Electrochemical noise –
Guidance for improving measurements and data analysis

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Introduction (1)

- Electrochemical Noise (EN): widely used since Iverson's paper in 1968 to study corrosion processes
- EN: promising technique to detect localized corrosion
- in the eighties, EN (random signal) was correctly measured with spectrum analyzers (due to the presence of anti-aliasing filters)
- since the nineties, personal computers with data acquisition cards or digital voltmeters often lead to improper EN measurements due to aliasing occurring during the analog-to-digital conversion
- aliasing problem currently ignored in many commercial potentiostats

➡ Round-Robin (RR) tests organized by ECG-COMON (European Cooperative Group on Corrosion Monitoring of Nuclear Materials) between 2006 and 2017
  - ZRA mode, three electrode configuration, ΔV and ΔI
  - mainly on dummy cells to check the EN measurement equipments with a well-defined noise level (thermal noise) in contrast to corroding electrodes

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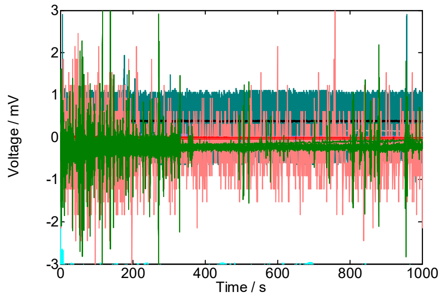
Introduction (2)

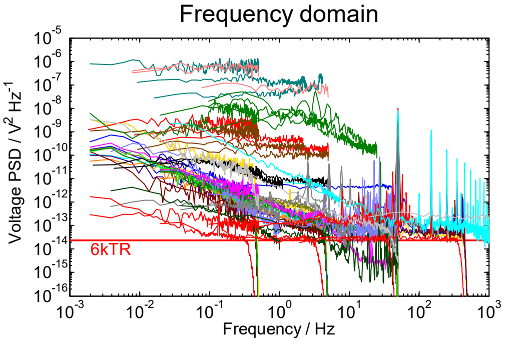
Analysis of the voltage fluctuations (R = 1 MΩ)

All results (77) in RR-2017

Time domain



Frequency domain



- ✓ Very large scatter : 8 decades in $V^2 Hz^{-1}$, so 4 decades in Volt!!
- ✓ Evidence of aliasing for many equipments: no PSD decrease at frequencies close to $f_s/2$ and bad overlap of the PSDs measured at different sampling frequencies f_s

- ➢ C2018-11040: "Electrochemical Noise Measurements with Dummy Cells: Evaluation of a Round-Robin Test Series", F. Huet, S. Ritter

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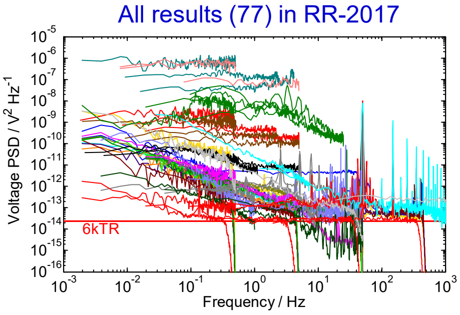
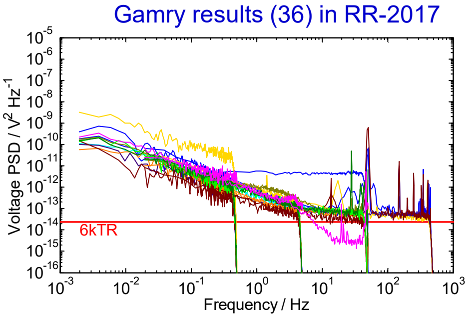
Introduction (3)

R = 1 MΩ

All results (77) in RR-2017



Gamry results (36) in RR-2017



- ✓ Lower scatter (2 decades at low frequency) and PSDs closer to thermal noise level
- ✓ Presence of anti-aliasing filters: PSD decrease observed at frequency close to $f_s/2$ and good overlap of the PSDs measured at different f_s
- ✓ However, some scatter still exists in voltage PSDs and larger scatter in current PSDs

➡ a tutorial for EN measurements is needed to train people to perform valid EN measurements

- ➢ first with using dummy cells for which the noise level is known
- ➢ then with a corrosion system

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Algorithm for PSD calculation with FFT

- algorithm
  - divide the time record in N sections (typically N = 10) of M data points (typically M = 2048, 1024…)
  - loop N times

