



TEG 097X: Electrochemical techniques for measuring corrosion
 Tutorials on Electrochemical Measurements for Monitoring Corrosion


ELECTROCHEMICAL NOISE
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 ECG-COMON (Round-Robin tests, noise guideline)


Corrosion 2018 – Phoenix – April 15, 2018


Outline of the presentation

- Generalities on Electrochemical Noise: origins, definition, examples...
- Electrochemical Noise Analysis: time domain, frequency domain
- Measurement technique:
 - various measurement problems
 - validation of the EN measurement
- Corrosion monitoring with noise resistance and noise impedance
- Measurement of electrolyte resistance fluctuations
- Conclusions and further information

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What is Electrochemical Noise?

- spontaneous fluctuations of
 - potential (galvanostatic control) 1 WE
 - current (potentiostatic control) 1 WE
 - potential and current (ZRA) 2 WE
- measured at corrosion potential (monitoring purpose)
 - or not (ex: passive domain to study pitting corrosion)
- no external signal applied (non-perturbative technique)
- main idea for field applications:
 - "listening" the noise to detect localized corrosion

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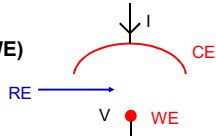
Origins of the noise

- for any physical system:
 - thermal noise (thermal vibrations of electrons)
 - shot noise (quantized nature of charge carriers)
 - 1/f noise (various origins, not clear)
- in the corrosion domain:
 - general corrosion
 - metastable pitting corrosion
 - other localized corrosion: crevice, IGSCC, TGSCC, cavitation...
 - hydrogen evolution (acidic media)
 - passage of solid particles (erosion) or oil droplets in brine...
 - flows enhance EN if corrosion controlled by mass transport
 - etc, etc...

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Electrochemical noise with 1 WE

One single working electrode (WE)



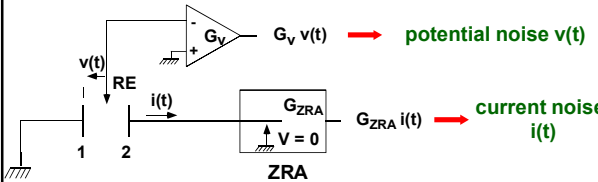
- galvanostatic control
 - $I = I_0$: $V = V_0 + v(t)$ $v(t) = \text{voltage noise}$
 - (ex: $I_0 = 0$ at corrosion potential)
- potentiostatic control
 - $V = V_0$: $I = I_0 + i(t)$ $i(t) = \text{current noise}$

➔ $v(t)$ or $i(t)$: information on the electrochemical processes


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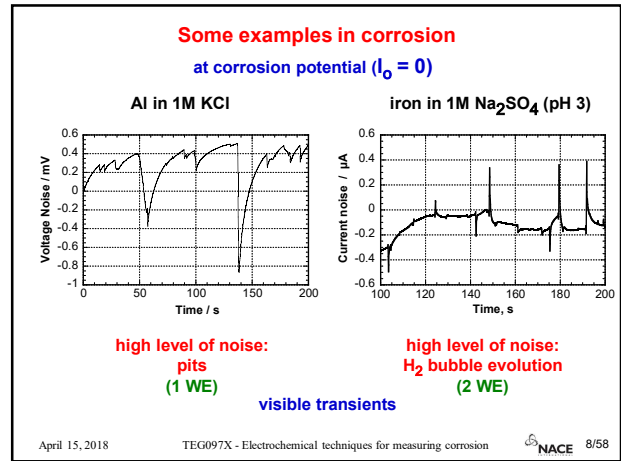
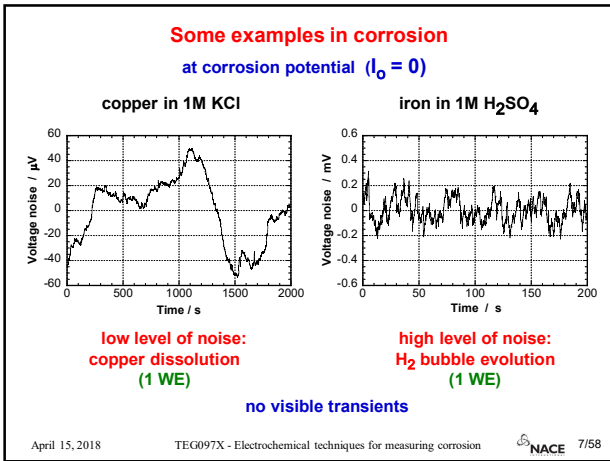
Electrochemical noise with 2 WEs

2 identical working electrodes: Eden, Hladky, John, Dawson, Corrosion / 86, Paper 274



- RE: true RE (SCE, SSE...) or 3rd identical electrode

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Electrochemical Noise Analysis

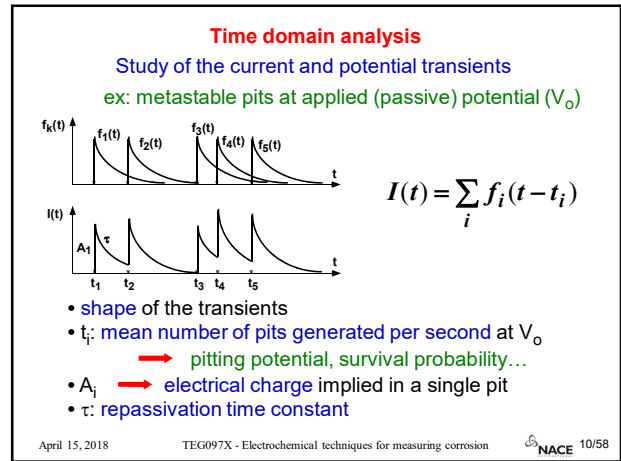
several methods (only "standard" methods are presented)

