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Hybrid Conducting Nanocomposites Coatings for Corrosion Protection

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1. Introduction

In the last years, conducting polymers (CPs) have arisen wide interest as electrode materials and they have reached a state of development that allow their use in various applications such as sensors, membranes for the separation of gas mixtures, corrosion protection, and so forth.

Recently, several studies in the fields of new materials have introduced the possibility to use CPs as suitable matrices to disperse nanostructured elements, such as nanoparticles or nanotubes. It has been shown that the introduction of nanostructures into a polymer matrix can improve the electrical conductivity and the mechanical properties of the original polymer matrix. The combination of conductive polymers with conductive particles (better if carbon nanostructures), producing a new class of materials known as *hybrid conducting nanocomposites*, has already shown some synergistic properties, with a variety of applications in the energy field.

The most interesting property of conducting polymers is their high (almost metallic) conductivity, which can be changed by simple oxidation or reduction, and also by bringing the material into contact with different compounds. Conducting polymers usually have a good corrosion stability when in contact with solution or/and in the dry state. For instance, polyaniline is stable in its leucoemeraldine and emeraldine states, even in 10 mol/l acid solutions. Furthermore, CPs can be deposited from a liquid phase, even in complex topographies. Redox processes combined with the intercalation of anions or cations can therefore be used to switch the chemical, optical, electrical, magnetic, mechanic and ionic properties of such polymers. These properties can be modified by varying the anion size and preparation techniques or by including other chemical species. As regards the preparation, CPs can be synthesised chemically or through electrochemical polymerisation. The electrochemical method is used more often because it is environmental friendly and presents several advantages. In fact polymeri-

sation media can be used repeatedly, and polymerisation rate can be controlled by varying potential values.

Among the CPs, polyaniline (PANI) has been one of the most studied because of its facile synthesis, electrical conductivity, low cost and environmental stability. It is characterised by different domains of conductivities, which refer to different oxidation states of the polymer. Although the synthesis of a PANI coating is direct and controllable, particular care has to be taken on choosing the proper polymerisation solution and electrochemical parameters, which affect the growth and properties of PANI. Moreover, PANI has good anticorrosion properties, depending on oxidation states, but the mechanism underlying the protective behaviour of PANI is still not completely clear. Most studies agree that PANI films have an active role in keeping the passivity of the metal substrate in acid solution, whereas others suggest the non conductive state of PANI performs better than that of a conductive one.

Recently CPs have been also used as the matrix of hybrid conducting nanocomposites containing carbon nanotubes (CNTs). Many efforts have been made to optimise the preparation of CPs-CNTs composites and different interaction mechanisms have been hypothesised and discussed in literature. Recent studies have shown that PANI could be used to functionalise and solubilise CNTs via formation of donor-acceptor complexes. Moreover, the possible presence of functional groups on the CNTs' surface can favour a chemical interaction of both the monomer and the polymer during its generation. Whatever interaction theory is adopted, the combination of PANI and CNTs has surely favorable effects on properties, also on corrosion protection.

This contribution will be divided in four sections. In the first part, conjugated polymers and their conducting mechanism will be treated. Then, a review of conjugated polymers applied to corrosion protection will be reported. Moreover, the proposed anticorrosion mechanisms occurring in conducting polymers and their composites will be reported by considering the most recent literature. In the third part, two methods used by the authors to obtain PANI-CNTs composite films will be described. The first method consists of an electropolymerisation process (EP) of ANI monomer during which the incorporation of CNTs in PANI matrix occurs. In the second method, PANI chains are treated to be able to encapsulate CNTs and so to make possible the formation of a nanocomposite film by Electrophoretic Deposition (EPD). Finally in the last part, the properties of the hybrid conducting nanocomposite coatings produced by both the methods, will be reported and discussed, also by comparing them with similar materials prepared by usual methods.

2. Conducting polymers: properties and synthesis mechanisms

Over the last twenty five years, the study and applications of conducting and electro-active conjugated polymers have reached a development state that enabled their use in various fields of technology, in form of electronic and optical devices, rechargeable batteries, sensors and biosensors, anticorrosion coatings, solar cells, etc. [1-3].

Conducting (or conjugated) polymers possess strong appeal as modifiers for electrode surfaces due to their electrical conductivity when doped by oxidant or reducing agents. This property is due to an extended π -electron system, over which electrons can be delocalised.

2.1. Conducting mechanism in conjugated polymers

A key requirement for a polymer to become electrically conducting is an overlap of molecular orbitals suitable to allow the formation of delocalised molecular wave functions. Besides this, molecular orbitals should be only partially filled, so that a free movement of electrons through the lattice is possible. In particular, a π -bonding, in which carbon orbitals are in the sp^2p_z configuration and the orbitals of the successive carbon atom along the backbone overlap, leads to electron delocalisation along the backbone of the polymer. The π -electron systems is composed by single and double bonds alternating along the polymer chain, and therefore responsible for electronic properties unusual for polymers, such as electrical conductivity, low ionisation potential, and high electron affinity. Thanks to their electronic configuration, CPs show a slight conductivity even in the neutral state but, when suitably doped, *i.e.* either partially oxidised or reduced, mobile charge carriers are generated and the electronic conductivity results to be strongly enhanced.

The conductivity of these materials can be explained by the “band theory”. According to this view, polymerisation causes the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) of each structural unit to form, altogether, π and π^* bands develop (Figure 1). In the terminology of solid-state physics these are the valence and conduction bands, respectively.

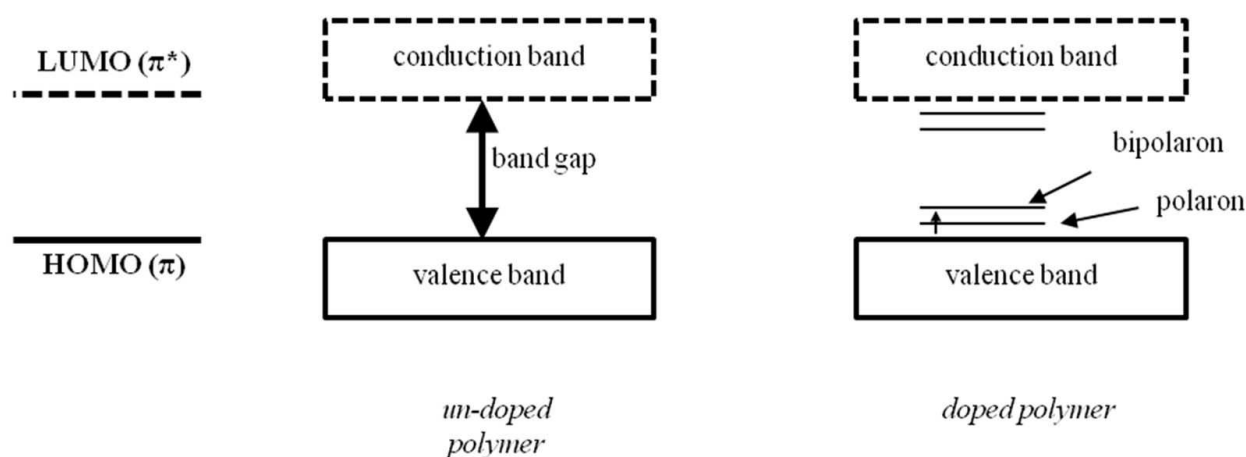


Figure 1. Schematic diagram of the evolution of the band structure of a CP.

In the neutral form, the valence band is filled and the conduction band is empty, the band-gap being typically 2-3 eV, which permits a low intrinsic conductivity. In simple terms, p-doping (by oxidation) can be viewed as the creation of ‘mobile’ holes in the valence band, and n-doping (by reduction) as the addition of ‘mobile’ electrons to the conduction band. However, these modification actually change the band structure, creating various midgap electronic states. By

p-doping, the removal of one electron from a segment of the chain creates a radical cation, i.e. a mobile polaron, generally delocalised over four to five structural units. The removal of a second electron creates a dication, so the combination of two polarons generates a mobile bipolaron. The formation of these charge carriers causes local distortions in the geometry of the chain and creates electronic states energetically located above the valence band. Similar valence and conduction bands arise when the polymer is n-doped [4-5].

All CPs, e.g. Polypyrrole, Polythiophene, Polyfuran, Polyaniline, Poly(phenylenevinylene), etc. (Figure 2) and most of their derivatives, undergo either p- and/or n-redox doping process during which the number of electrons associated with the polymer backbone changes. The electrical conductivity results from the existence of charge carriers (through doping) and their ability to move along the π -bonded "highway". Reversible doping of CPs, with associated control of the electrical conductivity over the full range from insulator to metal, can be accomplished either by chemical or electrochemical doping.

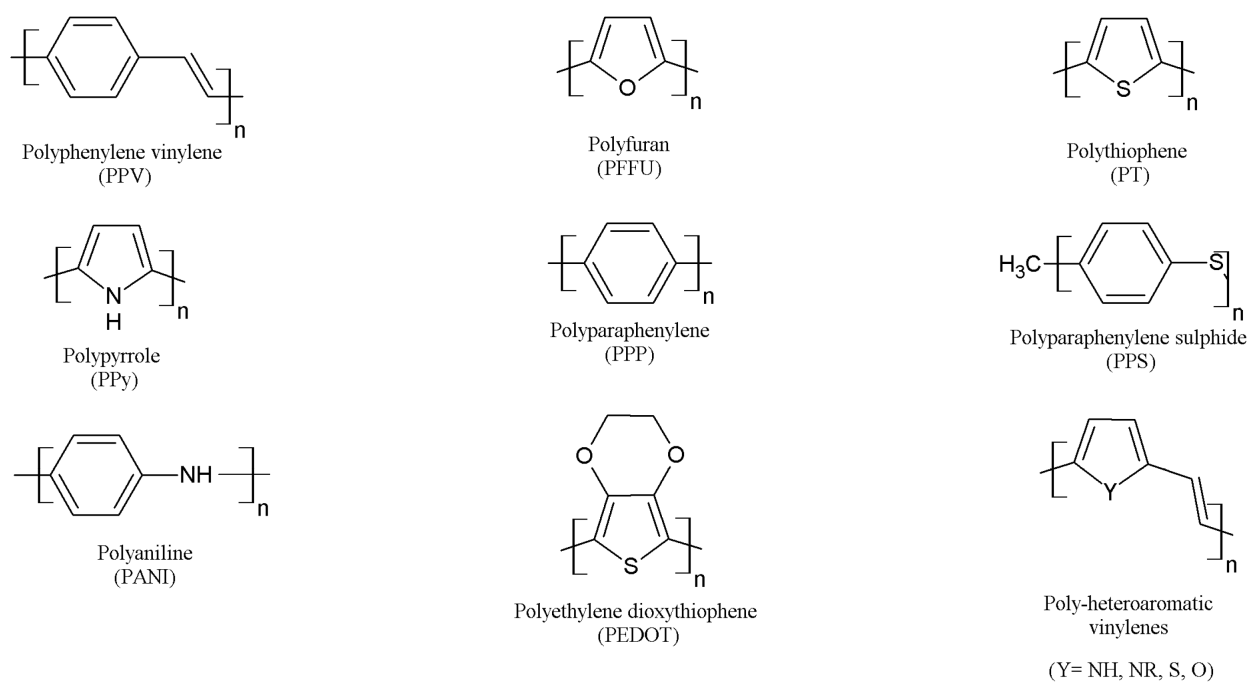


Figure 2. Chemical structures of some conjugated polymers.

