Project number: 263262 **Project acronym:** STEELCOAT

Project title: Development of Green Anticorrosion Coatings for Steel Protection based on Environmentally Friendly Nanoparticles and Conducting Polymers

Work package:	Lead beneficiary:	Participating organisation:
WP5: Enhanced fundamental understanding of corrosion protection systems	Trento	KTH

Tasks covered:

5.1 Molecular and microscopic understanding of the active corrosion protection mechanism	✔
5.2 Characterization of corrosion protection properties of the coating applied on the metal substrate using advanced electrochemical techniques	✔

Deliverable number and name	Delivery date (month)	Dissemination level	
D5.1 Understanding the role of conducting polymers	18	PU	✔

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1.   Summary

The role of conductive polymers in general, and Polyaniline (PANI) in particular, for the corrosion protection of steel is still a controversial issue, despite the large amount of literature available on this topic.

However a careful analysis of the experimental work available and a critical review of the results lead to the conclusion that some possible corrosion protection mechanisms can be excluded, some others are not dominating processes and finally only anodic protection action with following steel passivation can explain the corrosion protection action of PANI on steel.

A detailed description of the electrochemical action of PANI on steel is proposed.

The experimental results obtained with samples provided in the frame of the STEELCOAT project are a preliminary confirmation of this indication.

This is a fundamental results and starting point for considering the possible synergistic effect of PANI and nano-ceria in corrosion protection, as next step of the project.

2.   Background.

In the late 70's, the discovery that Polyacetylene (PAc) could transport electrical charge along its chains by Heeger, Shirakawa and MacDiarmid, for which they were awarded the Nobel Prize in Chemistry [1-3], gave scientists a new class of materials to be explored. Denominated nowadays as Intrinsic Conductive Polymers (ICP), these materials can combine the electronic and optical properties of a semiconductors and metals with the mechanical properties and ease of processing associated with polymers. After PAc other ICPs have arisen, Polyaniline (PANi), Polypyrrole (PPy) and Polythiophene (PT) for instance, with a wide possibility of applications, such as mechanical sensors, electromagnetic shielding (EMI), pH sensors and corrosion protection.

After the study reported by DeBerry, who demonstrated that electrodeposited Polyaniline film, was able to reduce the corrosion rate of the 400 series stainless steel in sulfuric acid solution by forming an oxide layer between the metal and PANi [4], ICP gained attention as promising candidates for anticorrosive applications.

Several literature review about the use of ICP as corrosion protection materials are available. As an example Tallman et al. [5] reviewed a number of publications with the use of Polyaniline (PANi) and Polypyrrole (PPy) as intrinsic conductive polymers for iron, steel and stainless steel corrosion protection. On the whole, there are clear evidences that ICP provide corrosion protection of steel, besides this, several operating corrosion protection mechanisms have been proposed, such as barrier protection, corrosion inhibition, anodic protection (ennobling effect) and others. However, due to several possible oxidation states of the polymer and different experimental parameters in the study of corrosion protection, it is difficult to achieve the complete understanding about the mechanisms. Every special situation should to be analyzed separately.

3.   Aim and Objective

The aim of this document is to describe the role of PANI as conductive polymer in controlling the corrosion rate of steel in different environments, focusing the protective mechanism.

This result will be used, together with similar consideration about the role of nano-ceria in corrosion protection of steel, to elucidate the corrosion protection action of the composite coating including PANI and nano-ceria.

4.   Corrosion mechanism of organic coatings with PANI

4.1.   Approach

The clarification of the influence of PANi on the corrosion protection mechanism of organic coatings will proceed with two different lines. Firstly, by carefully analyzing the literature in a critical way, a probable mechanism of corrosion protection will be identified. Following this hypothesis, some experimental results obtained in the SteelCoat project will be analyzed to verify the proposed mechanism for the studied coating materials.

4.2.   ICP and corrosion protection

Different kinds of Intrinsic Conductive Polymers (ICP) have been used for corrosion protection of metal substrates. Polyaniline (PANI), Polypyrrole, Polythiophene are the more frequently used polymer materials, while carbon steel, stainless steel, aluminum, magnesium, zinc and copper are possible substrates. The general problem is that every combination of polymer and substrate has a different corrosion protection mechanism.

In the SteelCoat project, the substrate is chosen as mild steel while the ICP used for developing new "green" coatings is Polyaniline (PANI). Even with this restriction, the mechanism of corrosion protection of steel by PANI is still a controversial issue.

The problem arises due to the fact that many studies have been carried out using a wide variation of experimental procedures, causing difficulties in trying to compare the results. In particular, the surface preparation, the coating deposition method, the corrosion environment and the test method, can be very different from one study to another study.

However, an effort has been made in this study to classify the corrosion protection mechanism. The possible mechanisms of corrosion protection of PANI on steel are essentially of three types:

- Barrier properties (involving a *physical action*)
- Corrosion inhibition (involving a *chemical action*)
- Anodic protection (involving an *electrochemical action*)

4.2.1.   Barrier properties

Organic coatings in general (including coatings with ICP as PANI) can protect metal substrates against corrosion following a general mechanism described in figure 1.

