
DETECTING “SELF-HEALING” EFFECTS

Evaluation of the anticorrosive properties of nanocontainers, micro- and nanocapsules in coatings

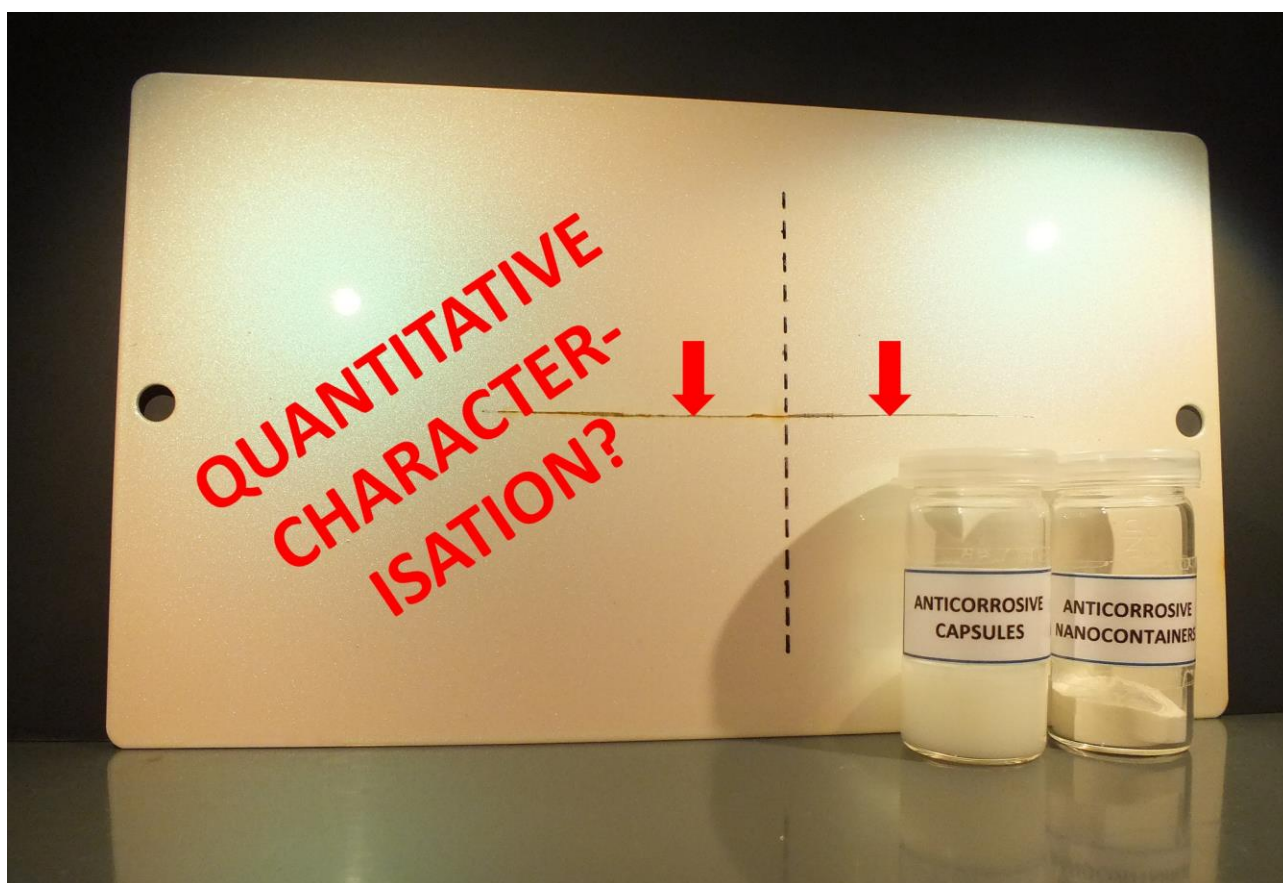
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Leader

Special nanocontainers, which act as reservoirs for the exchange of corrosive ions, as well as special micro- and nanocapsules, which contain corrosion inhibitors, can be introduced in an anticorrosive primer formulation. By this addition, the latter may be furnished with “self-healing” characteristics, which could appear as soon as the primer is harmed mechanically. Since such additions, however, do also affect the matrix continuity as well as the situation in the interfaces, a comprehensive evaluation of the performance of such “self-healing” primers cannot be done just by the eye. Here, electrochemical impedance spectroscopy (EIS) in combination with a thermo-cyclic electrolytic loading (TEL) is shown to contribute significantly to a representative evaluation of such systems.