2.2. Conducting polymers on electrodes – Electropolymerisation

To modify electrode surfaces, the CPs can be conveniently produced directly onto the electrode through an electrochemical polymerisation process. Various mechanisms have been proposed to explain the growth of CPs at electrodes. The first one was initially proposed by Geniès et al. [6] and finally proved by Andrieux et al. about 10 years later [7], consisting of an oxidative coupling mechanism.

Owing to the chemical diversity of compounds studied, a general scheme cannot be provided. However, it has been shown that the first step is the oxidation of monomers to form radical cations, electrochemical step (*E*). The second step is of chemical nature (*C*) and involves the coupling of two radicals to produce a di-hydro dimer dication. This leads to a neutral dimer by loss of two protons and concomitant re-aromatisation of the system, which constitutes the driving force of the whole chemical step. The oligomers produced are more easily oxidised than the starting monomer, so that they are converted into the relevant radicalic cationic form (*E*) and couple either with each other (*C*), or with monomer radical cations (*C*). Polymerisation proceeds then through successive electrochemical and chemical steps according to an $E(CE)_n$ mechanism, until the oligomer becomes insoluble in the electrolytic medium and precipitates onto the electrode surface (Figure 3) [8].

The chemical polymerisation proceeds similarly but it is commonly induced by a chemical oxidant, such as $FeCl_3$.

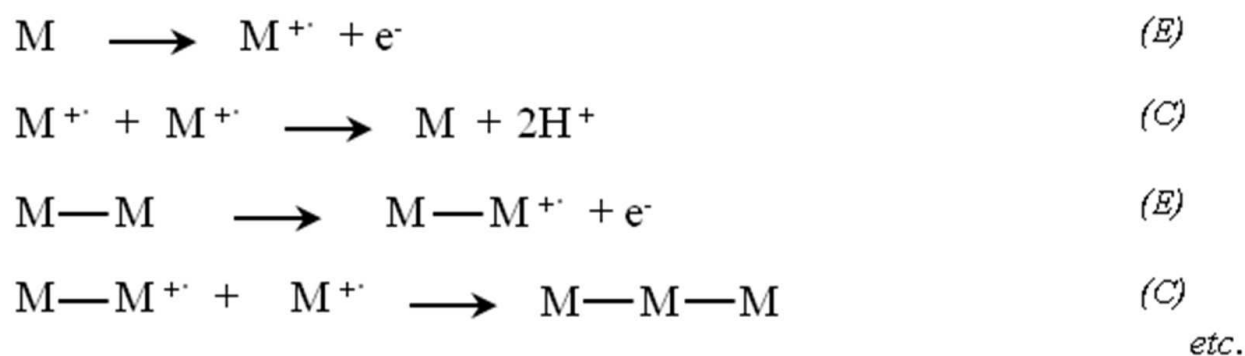


Figure 3. Mechanism of the first steps of the electrooxidation of electronically CPs.

Advantages of the electrochemical polymerisation over the chemical one, consists in reaction proceeding at room temperature and in controlling carefully the reaction rate. The electrode potential at which the monomer and the subsequently generated oligomers are oxidised is high enough to induce polymer p-doping. The coating progressively deposited becomes conductive and additional monomers in the solution are oxidised as well, so that the growth goes on. The thickness of the deposit can be more or less roughly controlled from few nanometers to more than 0.1 mm [9] by varying the experimental conditions, e.g. deposition potential and time, current intensity, number of cycles and potential scan rate, depending on technique chosen.

Cyclic voltammetry is most commonly used as a first approach to the study of the polymerisation process of a monomer, since it allows to 'follow' the different stages of the process. During cyclic voltammetry, the potential is varied linearly from a value at which no electrode reaction takes place to a value at which monomer oxidation and polymer deposition-doping occur. Reversing the scan to negative potentials, the discharge, i.e. the neutralisation of the p-doped polymer on the electrode, is observed in correspondence to a backward cathodic peak. In the following scans, the occurrence of an anodic/cathodic peak system at less anodic potentials than the monomer oxidation, growing in height scan by scan, can be observed. This

has to be ascribed to the charge/discharge of the polymer coating progressively formed on the electrode surface. Indeed, the occurrence of the polymerisation and film deposition is indicated by the increasing peak currents relative to oxidation/neutralisation of the polymer on subsequent cycles.

Electrodeposition of polymers by potential step techniques leads to a well-defined chronoamperometric response, showing a characteristic rising current-time transient in the initial stage, in most cases followed by a decay to an approximately constant value of the current. On a first approximation, charge collected at the potential at which monomer oxidation occurs is directly proportional to the amount of deposited polymer. At the same potential the polymer is oxidised and, therefore becomes conductive, allowing the current to flow and the deposit to grow.

Electrogeneration of CPs can be also performed through galvanostatic method. In this case, polymer formation and deposition occur by applying a constant current over a pre-fixed time length. The potential is concurrently modulated by an electrochemical apparatus. The coatings obtained through this technique are more homogeneous, especially when very low current densities are applied. Also in this case, the total charge spent in the electrochemical process is directly related to the amount of polymer chains deposited, i.e. with the thickness of the resulting film, reasonably hypothesising that the yield of polymer formation is constant over time.

2.3. Conducting polymers and their electrochemical doping — The polyanilines

The electrochemical doping of CPs was discovered by the MacDiarmid and co-workers in 1980, opening a new scientific direction [10]. The doping process definitely distinguishes CPs from all other types of polymers. Usually, an organic polymer, either an insulator or semiconductor, has low conductivity (10^{-10} - 10^{-5} S/cm). The doping process reversibly converts a polymer from insulator, or semiconductor, into a 'metallic' conducting regime ($\sim 1-10^4$ S/cm), with little or no degradation of the polymer backbone. Both the doping and the un-doping processes involve dopant counterions which stabilise the charge on the polymer backbone.

Among the CPs, Polyaniline (PANI) began to be investigated extensively some decades ago and attracted interest as a conducting material because of its low cost, straightforward synthesis that proceeds with high yield, environmental stability, and electrical conductivity. It is characterised by a relatively wide potential stability, a reproducible synthesis and a well-behaved electrochemistry showing different domains of conductivities, which refer to different oxidation states of the polymer.

The generalised formula of the base form of PANI consists of alternating reduced and oxidised repeat unit (Figure 4). The terms '*leucoemeraldine*', '*emeraldine*' and '*pernigraniline*' refer to the different oxidation states of the polymer where $y = 1, 0.5,$ and $0,$ respectively. PANI can be rendered conducting through two independent ways: oxidation of the leucoemeraldine base, or protonation of the emeraldine base. Depending on the oxidation state and the degree of protonation, PANI can be either an insulator or a conductor with different conductivity [11-12].