It is well established that most of the organic coatings with barrier effect permits the oxygen and water diffusion in quantities higher than the necessary amount for the corrosion rate measured on bare metal. It means that the reduction of oxygen and water availability at the metal surface, due to the presence of the coatings, is not sufficient to reduce remarkably the corrosion rate. It follows that both the anodic and the cathodic reactions can start, as shown in figure 1. However the cathodic and anodic reactions are only half of the total corrosion reaction and a balance of the two electrochemical reactions is necessary. In particular it is

necessary to have locally an electrical equilibrium balancing the electrical charge: electron and ions. In general it is not a problem for electrons to move, through the conductive metal, from one site to another, but several mobility problems can arise for ion diffusion. In the cathodic area there is an anion production (negative charge), and in the anodic site there is a cation production (positive charge). If the coating has a good adhesion (no lack of continuity at the metal-coating interface), the only possibility for balancing the charge is to move through the coating (from inside to outside or the opposite, or the lateral diffusion inside the coating, which is generally less probable because it involves a longer path) and this process is strongly hindered by the organic coatings. In this way the barrier organic coatings can reduce the corrosion rate of the metal substrate.
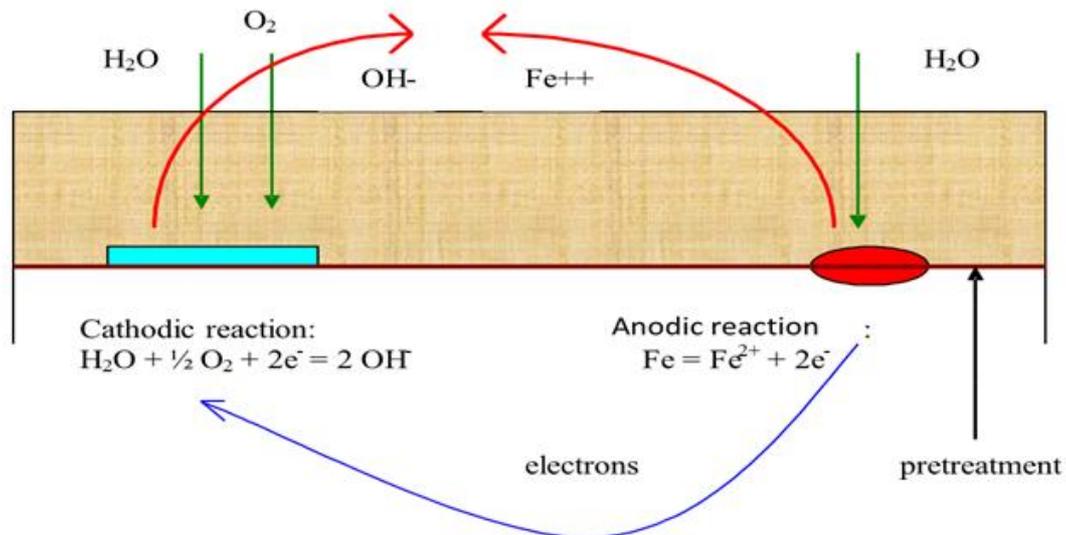

Figure 1: Cartoon of the barrier corrosion protection mechanism.

Applying this mechanism to PANI containing coatings, we can note several problems. Water permeability is, in general, not different from typical values of commercial organic coatings (as epoxy coatings); it means about 3-5% w/w of water uptake maximum. Moreover, oxygen permeability is not very different from traditional organic coatings. Actually, evaluation of oxygen transport is complicated by the problem that the oxygen diffusion rate is dependent on the oxidation state of PANI. The same is true for ions diffusion (the dominating barrier effect for normal coatings). The ion diffusion process is not reduced in PANI, actually it could be higher when PANI is in the salty state. These facts suggest that the barrier effect is not the predominant corrosion protection mechanism for polymer coatings with PANI. A further clear evidence to support this statement is the lower corrosion rate of coatings with PANI when scratched (defective coatings) in comparison with scratched traditional organic coatings. Even when the barrier effect is vanished, the presence of PANI can modify the corrosion process.

In conclusion, **barrier effect cannot be the dominant corrosion protection mechanism**.

4.2.2. Corrosion inhibition

The presence of organic compounds close to the metal surface in principle could affect both anodic and cathodic corrosion reactions. In this case the organic compound is called inhibitor.

Organic inhibitors are usually designated to act as film forming, protect the metal by forming hydrophobic film on the metal surface. In this way the corrosion rate is influenced. Their effectiveness depends on the chemical composition, their molecular structures, and their affinities to the metal surface. Because film formation is an adsorption process, the temperature and pressure in the system are the important factors.

