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
Analysis of the voltage fluctuations ($R = 1 \, \text{M} \Omega$) All results (77) in RR-2017

- Very large scatter: 8 decades in $V^2 \, \text{Hz}^{-1}$, 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 $f_s$

- 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
Algorithm for PSD calculation with FFT

- divide the time record in N sections (typically N = 10) of M data points (typically M = 2048, 1024…)
- loop N times
  
  \[
  \Psi_x(m\Delta f) = \frac{2}{T} |X_T(m\Delta f)|^2 = \frac{2}{M} \frac{1}{\Delta t} \sum_{n=0}^{M-1} x(n\Delta t) e^{-2\pi inm/M} \]

  - 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:

- 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" (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 $Z_n$

Practical work with dummy cells (1)

- 3 identical resistors in star arrangement (ZRA mode)

  $R = 100 \, M\Omega$

- thermal noise
  - at thermodynamic equilibrium ($I_o = 0$): $\Psi_V = 4kTR = 1.6 \times 10^{-20} \, V^2 \, Hz^{-1}$
  - 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 $\Delta V$ 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)


† Trade name
**Practical work on dummy cells (2):** $R = 10 \, \Omega$

**Measurement conditions**  
(fast, only for training)

**Potential measurement**  
(simple)

- Potential PSD / V
- Frequency / Hz

<table>
<thead>
<tr>
<th>$f_s$ (Hz)</th>
<th>1 kHz</th>
<th>100 Hz</th>
<th>10 Hz</th>
<th>2 Hz</th>
</tr>
</thead>
<tbody>
<tr>
<td>$f_s/N$</td>
<td>0.5 Hz</td>
<td>0.05 Hz</td>
<td>0.04 Hz</td>
<td>0.03 Hz</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Vch range</th>
<th>3 V</th>
<th>300 mV</th>
<th>30 mV</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vch gain</td>
<td>1</td>
<td>10</td>
<td>100</td>
</tr>
</tbody>
</table>

*Time record: no possible validation*  
*PSD: thermal noise measured!*

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**Practical work on dummy cells (3):** $R = 10 \, \Omega$

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

Choose I/E range so that $R_m > R$  
for $R = 10 \, \Omega$
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)

\[
\Psi_{\text{meas}} = \frac{\Psi_{\text{em}}}{R_m^2} + \frac{1}{1 + 4\pi^2 R_m^2 C^2 f^2} \left[ \frac{4kT}{R_m} \frac{1}{R_m} + \frac{\Psi_e}{4R^2} + \frac{2kT}{R} \right]
\]

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

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

I-E range and \( R_m \)

- \( R_m << R \): \( \Psi_{\text{meas}} \) too high because of the influence of \( \frac{\Psi_{\text{em}}}{R_m^2} \) and \( 4kT \frac{1}{R_m} \)
- \( R_m >> R \): \( \Psi_{\text{meas}} \) filtered at high frequency by \( C \) in parallel with \( R_m \)
- best value \( R_m = 20 \, \text{M}\Omega = 2R \)
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$^2$) 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:

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

- 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

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
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 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: