

Evaluation Techniques for the Corrosion Resistance of Self-Healing Coatings

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Self-healing coatings, materials that autonomically repair damage, are a method of extending the life of corrosion prevention coatings. The different types of self-healing coatings are briefly outlined. A review of the evaluation methods of the performance of self-healing coatings using electrochemical, surface and microscopy techniques are provided. Both global and local evaluation techniques are reviewed with emphasis on the most used electrochemical techniques as well as suggestions for alternative electrochemical techniques for self-healing coating evaluation.

Keywords: Self-healing, Corrosion, Electrochemical techniques, Coatings

Table of abbreviations:

Abbreviation	Meaning
AA	Aluminium alloy
AC	Alternating current
BTA	Benzotriazole
CI	Corrosion inhibitor
CLSM	Confocal laser scanning microscope
CPDP	Cyclic potentiodynamic polarization
CS	Carbon steel
EDX	Energy dispersive x-ray
EIS	Electrochemical impedance spectroscopy
ENA	Electrochemical noise analysis

EPMA	Electron probe microanalysis
LbL	Layer-by-layer
LDH	Layered double hydroxide
LPR	Linear polarization resistance
MS	Mild steel
OM	Optical microscope
OCP	Open circuit potential
P%	Protection efficiency
PEI	Poly(ethylene-imine)
PF	Phenol-formaldehyde
PMAA	Poly(methacrylic acid)
PP	Potentiodynamic polarization
PPy	Polypyrrole
PPT	Potentiostatic pulse testing
PU	Polyurethane
PVP	Poly(vinyl-pyrrolidone)
Ref.	Reference
SAP	Superabsorbent polymer
SECM	Scanning electrochemical microscope
SEM	Scanning electron microscope
SIET	Scanning ion-selective electrode technique
SKP	Scanning kelvin probe
SVET	Scanning vibrating electrode technique
UF	Urea-formaldehyde
WT%	Weight percent
XPS	X-ray photoelectron spectroscopy

1. INTRODUCTION

Corrosion is a critical problem in the industry worldwide. Pipelines, tanks and similar equipment are required to have regular maintenance due to corrosion and its associated effects. There are many ways to protect metals from corrosion such as corrosion inhibitors [1-3], cathodic protection [4] and coatings [5-7]. Corrosion inhibitors are typically used in a controlled environment to prevent corrosion and many inhibitors are not environmentally friendly [8]. Cathodic protection is used for metal-coated substrates, which are placed in contact with bulk electrolyte to inhibit corrosion. Coatings may be organic or metallic and act as barriers separating the metal surface from the corrosive environment or as sacrificial anodes. Metallic coatings are applied through plating a thin layer of

metal over the surface of the target one. Organic coatings are usually applied over the surface in the liquid form and allowed to cure into a solid surface which protects metal structures from corrosion.

Over time coatings lose their structural integrity and protective properties due to the formation of micro-cracks [9]. The micro-cracks are caused by thermal, chemical, or mechanical fatigue. The loss in protective properties of the coating allows the metal to interact with the environment leading to corrosion. Repairing or replacing traditional coatings requires human intervention; however, coatings with the ability to automatically heal damage are being developed [10-13]. In some cases, an external stimulus such as temperature change [14,15], externally applied radiation [16,17], pH changes [18,19], pressure changes [20], or mechanical action [21,22] is needed to initiate and sustain the self-healing. Such materials are non-autonomous self-healing materials. For example, shape memory materials have the ability to recover their original shape after deformation. This shape recovery does not occur unless the temperature is increased to the transition threshold [23,24]. On the other hand, autonomous self-healing materials have the ability to repair damage without external stimuli. Self-healing coatings are produced using many different materials such as macromolecular compounds [25], ceramics [26], metals [27] and composites [28]. Self-healing organic coatings may be achieved by two methods, either from functional corrosion inhibitors or from self-healing functionality in the coating structure.

Corrosion inhibitors are leached from the coating and come into direct contact with the metal and block the active sites on the metal surface. Corrosion inhibitors can have several disadvantages such as deactivation due to side interactions with the coating material or the loss of the coating integrity due to the leaching process. Encapsulation of corrosion inhibitors is a possible method to prevent both the side interactions of the inhibitor with the coating materials and the degradation of the coating integrity due to leaching [29].

Self-healing functionality can be included in the coating structure through many different techniques. For example, some polymers can absorb water and swell to cover and protect the substrate surface under the damaged area [30]. Another method to achieve self-healing performance in organic coatings is the sol-gel technique. Details of the sol-gel technique can be found in, for example, references [31-33].

Intrinsic self-healing coatings are healed via self-reactions such as hydrogen bonding [34], ionic coupling [35] or thermal reactions [36]. Extrinsic self-healing functionality can be achieved by embedding self-healing components in the coating structure. Two methods of embedding self-healing functionality in traditional polymer coatings include capsule and vascular based healing. Figure 1 shows a schematic of these two self-healing methods. In capsule based self-healing materials, shown in Figure 1a, the healing agent is contained in microcapsules. When the microcapsules are ruptured by damage, the healing agent is released and flows into the damaged region. For vascular self-healing materials, shown in Figure 1b, the healing agent is stored in hollow capillaries until damage ruptures the tubes and releases the healing agent [37,38].

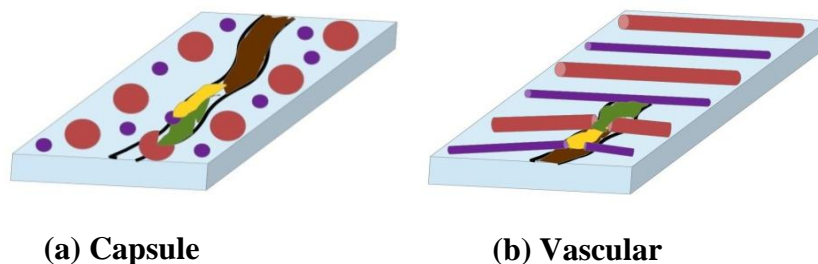


Figure 1. Two types of self-healing material approaches: (a) microcapsule based; (b) vascular based.

Even though there is a large number of possible self-healing coating materials and methods (for review see references [39], [40] and [41]), the corrosion of the metal substrate is an electrochemical process and therefore electrochemical testing techniques provide powerful tools to evaluate the corrosion protection efficiency of the different types of self-healing coatings. The electrochemical techniques for studying corrosion protection can be employed under atmospheric conditions and/or in bulk solutions. The techniques that are performed in atmospheric conditions are typically global techniques that evaluate the net performance of the entire coated substrate while the techniques used in bulk solution can be either local techniques that evaluate the coating performance at one specific location or global techniques. The common electrochemical techniques used in coating analysis include open circuit potential (OCP), potentiodynamic polarization (PP), electrochemical impedance spectroscopy (EIS), odd random phase multisine EIS (ORP-EIS), scanning vibrating electrode technique (SVET), scanning electrochemical microscope (SECM), localized electrochemical impedance spectroscopy (LEIS), scanning ion-selective electrode technique (SIET), electron probe microanalysis (EPMA), linear polarization resistance (LPR), electrochemical noise analysis (ENA), cyclic potentiodynamic polarization (CPDP), scanning kelvin probe (SKP) and hydrogen evolution reaction tests (HERT). Some of these techniques are used to evaluate and quantify the effects of the environmental and metallurgical parameters on the corrosion behavior of metals and alloys, while others are used to study the surface morphology, the mechanism of protection and the healing rate. A brief review of the electrochemical techniques that have been used for the evaluation of self-healing materials in the literature [42-45] and suggested methods for utilizing the techniques which have not been used for the evaluation of self-healing coatings follows. In addition to the electrochemical techniques, methods of evaluating the morphology of the coating after healing such as scanning electron microscope (SEM) or the elemental analysis of the coating using x-ray photoelectron spectroscopy (XPS) will also be discussed.

Currently there are no standards for evaluating the healing performance of self-healing coatings and there is no guidance to the types of experimental methods that will provide consistent information for evaluating and understanding the self-healing process in coatings. This review of the characterization techniques of self-healing coatings arises from the lack of information about self-healing coating characterization techniques in the literature. This review will not only help researchers understand the advantages and disadvantages of the characterization techniques for self-healing

coatings found in the open literature, but it also recommends new electrochemical evaluation techniques that can be used either separately or in combination with other surface analysis methods.