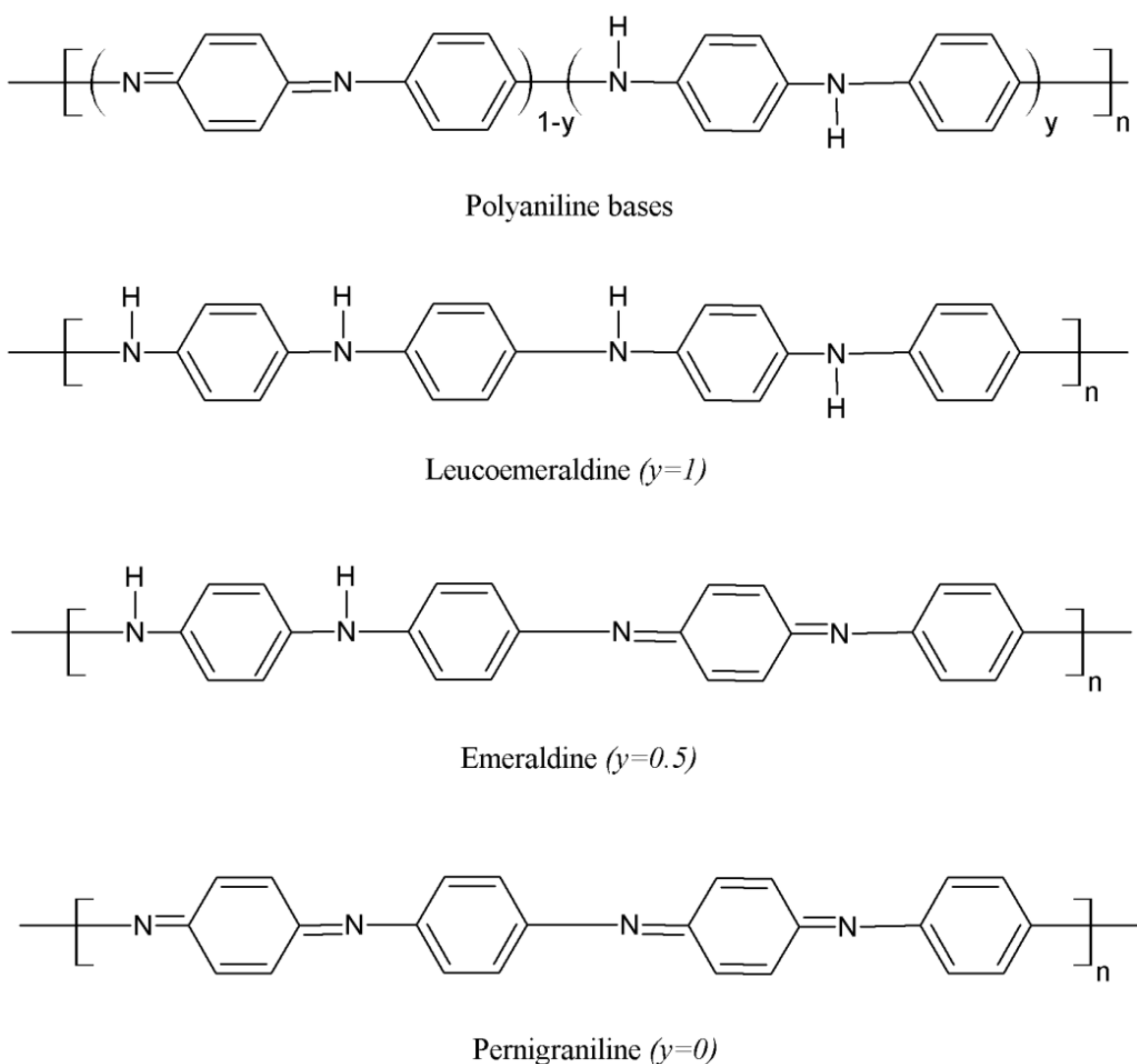


Figure 4. Different forms of PANI.

As an electrochromic polymer, PANI is one of the most promising materials because its colour can be controlled electrically. However, the electrochemical deposited PANI exhibits a significant resistivity, which is attributed to the lack of conducting pathways at the nanoscale associated with random deposition morphology. PANI is also characterised by an appreciable supercapacitive behaviour, although its mechanical stability is not so much good.

As mentioned before, PANI has shown to have good anticorrosion properties, also in controlling pitting corrosion resulting from the permeation and breakdown of the protective coating. In recent years, several methodologies have been proposed for the application of PANI coatings: (i) as a primer alone; (ii) as a primer coating with conventional topcoats or with other CPs films; (iii) blended with conventional polymer coatings, such as epoxy or polyurethane; (iv) as an anticorrosive additive to the paint formulation; (v) as a matrix where nanoparticles or nanostructures materials are incorporated.

3. Applications of conducting polymers as corrosion protective coatings

Since the first reported publications, the discussion on the potential of conducting polymers as promising candidates for a new generation of corrosion control coatings has opened. Although about more than a thousand publications have been published on this topic, their technical application has not yet made its breakthrough. The reason for this is that most coatings based on conducting polymers fail so far under practical corrosion conditions, as their efficacy depends on how they are applied.

In the recent years many papers have reported the use of CPs as materials for anti-corrosion coatings, applied on both ferrous and non ferrous metals, providing a potential cheap alternative to chromium and phosphate treatments and their pollution.

It is well known the corrosion process involves one or more oxidation reactions (affecting the metal under corrosion) and one or more reduction reactions (affecting O_2 or H ions and/or water). Both the reactions occur at the metal surface where a corrosion cell is established. To reduce the corrosion rate it is necessary to control the dynamics of the corrosion process, for example applying one or more coatings on the metal. Such a coating acts as a barrier between the metal and its environment, slowing down the rate at which water, oxygen, or ions from the environment reach the metal surface. Moreover, the coating can act as an active layer when it consists of or contains a material that can interact chemically or electrochemically with the metal, modifying the corrosion process or its rate.

The corrosion protection of metals can be done by a CP coating, such as highly conjugated organic polymer with some degree of electronic conductivity. As mentioned above, the conductivity of these polymers at the neutral state is typically quite low, ranging from insulating to semiconducting. After a partial oxidation (often referred to as p-doping), these polymers become highly conductive, as a metal. The partial reduction (referred as to n-doping) is possible although hard to maintain, especially in air. However, the use of n-doped conjugated polymers in corrosion protection is not diffused.

There are some possible interactions between an active metal and a CP. As the oxidized form of the polymer is electronically conductive, a non-redox interaction occurs when the metal is brought into electrical contact with the CP. In this case the electron moves from the metal, that is more active, into the CP, until the Fermi energy of the two phases are equal.

In the presence of an aerated electrolyte, the metal and the CP becomes a galvanic couple, where oxygen reduction can occur at the CP surface. In addition, an electron transfer from the metal (which becomes oxidized) to the CP (which becomes reduced) might be expected. In this case the oxidation capacity of the bulk polymer is significant. The electronic interactions between metal and CP depend on the quality of the mutual contact, influenced also by the eventual presence of an oxide layer interposed between them. On the other hand, the chemical interactions between metal and polymer or dopant anions occurring at the interface are equally important, because CP can assume the role of inhibitor coating.

Since the interactions between CP and metal are numerous and complex, it is hard to optimise coatings based on CPs that might successfully act for corrosion protection. So, initially in this

part of chapter, the proposed corrosion mechanisms occurring when CPs coat a metal will be reviewed. In literature several cases of ferrous and non ferrous metals coated by mono- and bi-layers based on CPs and their composites are reported. Our efforts will be devoted to report the most recent results, with particular attention to polyaniline, because of its potential practical applications. It is worth noting that a wide range of experimental methods were used to investigate the corrosion protection behaviour, it is therefore difficult to estimate the correct mechanism, also because opposite theories were depicted on the basis of experimental results obtained by different procedures. For each kind of structures based on CPs, the main data are reported in summarising tables, placed at the end of each sections (Tables 1-5).

3.1. CPs for protective mono-layer coatings

The first anticorrosion coatings based on CPs were made of pure polymers, in doped or undoped form. Their ability to transport and store charge has been believed to be the principal reason for their reliability to anodically protect metals against high corrosion rates. However the use of conducting polymers on active metals has been not common because of high positive potential required to form the polymers by electrochemical methods. For instance, to polymerize aniline potentials of the order of 1 V are needed. At these potentials, the most part of metals are corroded too rapidly to allow the formation of a conducting polymer on their surface. For this reason, the first CPs coatings were applied on inert metals, such as stainless steels, and it was only in the second half of the 1990s that PPy and PANI started to be grown on aluminum and iron electrodes.

The most ascertained mechanism of corrosion protection by a pure CP layer is based on two aspects: the physical barrier effect and the anodic protection. The first one is similar to that produced by a paint coating which inhibits the corroding substance from penetrating the substrate. So regarding the anodic protection, the conducting polymer works as an oxidant for the metal substrate, shifting the potential towards the passive state. However, these two aspects are not completely distinct, since in the presence of a CP coating the maximum current in the active-passive transition is limited by the barrier effect, and then the potential can be easily shifted to a higher potential in the passive state by the strongly oxidative property of the conducting polymer. Therefore, both the barrier effect and the oxidative capacity induce the anodic protection of the sustaining substrate.

An experimental evidence of this affirmation was given by Fang et al. [13] who described very clearly the mechanism of corrosion protection of PANI coating on stainless steel (SS). Moreover they demonstrated the mechanism of coating failure by means of experimental results. They affirmed that the electropolymerisation of PANI on SS substrate favours the passivation of the metal, that is held by the emeraldine state of PANI. Therefore, the corrosion protection ability of the PANI is mainly due to two factors: the positive potential of the emeraldine (EM) state of PANI, at which the SS substrate can be passivated, and the physical distance existing between metal substrate and environment.

Unfortunately, the electrodeposited PANI coating is intrinsically porous. This fact favours the access of corrosive species to the SS surface, where they react and produce some corrosion products. Then the adherence of the PANI coating to the substrate is worsened. The evidence

of the formation of an oxide layer at the interface between metal and CP coating was demonstrated by Hermas [14] by means of XPS analysis on SS after peeling off two different polymer coatings made of PANI and PoPD (Poly(o-phenylenediamine)). The passive films formed on SS during anodic polarization in a sulphuric acid solution is thinner than those formed on coated stainless steel under the same exposure condition. The polymer layer enhances the enrichment of chromium and nickel in the entire passive oxide, forming a more protective film than that formed during anodic polarization. Moreover, the type of the polymer influences the composition of the passive film. Indeed the amount of chromium, the main passivating constituent, is increased in the oxide film in the order: anodically passivated SS << PANI-SS < PoPD-SS, indicating that the conductive polymers induce a good passivation of the stainless steels, and that the best passivation is obtained by PoPD film. The passive films, particularly the outer layer of modified steels, contain a very low amount of water and sulphate species, revealing also a good resistance to pitting corrosion.

A scheme proposed for the corrosion inhibition of PANI on active metals is related to O₂ oxidising PANI to a partially oxidised and conducting form. The oxidised polymer acts as a catalyst between O₂ and the metal surface, removing electrons from the metal substrate and forming a passive oxide layer. Some evidence that this situation was not stable was reported. Kilmartin [15] used PANI and Poly(methoxyaniline) (also known as Poly-anisidine) to protect SS. He retained that PANI cannot remain in a partially oxidised state on pure iron in acid solutions, since the rate at which electrons are passed to PANI due to metal corrosion is greater than the rate at which the conducting polymer can be oxidised by O₂. However, even in a predominantly reduced state, any positively charged Polyaniline units can eventually pass their charge to substrate, forming a passivating iron oxide layer which serves to lower the rate of corrosion. In the presence of chloride, with higher rates of corrosion, the charge generated within the polymer film by the action of O₂ is not always produced rapidly enough to repair the passive film at the rate at which it is being broken down under the influence of chloride ions. In this case, the more catalytic material is available to passivate the metal, and the longer the system remains protected prior to the onset of pitting corrosion. Therefore there is a competition between Polyaniline being oxidised by dissolved O₂ and the underlying metal using up the Polyaniline charge to maintain a passive oxide film (Figure 5).

The majority of studies on corrosion protection by CPs reports on the doped form of the polymer, where an anion (dopant ion) is incorporated on oxidation, and is released upon reduction. The dopant ion has an important role in the control of corrosion mechanisms. When metal oxidation and polymer reduction result in a damage to the coating, a "special" dopant ion with inhibition function can be released by the coating and stops or slows down the corrosion [16] (Figure 6). If the anion is released as a consequence of anion exchange process, it can work as a physical barrier to prevent penetration of aggressive ions or to inhibit oxygen reduction.

