



**Mechanisms of Localized Corrosion and Electrochemical  
Methods (TEG 407X)**

**Electrochemical Noise - Guidance for Improving  
Measurements and Data Analysis  
(C2018 - 11042)**

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### **Introduction (1)**

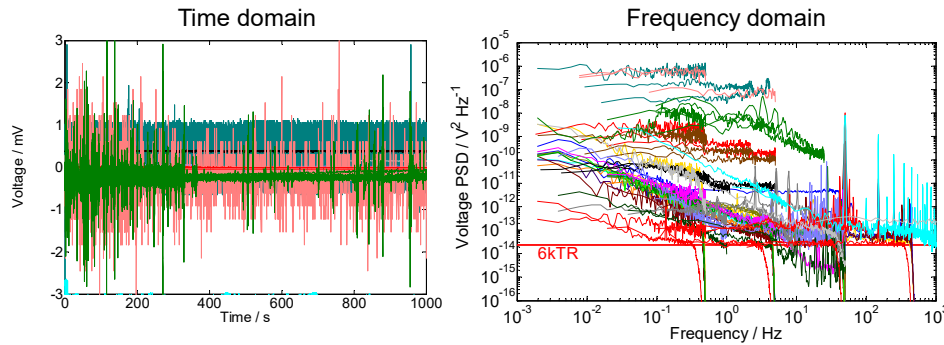
- **Electrochemical Noise (EN)**: widely used since Iverson's paper in 1968 to study corrosion processes
- **EN**: promising technique to detect localized corrosion
- in the eighties, EN (random signal) was **correctly measured with spectrum analyzers** (due to the presence of anti-aliasing filters)
- 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,  **$\Delta V$  and  $\Delta I$**
  - **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 ( $R = 1 \text{ M}\Omega$ )

All results (77) in RR-2017



- ✓ Very large scatter : 8 decades in  $\text{V}^2 \text{Hz}^{-1}$ , so 4 decades in Volt!!
- ✓ Evidence of aliasing for many equipments: no PSD decrease at frequency 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 (Wednesday, 9:25, room 131 A-B)

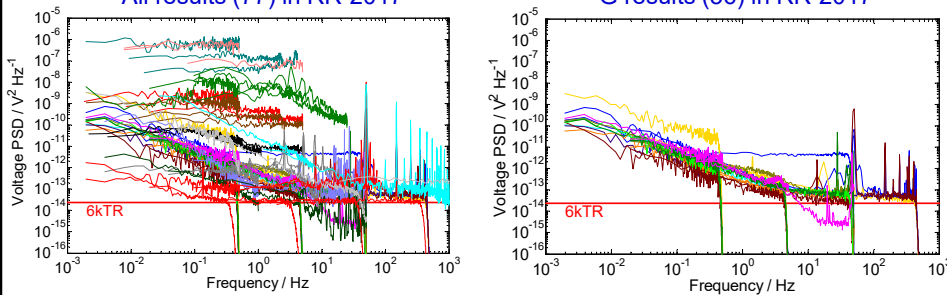
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## Introduction (3)

$R = 1 \text{ M}\Omega$

All results (77) in RR-2017

G 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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• **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

input file:  
time (s) potential (V) current (A) number N of sections into which file\_in will be divided to eliminate drift output file

Hann window  
(most often 1)

number M of points per section

• no character "blank" in the names of file\_in and file\_out  
• nbpoint\_section must be a power of 2

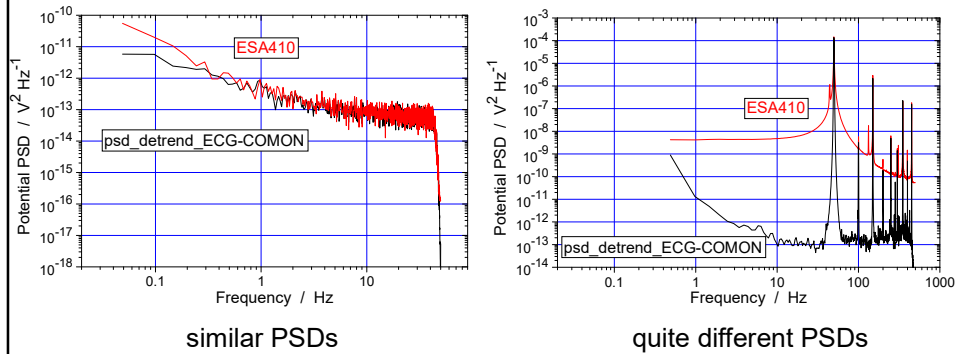
• **output file**

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

...