2. TECHNIQUES FOR EVALUATING THE SELF-HEALING COATINGS

Table I summarizes the corrosion protection coatings of different metals based on self-healing technology. The self-healing agent, healing approach, the type of self-healing, the coating material and the method of corrosion evaluation are also included in Table II. The most recent studies used several combinations of evaluation methods to provide more detailed information about the self-healing process.

Table I. Summary of corrosion protection coatings of different metals. Including self-healing agent, its type, healing approach and the method of corrosion evaluation.

Self-healing agent	Type of self-healing	Self-healing based on	Coating	Metal	Evaluation of corrosion	Ref.
Sodium silicate/cerium (III) nitrate	Intrinsic	Chemical reaction	1,2- bis (triethoxysilyl) ethane polymer	Zn	Polarization measurement	[46]
TiO ₂ / CI (Benzotriazole)	Intrinsic	Porous oxide interlayer	Hybrid Sol gel	AA 2024	EIS, SVET	[47]
(PEI/PSS) polyelectrolyte + benzotriazole	Intrinsic	LbL deposition nanocontainer	Hybrid epoxy-functionalized ZrO ₂ /SiO ₂ sol-gel	AA 2024	EIS, SVET	[48]
TiO ₂ particle-vinylester polymer composite	Intrinsic	Presence of the metal powder in polymer matrix	Fluorine resin (FLR) /powder Zn, Ti and Nb	AA 3003	EIS, OM	[49]
TiO ₂ + benzotriazole as (CI)	Intrinsic	Nanoporous reservoir	Hybrid Sol-gel	AA 2024-T3	EIS, SVET, SEM, EDX	[50]
Linseed oil	Capsule based -UF shell	Polymerization (In situ)	Epoxy resin	MS	Salt spray	[51]
Polydimethylsiloxane	Capsule based -UF shell	Polycondensation	Epoxy 828 + promoter + catalyst	Steel	SEM, PP	[52]
Polyurethane	Intrinsic	Thermal process	Shape memory polyurethane/ cerium ions	Pure Al	EIS	[53]
Molybdate/phosphate	Intrinsic	Permselective cation/ mobility of ions	Polypyrrol	CS	CLSM, OCP	[54]
Mg/Al and Zn/Al	Intrinsic	LDH deposition nanocontainer	Epoxy-primer + Epoxy-topcoat	AA 2024	EIS, SEM, EDX	[55]

hydroxide + vanadate ion						
Octyldimethylsilyloleate	Capsule based -UF shell	Polymerization (In situ)	Epoxy 828 + Ancamine 2500	AA 2024-T3	EIS, SVET	[56]
Mixture of epoxies (711+E51)	Capsule based -UF shell	Polymerization (In situ)	Anti-corrosion paint	Steel	Salt spray	[57]
Linseed oil	Capsule based -PF shell	Polymerization (In situ)	Epoxy resin	Steel	Visual inspection, OM	[58]
Hexamethylene diisocyanate (HDI)	Capsule based -PU shell	Polymerization (Interfacial)	Epalam 5015/5014	Steel	SEM, OM	[59]
Tung oil	Capsule based -UF shell	Polymerization (In situ)	Epoxy resin	CS	SEM, EIS	[60]
Octyldimethylsilyloleate	Capsule based -UF shell	Polymerization (In situ)	Epoxy 828 + Ancamine 2500	AA 2024-T3	SECM	[61]
Poly(ϵ -caprolatone)/polyurethane	Intrinsic	Thermal process	Shape memory polyurethane	AA2024-T3	SECM	[62]
Cellulose acetate / CI (Sodium benzoate)	Intrinsic	Porosity of the coating polymer	Porous polymer (cellulose acetate) /top coat	Steel	EIS, SEM, EDX	[63]
Titanium oxide	Intrinsic	Addition of nano-particles as a filler in coating matrix	Vinyl ester polymer	AA 5083	EIS, SEM, EDX	[64]
Perfluorooctyl triethoxysilane (POTS)	Capsule based -UF shell	Polymerization (In situ)	Epalam 5015/5014	CS	OM, EDX, SEM, polarization measurement	[65]
Linseed oil	Capsule based -UF shell	Polymerization (In situ)	Epoxy resin	CS	EIS, visual inspection	[66]
Linseed oil	Capsule based -UF shell	Polymerization (Emulsion)	Epoxy primer	Steel	EIS, SECM	[67]
Superabsorbent polymers	Intrinsic	Swelling effect	Vinyl ester polymer	CS	EIS, SEM, Polarization measurement	[68]
Linseed oil	Capsule based -UF shell	Polymerization (In situ)	Epoxy	Steel	Salt spray	[69]
Linseed oil	Capsule based-	Polymerization (Interfacial)	Polyurethane	Steel	Visual inspection	[70]

	Polyurea shell					
Linseed oil	Capsule based -UF shell	Polymerization (In situ)	Liquid epoxy paint	Steel	EIS, Tafel polarization	[71]
Potassium stannate	Intrinsic	Formation of metal hydroxide	Stannate-based coating	AZ91D Mg alloy	EIS, SEM, EDX, polarization measurement	[72]
3-caprolactone fiber	Intrinsic	Shape memory assisted self healing / heating	Shape memory epoxy matrix	Steel	OM, SEM	[73]
BTA-loaded silica/PMAA nanotube	Intrinsic	Double-walled hybrid nanotubes	SiO/ZrO hybrid coating/ CI	CS	Visual inspection	[74]
Epoxy resin	Capsule based -UF shell	Polymerization Interfacial	Interpenetrating polymer network (IPN)	MS	EIS, SVET	[75]

2.1. Electrochemical techniques

2.1.1. Open circuit potential (OCP)

The open circuit potential (OCP), also referred to as the free corrosion potential, is the electrical potential difference between two conductors in a specific electrolyte with zero current flow between them [76]. Monitoring the OCP over time can provide information about when the system has reached a steady state and when transitions between different states, such as passive and active behavior occur.

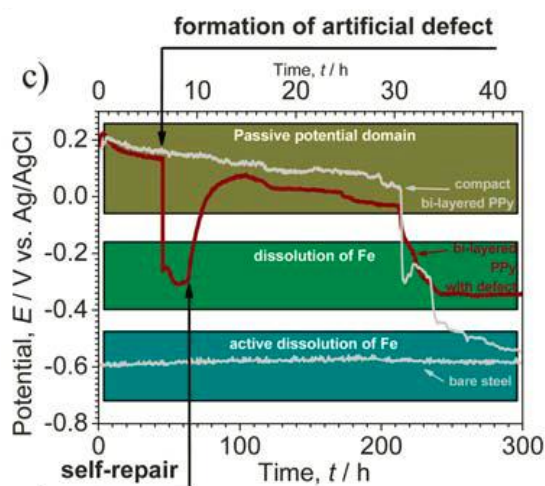


Figure 2. Open circuit potential for carbon steel coated with bi-layered PPy. An artificial defect was formed in the coating after 6 h of immersion in 3.5% NaCl solution (upper scale); for comparison OCPs for compact PPy film and bare steel are plotted (lower scale). This figure has been adapted from (ref. [54]).

Kowalski [54] et al. used the OCP to evaluate the self-healing ability of an intrinsically conducting polymer coating, polypyrrole (PPy) doped with molybdate, on a carbon steel substrate to repair defects in the coating and restore the passive state of the steel. The self-healing capability of the coating was investigated by creating defects in the coating while measuring the OCP in a 3.5 wt. % NaCl solution. The OCP over time is shown in Figure 2. A sudden decrease in the potential occurs when the defect is formed and the potential gradually returns to the passivation level indicating self-healing occurs. The healing is due to a synergistic effect of the unique permselectivity of the bi-layered PPy film and the catalytic action of polymolybdate anions. Typically, a stable OCP of intrinsically conducting polymer coated steel immersed in Cl^- solutions is difficult to obtain over long times (over 20h).

2.1.2. Potentiodynamic polarization (PP)

Potentiodynamic polarization is an electrochemical technique where the electrode potential is scanned continuously and the corresponding current density is recorded. The corrosion rate is evaluated through the Tafel extrapolation method.