    {
    linear detrending of x(t) if necessary
    remove the mean value of *x* (not informative since it corresponds to f = 0)
    multiply by the Hann window
    FFT
    PSD calculation: $$\Psi_x(m\Delta f) = \frac{2}{T}\left|X_T(m\Delta f)\right|^2 = \frac{2}{M}\Delta t\left|\sum_{n=0}^{M-1} x(n\Delta t)\, e^{-2i\pi m n / M}\right|^2$$
    }
  - average the *N* PSDs
  - if Hann: multiply the result by 8/3.
- psd-detrend_ECG-COMON.exe for PSD calculation on the ECG-COMON website (free access) (www.ecg-comon.org)

Some explanations on "psd-detrend_ECG-COMON.exe" (1)

- configuration file: config_psd-detrend_ECG-COMON.txt

file_in hanning (0 = no, 1 = yes) nb_section nbpoint_section detrend (0 = no, 1 = linear) file_out

- file_in → input file: time (s) potential (V) current (A)
- hanning → Hann window (most often 1)
- nb_section → number N of sections into which file_in will be divided
- nbpoint_section → number M of points per section
- detrend → to eliminate drift
- file_out → output file

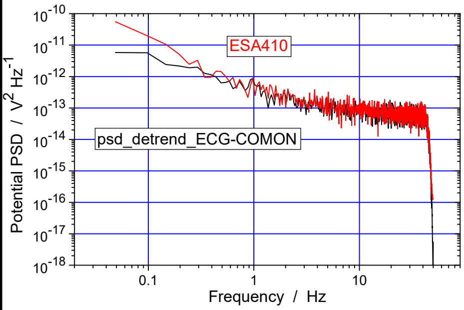
- no character "blank" in the names of file_in and file_out
- nbpoint_section must be a power of 2

- output file

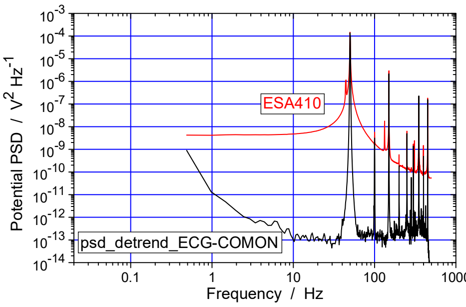
$$Z_n = \sqrt{\frac{\Psi_v}{\Psi_i}}$$

frequency	PSD_v	PSD_i	Zn
4.882813e-003	1.901942e-011	2.974846e-024	2.528520e+006
9.765625e-003	1.913229e-012	9.364153e-025	1.429385e+006
1.464844e-002	5.789599e-013	5.085475e-025	1.066985e+006
...			

Some explanations on "psd-detrend_ECG-COMON.exe" (2)



similar PSDs



quite different PSDs

✓ improvement in PSD calculation by equipment G is needed
✓ for the moment, it's preferable to use the ECG-COMON program to calculate PSDs and Z_n

Good new: Max Yaffe has recently corrected the PSD calculation in ESA410

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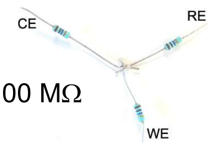
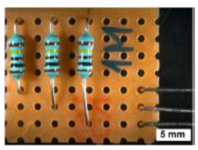
Practical work with dummy cells (1)

- 3 identical resistors in star arrangement (ZRA mode)



R = 100 MΩ



R = 1 MΩ

- thermal noise
  - ✓ at thermodynamic equilibrium ($I_o = 0$): $\Psi_V = 4kTR = 1.6 \times 10^{-20}$ R in V^2 Hz^{-1}
  - ✓ low amplitude as for passive electrodes
  - ✓ but known: $\Psi_V = 6kTR$, $\Psi_I = 2kT/R$ for 3 resistors in star arrangement
- EN measurements
  - ✓ potentiostat used: Gamry Ref600† with ESA410† software (v. 6.33)
  - ✓ measurements in ZRA mode to measure both ΔV and ΔI
  - ✓ measurements have to be performed at different sampling frequencies to check the overlap of the PSDs and validate the EN measurement
  - ✓ a Faraday cage was used (Al cooking paper)
- Guideline for an assessment of electrochemical noise measurement devices, S. Ritter, F. Huet, R.A. Cottis, Materials and Corrosion, 63 (2012) 297