Adsorption of organic inhibitors on a metal surface is strongly influenced by the ionic charge of inhibitors and the charge of the surface. The strength of adsorption bond is the dominant factor for soluble organic inhibitors. In this way organic inhibitors build up a protective film of adsorbed molecules on the metal surface, which provides a barrier against the dissolution of the metal in the electrolyte Figure 2). Because the coverage of metal surface is proportional to the inhibitors' concentration, the concentration of inhibitor in the medium is critical. For any specific inhibitor in any given medium there is an optimal concentration.
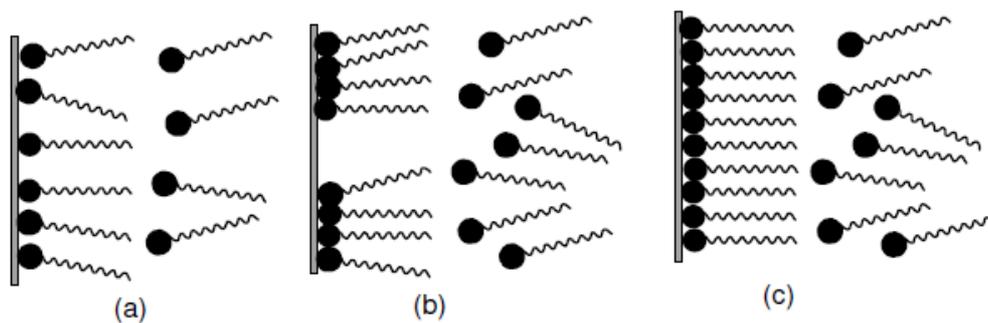

Figure 2: Different adsorption steps of an inhibitor on metal surfaces.

The inhibition effect of an organic compound is also significantly influenced by the mobility of the inhibitors, since it has to migrate to and adsorb on the metal surface. Monomeric aniline (before polymerization) has been proven to act as an organic inhibitor in several environments (acid environments and chlorides) on different substrates. The mechanism is a strong adsorption of aniline forming a hydrophobic surface layer, as in general for inhibitors. However, this behavior is not expected for PANI, because after polymerization the mobility of the molecular chains is strongly reduced. The only important consequence of polymerization, is that the adsorption could promote, in the case of PANI a good adhesion with the steel surface, influencing the long time durability of the coatings.

However, in conclusion, **any direct corrosion inhibition effect (chemical action) of PANI itself should be excluded**. The only possible inhibition effect is indirect and it is related to the released counter ions (e.g., phosphorous species) in doped PANI, which will be further discussed.

4.2.3. Anodic protection

Anodic protection is a corrosion protection strategy based on an anodic polarization by controlling the potential in a zone where the metal tends to be passive. In other words it is

an approach favoring passivity and stabilization. For this reason it can be used only for materials having passivation possibility. Iron (steel) can passivate, as shown in figure 3.
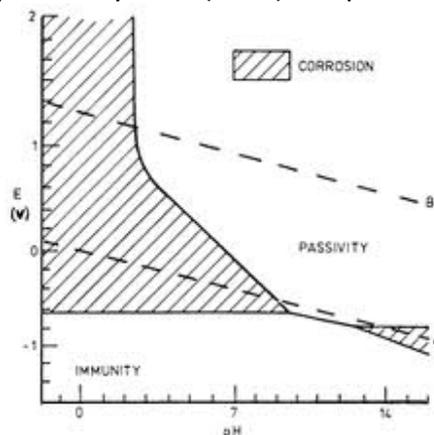

Figure 3. Simplified Pourbaix diagram (E-pH) for steel (iron), showing passivity areas.

From figure 3 it can be deduced that alkaline pH is necessary to promote passivation. This aspect must be considered carefully because it can be in conflict with PANI's pH stability. In other terms, to have an anodic protection action it is necessary to have a system in which both the passivation layer and the ICP based coating (PANI) are stable.

The general anodic protection mechanism of ICP is the following.

$$1/n\ M + 1/m\ CP^{m+} + y/n\ H_2O \quad \Longrightarrow \quad 1/n\ M(OH)_y^{(n-y)+} + 1/m\ CP^0 + y/n\ H^+ \qquad \text{(eq. 1)}$$
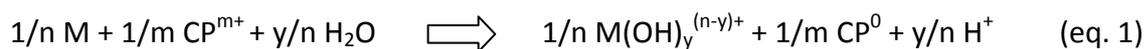
where M is the metal (Steel) and CP any electroactive conductive polymer

$$m/4\ O_2 + m/2\ H_2O + CP^0 \quad \Longrightarrow \quad CP^{m+} + mOH^- \qquad \text{(eq. 2)}$$

Many authors have tried to prove this mechanism by using different experimental approaches: open circuit potential measurements, metal surface analysis to identify the oxide layer, and surface analysis of CP to identify its oxidation state.

Many authors reported an increase of the OCP (moving to anodic direction) of steel coated with CP in comparison with bare steel (ennobling). Considering that the passivation potential of steel is expected to be between 0.5 and 1 V SCE, the observed ennobling can be an indication of passivation. However, it is important to keep in mind that the passivation potential is in general dependent on the local environment (pH, oxygen concentration, chlorides, etc.) normally unknown close to the corroding area.
Ennobling is a necessary condition for anodic protection, but it is not sufficient, since the OCP of coated steel is often increased also for barrier coatings because of the different corrosion conditions (concentration polarization and ohmic drop).