Aramaki [77] used the PP technique to measure the protection efficiency (P%) of 1,2-bis(triethoxysilyl)ethane containing a fine powder of ammonium heptamolybdate tetrahydrate as a protective polymer coat on an Fe electrode surface. The electrode was submerged in an aerated 0.1 M NaCl solution at 30 °C. The protection efficiency of the coating was calculated using the equation:

$$P (\%) = 100 (1 - i_{\text{corr}} / i_{\text{corr}}^{\circ}), \quad (1)$$

where, i_{corr} and i_{corr}° are the corrosion current densities with and without the coating respectively. The protection efficiency reached values up to 99 % in case of an unscratched coat. The self-healing ability of the coating was examined by scratching the coating with a knife edge. The protection efficiency of the scratched coat was then calculated to be 98.8 % indicating that self-healing occurred. The high protection efficiency was attributed to the formation of a passive film at the scratched surface due to the ammonium heptamolybdate tetrahydrate incorporated in the polymer coating. In addition, Aramaki used the same technique (PP) to detect the self-healing ability (by calculating the protection efficiency) of a thin film of a 1,2-bis(triethoxysilyl)ethane polymer coating [78]. This coating contained sodium silicate, cerium nitrate, and $\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}$ [79] on a zinc electrode surface.

Potentiodynamic polarization measurements have been used to evaluate the self-healing properties of scratched coated specimens immersed in a 0.5 wt% NaCl [68]. Four types of coatings were used: i) a superabsorbent polymer (SAP) coating with a 50 μm thickness, ii) a SAP coating layered with a plain vinyl ester polymer coating with a total coating thickness of 30 μm , iii) a vinyl ester, SAP-mixed polymer coating resulting in a 25 μm thickness, and iv) a plain vinyl ester coating with a 70 μm thickness. The SAP, consisting of spherical particles, will swell in corrosive solutions leading to some healing behavior. Figure 3 shows a schematic of the substrate and the swelled coating. The coating prohibits the diffusion of oxygen to the scratched surface of the substrate and inhibits the corrosion of the substrate. Figure 4 shows the polarization curves of the substrate in the corrosive

solution with and without a SAP coating. After healing the SAP-coated substrate resulted in a decrease in the cathodic current density. This indicates that the diffusion rate of the dissolved oxygen in the solution has decreased, and a self-healing effect has taken place.

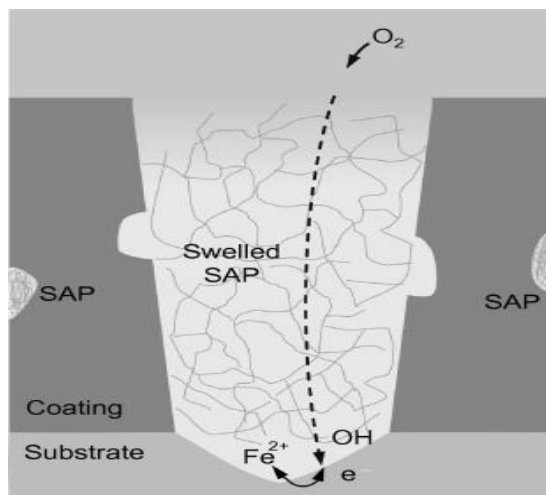


Figure 3. A schematic representation of the self-healing effect of the vinyl ester/SAP/vinyl ester coating (ref. [68]).

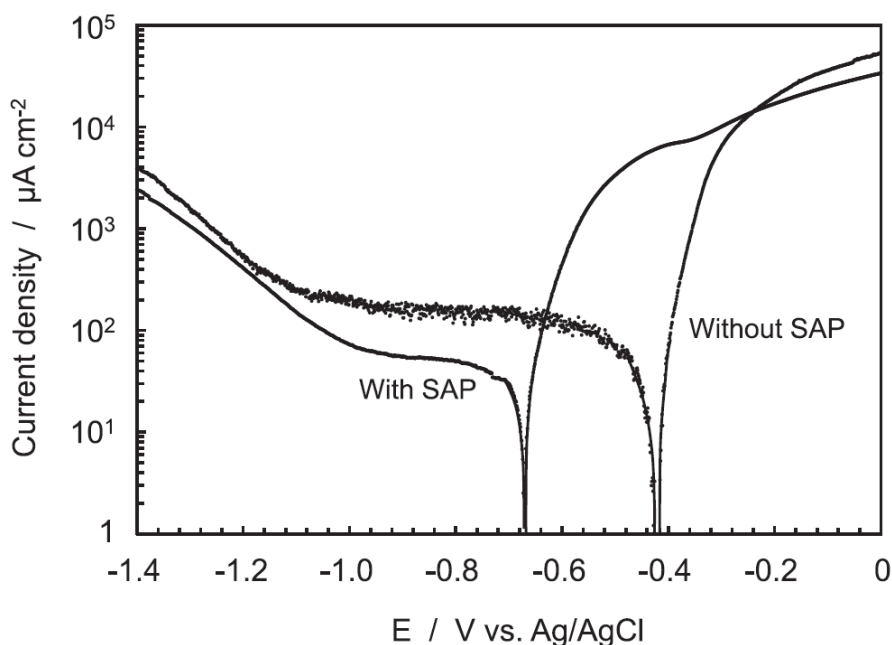


Figure 4. Bare substrate polarization curve in the corrosive solution with 1 wt.% of SAP and without SAP (ref. [68]).

Although the PP technique can be used to measure low corrosion rates, the reliability of this technique is limited by concentration polarization and IR drops (the voltage drop due to current flow in an electrolyte). Concentration polarization occurs at high reaction rates and prevents the electroactive

species from arriving at the electrode surface, resulting in inaccurate current density measurements. IR drops of coated substrates occur at high current densities and causes a non-linear Tafel behavior and prevents the use of the conventional DC polarization method. These limitations reduce the effectiveness of using polarization techniques to evaluate self-healing corrosion performance.

2.1.3. Electrochemical impedance spectroscopy (EIS)

In general, EIS is a transient technique where an excitation is applied to the system and the response (as a function of frequency) is observed. EIS is a non-destructive technique that characterizes bulk and interfacial properties of all sorts of materials (conductors, insulators and semiconductors). Many electrical parameters of the system can be determined in a single EIS experiment with an additional advantage that the signal can be averaged over long periods to achieve higher accuracy.

Yabuki [63] et al. studied the self-healing ability of coatings with varying pore sizes of porous polymer coatings using EIS. The coatings were comprised of cellulose acetate containing sodium benzoate as corrosion inhibitors. The coating with larger pores was considered to have higher self-healing capability since it had a larger polarization resistance. The largest polarization resistance was attributed to the diffusion of the corrosion inhibitor from the coating to the scratched area which formed a protective layer over the carbon steel. In later studies, Yabuki [49,64,68] et al. used several types of self-healing coatings such as a TiO₂ particle-vinylester polymer composite on aluminum alloy substrates and a multi-layer of vinyl-ester polymer followed by 5 wt% of a SAP and finally another layer of vinyl-ester polymers on steel. The polarization resistance of the 3-layer coating, shown in Figure 5, increased with time indicating a self-healing capability.

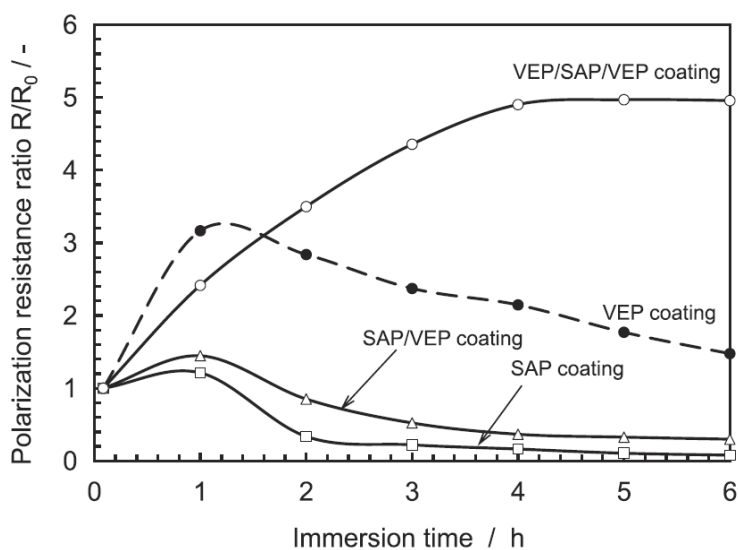


Figure 5. Polarization resistance ratio of the scratched specimen coated with a multilayer coating from ref. [68].