- analysis in the time domain: transient shape, SD, R_n ...
- analysis in the frequency domain: PSD

aim:

- investigate fundamental aspects of corrosion: mechanism, pitting domain...
- corrosion monitoring (in the field):
 - corrosion rate estimation
 - discriminate between various types of corrosion: uniform, pitting, intergranular, SCC...

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Time domain analysis

Standard deviation and root mean square (RMS): $I = I_0 + i(t)$

- standard deviation $\sigma_i = \sqrt{\langle i^2(t) \rangle}$
- root mean square $I_{rms} = \sqrt{\langle I^2(t) \rangle} = \sqrt{I_0^2 + \sigma_i^2}$

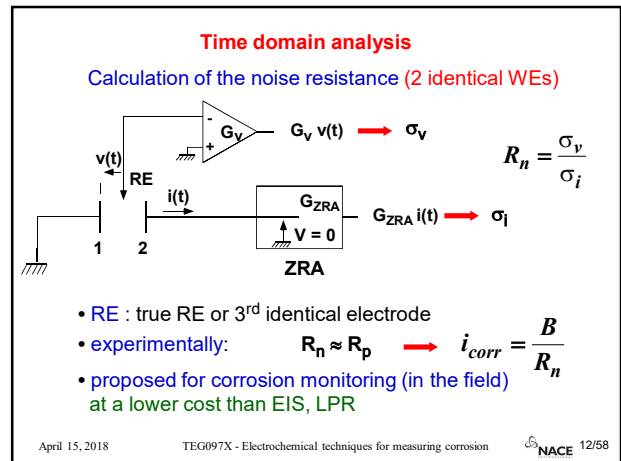
idea: estimation of the corrosion rate from σ_v or σ_i (not possible with a single WE)

"Pitting index": $PI = \frac{\sigma_i}{I_{rms}} = \frac{\sigma_i}{\sqrt{I_0^2 + \sigma_i^2}} \rightarrow 0 \leq PI \leq 1$

- uniform corrosion: $\sigma_i \ll I_0 \rightarrow PI \approx 0$
- localized corrosion: $\sigma_i \gg I_0 \rightarrow PI \approx 1$

but: conflicting results on the estimation of the degree of localized corrosion from PI

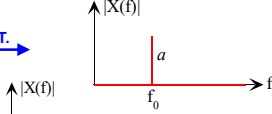
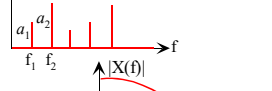
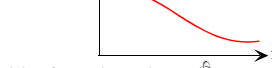
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Analysis in the frequency domain: power spectral density

time domain $x(t)$ $\xleftrightarrow[\text{Inverse Fourier T.}]{\text{Fourier transform}}$ frequency domain $X(f) = \int_{-\infty}^{+\infty} x(t) e^{-2\pi f t} dt$

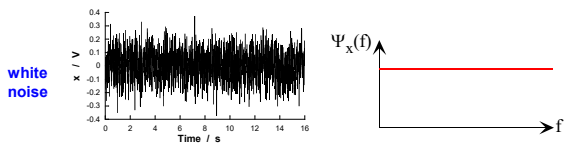
Some examples

- 1) pure sine wave $x(t) = a \sin(2\pi f_0 t + \phi)$ $\xrightarrow{\text{F. T.}}$ 
- 2) periodic signal $x(t) = \sum_i a_i \sin(2\pi f_i t + \phi_i)$ $\xrightarrow{\text{F. T.}}$ 
- 3) any signal (noise) $\xrightarrow{\text{F. T.}}$ 

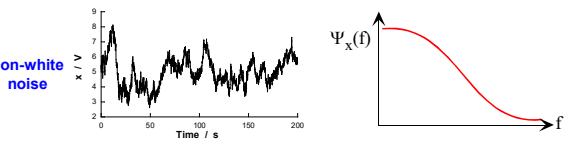
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Analysis in the frequency domain: power spectral density

$T =$ acquisition time $\text{PSD: } \Psi_x(f) = \frac{2}{T} |X(f)|^2$

white noise 

the most random signal

non-white noise 

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Analysis in the frequency domain: power spectral density

$x(t)$ $\xrightarrow{\text{Fourier transform}}$ $|X(f)|$

PSD: $\Psi_x(f) = \frac{2}{T} |X(f)|^2$

$x(t) =$ summation of sine waves $a_i \sin(2\pi f_i t + \phi_i)$

- at low frequency: a_i high \leftarrow large slow x variations
- at high frequency: a_i low \leftarrow small fast x variations

- maximum entropy method (MEM): **dangerous! never use it alone** (see Ref.)
- information from:
 - amplitude of the low-frequency plateau
 - cut-off frequency
 - slope of the decrease

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Algorithm for PSD calculation with FFT

loop N times

- { acquisition of M data points of $x(t)$
- linear detrending or not
- remove the mean value of x (not informative since corresponds to frequency 0)
- multiply by the Hann window
- FFT
- PSD calculation: $\Psi_x(m\Delta f) = \frac{2}{T} |X_T(m\Delta f)|^2 = \frac{2}{M} \Delta t \left| \sum_{n=0}^{M-1} x(n\Delta t) e^{-2\pi i m n / M} \right|^2$

average the N PSDs

if Hann: multiply the result by 8/3.