In addition, it has been proven that PANI can modify the steel surface conditions (electrochemical studies of bare steel and bare steel obtained after removal of the PANI layer exposed to the electrolyte). These results have been obtained using different techniques, as impedance measurements (charge transfer resistance), visual observation (change of color), XPS analysis (formation of Fe_2O_3, Fe_3O_4), mass spectroscopy, etc. It is important to remember that surface conditions depend on the PANI form, EB (emeraldine base) or ES (emeraldine salt).

A complete scheme describing the electrochemical action causing anodic protection, from Wesseling [6], is shown in figure 4.
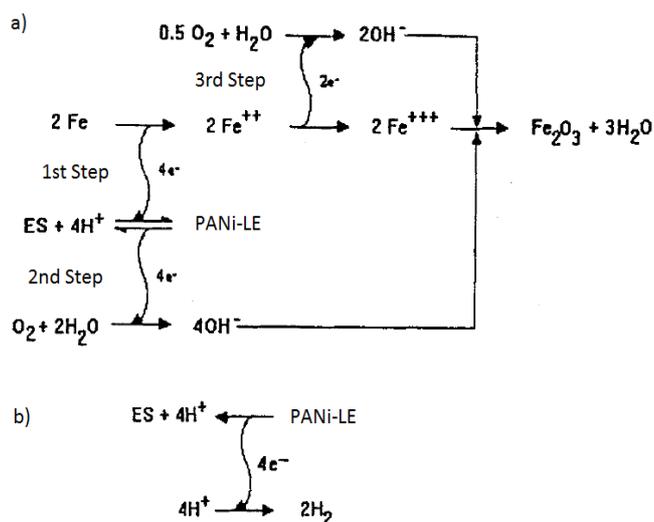

Figure 4: Wesseling scheme of anodic protection of PANI [6].

The main complication in understanding the anodic protection mechanism of PANI, is the fact that there are the different possible equilibrium states of PANI, as shown in figure 5.
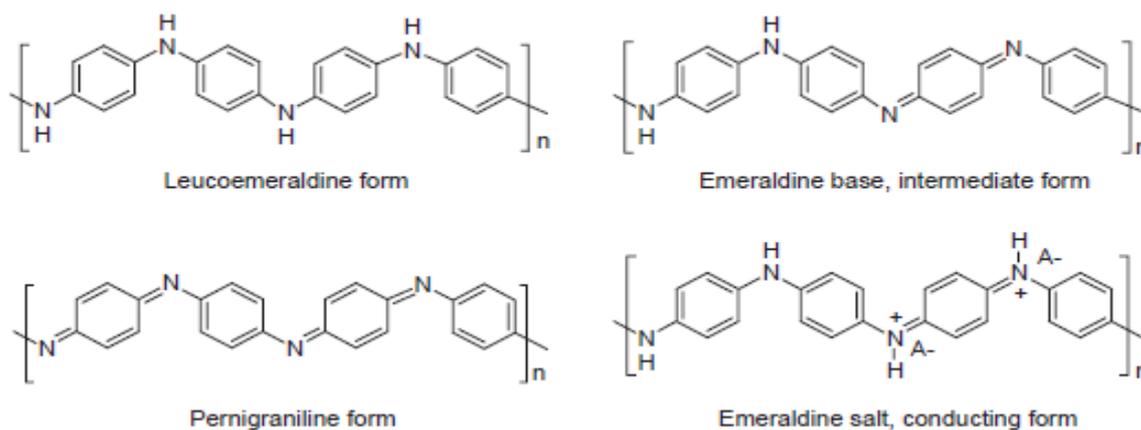

Figure 5: Possible PANI state Leucoemeraldine (LE), Emeraldine base (EB), Pernigraniline (PG) and the salty state Emeraldine salt (ES).

The oxidation state increases from LE (completely reduced form) to EB, to PG (fully oxidized). However not all the possible PANI states are conductive, actually PANI ES is the only really conductive form. In the salty form, anions are necessary for balancing the charge of salts.

Considering the salty and base states of Emeraldine, the equilibrium reactions of PANI includes not only redox reactions (changing LE, EB, PG), but also proton exchange reactions, passing from EB to ES (and the opposite) as shown in figure 6.
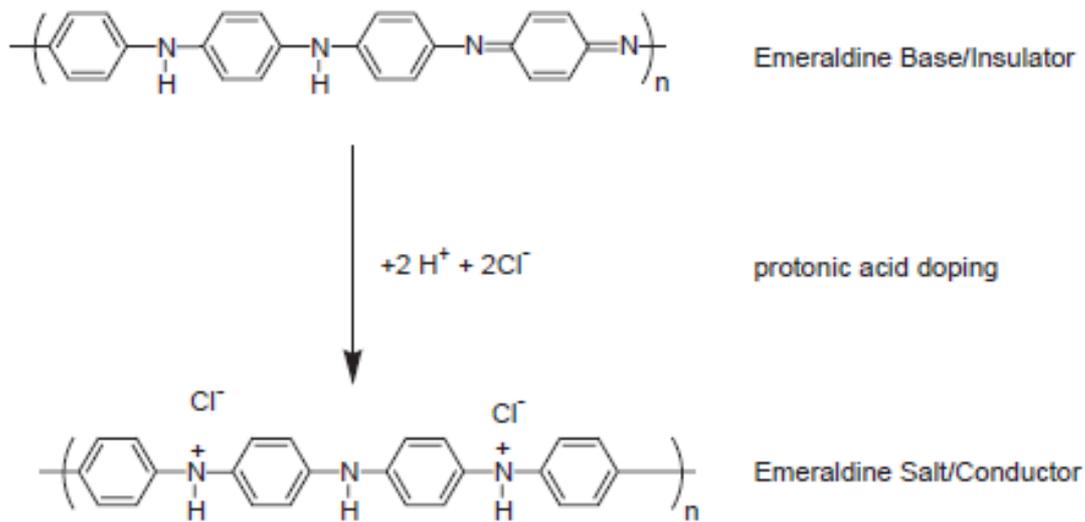
Figure 6: proton exchange reactions for Emeraldine PANI.

From figure 6 it is clear that anions are necessary (of course not only Cl-, but any other anion) for balancing the charge of salts. Therefore the ES is often called doped PANI (while EB undoped PANI).

XPS analysis proved the reduction of PANI from EB (or ES) to LE (with oxidation of steel as the coupled oxidation reaction). If the substrate is inert, this change is not measured.
Based on all these results and considerations, a conclusion can be drawn: **anodic protection is a possible corrosion protection mechanism for PANi on steel**, under specific restrictive conditions, i.e., the presence of PANI in the ES form and the presence of balancing anions.

A further corrosion protection mechanism has been proposed by Schauer [7] and it is depicted in figure 7.
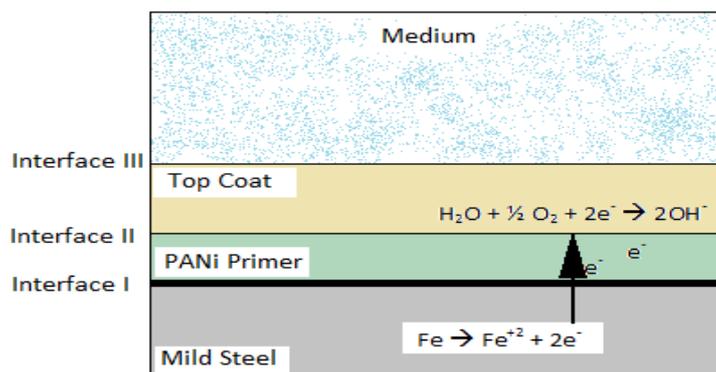

Figure 7: Schauer PANI protection mechanism [7].

The starting idea is that, being conductive and electroactive, PANI can shift the cathodic reaction interface from the metal surface to the PANI surface.
In this way the cathodic reaction can be the PANI reduction, followed by re-oxidation. PANI and iron ions form complex, able to reduce the kinetics of oxygen reduction.

With this mechanism there is a prevention of high pH formation (due to the cathodic reaction) at the metal surface. This prevention could stabilize the surface oxides and reduce cathodic disbonding. However, there are several problems for this mechanism. First of all, on one hand, high pH could promote cathodic disbanding; on the other hand, high pH could also promote passivation of the metal. Moreover, Emeraldine state is quickly reduced to LE, which is not conductive, and therefore the PANI layer cannot support anymore the cathodic reaction at the polymer surface. In other words, this mechanism could be effective only at the beginning, and should stop after a while. Another difficulty is to extend the mechanism to EB (undoped PANI), which is not conductive. Finally a problem is still present for the complete coating systems with top coat: the role and properties of the top coat.

In conclusion, **at the moment there are not enough experimental results supporting the shift of the cathodic interface as a relevant corrosion protection mechanism for PANi on stee**l.

A further critical issue in the PANI corrosion protection mechanisms is the role of counter ions. It has already been established that we need the ES form (salty form) to have conductive PANI and in this case we need negative counter ions. The release of anions during redox processes could affect the corrosion rate, both promoting corrosion if the ions are aggressive (as chlorides) or reducing the corrosion rate by complexation with Fe ions and causing a precipitation of insoluble salts (pseudo-passivation). This possible mechanism is very important in the case of contemporary presence of other ions (as in the case of nano-ceria) because of the formation of complex insoluble salts.

Moreover some released ions could act as inorganic corrosion inhibitors (as nitrates, sulfates, etc.)

The release of anions and the interaction between anions and iron or cerium ions must be carefully considered for the future in studying the synergistic effect of contemporary presence of PANI and nano-ceria.

5.   Preliminary results of STELLCOAT samples with PANI

5.1   Electrochemical measurements

The previously proposed mechanism must be compared with the experimental results obtained from STEELCOAT samples in order to validate the anodic protection mechanism.

In order to validate the mechanism we used a model system, consisting of a solventborne Alkyd (SYNOLAC) with and without 1% of PANI. We have previously determined that lower PANI content does not influence the coating behavior, even if 1% is still a very low amount.