† Trade name

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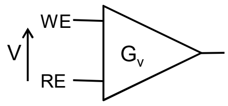
Practical work on dummy cells (2): R = 10 MΩ

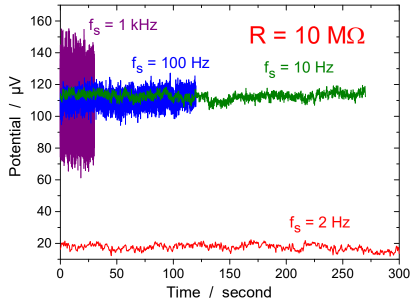
Measurement conditions
(fast, only for training)

Sampling frequency f_s	1 kHz	100 Hz	10 Hz	2 Hz
Number of points per section N	2 048	2 048	256	62
Number of sections	14	11	10	10
Measurement time T	30 s	4 min	4 min 30 s	5 min 30 s
Lowest analyzed frequency f_s / N	0.5 Hz	0.05 Hz	0.04 Hz	0.03 Hz

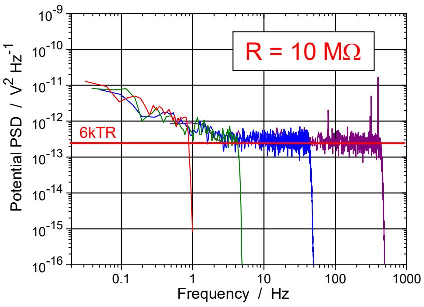
Potential measurement
(simple)



Vch range	3 V	300 mV	30 mV
Vch gain	1	10	100



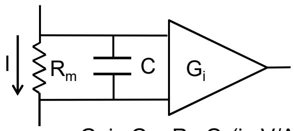
Time record: no possible validation



PSD: thermal noise measured !

Practical work on dummy cells (3): R = 10 MΩ

Current measurement: more difficult since 3 parameters have to be set (R_m, C, and G_i)



Gain G = R_m G_i (in V/A)

Ich range	3 V	300 mV	30 mV
Ich gain	1	10	100

Choose I/E range
so that
R_m > R

for R = 10 MΩ →

			I-E Stability (C)			
			Fast	Medium Fast	Normal	Slow
I-E range	R_m (Ω)	Effective gain (V/A)	frequency bandwidth (Hz)			
600 mA	0.2	5	500	500	500	500
60 mA	2	50	500	500	500	500
6 mA	20	500	500	500	500	500
600 µA	200	5×10^3	500	500	500	500
60 µA	2 k	5×10^4	500	500	500	80
6 µA	20 k	5×10^5	500	500	240	8
600 nA	200 k	5×10^6	500	500	24	800 m
60 nA	2 M	5×10^7	500	80	2.4	80 m
6 nA	20 M	5×10^8	50	8	240 m	8 m
600 pA	200 M	5×10^9	5	800 m	24 m	800 µ
60 pA	2 G	5×10^{10}	500 m	80 m	2.4 m	80 µ

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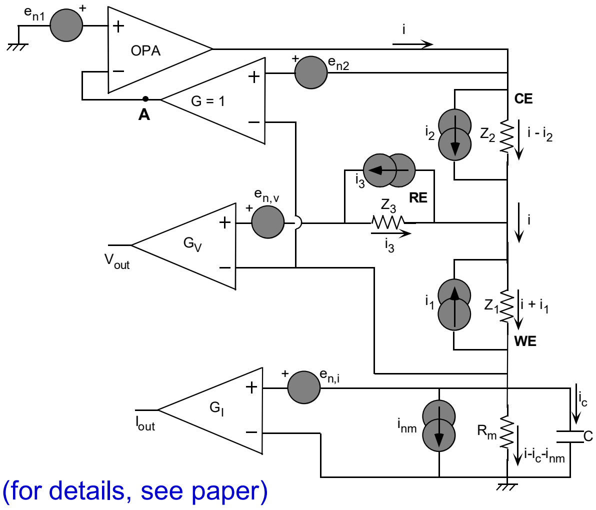
Practical work on dummy cells (4)



Schematic circuit of the potentiostat working in ZRA mode with predominant noise sources ($Z_1 = Z_2 = Z_3 = R$)

(for details, see paper)

$$\Psi_{I_{meas}} = \frac{\Psi_{e_{ni}}}{R_m^2} + \frac{1}{1 + 4\pi^2 R_m^2 C^2 f^2}\left[4kT\frac{1}{R_m} + \frac{\Psi_{e_n}}{4R^2} + 2kT\frac{1}{R}\right]$$