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Example: digital white noise (randn in Matlab)

$(f_0 = 1 \text{ Hz})$ $\text{PSD: } N = 1$ section of 1024 points

$\sigma_{\text{PSD}} / m_{\text{PSD}} = 101\%$ $\epsilon = \frac{1}{\sqrt{N}}$

$\text{PSD: } N = 10$ sections of 1024 points $\sigma_{\text{PSD}} / m_{\text{PSD}} = 31.3\%$

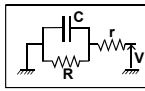
$\text{PSD: } N = 100$ sections of 1024 points $\sigma_{\text{PSD}} / m_{\text{PSD}} = 10.6\%$

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Example: thermal voltage noise of a R-C circuit

- measurement without ZRA, galvanostat (V amplifier only)
- thermodynamic equilibrium ($I_0 = 0$): $\Psi_V(f) = 4 k_B T \text{Re}(Z(f))$

$R = 100 \text{ M}\Omega$
 $r = 10 \text{ k}\Omega$
 $C = 15 \text{ nF}$

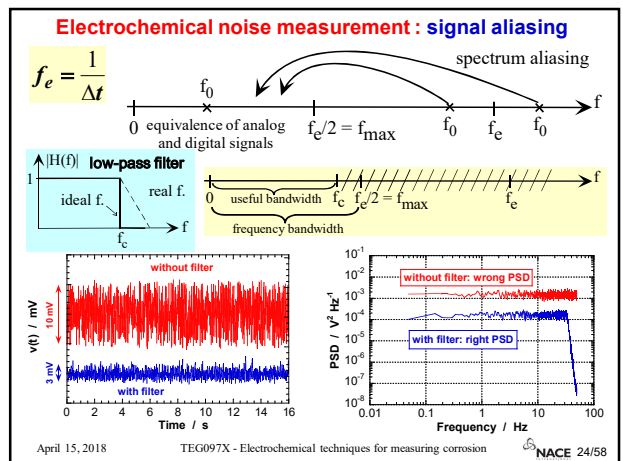
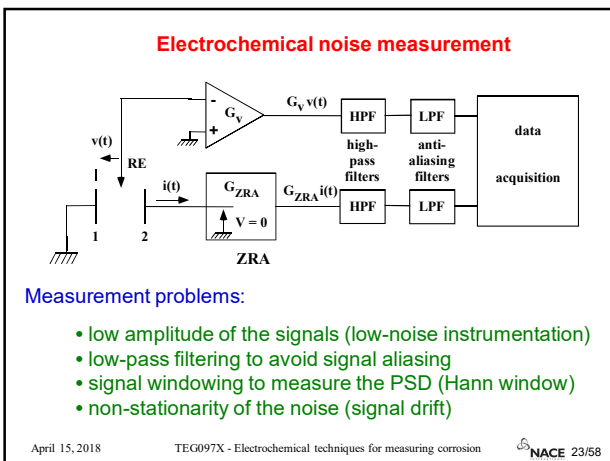
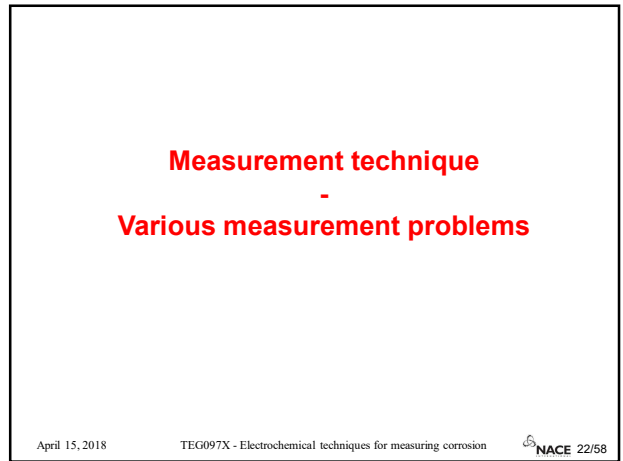
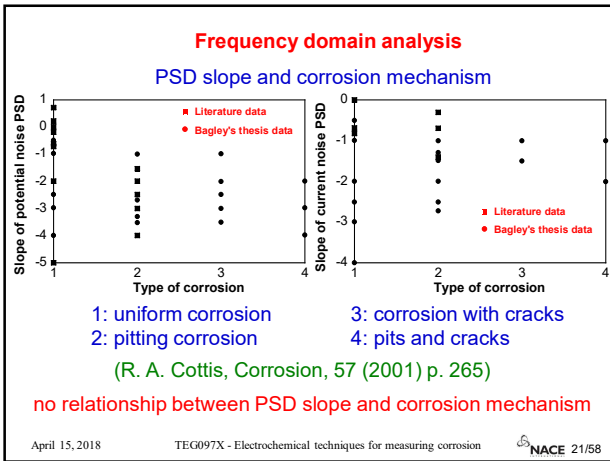
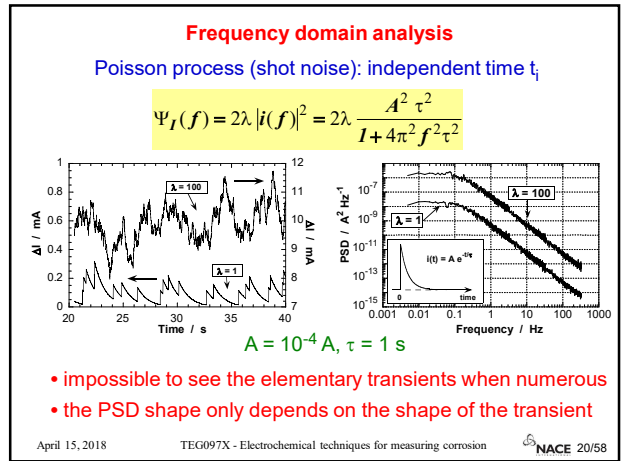
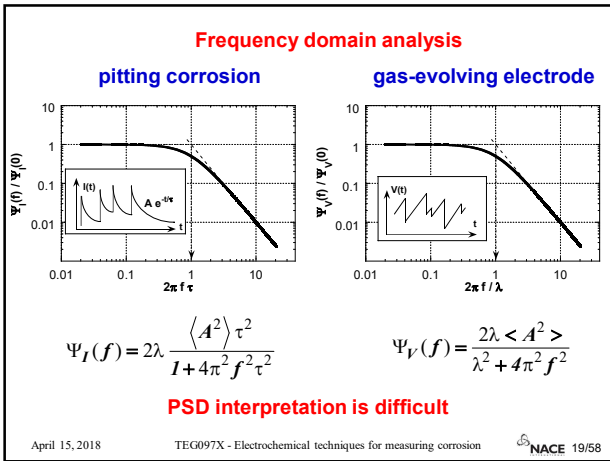