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

## Some explanations on "psd-detrend\_ECG-COMON.exe" (2)

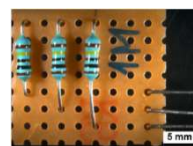
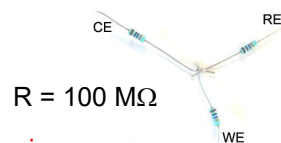


- ✓ improvement in PSD calculation by equipment G is needed
- ✓ for the moment, it's preferable to use the ECG-COMON program to calculate PSDs and  $Z_n$

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## Practical work with dummy cells (1)

- 3 identical resistors in star arrangement (ZRA mode)



$R = 1 \text{ M}\Omega$

- thermal noise

- ✓ at thermodynamic equilibrium ( $I_o = 0$ ):  $\Psi_V = 4kTR = 1.6 \times 10^{-20} \text{ V}^2 \text{ Hz}^{-1}$
- ✓ 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<sup>†</sup> with ESA410<sup>†</sup> software (v. 6.33)
- ✓ measurements in ZRA mode to measure both  $\Delta V$  and  $\Delta I$
- ✓ 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

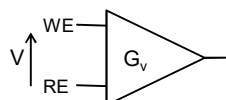
<sup>†</sup> Trade name

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### Practical work on dummy cells (2): $R = 10\text{ M}\Omega$

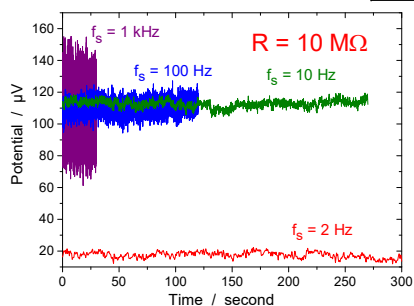
Measurement conditions  
(fast, only for training)

Potential measurement  
(simple)

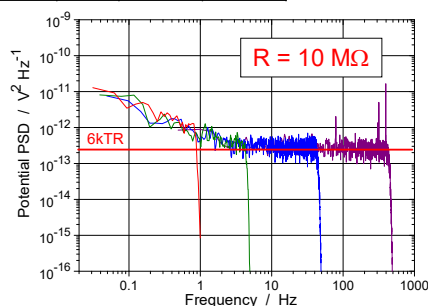


Sampling frequency $f_s$	1 kHz	100 Hz	10 Hz	2 Hz
Number of points per section N	2 048	2 048	256	62
Number of sections	14	11	10	10
Measurement time T	30 s	4 min	4 min 30 s	5 min 30 s
Lowest analyzed frequency $f_s / N$	0.5 Hz	0.05 Hz	0.04 Hz	0.03 Hz

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



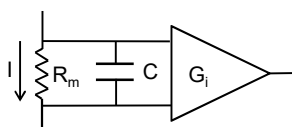
Time record: no possible validation



PSD: thermal noise measured !