Dominis et al. [17] studied how the type of the dopant anion used in the emeraldine salt (ES) form of PANI affects the corrosion rate of carbon steel. The differences in corrosion rate induced by different dopants used with the ES appear to be correlated with the galvanic activity between ES and carbon steel. Their results indicated that the coupling with PANI-ES

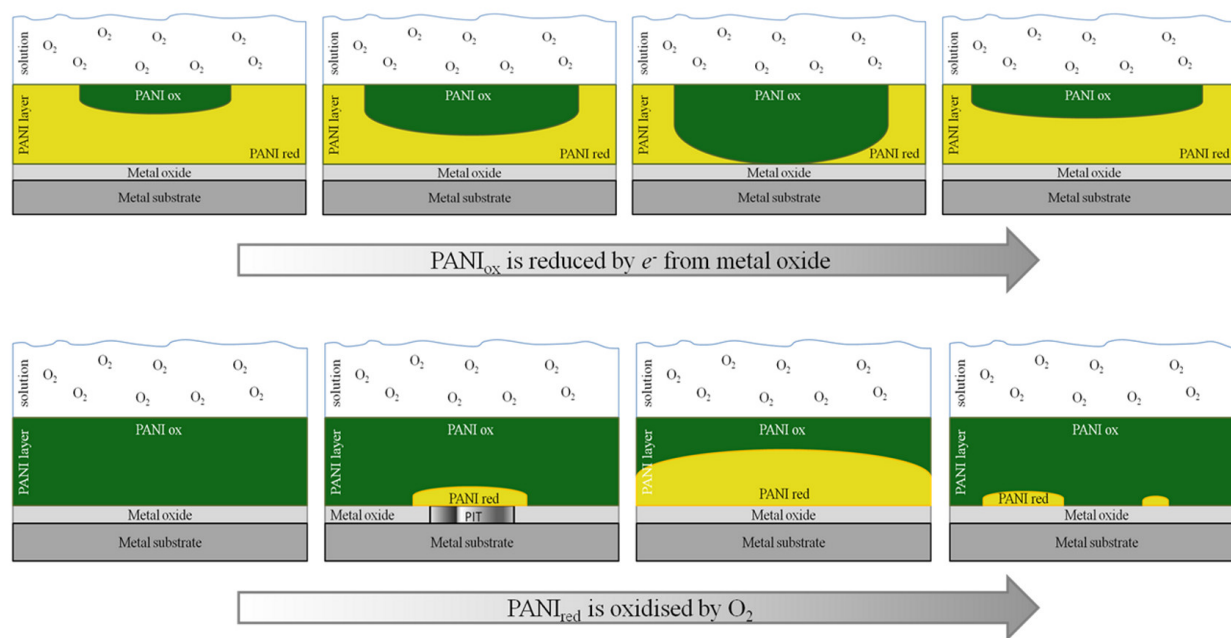


Figure 5. Schemes proposed for the corrosion inhibition of Polyaniline on active metals in chloride solutions.

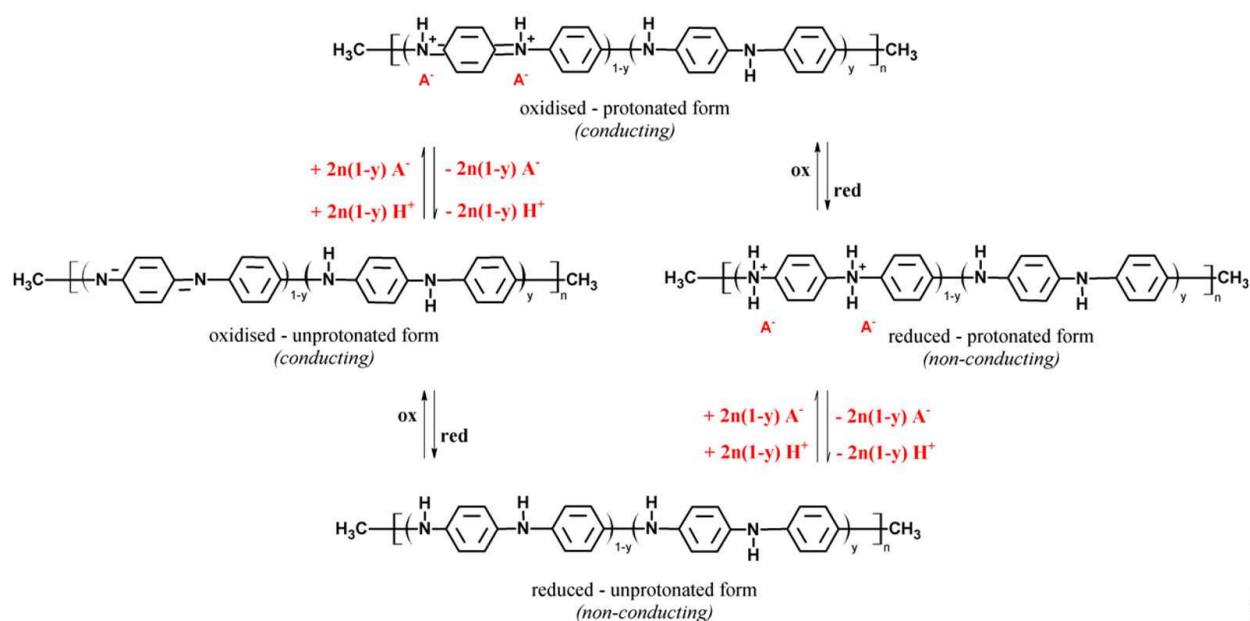


Figure 6. Reactions between the various forms of oxidised and reduced, protonated and unprotonated PANI.

does not passivate the steel under the test conditions used. Instead the steel behaves like a non-passivating metal with faster reduction of the polymer corresponding with a higher oxidation rate of the steel.

Different kinds of dopants, including organic and inorganic ions, have been used, often incorporated in the CP during its electrochemical synthesis. Among organic anions, doped

aliphatic and aromatic sulfonates provide good electrical and mechanical properties and good stability for the PPy layer. Inorganic ions, such as ClO_4^- or Cl^- , have also used as dopant in PPy, being easily released during reduction, and allowing the incorporation of other anions from an aqueous solution during the following oxidation [18].

In general, the polymerisation process, as well as the morphology and the adhesion to substrate, are influenced by the anion present on the electrode surface, the redox potential of the anion, and the ionic charge. The size of the counterions plays a particularly important role in the exchange of doped anions. In fact, the protection mechanism by dopant ions release works if the mobility of the anion is high enough to migrate through the CP film in a short time and to form a passive layer on the corroding metal [19]. In reference [20] different electrolytes in deposition of PPy films on oxidizable metals, such as copper, were used. Oxalic acid, sodium oxalate, sodium/potassium tartrate, and sodium salicylate were used as electrolytes and compared in terms of easiness for PPy deposition and film characteristics. Copper is efficiently passivated before Polypyrrole electrodeposition and a thin passivating layer is formed prior to the pyrrole electropolymerisation and prevents copper corrosion without inhibiting the polymer formation.

Mono-layer coatings based on CPs				
Type of polymer coating (s) and substrate	Method of coating deposition	Method of corrosion tests	REF.	Results
PANI on Zn-Co plated carbon steel	Cyclic voltammetry	EIS and Anodic polarisation in 3.5% NaCl	[85]	The corrosion potential for PANI on ZnCo plated steel shifts to more positive values with respect to uncoated steel and ZnCo coated steel. The polarisation resistance is maximum for PANI/ZnCo/steel and minimum for uncoated steel.
PANI on Al	Galvanostatic polarisation	Tafel polarisation and EIS in 1% NaCl	[89]	The pure PANI coating has a poor corrosion resistant behaviour due to galvanic action of PANI. A post – treatment in a Cerium salt solution increases the PANI coating performance.
Poly(aniline-co-m-amino benzoic acid) on steel	Cyclic voltammetry	Tafel polarisation and EIS in 1N HCl	[90]	The protection efficiency of copolymer coating is three times higher than that of pure PANI.
Poly(N-ethylaniline) (PNEA) on copper	Cyclic voltammetry	Potentiodynamic polarisation and EIS in 0.1M H_2SO_4	[91]	The corrosion rate of Cu is reduced by PNEA coatings electrodeposited at the lowest upper potential limit for shorter periods, by PNEA coatings electrodeposited at the highest upper potential limit for longer periods.
PPy on Al alloys	Galvanostatic activation and Galvanostatic deposition	Single-cycle anodic polarisation and subsequent repassivation Monitoring of OCP in 0.6M NaCl.	[92]	The nature of the substrate influences the structure and morphology of PPy films. The performance of PPy films depends on the corrosion test used and by the structural characteristic of films.