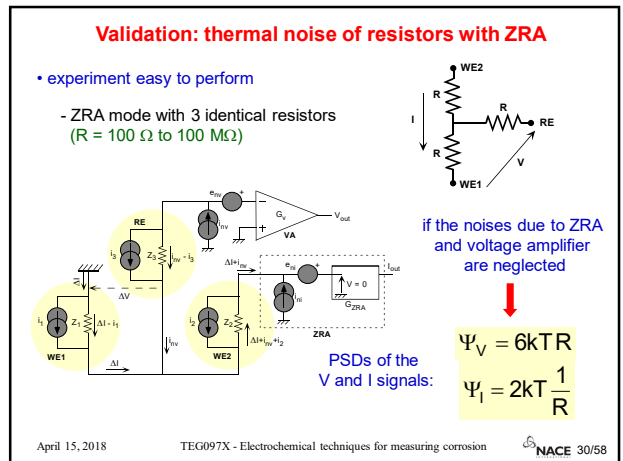
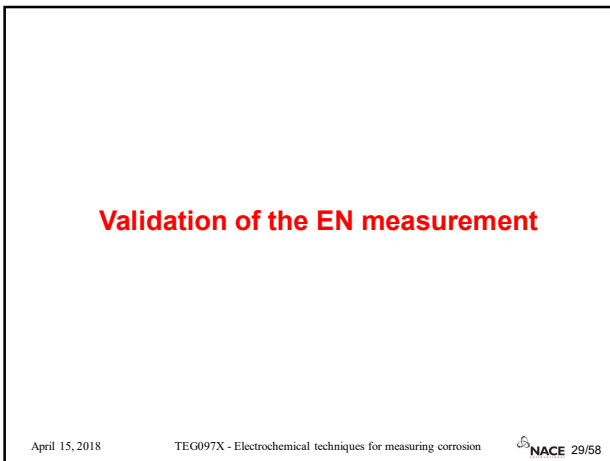
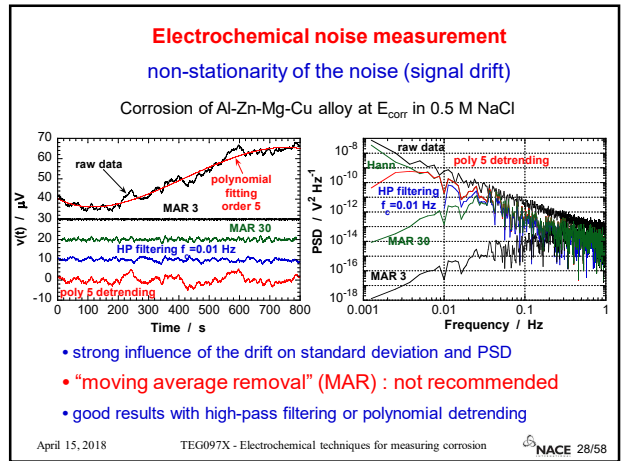
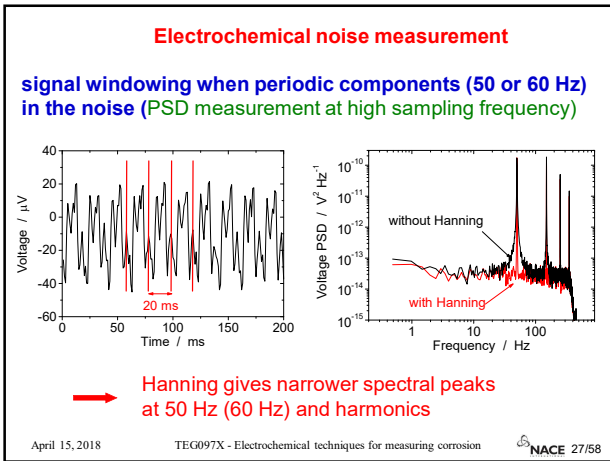
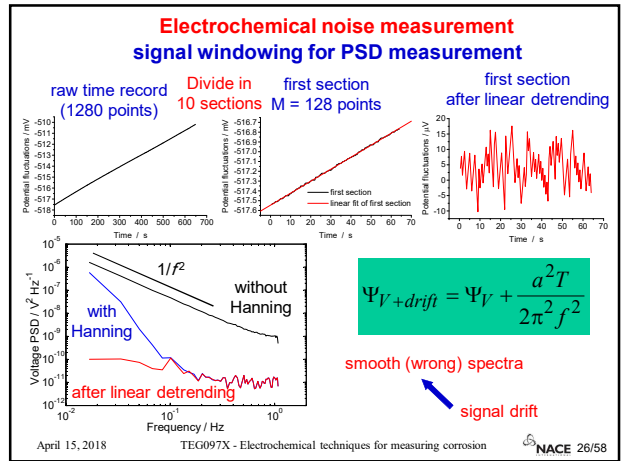
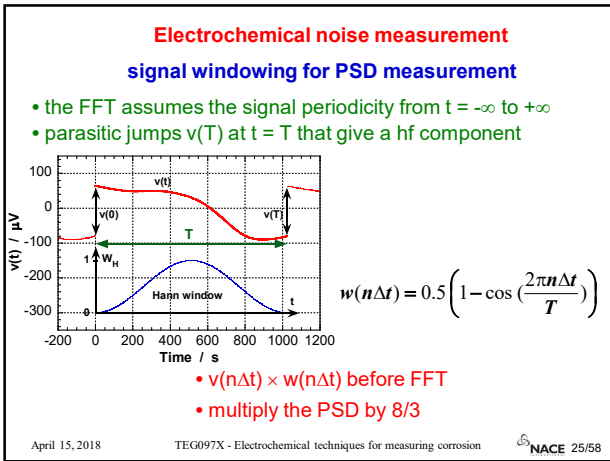
$\Psi_V(f) = 4kT \text{Re}(Z)$ $\Psi_V(f_s = 100 \text{ Hz})$ $\Psi_V(f_s = 10 \text{ Hz})$

