Application of local electrochemical probes for coatings studies

13/01/15
Introduction

Usual electrochemical techniques used to study coatings effect on corrosion behaviour are linear polarization (LP) and electrochemical impedance spectroscopy (EIS).

LP gives the global effect of the coating usually by showing reduced anodic activity on the sample.

EIS allows to model the electrochemical behaviour of metal/coating/electrolyte interface, accounting for the presence of pores for instance.

These techniques give a global response of the sample but further insights may be needed to actually identify and understand the specific mechanism responsible for corrosion inhibition and corrosion self-healing.

In this regard local probes give spatial insights at the microscale of the corrosion healing processes.

The following slides give some examples of results found in the literature and obtained using our instruments, M370/M470.

A general knowledge of each the local probes is required.

Enjoy!
Outline

1. SKP
2. LEIS
3. SVP
4. SECM
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Characterization of sol-gel coatings for magnesium alloys

The scanning probe is used to measure the surface potential of the various metal-coatings interface.

It can be shown that the surface potential increases as the content of the coating matrix in phosphonato-silane increases.

The measurement is performed in air without contacting the sample.

It is a direct reflection of the chemical binding of phosphonate functionalities at the magnesium substrate surface.

Work function difference between the probe and the sample. An area of $4.5 \times 6$ mm was scanned.

Characterization of X70 corrosion under a thin electrolyte layer

The system is a X70 steel sample covered by a thin electrolyte layer trapped between the metal and a coating (see scheme below).

Polarization curves are obtained for different electrolytes using as a reference the Kelvin probe.

A potentiostat is used to apply different current values to the sample while the potential of the sample is obtained by converting the surface potential measured by the probe.
Characterization of X70 corrosion under a thin electrolyte layer

Polarization curves obtained with various solutions, various electrolyte thicknesses are then compared between each other and with polarization curves of immersed samples.

Polarization curves of X70 steel in thin NS4 solution layer

Polarization curves of X70 steel in thin carbonate/bicarbonate (high pH) solution layer
1. SKP
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LEIS

Study of delaminated areas beneath organic coatings

Epoxy-vinyl primer with calcium ferrite, iron oxide and talc as pigments on carbon steel sheets.

LEIS used as Localised Electrochemical Impedance Mapping (LEIM) at one frequency.

LEIM carried out at 5 kHz:
(a) Before exposure in the salt spray chamber and after different exposure durations to the salt spray.
(b) 20 days.

One can see the cutter scribe mark.
Corrosion of steel under defected coating

LEIS is used to see differences in EIS spectrum between the coating and the defect

Nyquist diagrams of LEIS measured directly above the defect of 1000 µm in diameter as a function of immersion time.

Corrosion mechanisms and effect of the defect size can be investigated.

Nyquist diagrams of LEIS measured at intact coating.

3-D mapping of the impedance modulus at 50 Hz at two defects

Protection against Corrosion of AA2024-T3 by Sol-Gel Coating Modified with La and Mo-Enriched Zeolites

Sol-gel coatings with zeolites of various contents are studied. The healing mechanism of a scratch made on a 2024 sample is studied by scanning the LEIS probe over the sample immersed in a 1 mmol/L NaCl solution. The frequency of study is 77 Hz. The evolution of the local impedance allows to determine several healing mechanisms depending on the zeolite composition.

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A cathodic delamination study of coatings with and without mechanical defects.

The sample is coated with transparent vinyl varnish.

SVP measurements when sample immersed in 0.06 mol/L NaCl

Delamination starts on Zn particle.

Corrosion Science 82 (2014) 432–436
Silica nanoparticles as smart nanocontainers for intelligent anticorrosion coatings

SVET current density maps after 14 h of immersion in 0.1 M NaCl for the pure SNAP coatings (E) and the smart nanocontainers doped SNAP coating (H).

SVET is used to compare the healing efficiency of coatings doped with Silica nanoparticles. Silica nanoparticles efficiently suppress the corrosion activity by favoring self-healing mechanisms.

ACSNano (2013) 7 12 11397–11408
Self-healing anticorrosive organic coating based on an encapsulated water reactive silyl ester: Synthesis and proof of concept

SVET current density maps at the defect of a capsules-containing coating on AA2024-T3 after (a) 1 h, (b) 1 day and (c) 2 days immersed in 0.05M NaCl solution. Scanned area: $2 \times 3.5\text{mm}^2$. Current density legend: $\mu\text{A/cm}^2$.

With capsules, the scribe presents activity only in (a).

SVET current density maps at the defect of a clearcoat on AA2024-T3 after (a) 1 h (b) 1 day; and (c) 2 days immersed in 0.05M NaCl solution. Scanned area: $2 \times 4\text{mm}^2$. Current density legend: $\mu\text{A/cm}^2$.

Without capsules, the scribe activity increases with exposure time.
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A combined redox-competition and negative-feedback SECM study of self-healing anticorrosive coatings

(a) Optical micrograph of AA2024-T3 sample with bare and silyl-treated surface after 1 day immersion in 0.05 M NaCl solution. (b) SECM image of the transition area on (a) using the electroreduction of oxygen in solution as reaction at the tip. Scan rate: 40 μms⁻¹. Scanned area: 1.25 × 1 mm².

More reduction occurs on the silyl-covered area because O₂ is not consumed by corrosion, which is the case on the bare AA2024-T3, showing the corrosion protection effect of the coating.

Electrochemistry Communications 13 (2011) 1094–1097
SECM study of defect repair in self-healing polymer coatings on metals

SECM used in feedback mode. The tip is polarized at -0.6V/Ag/AgCl. The studied reaction is O₂ reduction over a scratch in a sample with shape-memory polyurethane coating.

Corrosion activity in the defect increased as a function of immersion time in the solution (Fig. 2b–d), and cathodic processes were mainly located at the top and bottom of the scratch.

(a) 4 h, b) 1 day, c) 2 days, d) 4 days of immersion in 0.05 M NaCl

Electrochemistry Communications 13 (2011) 169–173
SECM study of defect repair in self-healing polymer coatings on metals

One can see cathodic activity in the non-healed sample. In the non-healed sample, cathodic activity only occurs at a defect in the polymer. After 28 h, no sign of corrosion on the heat-treated polymer-coated sample.

Prior to thermal healing a) 1 day of immersion in 0.05 M NaCl
After thermal healing b) 4 h and c) 1 day of immersion in 0.05 M NaCl

Electrochemistry Communications 13 (2011) 169–173
Useful links

More references can be found here :
http://www.bio-logic.info/scanning-systems-scan-lab/scan-lab-literature/references/coatings/

Please also find some application notes here :
http://www.bio-logic.info/scanning-systems-scan-lab/scan-lab-literature/application-notes/

And the brochures here :
http://www.bio-logic.info/scanning-systems-scan-lab/downloads/brochures/

Requests can be placed here :
http://www.bio-logic.info/ask-for-a-quote-contact-us/

For more information on the techniques :
http://www.bio-logic.info/scanning-systems-scan-lab/scan-lab-literature/tutorials/