Main Text

One suggestion to achieve a more efficient and durable corrosion protection with coatings is the concept of self-healing, also known as self-repair, which aims at stopping the degradation processes in its early stage. This concept was published first about 20 years ago^{1,2}. Generally it bases on the use of encapsulated monomers, which start the healing action on being released from the capsule by a triggering crack. Several overviews of self-healing technology for polymers are given elsewhere³⁻⁶.

Regarding the corrosion protection of metal substrates with coatings, the self-healing effect can either be a restoration of the mechanical and barrier properties of the matrix or it can be the corrosion protection alone. Concerning the inhibition of corrosion processes at weakened and damaged sites in coatings, options for self-healing have been described in literature^{7,8}. The standard procedure involves the use of microcapsules, similar to those used for polymer self-healing, but filled with a liquid or soluble solid corrosion inhibitor. If such microcapsules are integrated into a coating and are destroyed by mechanical impact, the released contents are transported to the metallic substrate together with the corrosive medium. A direct contact of a corrosion inhibitor (e.g. benzotriazole, Ce^{3+} salts) with the metal at the damaged site initiates the corrosion inhibition and prevents premature degradation of the coating. A concept of nanocontainers or nanoreservoirs for self-healing of coatings is already described in literature^{9,10}, which relies on incorporation of corrosion inhibitors into porous or layer-structured nanoparticles.

Experimental

The liquid corrosion inhibitors G50 (HighTac) and Rewocoros AC 28 (Evonik) were encapsulated according to the following general procedure, which uses the so called “ouzo-effect”:

A mixture of inhibitor, monomer and ethanol is added to a well stirred aqueous solution of a surfactant. The contact between the hydrophobic and the aqueous phase leads to a diffusion process in the system. The ethanol diffuses into the aqueous phase leaving behind the anticorrosion agent. Small droplets are formed and stabilised by the surfactant. The actual nanocapsules are formed by surficial polymerisation from the emulsion. The polymerisation of the capsule membranes takes place at the interface of the resulting hydrophobic droplets in water and is initialised by the autoprotolysis of water.

Nanocontainers based on hydrotalcites (Pural®) and montmorillonites (Cloisite®) were synthesised and respectively modified with anions and cations by ion exchange. Different combinations of both of these nanocontainers were done and crushed together (particle size: 300 - 400 nm) in order to obtain a double container allowing the release of two types of components and the formation of protective precipitates (zinc molybdate: Nano91, calcium molybdate: Nano92).

Using Nano91, Nano92, the encapsulated versions of G50, Ø 150 nm, and Rewocoros AC 28, Ø 130 nm, (abbreviated: G50 c and Rew AC 28 c) as well as the liquid inhibitors themselves (abbreviated: G50 and Rew AC 28) the following primer formulations were generated:

Table 1: Formulations of test primers; numbers represent mass percentages

Components	Standard	G50	G50c	Rew AC 28	Rew AC 28c	Nano91	Nano92
Bayhydrol A 2227/1	30.62	30.96	30.21	30.58	30.21	30.96	30.78
Surfynol 104 BC	1.02	1.03	1.01	1.02	1.01	1.03	1.03
Borchi Gen SN 95	1.99	2.01	1.96	1.99	1.96	2.01	2.00
Crenox R-KB-4	5.26	5.31	5.19	5.25	5.19	5.31	5.29
Heucophos ZPA	16.23	16.41	16.01	16.21	16.01	16.41	16.33
resp. Inhibitor	0	0.10	1.01	0.10	1.01	0.10	0.10
Bayhydrol A 2227/1	14.34	14.50	14.15	14.32	14.15	14.50	14.59
Water demin.	6.07	5.21	5.99	6.07	5.99	5.21	5.24
STIT 2354*	15.39	15.39	15.39	15.39	15.39	15.39	15.49
Water demin.	9.07	9.07	9.07	9.07	9.07	9.07	9.13

