μF)	C <sub>3</sub> (nF)
Nominal values	5.1	100	1000	100	1000	100	1	100
	(5%)	(5%)	(5%)	(5%)	(5%)	(20%)	(5%)	(5%)
Experimental mean value	5.02	99.34	1001.52	99.79	-	108.18	1.01	99.09
Standard deviation	0.07	0.49	5.19	0.32	-	2.76	0.01	1.89
Accuracy, %	1.4	0.5	0.5	0.3	-	2.6	1.4	1.9

Fitting formula:  $Z(f) = R_{ohm} + \frac{R_1}{1 + j2\pi f R_1 C_1} + \frac{R_2}{1 + j2\pi f R_2 C_2} + \frac{R_3}{1 + j2\pi f R_3 C_3}$

## Results on the 2<sup>nd</sup> system: low-impedance electrochemical system

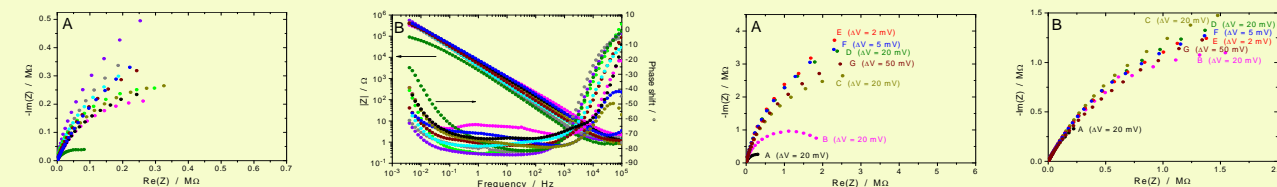


Large scatter in EIS data (galvanostatic mode, ΔI = 10 μA<sub>rms</sub>, immersion time 1h)

Large scatter in EIS data (potentiostatic mode, ΔV = 0.1 mV<sub>rms</sub>, immersion time 5h)

Large scatter in EIS data even with an excitation signal of amplitude higher (potentiostatic mode, ΔV = 1 mV<sub>rms</sub>, immersion time 9h): (A) Nyquist diagram; (B) and (C) Bode plots

## Results on the 3<sup>rd</sup> system: high-impedance electrochemical system



EIS data for the high-impedance electrochemical system (potentiostatic mode ΔV = 20 mV<sub>rms</sub>, immersion time 6 h): (A) Nyquist diagram; (B) Bode plots

EIS data for the high-impedance electrochemical system: influence of the immersion time and amplitude of the voltage excitation for two different participants using two different equipment

**Immersion time:**  
(A) 6h; (B) 24h; (C) 120h; and (D) 168h

**Amplitude of the voltage excitation:**  
(E) 2 mV; (F) 5 mV and (G) 20 mV; immersion time: 168h

## Conclusions

From these results, it can be concluded that with the actual commercially available instruments for EIS measurements it was relatively easy to produce good quality data. Differences were only obtained for the tested systems, the largest difference being obtained for the low-impedance system. Although well known, the importance of choosing the correct value of the perturbation amplitude for an EIS measurement was again demonstrated. This was much more sensitive for the active, low-impedance system than for the passive high-impedance system.