Mono-layer coatings based on CPs				
Type of polymer coating (s) and substrate	Method of coating deposition	Method of corrosion tests	REF.	Results
Poly (o-ethyl aniline) (POEA) on copper	Cyclic voltammetry	Potentiodynamic polarisation and EIS in 3% NaCl	[93]	The corrosion rate of POEA coated Cu is about 70 times lower than that of uncoated Cu.
PNEA on steel	Cyclic voltammetry	Tafel polarisation in 1M H ₂ SO ₄	[94]	The PNEA monolayer coating is less efficient than the bilayer coatings based on PNEA and PPy (see Table 2 – ref [94]).
	Cyclic voltammetry	Potentiodynamic polarisation in 0.2M H ₂ SO ₄	[13]	The corrosion protection ability of PANI increases with the increase of the thickness.
PANI on steel	Cyclic voltammetry	EIS and monitoring of OCP in 0.5M H ₂ SO ₄ and 0.5M HCl	[15]	The corrosion protective behaviour of PANI film depends on its oxidation state. The OCP oscillates after some hours of exposition to acid environment meaning a change from reduced to oxidised state of PANI.
	Cyclic voltammetry	Tafel polarisation in 1M H ₂ SO ₄	[21]	The corrosion performance of monolayer PANI coating is worse than that of bilayer PPy/PANI and PANI/PPy coatings (see Table 2 – ref [21]).
	Cyclic voltammetry	Potentiodynamic polarisation. EIS and monitoring OCP in 3% NaCl	[32]	The single PANI layer coating provides a worse protection than the bilayer PANI+POA coatings (see Table 2 – ref [32]). The corrosion rate of PANI coated steel is 35 times lower than that of uncoated steel.
	Galvanostatic deposition	Tafel polarisation in 3.5% NaCl	[95]	The corrosion rate of steel increases when the concentration of Aniline in the electrolytic solution increases from 0.1 to 0.4 M.
	Oxidative polymerisation	Potentiodynamic polarisation in 3.5% NaCl	[47]	The corrosion current on steel coated by PANI is better than uncoated steel but it is worse than PANI+TiO ₂ coatings (see Table 3 – ref [47, 48]).
	Cyclic voltammetry	Potentiodynamic polarisation and EIS in 0.5M NaCl	[96]	PANI acts as a worse protective layer than PoPD on steel against pitting corrosion.
	Oxidative polymerisation	Tafel polarisation and EIS in 3.5% NaCl	[97]	The corrosion current on PANI coated steel is 20 times lower than that on uncoated steel. The corrosion potential PANI coated steel is more positive of 300 mV than the uncoated steel.
PPy on steel	Cyclic voltammetry	Tafel polarisation in 0.1M HCl EIS in 0.5M NaCl, 0.1M HCl Potentiodynamic polarisation in 0.5M H ₂ SO ₄	[111]	All corrosion tests show the worst performance of PANI single coating with respect the single PPy coating, PANI/PPy and PPy/PANI bilayer coatings (see Table 2 – ref [111]).
	Cyclic voltammetry	Tafel polarisation in 1M H ₂ SO ₄	[21]	The corrosion performance of monolayer PPy coating is worse than that of bilayer PPy/PANI and PANI/PPy coating (see Table 2 – ref [21]).
	Galvanostatic deposition	Potentiodynamic polarisation, monitoring OCP, and EIS in 3.5% NaCl	[36]	PPy coating has worse anticorrosion properties than PPy + ZnO coating with 10 wt% of ZnO relative to PPy (see Table 3 – ref [36]).

Mono-layer coatings based on CPs				
Type of polymer coating (s) and substrate	Method of coating deposition	Method of corrosion tests	REF.	Results
	Cyclic voltammetry	Tafel polarisation in 0.1M HCl EIS in 0.5M NaCl, 0.1M HCl Potentiodynamic polarisation in 0.5M H ₂ SO ₄	[111]	All corrosion tests show the best performance of PPy single coating with respect to the single PANI coating, and PANI/PPy and PPy/PANI bilayer coatings.
Poly(o-anisidine) (POA) on steel	Cyclic voltammetry	Potentiodynamic polarisation, EIS and monitoring OCP in 3% NaCl	[32]	The single POA layer coating provides a worse protection than the bilayer PANI + POA coatings (see Table 2 – ref [32]). The corrosion rate of PANI coated steel is 9 times lower than that of uncoated steel.
Poly(o-methoxyaniline) on steel	Cyclic voltammetry	EIS in 0.5M H ₂ SO ₄	[15]	The corrosion protective behaviour of Poly(o-methoxyaniline) film depend on its oxidation state. The OCP oscillates after some hours of exposition to acid environment meaning a change in its oxidation state.
Poly(o-toluidine) (POT) on steel	Cyclic voltammetry	Potentiodynamic polarisation in 3% NaCl	[98]	The incorporation of CdO nanoparticles improves the corrosion protection of POT coating (see Table 3 – ref [98]).
PANI on iron	Oxidative polymerisation	Tafel polarisation and Monitoring OCP in 3.5% NaCl	[99]	The corrosion current on iron coated by PANI coating is almost 10 times lower than the uncoated iron
	Casting	Tafel polarisation in 1M H ₂ SO ₄ , 1M HCl and 3.5% NaCl	[100]	The corrosion protection of pure aniline is worse than the composite layer containing PANI and Clinoptilolite (see Table 3 – ref [100]).
Poly(o-phenylenediamine) (PoPD) on steel	Cyclic voltammetry	Potentiodynamic polarisation and EIS in 0.5M NaCl	[96]	PoPD acts as a better protective layer than PANI on steel against pitting corrosion.
	Cyclic voltammetry	Monitoring OCP in 3% NaCl	[101]	OCP is positive and increases gradually in time.

Table 1. Some examples of single layer coatings based on CPs for corrosion protection.

3.2. Layered structures based on CPs as protective coatings

A lot of attention has been devoted to study and improve the performances of coatings based on pure CP (doped or undoped), but their application to corrosion protection is subject to some limitations. There are mainly two reasons: the charge stored in the polymer layer (used to oxidise base metal and to produce passive layer) can be irreversibly consumed during the system redox reactions, and some intrinsic porosity cannot be avoided. Consequently, protective properties of the polymer coating may be lost with time.

In recent years, systems consisting of more than one layer have been adopted, generally formed by an inner highly electro-active layer and an outer more compact layer. The role of the superimposed layer should be not to block the corrosion reaction by isolation, but rather to lengthen the diffusion path of the corroding species to lower the corrosion rate at the interface metal/coating. Often the inner layer and the outer layer interact mutually improving the performances of the single layers.

A two-layer system that has been diffusely studied is that formed by PANI and PPy films deposited in alternating way [21-26]. In reference [27], PPy was electropolymerised in 0.25 M monomer and oxalic acid solution. From experimental results they argued a model pursuant to which $\text{Fe}_2(\text{C}_2\text{O}_4)_3$ is formed from oxidation of Fe^{2+} into Fe^{3+} , that derives in turn from $\text{FeC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$, produced in the cyclic voltammograms of steel in the presence of oxalate ions. Simultaneously, monomer oxidation starts on the surface, resulting a monomer cation radical attached to the steel surface while FeC_2O_4 dissolves. After complete dissolution of FeC_2O_4 , the steel surface is re-protected by the formed polymer, and the polymer including doping oxalate ions covers completely the iron substrate. On the basis of these theory, Hasanov [21] sustained that the oxidised form of PANI retaining dopant oxalate ions is a good conductor and helps to protect steel in the corrosive medium (Figure 7). The PANI and PPy layers are connected to each other by polar groups in the polymer matrix, forming a PANI/PPy coating on the steel surface with strong adsorption to steel. At the potential of the electropolymerisation, the iron oxalate is removed from the steel surface and therefore incorporated in the polymer matrix as dopant ions, and not bound directly to iron as iron oxalate. Moreover, Fe^{2+} ions from the dissolution of steel together with oxalate ions in the polymer matrix form iron oxalate on the steel surface in possible cracks or crevices, preventing further steel corrosion. Definitely, iron oxalate has a good diffusion barrier properties and is impermeable to corrosion-causing agents.

This mechanism proposed for the PPy/PANI coatings is arguable for other bilayer or multilayer conductive polymer coatings. The protection properties depend on the chemical structure of polymer coatings, on their adsorption on the metal surface, on the permeability of ions/molecules, on the transformation between redox states of polymers, and on their deposition order.

In reference [23] bilayer coatings, consisting of the inner conducting PPy doped with large dodecylsulfate ions (DS^-) and the outer conducting PANI doped with small SO_4^{2-} ions, were

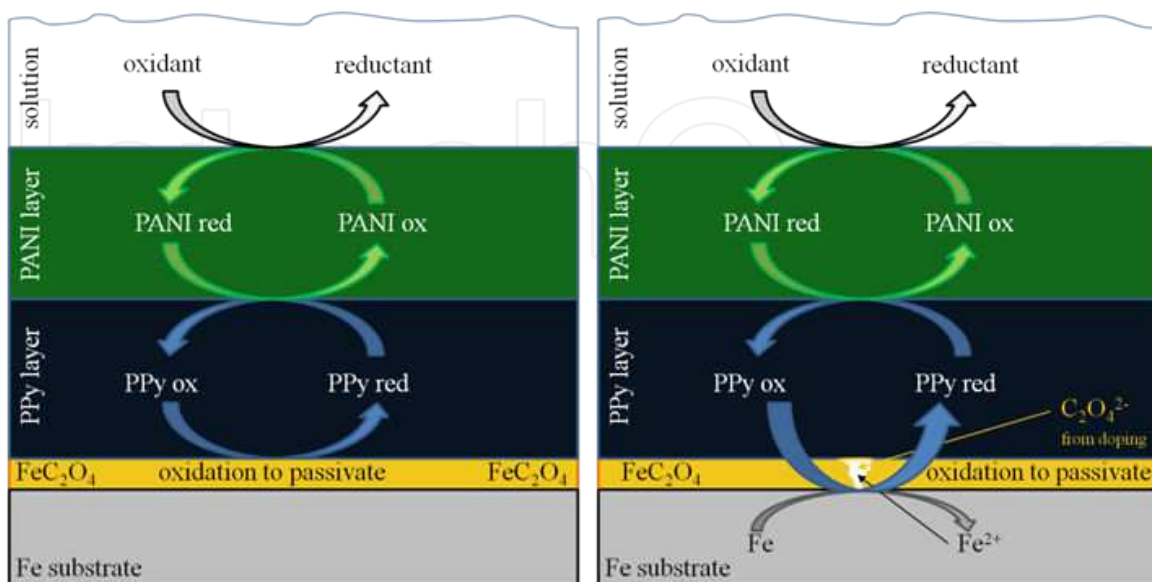


Figure 7. Proposed mechanisms of corrosion in PPy/PANI coated steel.

deposited on 304 SS for the bipolar plates of a PEMFC. The composite coatings inhibit the corrosion of the alloy significantly better than the single PPy coating. In fact, the composite coating shows a positive shift of the corrosion potential and a significant positive shift in the pitting corrosion potential with respect to the bare alloy. However, the free corrosion current density for the composite coatings is close to that of the bare steel, but significantly higher than that of the single PPy coatings, probably related to a contribution from the oxidation/reduction reaction of the polymer coatings, rather than to the corrosion of the substrate alloy. It was found that the composite coatings exhibited a greater chemical stability in HCl than the single PPy coating. This may be due to the bilayer coating acting as better barriers to trap chloride and more efficient oxidisers to maintain the metal in the passivity domain. The different ions permselectivity of the PPy underlayer and the PANI top layer increases the barrier effects of the composite coating. Moreover, the external PANI having a higher redox potential can oxidise the internal PPy layer in situ, thus maintaining the anodic protection effect of the composite coating.