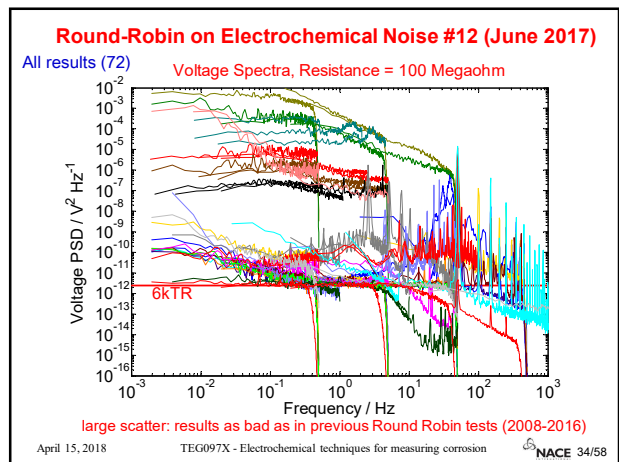
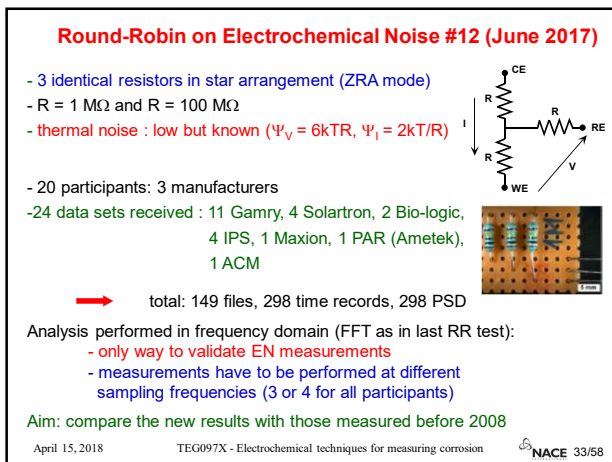
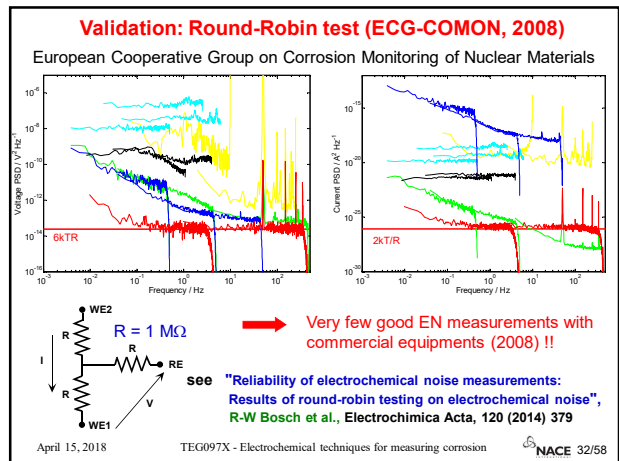
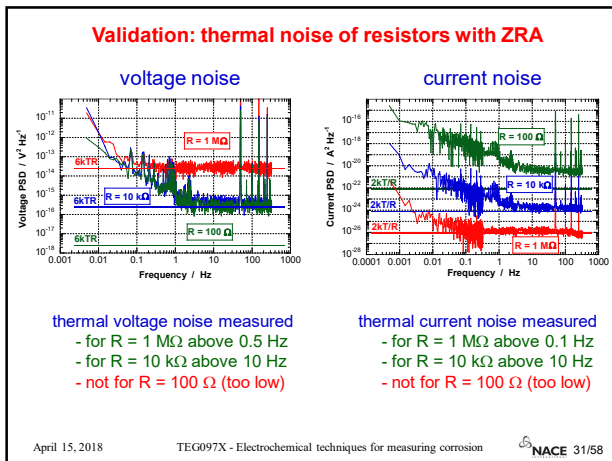
$\Psi_V(f) = 4k_B T \left(r + \frac{R}{1 + 4\pi^2 f^2 R^2 C^2} \right)$