EIS has also been used to demonstrate the self-healing capability of a coating containing urea-formaldehyde microencapsulated silyl ester [octyldimethylsilyloleate] by Garcia [56] et al. They compared the impedance of four specimens: bare aluminum, aluminum coated with silyl ester, aluminum with a scratched clear coat, and aluminum with a scratched coating containing microcapsules. The impedance of the aluminum coated with silyl ester was higher than the impedance of the bare aluminum. Additionally, the impedance of the coating containing microcapsules was higher than that of the clear coat indicating that the microcapsules healed the scratch and protected the aluminium from corrosion.

Neema [75] et al. studied the self-healing ability of microcapsules containing epoxy resin which was embedded in an interpenetrating polymer network (silicon polymer, acrylic monomers and additives) using EIS. The resistance of scratched coated steel after one hour of immersion in 0.05 molar NaCl was $9.64 \times 10^4 \Omega \text{ cm}^{-2}$, the resistance of the same specimen after 24 hours of immersion increased to $2.44 \times 10^7 \Omega \text{ cm}^{-2}$. This increase in the resistance, and therefore the associated reduction in the corrosion rate, was attributed to self-healing functionality.

The main difficulty of obtaining consistent results with the EIS technique is choosing the proper form of the equivalent circuit used in modeling the EIS curves. Depending on the specific form of the equivalent circuit there can be numerous parameters involved in creating the best fit of the EIS data. The effective resistance of the coating will be one of the parameters of the model. Thus, if an inappropriate model is chosen, or some of the model parameters are fixed at incorrect values, the calculated coating resistance can be incorrect. In addition, as the healing system evolves, the model may need to be altered to account for the new coating structure.

Another difficulty is the linear response of the system to the perturbation signal which is not always the case in corrosion where many corrosion and electrochemical processes are non-linear e.g. pitting corrosion.

Jorcin [80] investigated the physical self-healing properties of shape memory polyurethanes (SMPUs) with cerium ions on top of a pure aluminum substrate using odd random phase multisine EIS. The advantages of this EIS technique are; (i) the rapid detection for the onset of the corrosion process, (ii) the unimportance of the linearity or stationarity of the system (iii) the lack of need to use any equivalent circuit for fitting the impedance data in order to obtain the coating resistance or the polarization resistance in order to follow the coatings' integrity status [81].

Open Circuit Potential, Potentiodynamic Polarization, and Electrochemical Impedance Spectrometry measure the global (averaged) response of the specimen and provide data about the overall surface activity and the general performance of the self-healing coatings. The local performance of the coating at the defect location and the distribution of the ions consumed or released at the active sites are not characterized by the above techniques. Local data near the defect can also provide critical information for the development of self-healing coatings. Thus, identification and quantification of the different ions produced or consumed during the degradation and healing is very important to understand the self-healing phenomenon. Therefore, localized techniques can be used to provide quantitative information about the active species as well as the mechanism and/or the rate of self-healing process at the defect.

2.1.4. Scanning vibrating electrode technique (SVET)

The scanning vibrating electrode technique (SVET) is an in situ technique used to study galvanic activity by measuring potential gradients over a current source within an electrolyte. A solitary electrode is vibrated perpendicular to the surface being studied using a piezoelectric vibrator. The potential is recorded at the highest and lowest probe positions, resulting in a sinusoidal AC signal. SVET can be used to study the corrosion protection and the self-healing properties of coatings. The SVET technique can measure the local distribution of anionic and cationic fluxes along the coated surface. These fluxes correspond to cathodic and anodic corrosion current, respectively. Thus the ionic fluxes in the defect can be directly correlated to the corrosion activity. SVET has also been used to provide information about inhibitor release in coatings [82-85].

SVET was used to evaluate the self-healing ability of the silyl ester (octyldimethylsilyloleate) healing agent encapsulated in urea-formaldehyde microcapsules [56]. SVET mapped the current densities at the defect of a scratched coated aluminum alloy immersed in a 0.05 molar NaCl solution. In this case, no local anodic and cathodic zones were identified along the scratch.

Neema [75] et al. also used SVET to evaluate the self-healing ability of the scratched interpenetrating polymer network previously described. After 24 hours of immersion in 0.05 molar NaCl, no anodic current density was observed at the scratch, which was attributed to the self-healing of the coating. Once again the self-healing constituents lead to the formation of a passive polymer film over the scratch.

Although SVET is a powerful technique that can be used to measure the local distribution of ionic fluxes, it does not measure the local reactivity and it cannot differentiate between the chemical nature of the species that generate the electric field.

2.1.5. Scanning ion-selective electrode technique (SIET)

The scanning ion-selective electrode technique uses an ion-selective electrode with three-dimensional position control, a reference electrode and a video camera with a long distance lens. Potentiometric measurements are conducted in a two electrode galvanic cell under zero current conditions. The potential difference between the ion-selective electrode and the reference electrode is measured and combined with the precise location data of the ion-selective electrode.

Montemor [86] et al. evaluated the corrosion activity and the self-healing processes of a modified epoxy coating containing nano-additives filled with mercaptobenzothiazole as a corrosion inhibitor. The pH around a defect was mapped using the SIET and indicated that the inhibitors are released into the defect area. Therefore, SIET can be used to investigate the local activity of different ionic species in the medium. However, each ion-selective electrode only measures for a specific ion; for example, a hydrogen-selective microelectrode detects the hydrogen ion concentration (pH), while a magnesium-selective microelectrode is used to detect Mg^{2+} .

2.1.6. Localized electrochemical impedance spectroscopy (LEIS)

In the LEIS technique a five electrode configuration is used. The five electrodes are comprised of the traditional three electrodes, the counter, the reference, and the substrate working electrode along with a probe (Pt bi-electrode) to measure the local potential. Impedance can be evaluated locally by measuring the local current density in the vicinity of the working electrode.

Snihirova [87] et al. used LEIS to evaluate the corrosion protection and the self-healing ability of water-based epoxy primers modified with layered double hydroxides containing corrosion inhibitors on an aluminum substrate. It was found that the coating inhibits early stage corrosion. The presence of the chromate in the coating creates a stable passivating layer that provides some self-healing capability for defects of different sizes.

LEIS is capable of providing local data about impedance changes near the damage site in a coating but one limitation of the LEIS technique is that the tip must be kept at a constant distance from the surface of the coating. Unfortunately, the natural roughness of the surface creates problems with the LEIS technique [88].

2.1.7. Scanning electrochemical microscope (SECM)

A scanning electrochemical microscope (SECM) is an electrochemical imaging technique used to detect charge transfer near a metal surface [89-95]. The SECM uses an ultramicroelectrode tip that is kept at a constant height above the specimen to be tested. A potential is applied to the tip and the current variation due to the change in the local concentration of the electroactive species is recorded creating an SECM map.

Gonzalez-Garcia [62] et al. used SECM to study the healing efficiency of a shape-memory polyurethane on an aluminum substrate before and after the thermally induced healing of a scratch on the coating. SECM was used to monitor the onset of the reduction of oxygen during the corrosion process. The SECM map showed that after healing, the coating system reduced the corrosion activity in the healed area. Moreover, they introduced a new approach to the use of SECM to investigate the corrosion protection and the self-healing ability of epoxy-coating containing encapsulated silyl-ester (octyldimethylsilylolate) [61]. In this work, they combined the oxygen detection experiment (regular redox-competition SECM mode of measurements), to monitor the onset of the oxygen reduction during the corrosion process, with measurements using an electrochemical mediator in solution (negative-feedback mode). SECM measurements showed that silyl ester can effectively heal the surface damage of the substrate by forming a homogeneous protective layer at which the oxygen behaved as a conventional electrochemical mediator.

Pilbath [67] et al. followed the self-healing of a healing system consisting of microcapsules containing linseed oil. The oxidation and reduction currents during the corrosion process were measured along a scratch with the SECM method. Comparing the scratched coated specimens with and without microcapsules, the effect of the self-healing properties of linseed oil was evaluated.