In a proton exchange membrane fuel cell (PEMCF) stack, a good bulk conductivity is required because bipolar plates separate cells and carry current from cell to cell. A good surface conductivity is required and hence a low resistance surface contact must be kept. For this reason, the usual methods for corrosion protection producing insulating surfaces are not applicable to PEMFC. The use of conducting polymers should be useful but these polymers should not be faced with a passive oxide films, as usually occurs in the cases described above.

Recently many efforts have been made to use aluminum instead of steel as a material for bipolar plates. In addition to low cost and weight, the aluminum can provide bulk corrosion resistance, although even slight corrosive attack from free ions that contaminate the Nafion[®] membrane in the cell can occur. In addition to some evidences of corrosion of aluminum bipolar plates, the surface oxide which gives aluminum corrosion resistance prevents good electrical contact between the fuel cell electrode and the aluminum bipolar plate. For all these reasons it should be favourable to protect aluminum from corrosion by coatings based on conducting polymers. In reference [22] it is reported the electrochemically deposition of PPy and PANI on 6061 Al, after galvanostatic activation of aluminum. Whereas the corrosion resistance of the PPy coated samples shows no significant improvement from those of the uncoated plates, the PANI coated samples demonstrate a very good corrosion resistance and only a slightly higher contact resistance than that of the standard graphite plates. Since the conductivity of Polyaniline increases with its degree of oxidation, it is expected that in the acid environment of a fuel cell the contact resistance will be even lower.

Several PANI derivatives have been studied [15, 28-31]. In [32] it was reported on a bi-layered composites of PANI and Poly(o-anisidine) (POA). PANI coatings provide much better protection to stainless steel than Poly(2-anisidine) films. Both combinations of the bi-layered composite coatings, i.e., POA/PANI (POA on top of the PANI) and PANI/POA (PANI on top of the POA) give a more effective protection to carbon steel substrate than a single layered PANI or POA coating. However, the corrosion protection offered to carbon steel depends on the deposition order of polymer layers in the composite. The PANI/POA composite provides

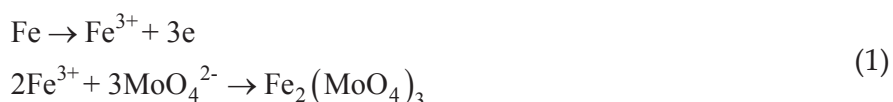
a better protection to carbon steel against corrosion than POA/PANI coating, and anyway the bi-layered composites prevent steel corrosion for longer time.

As previously mentioned, for corrosion protection by conductive polymers, two mechanisms have been proposed: one is the physical barrier effect, and the other is the anodic protection. On the barrier effect, the polymer coating works as a barrier against the penetration of oxidants and aggressive anions, protecting the substrate metals. On the anodic protection, the conducting polymer with the strongly oxidative property works as an oxidant to the substrate steel, potential of which is shifted to that in the passive state.

There is a wide risk of the localized corrosion connected with the anodic protection, because when steels covered with the conducting polymer are immersed in a solution containing chloride or bromide ions, the anions doped in the CP can be exchanged with the chloride/bromide anions in the solution. The chloride/bromide anions penetrate the CP towards the substrate steels, and then induce the breakdown of the surface passive oxide film, followed by a pitting corrosion.

When looking at the CP as a charged membrane, the immobile anions with a large mass can be considered to have fixed sites with a negative charge. In the channel between the negatively charged sites, the cations can be mobile whereas the movement of the anions is greatly inhibited. Therefore, the membrane exhibits cationic permselectivity. In such a way, under the situation where the dopant anions are large enough, the anions in the solution are excluded from the CP and the metal substrate is protected against the pitting corrosion. An example of this mechanism was depicted by Kowalski [33-34] who protected a steel substrate by a PPy layer, with the inner part doped with phosphomolybdate ions (PMo). PMo works as a passivator which stabilises the passive state of steels and facilitates the formation of passive oxide. For the outer layer, the PPy doped with dodecylsulfate (DoS) is used. The outer layer can inhibit the anions from penetrating in the PPy layer. The results show that the steel covered with the bilayered PPy, about 5 μm thick consisting of PPy-PMo/PPy-DoS, exhibits a good passivation and no corrosion products are observed. It was assumed that PMo ions doping the inner PPy stabilises the passive oxide and helps the maintenance of the passive state of the substrate steel.

This kind of bilayer coatings also show an interesting self-healing property in which the passive oxide is spontaneously repaired after it develops small defects. After the coating and passive oxide are locally flawed, PMo in the PPy layer is hydrolysed and decomposes to molybdate and phosphate ions, and then both ions arrive at the flawed sites. The molybdate ions react with ferric ions on the flawed site to produce the ferric molybdate film. The salt film gradually changes into the passive oxide on the damaged site, according to following reactions [35]:



In the experiment conducted by Kowalsky, a PPy layer receives the small flaw and then is immersed in a 3.5% sodium chloride solution. Initially, the open circuit potential fall down. When the corrosion is continuing at the defect site, the potential decreases to that of bare steel. The potential, however, rises up and recovers in the passive potential region. After that, the potential maintains the high potential in the passive region. Raman scattering spectroscopy reveals the molybdate salt is formed and a salt layer of ferric molybdate is reformed on the site of flaw.

One can argue that in designing a bilayer system coating for the corrosion protection, two important factors have to be considered: one is the stabilization of the passive film on the steel by action of dopant ions in the inner CP layer, and the other is the control of ionic permselectivity by organic dopant acid ions in the outer CP layer.

3.3. Composite structures based on CPs as protective coatings

Porosity and anion exchange properties of CPs could be disadvantageous, particularly when pitting corrosion starts caused by small aggressive anions. An interesting alternative, that has been established more recently, has been to consider composite systems based on conducting polymers.

Composite materials usually consist of a polymer matrix in which fibres and/or small filler particles are thoroughly dispersed. Silicon dioxide or titanium dioxide particles, for example, comprise some of the common fillers in composite materials such as plastics and films. Recently, conducting polymer/inorganic nanocomposites have also attracted more and more attention. These composite materials have shown better mechanical, physical and chemical properties, due to combining the qualities of CP and inorganic particles.

Fillers play an important role in the improvement of polymers matrix properties and each filler, with its volume fraction, shape and size, may have an effect on one or more particular properties. Size reduction of filler particles to nano-scale causes them to show different properties compared to those exhibited in micro scale sizes. At the same way, the reduction of filler particle size in polymer composites strongly affects the final properties of composites.

Nanocomposite materials based on PPy were studied in [36]. PPy-ZnO nanocomposite films with 10%wt nanorod ZnO loading are prepared by electropolymerisation from a monomer solution on mild steel. The role of the nano particles is to increase the barrier effect of the polymer matrix, improving its protecting properties. The reported excellent anticorrosion protection is attributed to the size and shape of nanorod, which is small in size and has a large aspect ratio. For small particles, free space between particles and polymer is far lesser than that of larger particles. Thus electrolyte is harder to penetrate through the pores in coating film where nano-pigment are added. In addition, due to longer diffusion path in nanocomposite coating, the water and ions need more time to arrive at the substrate. Moreover, from Electro-mechanical Impedance Spectroscopy (EIS) measurements it was found that although the initial value of coating resistance for the PPy and PPy-ZnO coatings are close to each other, the resistance of the PPy coating decreases sharply and becomes much lower than that of the PPy-ZnO coating. Therefore, it was supposed that the protection life-time of the PPy-ZnO nano-

Layered structures based on CPs				
Type of polymer coating (s) and Substrate	Method of coating deposition	Method of corrosion tests	REF.	Results
PANI/POA on low carbon steel	Cyclic voltammetry	Potentiodynamic polarisation, EIS and monitoring OCP in 3% NaCl	[32]	The bilayer coating provides a better protection than the single layered PANI or POA coatings. The corrosion rate of PANI/POA coated steel is 88 times lower than that of uncoated steel.
POA/PANI on low carbon steel	Cyclic voltammetry	Potentiodynamic polarisation, EIS and monitoring OCP in 3% NaCl	[32]	The bilayer coating provides a better protection than the single layered PANI or POA coatings. The corrosion rate of POA/PANI coated steel is 44 times lower than that of uncoated steel.
PANI/PPy on steel	Cyclic voltammetry	Tafel polarisation in 1M H ₂ SO ₄	[21]	The corrosion performance of bilayer coating is better than that of monolayer PPy and PANI coating.
PANI/PPy on zinc	Galvanostatic deposition	Potentiodynamic polarisation and EIS in 3.5% NaCl	[25]	The corrosion potential and the corrosion current depend on the galvanostatic deposition parameters. The protection efficiency is 94.3% for the bilayer film and 92.9% for single PPy film.
PPy/PANI on steel	Cyclic voltammetry	Tafel polarisation in 1M H ₂ SO ₄	[21]	The corrosion performance of bilayer coating is better than that of monolayer PPy and PANI coatings. The highest inhibition efficiency is that of PPy/PANI coating.
PPy/PANI on steel	Galvanostatic deposition for PPy and Cyclic voltammetry for PANI	Potentiodynamic polarisation, EIS and monitoring OCP in 0.3M HCl	[23]	The bilayer coating shows a better corrosion protection than the single PPy coating, with a shift of about 500 mV of pitting corrosion potential and a good stability for up 36 days.
PPy/PANI on steel	Potentiostatic deposition	EIS and monitoring OCP in 3.5% NaCl	[24]	The bilayer film has a better anticorrosive behaviour than the monolayer films based on PPy and PANI.
PPy/PANI on steel	Cyclic voltammetry	Tafel polarisation in 0.1M HCl, EIS in 0.5M NaCl, 0.1M HCl, Potentiodynamic polarisation in 0.5M H ₂ SO ₄	[111]	All corrosion tests show a worse performance of PPy/PANI bilayer coating with respect to single PANI coating and PANI/PPy bilayer coating.
PPy-PMo/PPy-DoS on steel	Oxidative polymerisation	Monitoring OCP in 3.5% NaCl	[19]	The steel coated by the PPy based bilayer coating is kept passive for about 200 hours in NaCl environment.
PPy/PNEA on steel	Cyclic voltammetry	Tafel polarisation in 1M H ₂ SO ₄	[94]	The bilayer coating is more efficient than PNEA monolayer coating.
PNEA/PPy on steel	Cyclic voltammetry	Tafel polarisation in 1M H ₂ SO ₄	[94]	The bilayer coating is more efficient than PNEA monolayer coating.