The impedance measurement results (EIS spectra) obtained during the first 5 days of immersion in the testing solution (0.3% Na_2SO_4) are presented in figure 8 for the coating including PANI, and in figure 9 for the equivalent coating without PANI on carbon steel as the control system. In both cases, the coating thickness was around 30 µm.

The low frequency impedance is an indication of the protective properties of the coating, and the spectra in figure 8 show an increases of this value, starting from about $2 \cdot 10^8$ ohm·cm^2 at the beginning and progressively reaching $2 \cdot 10^9$ ohm·cm^2 after 120 hours of immersion (an increases of a factor 10!).

This behavior is not observed for the equivalent coating without PANI (figure 9), where all the low frequencies values are lower than the initial one, and indicate an opposite trend.

Following the previously described mechanism, the protective behavior could be explained by an ennobling of the substrate. It means that the free corrosion potential of steel should increases during exposure.

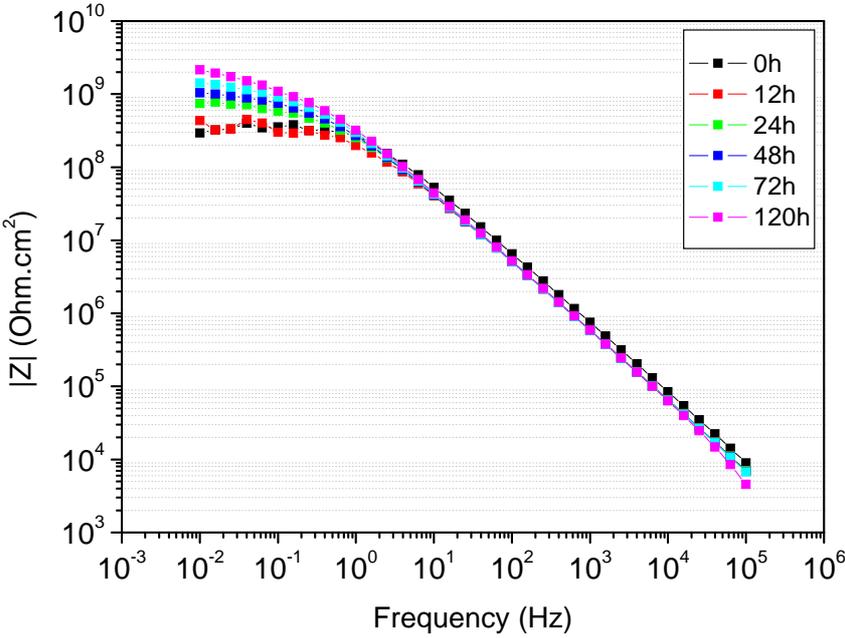The free corrosion potential (OCP) of the coating with PANI is shown in figure 10.

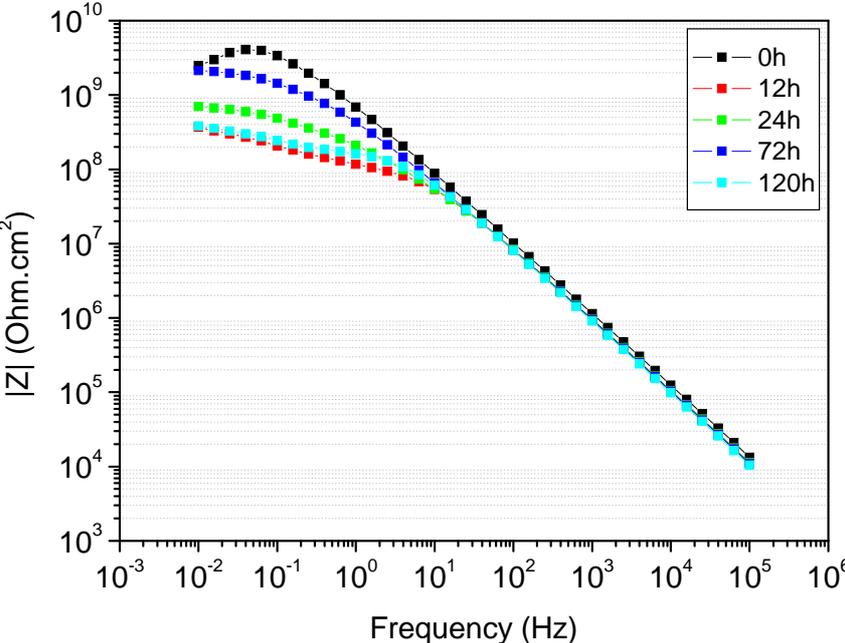Figure 8: Solventborne (SYNOLAC) Alkyd with 1.0 wt% PANI (Enthone-CP-W1)