### Practical work on dummy cells (3): $R = 10\text{ M}\Omega$

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

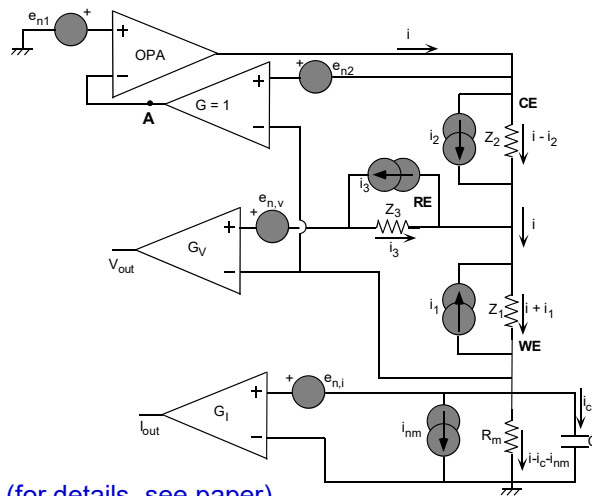
Choose I/E range  
so that  
 $R_m > R$

for  $R = 10\text{ M}\Omega$  →

			I-E Stability (C)			
			Fast	Medium Fast	Normal	Slow
I-E range	$R_m (\Omega)$	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 $\mu$ A	200	$5 \times 10^3$	500	500	500	500
60 $\mu$ A	2 k	$5 \times 10^4$	500	500	500	80
6 $\mu$ A	20 k	$5 \times 10^5$	500	500	240	8
600 nA	200 k	$5 \times 10^6$	500	500	24	800 m
60 nA	2 M	$5 \times 10^7$	500	80	2.4	80 m
6 nA	20 M	$5 \times 10^8$	50	8	240 m	8 m
600 pA	200 M	$5 \times 10^9$	5	800 m	24 m	800 $\mu$
60 pA	2 G	$5 \times 10^{10}$	500 m	80 m	2.4 m	80 $\mu$

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### Practical work on dummy cells (4)



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

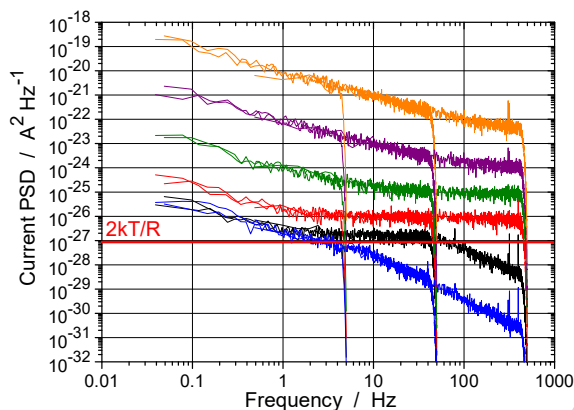
(for details, see paper)

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

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### Practical work on dummy cells (5): $R = 10 \text{ M}\Omega$

I-E Stability "Fast",  $I_{ch} = 30 \text{ mV}$



I-E range and  $R_m$

60  $\mu\text{A}$ ,  $R_m = 2 \text{ k}\Omega$

6  $\mu\text{A}$ ,  $R_m = 20 \text{ k}\Omega$

600 nA,  $R_m = 200 \text{ k}\Omega$

60 nA,  $R_m = 2 \text{ M}\Omega$

6 nA,  $R_m = 20 \text{ M}\Omega$

600 pA,  $R_m = 200 \text{ M}\Omega$

-  $R_m \ll R$ :  $\Psi_{I_{\text{meas}}}$  too high because of the influence of  $\frac{\Psi_{e_{ni}}}{R_m^2}$  and  $4kT \frac{1}{R_m}$

-  $R_m \gg R$ :  $\Psi_{I_{\text{meas}}}$  filtered at high frequency by C in parallel with  $R_m$

- best value

$R_m = 20 \text{ M}\Omega = 2R$ :

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

### 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)

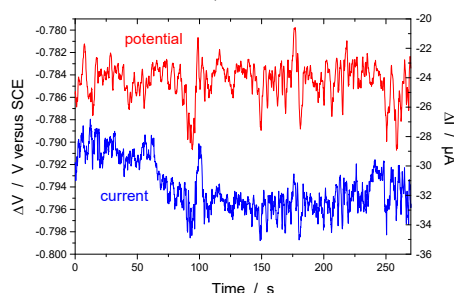
- 2 identical Al disk electrodes ( $\phi = 2.5$  cm,  $S = 4.9$  cm<sup>2</sup>) faced each other ( $d = 1$  cm)
- RE = SCE
- no Faraday cage was used

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

➔ both electrodes at corrosion potential

another way to validate EN measurements:

$$Z_n(f) = \sqrt{\frac{\Psi_v(f)}{\Psi_i(f)}} = |Z(f)| \quad \text{if - a true RE is used (SCE, SSE...)} \\ \text{- EN higher than instrumentation noise}$$