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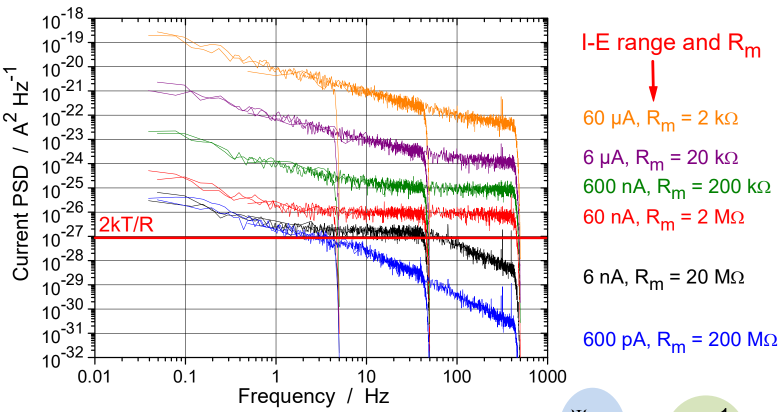
Practical work on dummy cells (5): R = 10 MΩ

I-E Stability "Fast", Ich = 30 mV



- $R_m \ll R$: $\Psi_{I_{meas}}$ too high because of the influence of $\frac{\Psi_{e_{ni}}}{R_m^2}$ and $4kT\frac{1}{R_m}$
- $R_m \gg R$: $\Psi_{I_{meas}}$ filtered at high frequency by C in parallel with R_m
- best value $R_m = 20\ \text{M}\Omega = 2R$:

$$\Psi_{I_{meas}} = \frac{\Psi_{e_{ni}}}{R_m^2} + \frac{1}{1 + 4\pi^2 R_m^2 C^2 f^2}\left[4kT\frac{1}{R_m} + \frac{\Psi_{e_n}}{4R^2} + 2kT\frac{1}{R}\right]$$

Measurement procedure for EN measurements in ZRA mode

- ✓ Connect all electrodes. Toggle cell on.
- ✓ Input file name, choose ZRA mode, sampling frequency f_s, test time (at least 10 N / f_s).
- ✓ Set Device/I-E Stability according to f_s (usually 'Fast', see Table 2).
- ✓ Set Device/Ich Filter and Vch Filter to 1 kHz if f_s > 5 Hz, or to 5 Hz otherwise.
- ✓ Set all I-E range, Current channel, Voltage channel to auto mode, let the software choose a measure range without overload.
- ✓ Set all I-E range, Current channel, Voltage channel to manual mode. Try to decrease I-E range down to get a minimum setting without overload.
- ✓ Decrease voltage channel and current channel manually down to get a minimum range without overload.
- ✓ If the EN is expected to increase during the experiment, it may be necessary to use higher I/E, voltage, and current ranges.
- ✓ Start to record EN data.
- ✓ Observe the overload indicators. Once the overload warning occurs, the data may be unreliable.
- ✓ When the test is finished, toggle cell off.

Practical work on pitting corrosion of aluminum (1)

- 2 identical Al disk electrodes (ϕ = 2.5 cm, S = 4.9 cm²) facing each other (d = 1 cm)
- KCl 1M, RE = SCE,
- no Faraday cage was used

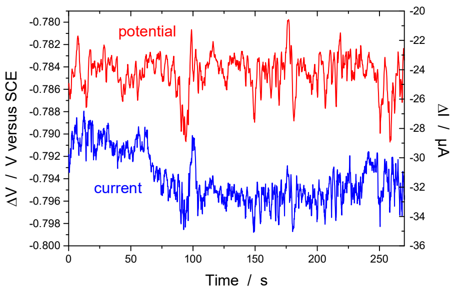
symmetric system: V = 0 applied between the WE and CE (ZRA mode)