• good overlap of the 2 PSDs (validation of EN measurement)

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- ### Some advices for EN measurements
- validation of EN measurements can only be performed in the frequency domain (PSD)
 - it is important to perform measurements at different sampling rates to check the overlapping of the PSDs
 - never use the auto-range of the measurement device
 - see "Guideline for an assessment of electrochemical noise measurement devices", S. Ritter, F. Huet, R.A. Cottis, Materials and Corrosion, 63 (2012) 297
 - based on ECG-COMON's work (www.ecg-comon.org)
 - on the website (free access): [psd_ECG-COMON.exe](#) for PSD calculation
- C2018-11042: "Electrochemical Noise - Guidance for Improving Measurements and Data Analysis", F. Huet, K. Ngo (Monday, 9:10, room 228 A-B)
- 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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Corrosion monitoring with noise resistance and noise impedance

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Corrosion monitoring with EN

$R_n = \frac{\sigma_v}{\sigma_i}$

if $R_n = R_p \rightarrow i_{corr} = \frac{B}{R_n}$

- $R_n = R_p$?
- model + experiments with U. Bertocci (6 papers in J. Electrochem. Soc. since 1997)
- 2 cases: - 2 identical electrodes + true RE (scheme #1)
- 3 identical electrodes (scheme #2)
- noise impedance: $Z_n(f) = \sqrt{\frac{\Psi_V(f)}{\Psi_I(f)}}$

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Corrosion monitoring with EN

bubbles, pits, cracks...

- $i_1, i_2 =$ current noise sources (cannot be measured)
- only $\Delta I(t)$ and $\Delta V(t)$ can be measured
- Ohm's law in the frequency domain (for $R_s \approx 0$):
- for ΔI : $-Z_1(i_1 - \Delta I) + Z_2(\Delta I + i_2) = 0$
- for ΔV : $\Delta V = -Z_1(i_1 - \Delta I)$

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Corrosion monitoring with EN: current distribution

$-Z_1(i_1 - \Delta I) + Z_2(\Delta I + i_2) = 0$ gives $\Delta I(f) = \frac{Z_1(f)i_1(f) - Z_2(f)i_2(f)}{Z_1(f) + Z_2(f)}$

- for 2 identical WEs: $Z_1 = Z_2 (= Z)$
 $\Delta I(f) = \frac{1}{2}(i_1(f) - i_2(f))$ or $\Delta I(t) = \frac{1}{2}(i_1(t) - i_2(t))$
- with a pit on WE #1 and nothing on WE #2 ($i_2 = 0$)
 $\Delta I(t) = \frac{1}{2}i_1(t)$
 $i_1(t) - \Delta I(t) = \frac{1}{2}i_1(t)$

only half of the current i_1 is measured by the ZRA!

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Corrosion monitoring with EN: current distribution

- WE #1 and 2 : SS316L, diameter 1.5 cm
- WE #3 : iron, diameter 250 μ m
- 0,06 M NaCl
- 3 ZRA for measuring the 3 currents I_{w1}, I_{w2}, I_{w3}

- cathodic processes on WE #1 and #2 $\Delta I_1 = \Delta I_2$
- current measured by the ZRA: $\Delta I_2 = \frac{1}{2} \Delta I_w$

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Corrosion monitoring with EN: noise impedance

- for 2 identical WEs (scheme #1): $\Delta I(f) = \frac{1}{2}(i_1(f) - i_2(f))$
- $\Delta V = -Z_1(i_1 - \Delta I)$ gives $\Delta V(f) = -\frac{Z(f)}{2}(i_1(f) + i_2(f))$
- hence the PSDs: $\Psi_I(f) = \frac{1}{4}(\Psi_{i_1}(f) + \Psi_{i_2}(f))$
 $\Psi_V(f) = \frac{|Z(f)|^2}{4}(\Psi_{i_1}(f) + \Psi_{i_2}(f))$
- noise impedance: $Z_n(f) = \sqrt{\frac{\Psi_V(f)}{\Psi_I(f)}} = |Z(f)|$
- ∇ the origin of the noise : bubbles, pits, cracks...
- ∇ the level of the noises i_1, i_2
- measurement of $|Z|$ from the internal noise (without external excitation)