SECM is a very good technique for evaluating self-healing performance. It is highly specific and can measure smaller and faster phenomena due to its very small probe tip. In addition, by altering

the position of the probe tip the surface topography can be mapped [96]. SECM can also be used to probe the kinetics of reactions for small portions of the substrate which will provide insight into the possible mechanisms of the electrochemical processes [62].

2.2. Non-electrochemical techniques

The methods described in the previous sections are electrochemical based. Although these methods are very effective for determining the self-healing ability and/or the self-healing rate of coatings, there is no morphological or phase information about the damaged surface. Non-electrochemical methods, specifically, optical microscope (OM), scanning electron microscope (SEM) and confocal laser scanning microscopy (CLSM) can be used for surface analysis; and energy dispersive x-ray (EDX), electron probe microanalysis (EPMA) and x-ray photoelectron spectroscopy (XPS) can be used for elemental analysis helping to study the self-healing mechanism.

2.2.1. Optical Microscopy (OM)

Jadhav [58] et al. used an optical microscope to investigate the self-healing performance of steel coated with epoxy containing linseed oil encapsulated in phenol-formaldehyde microcapsules. The corrosion in 5% NaCl aqueous solution due to a scratch in the epoxy with and without microcapsules was evaluated. The corrosion of the damaged area also was monitored by visual inspection using a digital camera. From this method, it was concluded that the linseed oil is an effective healing agent. While digital images can provide a quick assessment of the viability of a particular self-healing system, the amount of corrosion can be difficult to quantify, especially if released self-healing chemicals alter the appearance of the coating.

2.2.2. Scanning Electron Microscope (SEM)/Energy-dispersive x-ray (EDX)

Huang [59] et al. evaluated self-healing epoxy coatings containing polyurethane (PU) microcapsules of hexamethylene diisocyanate (HDI) on a steel substrate using SEM. SEM images of the scratched regions of control specimens and the self-healing specimens before and after immersion in salt water for 48 hours showed evidence of corrosion protection and effective self-healing. Zhao [97] et al. demonstrated the effectiveness of epoxy resin as a self-healing agent using both optical and electron microscopy. The self-healing coating was prepared by combining 10 wt% microencapsulated epoxy resin and a 2 wt% catalyst solution in an epoxy resin matrix. It was found that the self-healing samples showed no visual evidence of corrosion.

Yabuki [64] et al. used a SEM to evaluate the self-healing capability of a coated aluminium alloy with and without TiO₂. EDX was used to determine the chemical composition near the scratch in the coating. EDX results showed that a carbon containing 2 μm thick film formed on the coated aluminum substrate at the site of the scratch. This is attributed to the dissolution of bisphenol A (BPA), which is a chemical precursor of the polymer coating, leading to formation of a film at the defect area.

The SEM is a very useful tool for evaluating the presence of a self-healing film in the scratched area of a specimen. Information about the progression of corrosion protection, the mechanisms of how the film is formed, or additional experiments with a particular specimen is impossible after applying the conductive coating needed for imaging with the SEM. The SEM method does not allow analysis of the pre-healed specimen (morphology of the defect before healing, coating resistance to corrosion immediately after damage, etc.) and only provides data at the end of the experiment.

2.2.3. Confocal laser scanning microscopy (CLSM)

The self-healing ability of an intrinsically conducting polymer coating (PPy) doped with molybdate ions on a carbon steel substrate was evaluated with confocal laser scanning microscopy (CLSM) [54]. The scratched specimen was submerged in a 3.5 wt% NaCl solution and the resulting CLSM images are shown in Figure 6a and 6b. This coating system resulted in the passivation of the iron. Counter ions in the inner layer of the coating reacted with iron ions in the coating containing iron molybdate to create a passivation layer and block the iron dissolution. CLSM can be used with thick materials and provide images at various depths, unlike the SEM which deals only with the surface. CLSM can be used to evaluate the damage site before and after healing. It can produce images of the surface morphology as well as slices of the substrate (one level at a time).

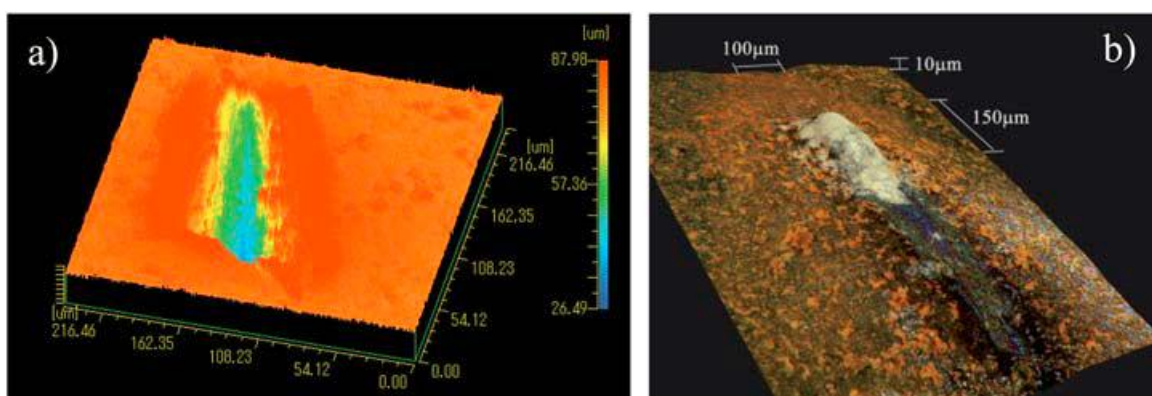


Figure 6. Confocal laser scanning microscopy 3D images of an artificial defect formed in bi-layered PPy coating electrodeposited on carbon steel a) as formed, b) after self-repair (ref. [54]).

2.2.4. X-ray photoelectron spectroscopy (XPS)

Aramaki [46] used XPS and electron-probe microanalysis to investigate the self-healing mechanism of a scratched coating of 1,2-bis(triethoxysilyl)ethane containing sodium silicate and cerium nitrate on treated zinc electrodes. No pitting corrosion occurred at the scratches after submersion in a 0.001 molar cerium nitrate solution. XPS revealed that a passive film composed of $\text{Zn}(\text{OH})_2$, ZnSi_2O_5 and $\text{Ce}^{3+}\text{Si}_2\text{O}_5^{2-}$ complex was formed on the scratched surface and deposition of $\text{Si}_2\text{O}_5^{2-}$ compounds occurred at the scratch where Cl^- was accumulating, resulting in suppression of

pitting corrosion. The key feature of the XPS technique is that it can detect the chemical species formed before and after the self-healing process. This can provide local information about the chain of reactions and mechanisms of self-healing.

2.2.5. Electron probe microanalysis (EPMA)

EPMA is an analytical technique that is used to analyze very small amounts of material by bombarding the material with a narrow beam of electrons and examining the resulting X-ray emission spectrum.

Aramaki [98] prepared a coating of 1,2-bis(triethoxysilyl)ethane polymer containing sodium silicate and cerium nitrate on a zinc electrode which was scratched and immersed in a NaCl solution. The coating was evaluated with EPMA which showed that the coating had some self-healing ability since the pitting corrosion at the scratches are suppressed due to the formation of passive film composed of $\text{Zn}(\text{OH})_2$, ZnSi_2O_5 and $\text{Ce}^{3+}\text{Si}_2\text{O}_5^{2-}$. Aramaki examined the self-healing capability of various modified coatings on zinc [99-101] and iron [102] electrodes. EPMA is a local technique which can supply information about the types of species as well as its migration in the vicinity of a coating scratch giving rise to complete information of the mechanism and kinetics of the self-healing process.

2.3. Suggested electrochemical techniques

The electrochemical techniques in this section have not been used to investigate the self-healing ability of coatings in the open literature, however, they should be considered as possible tools for studying the performance of a self-healing coating.

2.3.1. Linear polarization resistance (LPR)

This technique enables the calculation of polarization resistance and hence the corrosion rate. The polarization resistance is determined by monitoring the current caused by a small potential between two electrodes. If corrosion is occurring rapidly, a large number of ions will be present in the solution, resulting in a high current and low polarization resistance. The LPR can be used to monitor corrosion within a relatively small potential perturbation and has extremely fast response times. Using LPR effectively requires knowledge about the Tafel slope for the system under observation. This method is a global method and will not provide localized data. Its main advantage is the very fast response time of the polarization resistance and therefore provides an almost instantaneous information about the corrosion rate.

