Electrochemical assessment of protection systems for metal artefacts

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Outline

- New protection systems for heritage?
- Pros and cons of electrochemical techniques
- Rp: fundamentals and applications
- EIS: fundamentals and applications
- Evaluation of innovative coatings in the PROMET project.
Need of new protection systems

- Improved efficiency
- Lower toxicity
- Specific needs for cultural heritage conservation:
  - Reversibility/re-tratability
  - Respect to original object and surface
  - Transparency, good visual aspect
  - Reproducibility issues
Testing new protection systems

- Tests in laboratory coupons
  - Difficult (impossible?) to reproduce composition and corrosion layers

- Tests in real objects:
  - Not uniform in composition, microstructure and patina/corrosion products
  - Unique value of each object

- Combination of both, specific protocols and non-destructive and highly sensitive techniques
Testing new protection systems

• Natural exposure
  – Very reliable, but very slow

• Accelerated tests in climatic chambers
  – Fast, but too accelerated
  – Well established for industrial applications (for instance, salt fog test)
  – Better for comparison purposes
  – Not applicable to real objects

• Electrochemical tests
Electrochemical tests

• Advantages
  – Very high sensibility
  – Measure instantaneous corrosion rate and are not destructive: evolution of protection/corrosion with time
  – Measure in real conditions: even on real objects!
  – Relatively simple and inexpensive equipment

\[
\begin{align*}
1 \text{ nA/cm}^2 & \quad \text{Fe} \rightarrow \text{Fe}^{2+} \\
& \quad 1 \text{ hour} \\
& \quad 1,04 \cdot 10^{-8} \text{ g}
\end{align*}
\]
Electrochemical tests

• Disadvantages
  – Usually need a bulk electrolyte: not real atmospheric conditions
  – Interpretation might be not easy in some cases (EIS)
Polarization resistance ($R_p$)

- At $E_{corr}$, the slope of the V/I curve is proportional to the corrosion rate.
- Stern and Geary (1957):

\[
R_p = \frac{B}{i_{corr}}
\]

\[
B = \frac{b_a b_c}{2.3 (b_a + b_c)}
\]
Polarization resistance (Rp)

- Potential sweep from ± 10 mV vs. Ecorr
- Usually not employed for coatings due to the very high resistance of the coating
- Fast and easy to interpret
**Electrochemical Impedance Spectroscopy (EIS)**

- Based on the application of a AC low amplitude (typically 10 mV) potential signal

  - **Perturbation:** \( E(t) = E_0 \cos(\omega t) \)
  
  - **System response:** \( I(t) = I_0 \cos(\omega t - \phi) \)
  
  - **Response function:** \( Z(\omega) = E/I \)

- Frequency swept from 100 kHz to 1 mHz
Electrochemical Impedance Spectroscopy (EIS)

- The most important technique for evaluation of corrosion protection coatings in the last 30 years
- Allows for the measurement of the properties of high resistance coatings
- Can obtain information of different processes/parts of your system: electrolyte, coating, corrosion processes, etc.
History of use of EIS for CH

• Pioneer work: Price, Hallam *et al.*, Metal 95
• *In situ* evaluation of CH objects (Letardi, Metal 98)
• Very important increase of the use of EIS in CH in the last years
PROMET project

- PROMET:
  “Innovative conservation approaches for monitoring and protecting ancient and historic metals collections from the Mediterranean basin”
  - 6º Framework Program E.U. INCO-MED
  - November 2004 - April 2008
  - 21 partners from 11 mediterranean countries
  - Spain: CENIM-CSIC & UAM
Protocol to study new protection systems

Study of real objects

New products selection

Artificially corroded coupons

Laboratory tests

Naturally corroded coupons

Laboratory tests

Real exposure

Final list of products

Application in real heritage objects
Experimental

- Material: low carbon steel (0.14%)
- Coatings
  - New: Poligen ES91009 (BASF)
    - Ready to use liquid polyethylene wax emulsion
    - Dries in 24 h.
    - Non toxic and environmentally safe
  - Traditional: Paraloid B-72 and Renaissance
- With and without corrosion inhibitor additives
- Electrochemical tests (Rp and EIS)
## Coatings tested