*Curing agent formulated by and obtained from Covestro, which consists of 77.20% Desmodur N 3900, 19.30% Butoxyl and 3.50% Dynasilan Glymo

According to table 1 “mixed” inhibitor formulations were manufactured additionally, which contained G50c and Nano91 or Nano92 in the ratios 1:1, 1:0.6 and 1:0.3.

Using a doctor blade the primer formulations were applied on degreased steel panels (Gardobond C) resulting in dry film thicknesses of $25 \pm 2 \mu\text{m}$. Two PVC tubes (Ø 25 mm, h = 20 mm) were glued to the surface of the film. In one of which, a 6 mm long and 0.5 mm wide slit was inflicted centrally, which met the substrate. After conditioning for 7 days, the PVC tubes were filled with 7 ml Harrison solution and sealed

with a glass plate, $d = 0.1$ mm. These samples were exposed to a thermocyclic electrolytic loading (TEL sinusoidal cycling between 20 °C and 70 °C in periods of 1 h)¹¹ and characterized by EIS (ATLAS 0441 High Impedance Analyzer) using a Pt wire as counter electrode (two electrode geometry; modulation amplitude: 15 mV, frequency range: 100 kHz – 0.1 Hz) after defined intervals of TEL. Simulation of EIS spectra was performed using ZView 3.1.

Results

EIS spectra obtained from the sample areas without and with artificially inflicted defect were simulated corresponding to the equivalent circuit models depicted in Fig. 1. The left model implies pores, which reach the substrate. By these the electrolyte solution meets the substrate and induces corrosion. The model at the right additionally includes a defect, which acts as an additional, significantly larger path for the charge carriers between the substrate and the counter electrode. This means, here, the part of charge carriers migrating through coating pores is very small. In cases, in which the mesh size of the matrix is in the range of the charge carrier sizes, charge transfer is determined by a molecular diffusion mechanism. This non-linear behavior (“anomalous diffusion”) could be simulated by a Finit Layer Warburg element (FLW; here: W_s)¹². Due to the finding that all EIS spectra obtained from the injured areas of the primer samples during the TEL are consistent with the right equivalent circuit model in Fig. 1, it may be supposed that the corrosion layer growing in the defect (fractionally under participation of liquid inhibitors, which origin from broken capsules) acts as a second “coating” provided with diffusion paths in the size of the charge carriers. Here, “ R_{coat} ” could be regarded as a measure for the formation of corrosion in the defect, whereas R_{coat} (as relevant in the model without defect) is of low meaning by trend. In both models, however, R_{corr} and C_{dl} (not depicted in the sketches) represent the extent of undercutting corrosion and delamination, respectively.