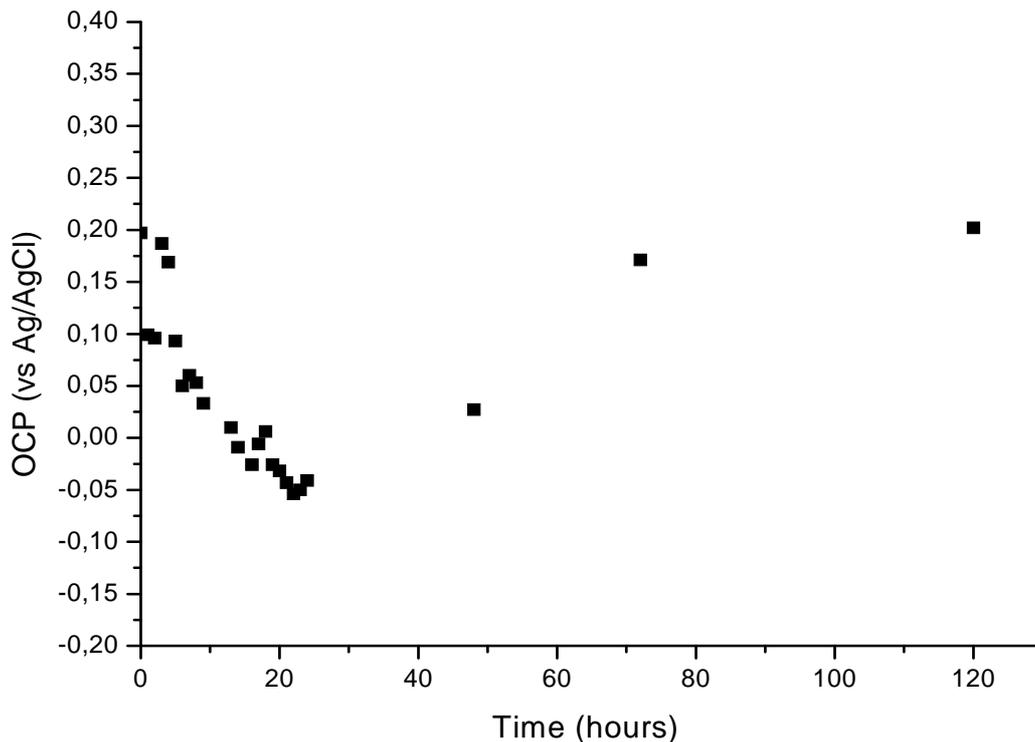Figure 9: Solventborne (SYNOLAC) Alkyd clear coat (ARKEMA.F6.S1)

Figure 10: OCP evolution of Solventborne (SYNOLAC) Alkyd 1.0 wt% PANI (Enthone-CP-W1)

In figure 10 it is possible to distinguish clearly 2 parts. During the first day of immersion there is an initial drop of the OCP value, and an actual measurement of the lowest free corrosion potential was around -0.05 mV vs Ag/AgCl. This is because the water uptake progressively permits the contact of the electrolyte with the metal substrate. After this initial immersion period, an increase of the OCP value is visible, reaching a nobler value around +0.200 mV vs Ag/AgCl. This is a clear indication of the anodic ennoblement by the PANI containing coating.

5.2   In-situ AFM measurements

The samples used for in-situ AFM study (performed at the Royal Institute of Technology, KTH, Sweden) are from the same batch of production (supplied by the same company, Arkema, France) as those for the EIS measurements (obtained at the University of Trento, Italy) so the AFM and EIS results can be compared directly, which enable correlation between the micro- and nano-structure of the coating as well as their change occurring in water and corrosive solution and the corrosion protection performance of the coating.
The in-situ AFM images show that, the solventborne alkyd coating on carbon steel (reference sample) has a very smooth surface, with a roughness of less than 10 nm on an area of 50 μm size. The coating is very stable during exposure in 3% NaCl solution. Examples of the AFM images are shown in Figure 11.
For the solventborne alkyd coating with 0.5% PANI, the AFM images reveal the presence of submicron and micron sized PANI particles in the coating. The coating is quite uniform although the roughness increased to several tens of nanometers on an area of 80 μm size. This coating is also very stable during the exposure in 3% NaCl solution. In fact, it was observed that the depth of a small shallow pinhole decreased slightly during the exposure.
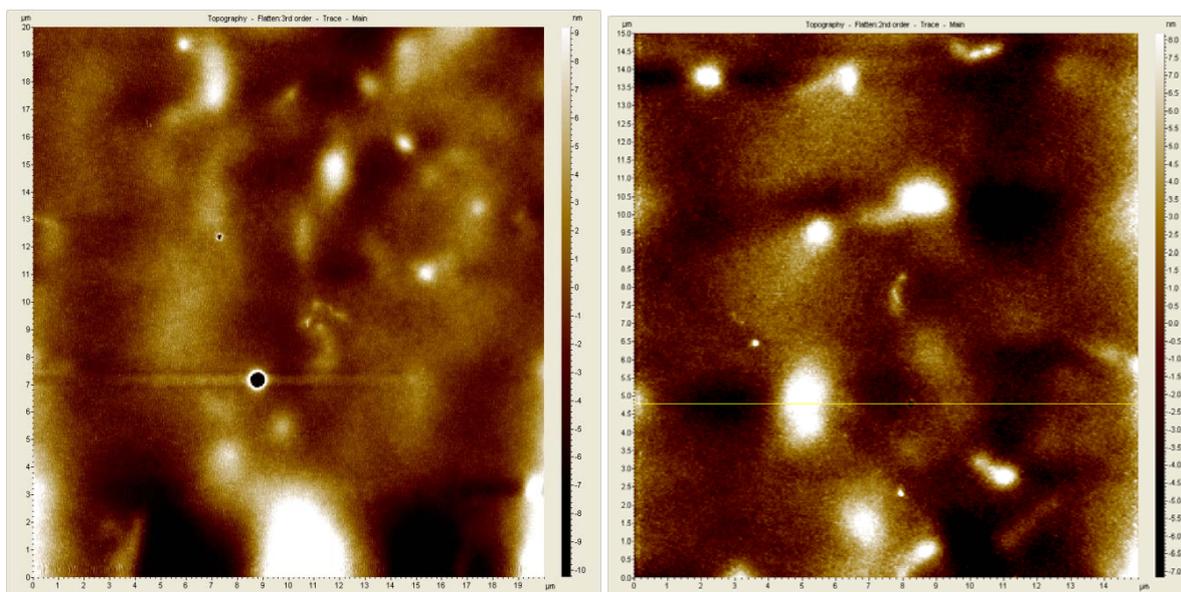
Figure 11. AFM images for the solventborne alkyd coating with 0.5 % PANI, obtained in air (left, 20x20 μm), and after 18 hours' exposure in 3% NaCl solution (right, 15x15 μm).