2.3.2. Electrochemical noise analysis (ENA)

EN is another global technique which is defined as the spontaneous random fluctuation of the current (or potential) crossing a metal/electrolyte interface under potentiostatic (or galvanostatic)

control [103-105]. EN has many modes of measurements that can monitor corrosion of metals and alloys depending on the measured current and/or potential fluctuations. One of the most common analysis techniques is to calculate the noise resistance (R_n) and noise impedance (Z_n) from the current and potential noise data. R_n is defined as the ratio between the standard deviation of the fluctuating potential and the standard deviation of the fluctuating current. Z_n is calculated by dividing the power spectral density of the potential noise by the power spectral density of the current noise. In general, analysis techniques of EN can be divided into current measurement and potential measurement sequence dependent techniques and sequence independent techniques.

For passive or coated metallic materials, the fluctuations in the current and potential indicate that passivity, coating breakdown or both has begun. From the beginning of the experiment until the start of the current and potential fluctuations is defined as the corrosion incubation period. The length of the corrosion incubation period is directly related to the corrosion resistance of the coating. In addition, monitoring and comparing Z_n for a self-healing coated metal or alloy before and after the healing process can give valuable information about (i) the healed area or the efficiency of the healing process, (ii) the needed time per unit area for a complete healing, (iii) the area limitation regarding the healable scratches and (iv) the corrosion rate of the metal or alloy during the healing process [106].

EN allows corrosion rate and incubation period measurements for many difficult to measure forms of corrosion (e.g. crevice corrosion with a self-healing coating, pitting, and stress corrosion cracking [107]) in very low conductive media where other techniques (AC, DC or EIS) fail. EN can also be used where the signal to be measured is very small, typically due to a high resistance of the electrolyte. On the other hand, the disadvantages of this technique are its dependence on the Tafel slopes (or assuming they are 0.12 V/decades, which is not always correct) and the errors introduced in the measurement of the noise due to the electrodes' asymmetry and area.

2.3.3. Cyclic potentiodynamic polarization (CPDP)

Usually self-healing coatings are designed to protect metals and alloys against uniform corrosion. For localized corrosion beneath the coatings e.g. pitting and crevice, CPDP is a common global technique that can be used to estimate the vulnerability of a metal or alloy to these forms of corrosion [108]. It is based on cycling the potential from the open circuit potential, E_i , to potentials beyond the breakdown potential, E_b , (e.g. pitting potentials) at a constant rate. The potential at which the metal/electrolyte system repassivates is called the repassivation potential, E_p , and is where the measured current during the reverse scan intersects with the passive current measured during the forward scan. E_p is usually in the microampere range and the higher the E_p , the more resistant the metal is to localized corrosion.

The CPDP technique can be extended to evaluate self-healing coatings and determine if crevice or pitting corrosion is occurring under the coating using the E_p as an indicator of the status of the metal under the coating. In addition, the value of the passive current can be used whether crevice corrosion is taking place under the self-healing coating. A high passive current (in the range of milliamperes) usually indicates crevice corrosion is occurring under the coatings.

As with any other electrochemical techniques, the uncompensated solution resistance affects the repassivation potential measurements significantly, so the solution should be highly conductive. A minimum electrolyte concentration of 0.15 M is required to provide valid repassivation potential measurements. Furthermore, the data and its interpretation can be significantly affected by experimental parameters such as the scan rate and the apex current.

2.3.4. Potentiostatic pulse testing (PPT)

PPT is an efficient global technique for detecting the early stages of a coating degradation [109,110] which standard EIS cannot detect. Typically, PPT can be used in cases where the low frequency impedance is higher than the input impedance of the EIS equipment. Both PPT and EIS are based on the analysis of the current response analysis to time varying potential changes. PPT uses square pulses of 0.1 ~ 2.0 V instead of Sine waves as are used in standard EIS [109]. One of the main disadvantages of using the PPT technique is its inability to obtain values for all the equivalent circuit components simultaneously. Furthermore, there are some parameters which cannot be determined using PPT, e.g. coating capacitance, but they are typically not vital for determining the overall corrosion resistance or the early stages of a coating degradation [111]. Similar to CPDP, the data obtained from PPT and its interpretation can be significantly affected by experimental parameters such as the sampling rate and current range used. Thus, unlike EIS, PPT tests with different measuring conditions should be performed repetitively to ensure the quality of the data.

2.3.5. Scanning Kelvin probe (SKP)

The Kelvin probe is made from an inert metal wire (Pt, Cr/Ni) with one end of the probe connected to a support via a pin connector while the other end is positioned in close proximity to the sample surface. The end close to the sample surface is called the Kelvin probe tip. The tip is tapered but has a flat end. This technique SKP is used to determine the difference in the relative work function between the probe and the sample which simply describes the energy required to liberate an electron from the surface of a conductor.

The SKP is a technique for studying the corrosion not only at the surface of the material but also at buried interfaces of coated samples. SKP can also be used for studying corrosion under electrolyte droplets, where it provides direct information about the distribution and activity of local cathodes and anodes and how these are affected by the substrate composition and inhibitors in the electrolyte [112]. Although the SKP measurement cannot be performed in full immersion, using a reservoir of solution adjacent to a coating delamination makes it possible to measure quantitatively the delamination rate of organic coatings at defects [113] and then the behavior under immersion conditions could be simulated.

2.3.6. Hydrogen Evolution Reaction test (HERT)

The HER takes place when a polarized coated metal electrode is placed in an electrolyte at potentials lower than the potential of hydrogen evolution on the metal. The HER technique is a global

technique that can measure the decrease in the HER cathodic current due to self-healing. The HER cathodic current near the damaged area will be directly proportional to the surface area of the electrode. As the self-healing process progresses, the surface area of the electrode which is in direct contact with the corrosive electrolyte is decreasing, which results in a decrease in the measured cathodic current. If the healing process resulted in a complete polymeric layer at the damage location, then the HER cathodic current will be nearly zero. A disadvantage of the HER technique is that it provides mainly qualitative data and no corrosion parameters can be concluded from the data.

3. SUMMARY AND CONCLUSION

Self-healing coatings are a robust method of corrosion protection that can autonomically repair damage and prolong the useful life of the coating. Evaluation of the performance of self-healing coatings can be performed either globally or locally. The main disadvantages of the techniques used in evaluating self-healing performance are as follows: complexity in obtaining a stable potential due to the non-electrochemical nature of the coating as in OCP, limitations arising from the concentration polarization and IR drops as in PP and difficulty in the proper construction of the equivalent circuits as in the EIS. The electrochemical techniques PP and EIS provide quantitative results about the self-healing process where the protection efficiency and the rate of corrosion and therefore the rate of self-healing can be calculated using these techniques. These methods provide global information about the self-healing process and do not provide details of the local reactions occurring at the damage site. On the other hand, addressing the processes occurring locally at the solid/liquid interfaces may provide a key for investigating the mechanisms of the respective electrochemical reactions as well as the active species involved in the latter. For instance, SVET can measure the local distribution of fluxes but cannot differentiate the nature of the species that are responsible for generating the electric field. SIET can investigate the local activity of different ionic species however, it detects only a single specific ion in the medium. Therefore, a combination of SVET and SIET provides a powerful way of investigating both the distribution and type of the active species involved in the electrochemical process. Although, LEIS can probe valuable information about the changes of the impedance in a small area, it does not give information about the topology of the surface. SECM is capable of providing valuable information about the topology of the surface, it is highly specific and able to provide measurements of the smaller and faster phenomena. Moreover, SECM can give information about the kinetics and mechanisms of the electrochemical processes and therefore considered one of the best techniques for self-healing coating evaluation.

Different scanning microscope methods, such as SECM, are used to supply mechanistic details about the self-healing process. In addition, XPS and EDX are used to detect the different materials formed upon self-healing. Due to the limitations of some of the electrochemical techniques used in evaluating self-healing coatings, a few more possible methods of obtaining useful data about the coatings behavior, e.g. LPR might provide more instantaneous corrosion behavior to enable researchers to better understand and characterize self-healing effects. It is recommended to combine local and global electrochemical techniques described above along with the non-electrochemical

methods to create a more complete picture of the self-healing performance including the mechanisms involved in the complicated processes of the self-healing of corrosion control coatings.