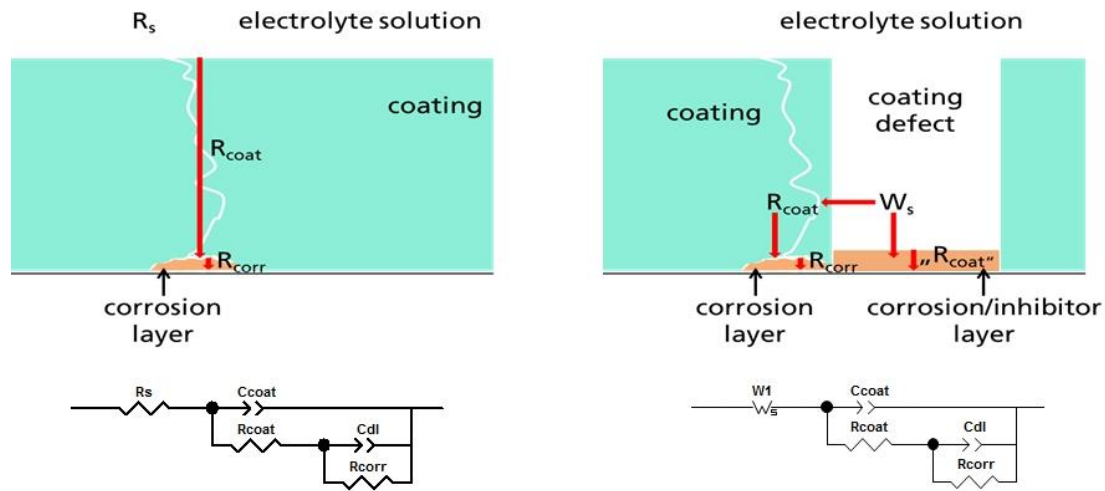


Figure 1: Charge carrier paths (red arrows) and equivalent circuit model for the primers without (left) and with (right) artificially inflicted defect under electrolyte impact; the capacitive elements are in parallel to the resistive ones (not depicted)

Exemplarily, Fig. 2 shows the EIS data obtained before TEL (0 h) and after 21 h, 94 h and 178 h of TEL of the Rew AC 28 c primer.

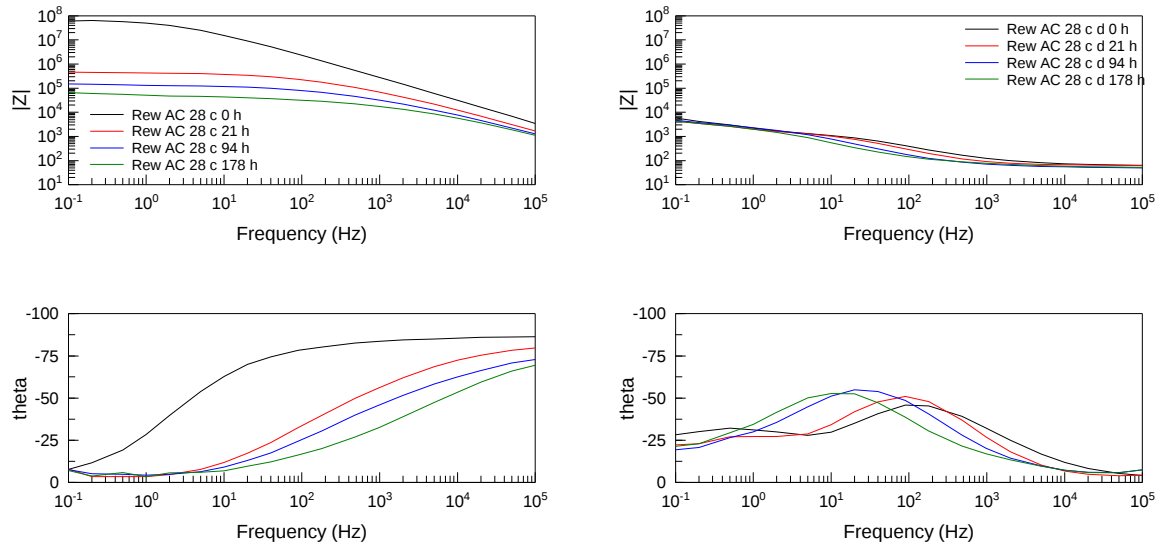


Figure 2: EIS data of an intact (left) and injured (right) area of the TEL affected Rew AC 28 c primer

Systematic interpretation of EIS data possible

As expected, the barrier is significantly decreased in the case of the injured sample areas, and electrochemical processes in fact occur already before the thermocycling is processed. All such spectra could be simulated consistently by the respective equivalent circuit model displayed in Fig. 1 by low standard deviation (typically $\chi^2 < 0.001$, $\sum W_i X_i^2 < 0.025$). This allows interpreting the data systematically.

Particulate additives affect barrier

Fig. 3 displays the shifting of the parameters R_{por} and C_{dl} obtained from EIS performed in intact areas between 0 h and 178 h of TEL. Especially the G50 and G50 c containing primers exhibit larger barrier properties than the Standard formulation initially. After 178 h, however, the barrier properties of the Standard formulation exceed the barrier properties of all other primer formulations except for Rew AC 28. The finding that especially the formulations, which contain capsules (“c”) or nano containers show lower barrier properties than the Standard can easily be attributed to a disturbance of the matrix continuance caused by the introduction of the mentioned particulate additives.