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Corrosion monitoring with EN: noise impedance

- corrosion of iron in 1M Na_2SO_4 (pH 3), RE = SSE (scheme #1)

- noise due to hydrogen-bubble evolution
- $Z_{n,1}(f) = |Z(f)|$ ← 2 identical WEs + true RE

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Corrosion monitoring with EN: 3 identical WEs (scheme #2)

$Z_1 = Z_2 = Z_3 (= Z)$

$$Z_{n,2}(f) = |Z(f)| \sqrt{1 + \frac{4\Psi_{i_3}(f)}{\Psi_{i_1}(f) + \Psi_{i_2}(f)}}$$

- Z_n depends on the noise of each electrode
- if the electrodes are identically noisy (same PSD):

$$Z_{n,2}(f) = \sqrt{3} |Z(f)|$$
- doubtful assumption for discontinuous processes (pitting)

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Corrosion monitoring with EN: 3 identical WEs (scheme #2)

- corrosion of iron in 1M Na₂SO₄ (pH 3), RE = SSE + RE = iron

- noise due to hydrogen-bubble evolution
- $Z_{n,2}$ is not equal to $\sqrt{3} |Z|$ for each frequency because of the noise of the iron RE
- when possible, it is safer to work with a true RE

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Corrosion monitoring with EN: noise resistance

$$R_n = \frac{\sigma_v}{\sigma_i} = \sqrt{\frac{\int_{f_{min}}^{f_{max}} \Psi_I(f) |Z(f)|^2 df}{\int_{f_{min}}^{f_{max}} \Psi_I(f) df}}$$

- R_n depends on:
 - the frequency bandwidth analysed (f_{min} , f_{max})
 - the impedance $Z(f)$ of the electrodes
 - the PSD of the current noise
- roughly:
 - when $|Z| = R_p$ for $f > f_{min}$ then: $R_n = R_p$
 - if not (coated electrodes, stainless steels...): $R_n \neq R_p$

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Corrosion monitoring with EN: asymmetric systems

- same equivalent circuit with Z_a et Z_c instead of Z_1 et Z_2
- $Z_n(f) = |Z_a(f)Z_c(f)| \sqrt{\frac{\Psi_{i_a}(f) + \Psi_{i_c}(f)}{|Z_a(f)|^2 \Psi_{i_a}(f) + |Z_c(f)|^2 \Psi_{i_c}(f)}}$
- $Z_n(f)$ and R_n depend:
 - on the impedance of each electrode Z_a et Z_c
 - on the noise level on each electrode Ψ_{i_a} et Ψ_{i_c}
- it is necessary to measure Z_a et Z_c for the noise analysis

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Corrosion monitoring with EN: asymmetric systems

- 2 identical carbon steel electrodes (diameter 0.6 cm), RE = SCE, 0,1 M citric acid (pH = 2), $V_{bias} = 350$ mV, $V_{anode} = -0.509$ mV/SCE

- noise due to hydrogen-bubble evolution
- $\Delta i(t)$ and $\Delta V(t)$ show the processes (bubbles) on the cathode!
- Z_n gives the impedance of the anode at low frequency!

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Preliminary conclusions

- electrochemical noise used essentially in corrosion
- the current noise allows discrimination between uniform and localised corrosion (weight loss, LPR, Z)
- with 2 WEs: measurement of both $i(t)$ and $v(t)$ $\rightarrow Z_n$ et R_n
 - when $R_n = R_p$: estimation of i_{corr}
 - if not: corrosion monitoring with R_n
- impedance measurement with EN (no excitation signal) \rightarrow low-cost instrumentation
- common use: 2 identical WEs
 - the analysis of asymmetric systems is more difficult

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Measurement of electrolyte resistance fluctuations

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Measurement of electrolyte-resistance fluctuations

- between WE and RE
- between 2 identical electrodes
- purely ohmic quantity
- detect changes in the resistivity of the solution close to the electrode
- applications to two-phase systems: oil in water, gas-evolving electrode...

$$V = E + R_e I \rightarrow \Delta V = \Delta E + \Delta R_e I \quad \text{if } I \text{ is constant}$$

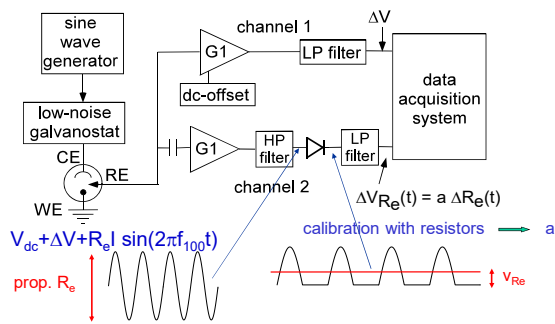
↑
simultaneously measured

at $I = 0$: different information in ΔV and ΔR_e

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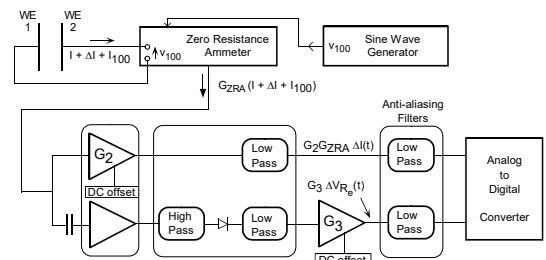
Measurement of ΔV and ΔR_e

$$V = E + R_e I \text{ at constant } I \rightarrow \Delta V = \Delta E + \Delta R_e I$$