<table>
<thead>
<tr>
<th>Organic coating</th>
<th>Clean surface—brushing (set 1)</th>
<th>Pre-corroded surface—immersion (set 2)</th>
<th>Clean surface—immersion (set 3)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Specimen</td>
<td>Thickness (µm)</td>
<td>Standard deviation</td>
</tr>
<tr>
<td>Without organic coating</td>
<td>0</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Renaissance™</td>
<td>1</td>
<td>1</td>
<td>0</td>
</tr>
<tr>
<td>Poligen™ ES-91009</td>
<td>2</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>Poligen™ ES-91009 + M435º</td>
<td>2a</td>
<td>3</td>
<td>3</td>
</tr>
<tr>
<td>Poligen™ ES-91009 + M370º</td>
<td>2b</td>
<td>4</td>
<td>4</td>
</tr>
<tr>
<td>Paraloid™ B-72º</td>
<td>3</td>
<td>7</td>
<td>4</td>
</tr>
<tr>
<td>Paraloid™ B-72 + M435</td>
<td>3a</td>
<td>6</td>
<td>4</td>
</tr>
<tr>
<td>Paraloid™ B-72 + M109º</td>
<td>3b</td>
<td>6</td>
<td>4</td>
</tr>
<tr>
<td>Paraloid™ B-72 + Alkaterge-Tº</td>
<td>3c</td>
<td>10</td>
<td>5</td>
</tr>
</tbody>
</table>

*C* pre-corroded specimen, coated by immersion, *N* non-artificially aged coating, *A* artificially aged coating, *X* clean specimen, coated by immersion
Experimental setup

• Polarization resistance \((R_p)\)
  – -10→+10 mV vs. OCP
  – 0,16 mV/s

• Electrochemical Impedance (EIS)
  – 64 kHz → 1mHz, 10 mV, 0 V vs. OCP

• PAR 273A
  Solartron 1250
Experimental setup

Reference electrode

Platinum mesh (counter electrode)

4.15 cm² working electrode
Rp tests

• Clean samples

<table>
<thead>
<tr>
<th>ID</th>
<th>Coating</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>No coating (Blank)</td>
</tr>
<tr>
<td>1</td>
<td>Renaissance wax</td>
</tr>
<tr>
<td>2</td>
<td>Poligen ES 91009</td>
</tr>
<tr>
<td>2a</td>
<td>Poligen ES 91009 + M435 inhibitor</td>
</tr>
<tr>
<td>2b</td>
<td>Poligen ES 91009 + M370 inhibitor</td>
</tr>
<tr>
<td>3</td>
<td>Paraloid B-72 (15% Acetonae)</td>
</tr>
<tr>
<td>3a</td>
<td>Paraloid B-72 + M435 inhibitor</td>
</tr>
<tr>
<td>3b</td>
<td>Paraloid B-72 + M109 inhibitor</td>
</tr>
<tr>
<td>3c</td>
<td>Paraloid B-72 + Alkaterge-T</td>
</tr>
</tbody>
</table>

\[
B = \frac{b_a b_c}{2.3(b_a + b_c)}
\]

\[
R_p = \frac{B}{i_{corr}}
\]

*Electrochemistry in Historical and Archaeological Conservation*
Lorentz Center. Leiden. 11-15 January 2010
R̂p tests

• Pre-corroded and aged samples

<table>
<thead>
<tr>
<th>ID</th>
<th>Coating</th>
</tr>
</thead>
<tbody>
<tr>
<td>NC</td>
<td>No coating (Blank)</td>
</tr>
<tr>
<td>TC1</td>
<td>15% Paraloid B-72 in acetone</td>
</tr>
<tr>
<td>TC2</td>
<td>Renaissance wax</td>
</tr>
<tr>
<td>C1</td>
<td>Poligen ES 91009</td>
</tr>
<tr>
<td>C2</td>
<td>Poligen ES 91009 + M370</td>
</tr>
<tr>
<td>C3</td>
<td>Poligen ES 91009 + M435</td>
</tr>
<tr>
<td>C4</td>
<td>15% Paraloid B-72 in acetone + Alkaterge-T</td>
</tr>
<tr>
<td>C5</td>
<td>15% Paraloid B-72 in acetone + M109</td>
</tr>
</tbody>
</table>
EIS results

Sin recubrimiento

![EIS graph showing impedance and phase angle vs. frequency for different coatings.](image)
EIS results