→ both electrodes at corrosion potential

another way to validate EN measurements:

$$Z_n(f) = \sqrt{\frac{\Psi_V(f)}{\Psi_i(f)}} = |Z(f)|$$

if - a true RE is used (SCE, SSE…)
- EN higher than instrumentation noise

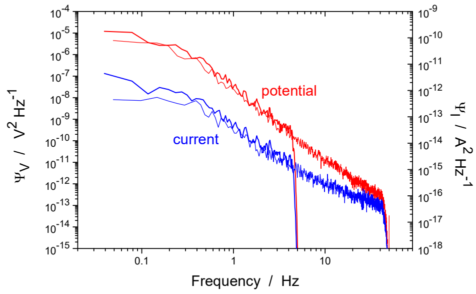


high noise due to pitting
$\Delta V \approx 4\ mV_{pp}$, $\Delta I \approx 4\ \mu A_{pp}$

no visible transients (too many pits)

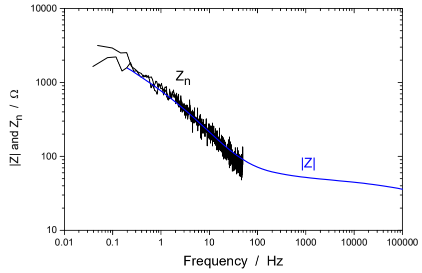
Practical work on pitting corrosion of aluminum (2)

symmetric system:



good overlap of the PSDs

first validation of the noise measurements



Z_n (f) = |Z(f)|

second validation of the noise measurements

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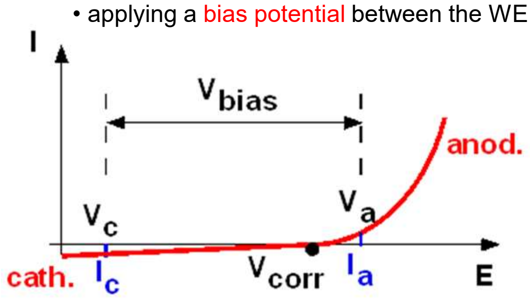
Practical work on pitting corrosion of aluminum (3)

asymmetrics systems

- sometimes used to have only one corroding electrode
  - electrodes of different materials (cathode in Pt and small size)
  - bias potential applied between identical electrodes
- identical electrodes cannot be used
  - in SCC investigations, only one electrode is under stress
  - in crevice corrosion studies, crevice attack occurs on one electrode only

practical work

- using the same Al electrodes as before
- applying a bias potential between the WE and the CE



one electrode acts as an anode, the other as a cathode

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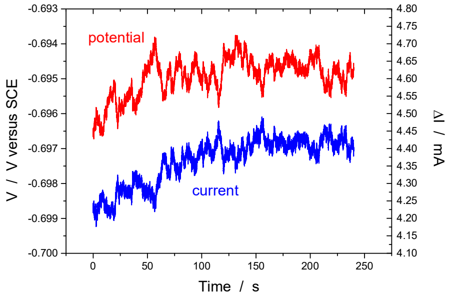
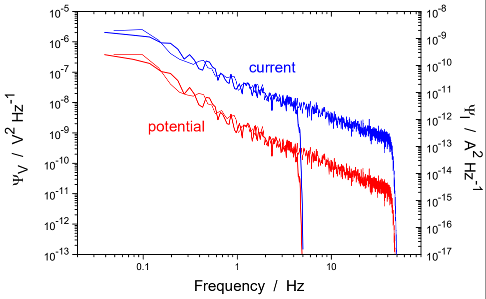
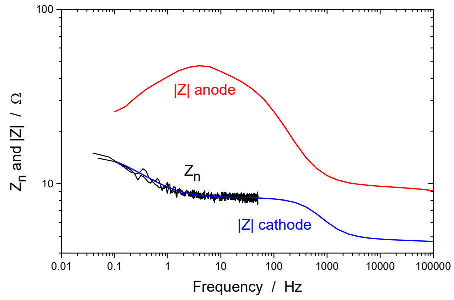
Practical work on pitting corrosion of aluminum (4)







good overlap of the PSDs
first validation of the noise measurements

Z_n (f) = |Z(f)| of the cathode
due to the high noise on the anode!

EN analysis is more difficult
for asymmetric systems

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Conclusions

- validation of EN measurements can only be performed in the frequency domain by checking the overlap of PSDs measured at different sampling rates
- ECG website (free access): psd_ECG-COMON.exe for PSD calculation
- good PSD measurements (= good PSD overlaps) for very few commercial potentiostats (Gamry† with ESA410†, Bio-logic†?, IPS†?)
- even with good equipments, data provided by common users are often wrong: they do not set right values to the parameters of the setup for ENM

→ practical course on dummy cells and a corrosion system

it is now possible to perform valid EN measurements
with a commercial potentiostat

† Trade name

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