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Electrolyte Resistance Measurement (2 WEs + ZRA)



$$\Delta v_{R_e}(t) = b \Delta \left(\frac{1}{R_e(t)} \right) = -b \frac{\Delta R_e(t)}{R_e^2}$$

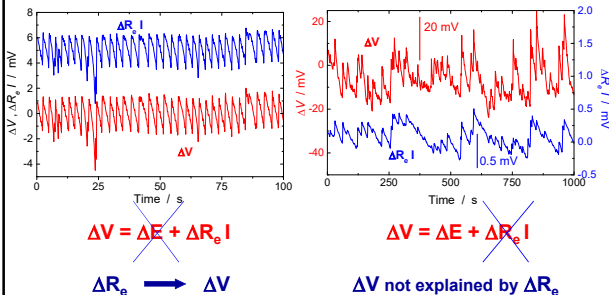
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First example of ΔR_e measurements (one WE)

hydrogen evolution on Fe ($\phi = 5 \text{ mm}$) / 1 M H_2SO_4

$I = -100 \text{ mA}$ (500 mA/cm^2)

$I = -1 \text{ mA}$ (5 mA/cm^2)

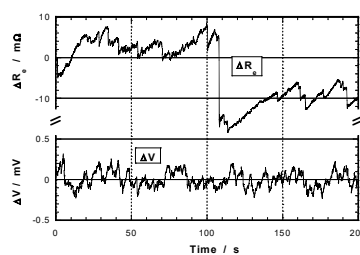


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First example of ΔR_e measurements: one WE

hydrogen evolution on Fe ($\phi = 5 \text{ mm}$) / 1 M H_2SO_4

at corrosion potential: $I = 0 \rightarrow \Delta V = \Delta E$

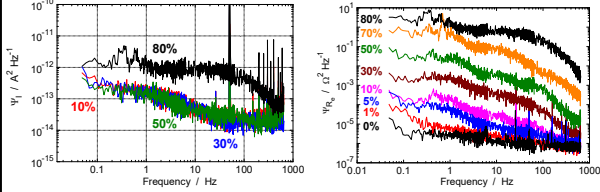
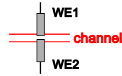


- ΔR_e and ΔV : complementary information
- $\Delta R_e \rightarrow$ sensor of bubble evolution

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Second example of ΔR_e measurements: 2 WE

- oil + 3% NaCl mixture in a flow-loop cell ($v = 1.9$ m/s)
- 2 iron disks ($\phi = 5$ mm) connected with ZRA
- volumetric oil content: $0\% < \text{VOC} < 80\%$



$\Psi_{i(0)}$ varies within only 1 decade for $\text{VOC} \leq 75\%$

$\Psi_{R_e(0)}$ varies within 6 decades for VOC between 0% and 80%

ΔR_e → sensor for monitoring o/b composition between 2 coupons

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Conclusions

- ✓ EN used in corrosion
 - detection of localized corrosion
 - monitoring corrosion rate in the field (EIS in the lab)
 - use EN in combination with other techniques: EIS, LPR...
- ✓ Be careful in measuring the noise
 - possible to validate EN measurements
 - necessary to test commercial equipments
 - participate or organize Round-Robin tests
- ✓ Read good literature on EN for data interpretation

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Further information

- ✓ Corrosion Testing Made Easy – Electrochemical Impedance and Noise, R. A. Cottis and S. Turgoose, NACE International, Houston, Texas, 1999; ISBN: 157590-093-9, 2000
- ✓ The interpretation of EN data, R. A Cottis, Corrosion, 27 (2001) 265
- ✓ Guideline for an assessment of electrochemical noise measurement devices, S. Ritter, F. Huet, R.A. Cottis, Materials and Corrosion, 63 (2012) 297
- ✓ Reliability of electrochemical noise measurements: Results of round-robin testing on electrochemical noise*, R-W Bosch et al., Electrochimica Acta, 120 (2014) 379
 ← ECG-COMON (www.ecg-comon.org)
- ✓ The Electrochemical Noise Technique, F. Huet, Analytical Methods in Corrosion Science and Engineering, eds P. Marcus, F. Mansfeld, CRC Press, Series: Corrosion Technology, Volume 22, p. 507-570 (2006)
- ✓ Analysis of electrochemical noise by power spectral density applied to corrosion studies : MEM or FFT? U. Bertocci et al. J. Electrochem. Soc. 145 (1998) 2780
- ✓ Noise resistance applied to corrosion measurements: series of 6 papers, U. Bertocci, F. Huet et al., J. Electrochem. Soc. (1997 – 2002)

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Thank you for your attention

if you want:

- a copy of the slides
- ask any question
- I test the EN measurements you performed with your commercial equipment
- participate to noise Round-Robin tests

→ email to francois.huet@upmc.fr

- > C2018-11042: "Electrochemical Noise - Guidance for Improving Measurements and Data Analysis", F. Huet, K. Ngo (Monday, 9:10, room 228 A-B)
- > 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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