Sin recubrimiento

\[ Z_{CPE} = \frac{1}{Y_0 (j \omega)^\alpha} \]

\[
\begin{array}{ccc}
\text{CPE1} & \text{Y0} & \alpha & R_1 \\
\text{F/cm}^2 \text{s}^{(1-\alpha)} & \text{Ω cm}^2 & \\
2.8 \times 10^{-3} & 0.74 & 2681
\end{array}
\]
EIS results

Rennaissance wax

<table>
<thead>
<tr>
<th>CPE₁</th>
<th>CPE₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Y_0)</td>
<td>(Y_0)</td>
</tr>
<tr>
<td>(\alpha)</td>
<td>(\alpha)</td>
</tr>
<tr>
<td>(R_1)</td>
<td>(R_2)</td>
</tr>
<tr>
<td>F/cm²·s(^{(1-\alpha)})</td>
<td>F/cm²·s(^{(1-\alpha)})</td>
</tr>
<tr>
<td>(\Omega) cm²</td>
<td>(\Omega) cm²</td>
</tr>
<tr>
<td>0.4 (\times 10^{-3})</td>
<td>0.3 (\times 10^{-3})</td>
</tr>
<tr>
<td>0.8</td>
<td>0.79</td>
</tr>
<tr>
<td>22.86</td>
<td>2960</td>
</tr>
</tbody>
</table>
EIS results

Poligen ES 91009

<table>
<thead>
<tr>
<th>CPE1</th>
<th>CPE2</th>
</tr>
</thead>
<tbody>
<tr>
<td>$Y_0$</td>
<td>$\alpha$</td>
</tr>
<tr>
<td>$F/cm^2s^{(1-\alpha)}$</td>
<td>$\Omega$</td>
</tr>
<tr>
<td>$0.4 \times 10^{-3}$</td>
<td>0.76</td>
</tr>
<tr>
<td>$1.17 \times 10^{-6}$</td>
<td>0.76</td>
</tr>
<tr>
<td>$8.89 \times 10^{-9}$</td>
<td>0.96</td>
</tr>
</tbody>
</table>
EIS results

Paraloid B72

<table>
<thead>
<tr>
<th>CPE₁</th>
<th>Y₀</th>
<th>α</th>
<th>R₁</th>
<th>Y₀</th>
<th>α</th>
<th>R₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>F/cm² s^(1-α)</td>
<td>Ω cm²</td>
<td>F/cm² s^(1-α)</td>
<td>Ω cm²</td>
<td>F/cm² s^(1-α)</td>
<td>Ω cm²</td>
<td></td>
</tr>
<tr>
<td>2.95 × 10⁻⁷</td>
<td>0.56</td>
<td>16725</td>
<td>4.6 × 10⁻⁶</td>
<td>0.5</td>
<td>34825</td>
<td></td>
</tr>
<tr>
<td>0.39 × 10⁻³</td>
<td>0.5</td>
<td>407</td>
<td>1.2 × 10⁻³</td>
<td>0.82</td>
<td>1395</td>
<td></td>
</tr>
<tr>
<td>4.53 × 10⁻⁷</td>
<td>0.65</td>
<td>32228</td>
<td>1.0 × 10⁻⁶</td>
<td>0.63</td>
<td>1.29 × 10⁶</td>
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</tr>
<tr>
<td>2.14 × 10⁻⁷</td>
<td>0.65</td>
<td>8031</td>
<td>7.6 × 10⁻⁶</td>
<td>0.54</td>
<td>28949</td>
<td></td>
</tr>
</tbody>
</table>
Conclusions

- Electrochemical tests give a quantitative information of the protection provided by different coatings in a short time
  - Rp provide quick and easy to interpret results
  - EIS provide in-depth information on the corrosion and protection mechanisms
Conclusions

• The addition of corrosion inhibitor additives did not provide and improvement of the protection, and in some cases have a negative effect.

• Poligen ES91009 provides better protection than Paraloid B72 when applied in thick layers

• Rennaissance provides very little protection
PROMET: additional information

- CSSIM conference proceedings “Strategies for saving our cultural heritage”
- Book “Metals and Museums in the Mediterranean. Protecting, preserving and interpreting”
Further reading

Acknowledgments

• Organizers of the workshop
• PROMET project E.U.
• Colleagues in the PROMET
• Prof. José María Bastidas

Thanks for your attention!