Table 2. Some examples of layered coatings based on CPs for corrosion protection.

composite coating is longer than that of the pure PPy coating for the following reasons: (a) the existence of ZnO nanorods increases the deviousness of diffusion pathway of corrosive species; (b) PPy-ZnO coating is more compact compared with the PPy coating.

A particular use of PPy is as modifier of alumina nanoparticles, before using as coating filler [37]. It is known that additives, such as nanoparticles or nanoflakes, prevents the uniform diffusion through intermolecular pores into an anticorrosion coating. Tallman suggested to take a vantage from the capacity of CPs changing their volume during undoping. Therefore, modifying alumina particles with PPy, and inducing a swelling of the PPy, the voids formed in the coating during its lifetime by ageing, are filled. At the same time, the swollen PPy absorbs additional moisture that penetrates from the outside and blocks transfer of ion permeating inside coating.

The enhanced barrier effect is also the reason of the incorporation of a layered material such as smectite clays (e.g. montmorillonite) in CPs. Nanocomposed based on clays and polymer have been diffusely prepared in past decades due their improved gas barrier, thermal stability, mechanical strength, fire retardant and anticorrosive properties. It has been shown that the montmorillonite (MMT) enhances the anticorrosive effect of Polyaniline and Polypyrrole coatings because of the enhancement of the barrier property of the CP [38-40]

Generally, two kinds of MMT are used: organophilic montmorillonite (O-MMT) and hydrophilic montmorillonite (Na-MMT). The preparation of PANI/MMT nanocomposites with hydrophilic and organophilic nanoclay particles is successfully performed by in situ polymerisation method [41] and therefore different structures of PANI/MMT nanocomposites are obtained. It was found that the incorporation of MMT nanoparticles in PANI matrix, promotes the anticorrosive efficiency of PANI/MMT nanocomposite coatings on iron samples. Comparison of the corrosion rate shows that the anticorrosive properties of PANI/Na-MMT nanocomposite coating is better than PANI/O-MMT and pure Polyaniline coating in 3.5% NaCl but not in 1M H₂SO₄, where the corrosion rate of PANI/O-MMT nanocomposite coated samples is lower. This behaviour is attributed to the hydrolysis of Na-MMT in H₂SO₄ solution which causes changes in the structure of MMT.

However, enhanced corrosion protection of PANI/MMT nanocomposite compared to pure PANI coated samples results from silicate nanolayers of clay dispersed in PANI matrix which increase the deviousness of diffusion pathway of corrosive agents such as oxygen gas, hydrogen and hydroxide ions.

An improvement of anticorrosive properties of PANI is also observed after introducing metal particles such as Zn particles. Zinc, as a transition metal, has conducting and semiconducting properties together with potential ability to cathodic sacrificial protection of metals against corrosion. More recently zinc rich coatings have been applied for the protection of mild steel against corrosion. Also zinc dust and inorganic zinc salts have been used as anticorrosive fillers in conducting PANI coating matrices [42-46]. It has been demonstrated that zinc particles can improve the barrier properties of a PANI coating on copper by the formation of voluminous zinc corrosion products within the pores of PANI coating [43].

Also in cathodic protection of metals by zinc particles, the conducting PANI can play the role of conductance between the zinc particles and the metal surface. Olad [39-40] found out that incorporation of zinc nanoparticles and zinc micro-size particles produces an effective PANI/Zn nanocomposite and PANI/Zn composite coatings on iron, respectively. The electrical conductivity of both nanocomposite and composite systems are correlated with the zinc content, and it is higher when Zn particles are nanosized.

A similar behaviour has been found in the anticorrosive properties of PANI/Zn coatings because the synergetic effect of zinc nanoparticles is more than that of micro sized particles.

Among various inorganic particles, titanium dioxide (TiO_2) nanoparticles have attracted attention due to their excellent properties such as a charge carrier, oxidizing power, non toxicity, chemical and photo stability. Nanostructured TiO_2 can be used to develop multifunctional devices with unique mechanical, chemical, electrical, optical and magnetic properties. Conductive PANI/ TiO_2 nanocomposites combine the qualities of PANI and nanocrystalline TiO_2 within a single material, thereby developing multifunctional materials with combined properties which have very strong potential applications.

Rathod [47] and Radhakrishnan [48] are in agreement when suggesting that the corrosion protection of PANI/ TiO_2 coating is based on almost three factors. The first is the barrier effect formerly cited, preventing oxygen and moisture from reaching the metal substrate. In the specific case of TiO_2 is increased by the nano scale of the additive. Moreover, since that PANI polymerisation is carried out in the presence of a nano- TiO_2 dispersed in the reaction medium, the PANI forms around these particles giving a core-shell type structure: the core being TiO_2 with the shell formed by PANI. This type of structure give rise to higher surface area for PANI as compared to the particles made wholly from PANI.

The second factor relies on the role of PANI in corrosion protection, that is its redox behaviour. PANI captures the ions liberated during the corrosion reaction of steel in the presence of NaCl, water and oxygen, becomes doped and liberates the dopant ions which form a passivating layer even when the corrosion process at the substrate has started. Thus, it acts as a self healing coating with improved corrosion resistance.

As third factor, there is also a charge trapping process because TiO_2 is n-type with a band gap of 3.13 eV while PANI is p-type with band gap of 2.1 eV, and this gives rise to potential barrier formation at the interface. It is quite likely that both these species may form p-n junctions, which prevent charge transport across the layer. In other words, the synergetic action between TiO_2 and PANI hinders the process of electron or charge to transfer across the film, the barrier property of the coating get enhanced, and therefore the flow of electron or ions in and through the film is hindered. All the factors lead to much better performances than the single component system, that are pure nano- TiO_2 and pure PANI coatings.

A diffused use of CPs, and in particular of PANI, with epoxy has been made in the last five years. PANI has been introduced in a resin in form of pigments [49-50], fibres [51-52], nanoparticles [53], or as additive [54-55]. Moreover, the effectiveness of both the emeraldine base (EB) and the emeraldine salt (ES) form of PANI for corrosion protection has been studied. In reference [56] it was observed that from corrosion tests with an aggressive saline solution,

the epoxy + PANI-EB formulation provides more protection than the epoxy + PANI-ES. The comparison of these results with those obtained for other epoxy coatings containing conducting polymers as anticorrosive additives, indicates that the protection mechanism of PANI-EB is based on the ability of this polymer to store charge. Moreover, as the highest protection is observed by epoxy + PANI-EB paint, it is concluded that the mechanism based on the electroactivity of partially oxidised polymers is more effective than that based on the interception and transport of electrons.

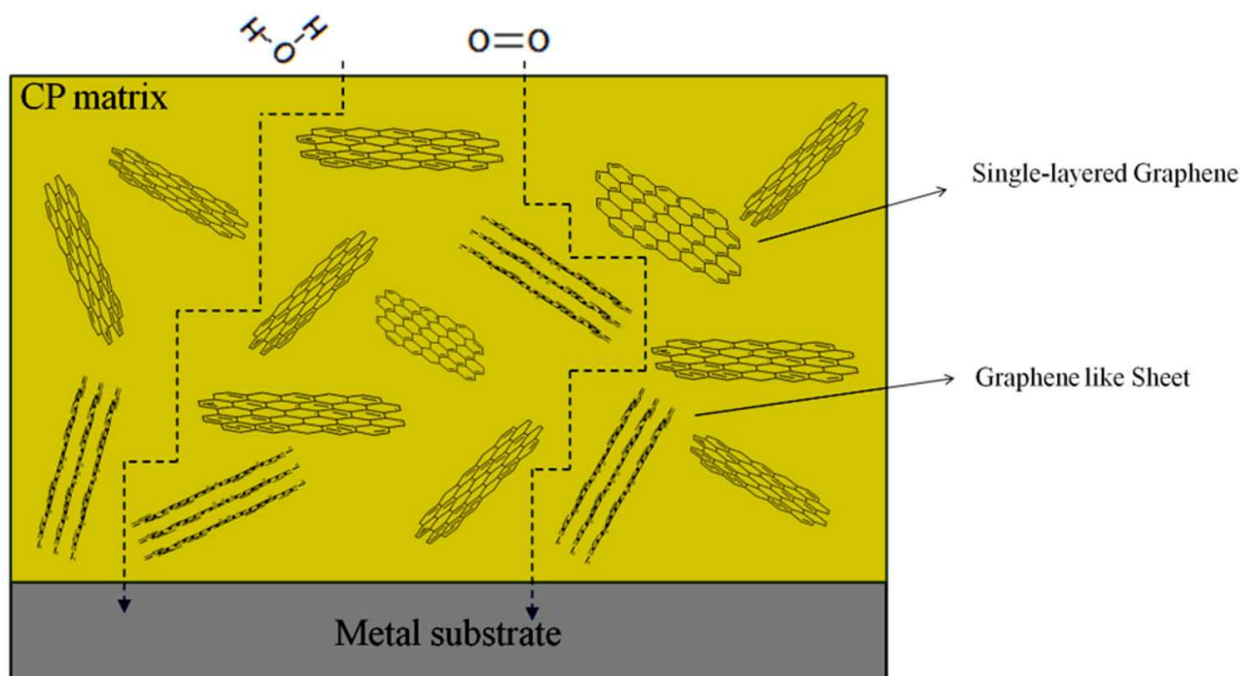


Figure 8. Scheme of the hypothesised retarding effect of graphene on gas diffusion.