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Reference

1. P. Chatterjee, M.K. Benerjee and K.P. Mukherjee, *Ind. J. Technol.*, 29 (1991) 191.
2. F. Bentiss, M. Lagrenee, M. Traisnel and J.C. Hornez, *Corros. Sci.*, 41 (1999) 789.
3. F. Bentiss, M. Traisnel and M. Lagrenee, *Corros. Sci.*, 42 (2000) 127.
4. A.W. Peabody, *Peabody's Control of Pipeline Corrosion*, 2nd Ed., NACE International (2001).
5. J.B. Mohler, *Electroplating and Related Processes*, Chemical Publishing Co (1969).
6. N. Sato, *Corros. Sci.*, 31 (1990) 1.
7. P.A. Schweitzer, *Corrosion of Linings and Coatings: Cathodic and Inhibitor Protection and Corrosion Monitoring*, CRC press, Florida, USA (2007).
8. P.B. Raja and M.G. Sethuraman, *Material Lett.*, 62 (2008) 113.
9. X. Shi, B.M.D. Fernando and S. Croll, *J. Coat. Technol. Res.*, 5 (2008) 299.
10. D.O. Grigoriev, K. Kohler, E. Skorb, D.G. Shchukin and H. Mohwald, *Soft Matter.*, 5 (2009) 1426.
11. H. Jin, G.M. Miller, N.R. Sottos and S.R. White, *Polymers*, 52 (2011) 1628.
12. J. Lee, D. Bhattacharyya, M.Q. Zhang and Y.C. Yuan, *Express Polym. Lett.*, 5(3) (2011) 246.
13. H.H. Noh and J. Lee, *Express Polym. Lett.*, 7(1) (2013) 88.
14. X. Chen, M.A. Dam, K. Ono, A. Mal, H. Shen and S.R. Nutt, *Science*, 295 (2002) 1698.
15. Q. Tian, Y.C. Yuan, M.Z. Rong and M.Q. Zhang, *J. Mater. Chem.*, 19 (2009) 1289.
16. Y. Chujo, K. Sada and T. Saegusa, *Macromolecules*, 23 (1990) 2693.
17. C.M. Chung, Y.S. Roh, S.Y. Cho and J.G. Kim, *Chem. Mater.*, 16 (2004) 3982.
18. A. Yabuki and M. Sakai, *Corros. Sci.*, 53 (2011) 829.
19. A. Yabuki and R. Kaneda, *Mater. Corros.*, 60 (2009) 444.
20. M.A.M. Rahmathullah and G.R. Palmese, *J. Appl. Polym. Sci.*, 113 (2009) 2191.
21. S.H. Cho, M. Andersson, S.R. White, N.R. Sottos and P.V. Braun, *Adv. Mater.*, 18 (2006) 997.
22. H.R. Williams, R.S. Trask and I.P. Bond, *Smart Mater. Struct.*, 16 (2007) 1198.
23. W. Ni, Y.T. Cheng and D.S. Grummon, *Appl. Phys. Lett.*, 80 (2002) 3310.
24. A. Lendlein and S. Kelch, *Angew. Chem. Int. Ed.*, 41 (2002) 2034.
25. T.F. DaConceicao, N. Scharnagl, W. Dietzel, D. Hoeche and K.U. Kainer, *Corros. Sci.*, 53 (2011) 712.
26. J. Gao and J. Suo, *Surf. Coat. Technol.*, 206 (2001) 1342.
27. D.A. Koleva, N. Boshkov, V. Bachvarov, H. Zhann, J.H.W. de Wit and K. van Breugel, *Surf. Coat. Technol.*, 204 (2010) 3760.
28. E.M. Moustafa, A. Dietz and T. Hochsattel, *Surf. Coat. Technol.*, 216 (2013) 93.
29. D. Borisove, H. Mohwald and D.G. Shchukin, *ACS Appl. Mater. & Interfaces* 5 (2013) 80.
30. A. Yabuki and K. Okumura, *Corros. Sci.*, 59 (2012) 258.
31. M.F. Montemor, W. Trabelsi, S.V. Lamaka, K.A. Yasakau, M.L. Zheludkevich, A.C. Bastos and M.G.S. Ferreira, *Electrochim. Acta*, 53 (2008) 5913.
32. M.F. Montemor, M.G.S. Ferreira and R. Pinto, *Electrochim. Acta*, 54 (2009) 5179.

33. N.C. Rosero-Nadarro, L. Paussa, F. Andreatta, Y. Castro, A. Duran, M. Aparicio and L. Fedrizzi, *Prog. Org. Coat.*, 69 (2010) 167.
34. P. Cordier, F. Tournilhac, C. Soulie-Ziakovic and L. Leibler. *Nature*, 451 (2008) 977.
35. S.J. Kalista, T.C. Ward and Z. Oyetunji. *Mech. Adv. Mater. Struct.*, 14 (2007) 39.
36. S.A. Hayes, W. Zhang, M. Branthwaite and F.R. Jones. *J. Roy. Soc. Interface*, 4 (2007) 381.
37. K.S. Toohey, N.R. Sottos, J.A. Lewis, J.S. Moore and S.R. White, *Nat. Mater.*, 6 (2007) 581.
38. H.R. Williams, R.S. Trask and I.P. Bond, *Smart Mater. Struct.*, 16 (2007) 1198.
39. S.J. Garcia, H.R. Fischer and S. van der Zwaag, *Prog. Org. Coat.*, 72 (2011) 211.
40. E.B. Murphy and F. Wudl, *Prog. Polym. Sci.*, 35 (2010) 223.
41. A. Stankiewicz, I. Szczygiel and B. Szczygiel, *J. Mater. Sci.*, 48 (2013) 8041.
42. A.N. Khramov, N.N. Voevodin, V.N. Balbyshev and M.S. Donley, *Thin Solid Films*, 447–448 (2004) 549.
43. W. Trabelsi, P. Cecilio, M.G.S. Ferreira and M.F. Montemor, *Prog. Org. Coat.*, 54 (2005) 276.
44. D. Fix, D.V. Andreeva, Y.M. Lvov, D.G. Shchukin and H. Mohwald, *Adv. Funct. Mater.*, 19 (2009) 1720.
45. A.C. Balaskas, I.A. Kartsonakis, L-A. Tziveleka and G.C. Kordas, *Prog. Org. Coat.*, 74 (2012) 418.
46. K. Aramaki, *Corrosion (Houston)*, 44 (2002) 1621.
47. S.V. Lamaka, M.L. Zheludkevich, K.A. Yasakau, M.F. Montemor, P. Cecilio and M.G.S. Ferreira, *Electrochem. Commun.*, 8 (2006) 421.
48. D.G. Shchukin, M. Zheludkevich, K. Yasakau, S. Lamaka, M.G.S. Ferreira and H. Möhwald, *Adv. Mater.*, 18 (2006) 1672.
49. A. Yabuki, H. Yamagami and K. Noishiki, *Mater. Corros.*, 58 (2007) 497.
50. S.V. Lamaka, M.L. Zheludkevich, K.A. Yasakau, R. Serra, S.K. Poznyak and M.G.S. Ferreira, *Prog. Org. Coat.*, 58 (2007) 127.
51. C. Suryanarayana, K.C. Rao and D. Kumar, *Prog. Org. Coat.*, 63 (2008) 72.
52. P.V. Braun, S.H. Cho and S.R. White, *Adv. Mater.*, 21 (2009) 645.
53. J.B. Jorcin, G. Scheltjens, Y.V. Ingelgern, E. Tourwe, I.D. Graeve, G.V. Assche, B.V. Mele, H. Terryn and A. Hubin, *Electrochim. Acta*, 55 (2010) 6195.
54. D. Kowalski, M. Ueda and T. Ohtsuka, *J. Mater. Chem.*, 20 (2010) 7630.
55. M.L. Zheludkevich, S.K. Poznyak, L.M. Rodrigues, D. Raps, T. Hack, L.F. Dick, T. Nunes and M.G.S. Ferreira, *Corros. Sci.*, 52 (2010) 602.
56. S.J. Garcia, H.R. Fischer, P.A. White and A.E. Hughes, *Prog. Org. Coat.*, 70 (2011) 142.
57. L. LePing, Z. Wei, X. Yi, W. HongMei, Z. Yang and L. WuJun, *Chinese Sci. Bull.*, 57 (2011) 439.
58. S.R. Jadhav, G.D. Hundiware and P.P. Mahulikar, *J. Appl. Poly. Sci.*, 119 (2011) 2911.
59. M-X. Huang and J-L. Yang, *J. Mater. Chem.*, 21 (2011) 11123.
60. M. Samadzadeh, S.H. Boura, M. Peikari, A. Ashrafi and M. Kasiriha, *Prog. Org. Coat.*, 70 (2011) 383.
61. Y. Gonzalez-Garcia, S.J. Garcia, A.E. Hughes and J.M.C. Mol, *Electrochem. Commun.*, 13 (2011) 1094.
62. Y. González-García, J.M.C. Mol, T. Muselle, I. De Graeve, G. Van Assche, G. Scheltjens, B. Van Mele and H. Terryn. *Electrochem. Commun.*, 13 (2011) 169.
63. A. Yabuki and T. Nishisaka, *Corros. Sci.*, 53 (2011) 4118.
64. A. Yabuki, W. Urushihara, J. Kinugasa and K. Sugano, *Mater. Corros.*, 62 (2011) 907.
65. M. Huang, H. Zhang and J. Yang, *Corros. Sci.*, 65 (2012) 561.
66. S.H. Boura, M. Peikari, A. Ashrafi and M. Samadzadeh, *Prog. Org. Coat.*, 75 (2012) 292.
67. A. Pilbath, T. Szabo, J. Telegdi and L. Nyikos, *Prog. Org. Coat.*, 75 (2012) 480.
68. A. Yabuki and K. Okumura, *Corros. Sci.*, 59 (2012) 258.
69. T. Nesterova, K.D. Johansen, L.T. Pedersen and S. Kiil, *Prog. Org. Coat.*, 75 (2012) 309.
70. P.D. Tatiya, R.K. Hedao, P.P. Mahulikar and V.V. Gite, *Ind. Eng. Chem. Res.*, 52 (2013) 1562.