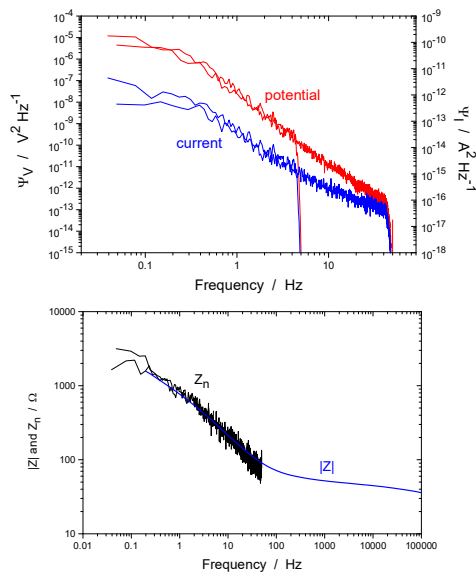
high noise due to pitting  
 $\Delta V \approx 4$  mV<sub>pp</sub>,  $\Delta I \approx 4$  μA<sub>pp</sub>

no visible transients (too many pits)

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## 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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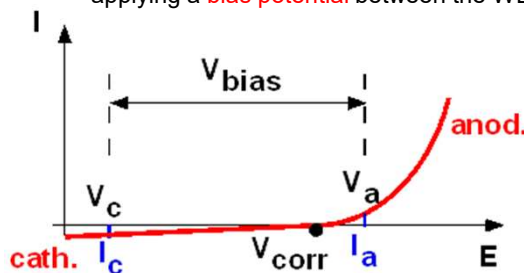
## Practical work on pitting corrosion of aluminum (3)

asymmetric 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

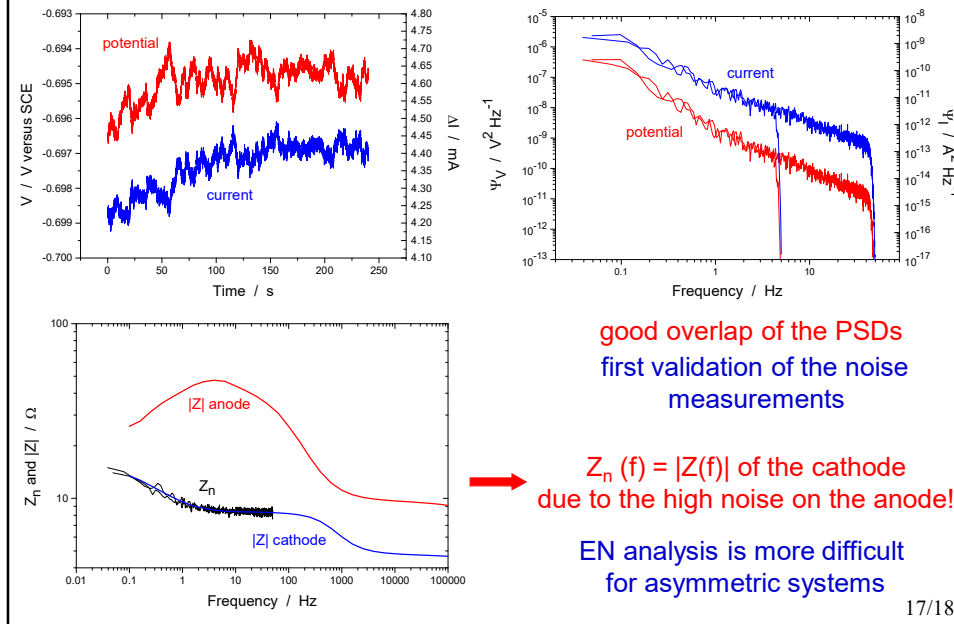


one electrode acts as an anode, the other as a cathode

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### Practical work on pitting corrosion of aluminum (4)



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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<sup>†</sup> with ESA410<sup>†</sup>, Bio-logic<sup>†</sup>?, IPS<sup>†</sup>?)
- even with good equipments, data provided by common users are often wrong: they do not set the right parameters in 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

- read 2 papers:

- Guideline for an assessment of EN measurement devices, S. Ritter, F. Huet, R. Cottis, *Materials and Corrosion*, 63 (2012) 297
- C2018-11040: "Electrochemical Noise Measurements with Dummy Cells: Evaluation of a Round-Robin Test Series", F. Huet, S. Ritter (Wednesday, 9:25, room 131 A-B)

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