Specifically varying effect on delamination resistance

Apparently, the introduction of the particular additives did also affect the adhesion in the substrate/coating interface. The increase of C_{dl} is by far largest for the primer G50 c. Such large C_{dl} values as observed for G50 c after TEL (around 10^{-4} Fcm^{-2}) can only be explained by the presence of blisters¹³. In fact, the impact of TEL should induce a build-up of internal stress, which easily could cause collapse of fragile capsules resulting in the spread of the liquid G50 inhibitor. Thus, such “empty” G50 capsules should behave like blisters and cause such extraordinary large C_{dl} values. In contrast, for Rew AC 28 c such an effect is not observed, which may be explained by the smaller dimension of these capsules and their better persistence under impact of TEL. All other systems, however, show improved delamination resistance in comparison to the standard. Especially the nanocontainers provide considerable adhesion persistence indicated by low increases of C_{dl} induced by TEL.

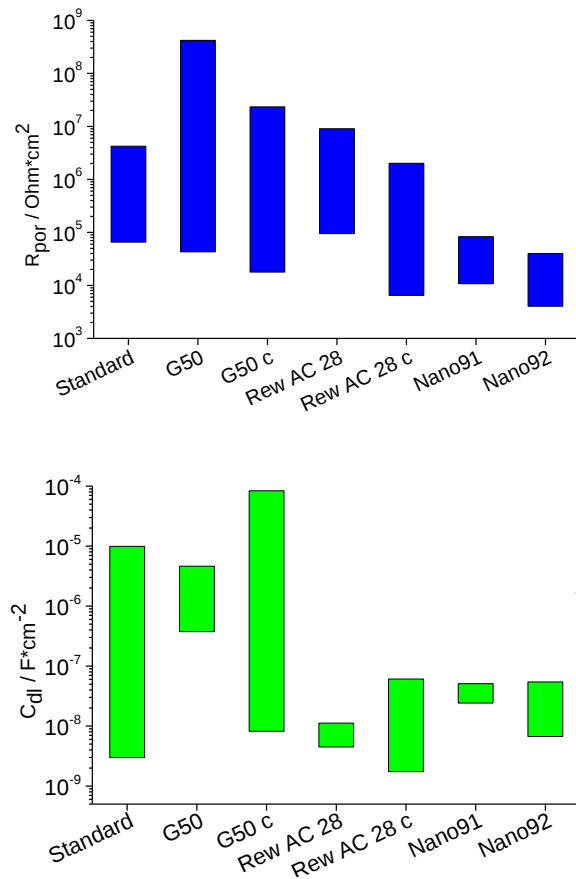


Figure 3: Shifts of R_{por} and C_{dl} obtained from EIS performed in intact areas between 0 h and 178 h of TEL; the red arrows figure the variation in time.

Further results

Further results obtained from primer areas with a defect suggest, that the presence of fragile capsules containing corrosion inhibitor could contribute to decelerate the corrosion processes in case of an inflicted injury. From this, one might expect that primer systems, which contain nanocontainers in the bottom and inhibitor containing capsules in the top volume could be promising candidates for powerful “self-healing” anticorrosive systems. In fact, very recent results obtained from such systems confirm this assumption impressively.

Results at a glance

- EIS in combination with a thermocyclic electrolytic loading (TEL) can be regarded as a powerful tool for a quantitative short-time evaluation of anticorrosive primers furnished with ion-exchanging nanocontainers and/or inhibitor containing micro- and nanocapsules.
- Continuously consistent equivalent circuit models were identified, which allow differentiated interpretations of the EIS data obtained from the intact and injured primer samples exposed to TEL.
- These data strongly suggest that two-layered primer systems (bottom: nanocontainers, top: nano-/microcapsules) could be promising candidates for powerful “self-healing” anticorrosive systems.

Acknowledgements

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