71. M. Kouhi, A. Mohebbi and M. Mirzaei, *Res. Chem. Intermed.*, 39 (2013) 2049.
72. A.S. Hamdy and D.P. Butt, *Electrochim. Acta*, 97 (2013) 296.
73. X. Luo and P.T. Mather, *ACS Macro Lett.*, 2 (2013)152.
74. G.L. Li, Z. Zheng, H. Mohwald and D.G. Shchukin, *ACS Nano*, 7 (2013) 2470.
75. S. Neema, M. Selvaraj, J. Raguraman and S. Ramu, *J. Appl. Polym. Sci.*, 127 (2013) 740.
76. K. Aramaki, K. Makotosakakibara and H. Nishihara, *J. Electrochem. Soc.*, 140 (1995) 1561.
77. K. Aramaki, *Corrosion (Houston)*, 55 (1999) 1020.
78. K. Aramaki, *Corros. Sci.*, 44 (2002) 1375.
79. K. Aramaki, *Corros. Sci.*, 44 (2002) 2621.
80. J.B. Jorcin, G. Scheltjens, Y.V. Ingelgem, E. Tourwé, G.V. Assche, I.D. Graeve, B.V. Mele, H. Terryn and A. Hubina, *Electrochim. Acta*, 55 (2010) 6195.
81. T. Breugelmans, E. Tourwé, Y.V. Ingelgem, J. Wielant, T. Hauffman, R. Hausbrand, R. Pintelon and A. Hubin, *Electrochem. Commun.*, 12 (2010) 2.
82. A.C. Bastos, O.V. Karavai, M.L. Zheludkevich, K.A. Yasakau and M.G.S. Ferreira, *Electroanal.*, 22 (2010) 2009.
83. J. He, V.J. Gelling, D.E. Tallman and G.P. Bierwagen, *J. Electrochem. Soc.* 147 (2000) 3661.
84. K. Ogle, V. Baudu, L. Garrigues and X. Philippe, *J. Electrochem. Soc.* 147 (2000) 3654.
85. A.C. Bastos, M.G.S. Ferreira and A.M. Simões, *Prog. Org. Coat.*, 52 (2005) 339.
86. M.F. Montemor, D.V. Snihirova, M.G. Taryba, S.V. Lamaka, I.A. Kartsonakis, A.C. Balaskas, G.C. Kordas, J. Tedim, A. Kuznetsova, M.L. Zheludkevich and M.G.S. Ferreira, *Electrochim. Acta*, 60 (2012) 31.
87. D. Snihirova, L. Liphardt, G. Grundmeier and F. Montemor, *J. Solid State Electrochem.*, 17 (2013) 2183.
88. W. Pernkopf, M. Sagl, G. Fafilek, J.O. Besenhard, H. Kronberger and G.E. Nauer, *Solid State Ionics*, 176 (2005) 2031.
89. R.M. Souto, Y. González-García and S. González, *Corros. Sci.*, 47 (2005) 3312.
90. R.M. Souto, Y. González-García, S. González and G.T. Burstein, *Corros. Sci.* 46 (2004) 2621.
91. R.M. Souto, Y. González-García, S. González and *Corros. Sci.*, 50 (2008) 1637.
92. R.M. Souto, Y. González-García, S. González and G.T. Burstein, *Electroanal.*, 21 (2009) 2569.
93. A.C. Bastos, A.M. Simões, S. González, Y. González-García and R.M. Souto, *Electrochem. Commun.*, 6 (2004) 1212.
94. S. González, L. Fernández-Mérida and R.M. Souto, *Electroanal.*, 21 (2009) 2640.
95. J.J. Santana, J. González-Guzmán, L. Fernández-Mérida, S. González and R.M. Souto, *Electrochim. Acta*. 55 (2010) 4488.
96. P. Sun, F.O. Laforge and M.V. Mirkin, *Phys. Chem. Chem. Phys.*, 9 (2007) 802.
97. Y. Zhao, W. Zhang, L. Liao, H. Wang and W. Li, *Physics Procedia*, 18 (2011) 216.
98. K. Aramaki, *Corros. Sci.*, 44 (2003) 1621.
99. K. Aramaki, *Corros. Sci.*, 45 (2003) 2361.
100. K. Aramaki, *Corros. Sci.*, 46 (2004) 1565.
101. K. Aramaki, *Corros. Sci.*, 47 (2005) 1285.
102. K. Aramaki and T. Shimura, *Corros. Sci.*, 52 (2010) 1464.
103. G.C. Barker, *J. Electroanal. Chem. & Interfac. Electrochem.*, 21 (1969) 127.
104. V.A. Tyagai, *Electrokhimiya*, 10 (1974) 5.
105. M. Fleischmann and J.W. Oldfield, *J. Electroanal. Chem. & Interf. Electrochem.*, 27 (1970) 207.
106. A. Lowe, H. Eren, Y.J. Tan, B. Kinsella and S. Bailey, *IEEE T. Instrum. Meas.*, 50 (2001) 1059.
107. R.A. Cottis, *Corrosion*, 57 (2001) 265.
108. ASTM Standards F2129 – 08, Standard Test Method for Conducting Cyclic Potentiodynamic Polarization, Measurements to Determine the Corrosion Susceptibility of Small Implant Devices.
109. P.C. Pistorius, in the Conference Paper of the 14th International Corrosion Council, Capetown, S.A., published on CD-ROM (1999).

- 110.R.D. Granata, K.J. Kovaleski, *Evaluation of High-Performance Protective Coatings by Electrochemical Impedance and Chronoamperometry*, in *Electrochemical Impedance: Analysis and Interpretation*, J.R. Scully, D.C. Silverman, M.W. Kendig (Eds.), ASTM, Philadelphia, PA (1993) 450
- 111.J. Kang and G.S. Frankel, *Z. Phys. Chem.*, 219 (2005) 1519.
- 112.C. Chen, C.B. Breslin and F. Mansfeld, *Mater. Corros.*, 49 (1998) 569.
- 113.M. Rohwerder, P. Leblanc, G.S. Frankel, M. Stratmann, *Analytical Methods in Corrosion Science and Engineering*, P. Marcus and F. Mansfeld, Eds. CRC Press, Boca Raton, FL (2006).

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