For the coating containing 1% PANI, the roughness is further increased to over 100 nm on an area of 50 μm in size. The in-situ AFM images reveal submicron and micron sized PANI particles dispersed in the coating, the presence of larger particles (likely PANI aggregates) of a few μm in size, and also μm-sized pinholes with depth of ca. 0.5 μm. During long term exposure in 3% NaCl solution, some large particles (aggregates) dissolve and disappear, which may lead to open-up of pinholes in the coating, however, no fast corrosion at the pinhole sites was observed. Figure 12 show examples of AFM images obtained during exposure in 3 % NaCl solution. The results suggest that the solution can penetrate though the coating, and react with the coating components. Nevertheless, the composite coating in general remains to be quite stable in the solution.
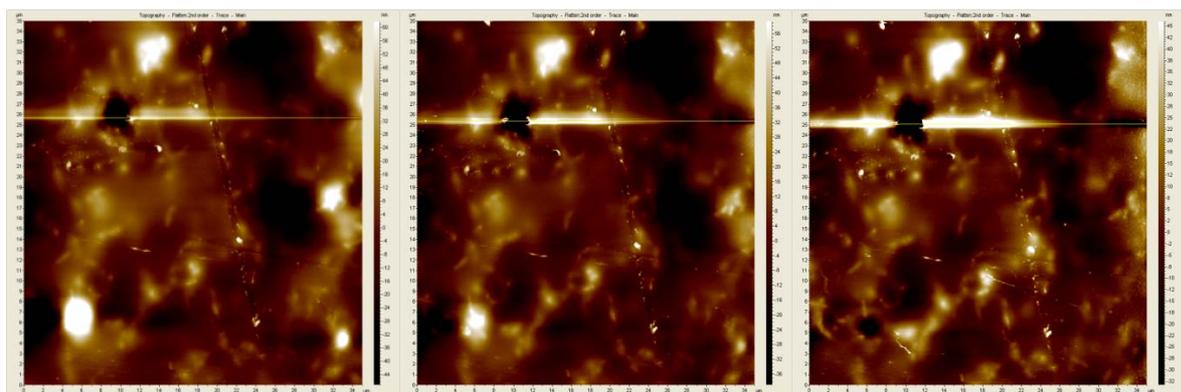

Figure 12. In-situ AFM images obtained for the solventborne alkyd coating with 1 % PANI, obtained after 10 hours (left), 15 hours (middle) and 21 hours (right) exposure in 3% NaCl solution (scan area: 35x35 μm).

Further in-situ AFM study should be carried out to investigate the action of PANI in the corrosion protection mechanism, in particular the control of corrosion in defects of the coating.

In summary, it is possible to conclude that the experimental results obtained with a model coating with PANI produced for the STELLCOAT project are in agreement with the proposed mechanism based on anodic protection and passivation of steel, even though further investigations are necessary to better elucidate the PANI action.

6.   Conclusion

The possible corrosion mitigation action of organic coatings including conductive polymers (PANI) on mild steel is due to an anodic protection mechanism inducing a passivation action on the steel surface.
This mechanism has been determined by analyzing the scientific literature and validating the hypothesis using model materials.

7.   Suggestions for Further Work

The future work in this direction will include verification of the proposed mechanism using all the polymeric matrixes chosen for making composite coatings in the project, including the validation of the mechanism also using surface analysis techniques (characterization of the passivation layer).
Further in-situ AFM study will be carried out to investigation the samples with defects, both natural pinholes and artificial defects (scratches) in the composite coatings, for a better understanding of the anodic protection action and the postulated self-repairing property.
The final step will be the study of the synergistic effect of the presence of PANI and other passivation inhibitors (as cerium oxides).

8.   References

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