More recently carbon nanostructures have been used as fillers in CP coatings, starting *de facto* the age of “hybrid conducting nanocomposites”. The first study on PANI/graphene composites as anticorrosion coating material is that of Chang et al. [57]. They obtained graphene-like sheets grafted with 4-aminobenzoyl groups by Friedel–Crafts acylation with 4-aminobenzonic acid (ABA) in polyphosphoric acid (PPA)/phosphorous pentoxide (P_2O_5). The subsequent chemical oxidation polymerisation of the aniline monomers with different amounts of 4-aminobenzoyl group- functionalised graphene-like (ABF-G) sheets is conducted in ammonium persulfate (APS)/1.0 M aqueous hydrochloric acid to yield Polyaniline /graphene composites (PAGCs). By comparing gas barrier properties of PAGCs with those of Polyaniline/clay composites (PACCs), it is argued PAGCs are more suitable anticorrosion coating materials than PACCs. This also suggests that polymer/graphene

composites are a potential advanced anticorrosion coating candidate to replace traditional polymer/clay composites, where the diffusing gas molecule would encounter a more tortuous path in traversing the polymer/graphene composite coatings (Figure 8).

Also carbon nanotubes (CNTs) were introduced in PANI matrix, to form composite materials with enhanced electrical properties [58-62] by facilitating charge-transfer processes between the two components. Hermas [63] obtained anticorrosion coatings on a stainless steel surface by in situ electropolymerisation of PPy-oxidised multi-walled carbon nanotubes and PPy-oxidised single-walled carbon nanotubes composites on from 0.1 M oxalic acid by using cyclic voltammetry. The results show that the addition of the oxidised carbon nanotubes greatly enhances the electropolymerisation process, especially in the case of oxidised single walled carbon nanotubes.

Similar results are reported in [64], referring to electrodeposition of a nano-composite coating made of oxidised CNTs and Poly(o-phenylenediamine) (PoPD) on a stainless steel. Also in this case the presence of the CNTs enhances the deposition of the PoPD and this enhancement is more significant in the presence of single walled carbon nanotubes (SWCNTs) by comparison to multi-walled carbon nanotubes (MWCNTs). The nano-composite coating keeps the stainless steel in a passive state in an acidic solution.

The functionalisation of CNTs plays an important role in the preparation process of a CP-CNT nanocomposite material. For example, if single-walled carbon nanotubes (SWCNTs) are covalently functionalised with a water soluble conducting polymer, they acquire an excellent solubility in water and a high potential for covalent immobilisation of various dopants.

In [65] nanocomposite films based on Polyaniline, functionalised single-walled carbon nanotubes and different dopants are studied. These nanoporous composite films are grown electrochemically from aqueous solutions such that constituents are deposited simultaneously onto a substrate electrode. The composite films consist of nanoporous networks of SWCNTs coated with polymeric film. Cyclic voltammetry and electrochemical impedance spectroscopy demonstrate that these composite films have similar electrochemical response rates to pure polymeric films but a lower resistance and much improved mechanical integrity. The negatively charged functionalised carbon nanotubes serve as anionic dopants during the electro polymerisation to synthesise polymer-CNTs composite films. The specific electrochemical capacitance of the composite films has a significantly greater value than that for pure polymer films prepared similarly. The higher capacitance of the composite films results obviously from the contribution of the embedded functionalised SWCNTs that provide interconnected pathways for electrons through the functionalised SWCNTs and ions through the pore network or the direct interaction between the delocalised electrons on polymer chains and the functionalised SWCNTs. For this reason, PANI-CNTs composites have been particularly studied for using as supercapacitors. Nevertheless, these hybrid nanocomposite materials have shown to have good corrosion protection properties, as reported in the following section.

Composite layers based on CPs				
Type of polymer coating (s) and Substrate	Method of coating deposition	Method of corrosion tests	REF.	Results
PPy+ZnO on steel	Galvanostatic deposition	Potentiodynamic polarisation, monitoring OCP, and EIS in 3.5% NaCl	[36]	PPy+ZnO coating with 10wt% of ZnO relative to PPy has better anticorrosion properties than the pure PPy coating.
PPy+MMT on steel	Dip coating	Tafel polarisation in 5% NaCl	[39]	Increasing the MMT content in PPy from 0 to 10wt%, the corrosion current decreases and the corrosion potential shifts to nobler potential values.
PPy +Al₂O₃ on Al alloy 2024T3	Painting	EIS in DHS	[37]	The coating impedance increases when the Alumina nanoparticles content increases.
PANI+Na-MMT on iron	Casting	Tafel polarisation in 1M H ₂ SO ₄ and 3.5% NaCl, Monitoring OCP in 1M HCl	[41]	The anticorrosion behaviour of PANI+Na-MMT is better than PANI and PANI+O-MMT in NaCl, but worse than PANI and PANI+O-MMT in H ₂ SO ₄
PANI+O-MMT on iron	Casting	Tafel polarisation in 1M H ₂ SO ₄ and 3.5% NaCl, Monitoring OCP in 1M HCl	[41]	The anticorrosion behaviour of PANI+O-MMT is better than PANI and PANI+Na-MMT in H ₂ SO ₄ , but worse than PANI and PANI+Na-MMT in NaCl .
PANI+ Sulfonated chitosan (S-CTS) on steel	Chemical synthesis	EIS and polarisation curves in 3.5% NaCl	[105]	The best corrosion inhibition is obtained for a S-CTS/ Aniline ratio equal to 2:1. The maximum value of the inhibitive efficiency is 92.3%.
Dodecylbenzenesulfonic acid-doped Polyaniline nanoparticles [n-PANI (DBSA)] on steel	Casting	EIS in 3.5% NaCl	[106]	n-PANI (DBSA) coating shows a coating resistance and a coating capacitance stable up to 77 days.
Benzoate-doped PANI on steel	Galvanostatic deposition	Potentiodynamic polarisation in 3% NaCl, outdoors and in atmosphere	[107]	Benzoate-doped PANI coatings could protect steel in the three different environments for a limited period of time, even when the coatings are partially applied.
PANI+Zn on iron	Casting	Tafel polarisation and Monitoring OCP in 0.1M HCl	[42]	The corrosion rate values of PANI+Zn coatings with a different Zn content are lower than of pure PANI, but their kinetic anticorrosive properties get worse with increasing the zinc content.
	Casting	Tafel polarisation and Monitoring OCP in 0.1M HCl, 0.1M H ₂ SO ₄ , and 3.5% NaCl	[43]	In all the corrosive environments, the incorporation of Zn nanoparticles increases the anticorrosive efficiency on PANI coating.
Anodic Alumina with PANI+TiO₂ on Al alloy AA2024T3	Potentiostatic deposition	Potentiodynamic polarisation in 5mM NaCl and 0.1M Na ₂ SO ₄	[108]	The coating containing TiO ₂ nanoparticles protects the substrate against the corrosion better than pure PANI and coatings based on PANI containing ZrO ₂ particles.

Composite layers based on CPs				
Type of polymer coating (s) and Substrate	Method of coating deposition	Method of corrosion tests	REF.	Results
Anodic alumina with PANI+ZrO₂ on Al alloy AA2024T3	Potentiostatic deposition	Potentiodynamic polarisation in 5mM NaCl and 0.1M Na ₂ SO ₄	[108]	The coating containing ZrO ₂ nanoparticles protects the substrate against the corrosion better than pure PANI but worse than coatings based on PANI containing TiO ₂ particles.
PANI+TiO₂ on steel	Dip coating	Tafel polarisation and Monitoring OCP in 3.5% NaCl	[48]	The corrosion protection property of PANI+TiO ₂ coatings depends on TiO ₂ content. When the TiO ₂ content increases, the OCP shifts to nobler potentials but the corrosion current increases.
PANI+TiO₂ on steel	Oxidative polymerisation	Potentiodynamic polarisation in 3.5% NaCl	[47]	The corrosion current of PANI+TiO ₂ coatings on steel is better than the single component system (pure PANI or nano-TiO ₂). The corrosion protection property of PANI +TiO ₂ coatings depends on TiO ₂ content and it is better when TiO ₂ /aniline weight ratio is 0.05.
POT + CdO on steel	Cyclic voltammetry	Potentiodynamic polarisation in 3% NaCl	[98]	The incorporation of CdO nanoparticles improves the corrosion protection of POT coating.
PANI+ZnO on iron	Oxidative polymerisation	Tafel polarisation and Monitoring OCP in 3.5% NaCl	[99]	The corrosion current on iron coated by PANI+ZnO coating is almost 30 times lower than the uncoated iron.
PANI+PVC+ZnO on iron	Oxidative polymerisation	Tafel polarisation and Monitoring OCP in 3.5% NaCl	[99]	The corrosion current on iron coated by PANI+PVC+ZnO coating is almost 200 times lower than the uncoated iron.
PANI + Clinoptilolite (Clino) on iron	Casting	Tafel polarisation in 1M H ₂ SO ₄ , 1M HCl and 3.5% NaCl	[100]	The encapsulation of PANI in the Clino channels and the dispersion of Clino layers in PANI matrix enhances the corrosion protection of composite layer with respect to pure Aniline.
Methyl Orange (MO)-doped PANI on steel	Painting	Monitoring OCP in 5% HCl, 3.5% NaCl and 5% NaOH	[109]	MO composite coatings act as "corrosion indicators".
MO-PANI/ Castor Oil Polyurethane (COPU) on steel	Painting	Monitoring OCP in 5% HCl, 3.5% NaCl and 5% NaOH	[109]	MO composite coatings act as "corrosion indicators". The corrosion protection is improved by the MO-PANI nanoparticles in COPU.
PANI+SiO₂ on Al	Dipping	Potentiodynamic polarisation in 0.5M NaCl	[112]	The corrosion protection ability of PANI+SiO ₂ coating decreases when the TEOS (precursor of SiO ₂) increases.

Table 3. Some examples of composite coatings based on CPs for corrosion protection.

CPs mixed to Epoxy				
Type of polymer coating (s) and Substrate	Method of coating deposition	Method of corrosion tests	REF.	Results
PANI with epoxy on steel	Immersion and solvent evaporation	Immersion in 3.5% NaCl	[54]	The epoxy coating containing a very low PANI concentration (0.3wt%) provides the best corrosion protection with respect to the unmodified epoxy coating.
	Air spray	EIS in 3.5% NaCl	[50]	The PANI pigmented paint coating shows a capacitive behaviour.
	Immersion and solvent evaporation	Immersion in 3.5% NaCl	[56]	The epoxy coating modified with PANI-EB performs better than both the unmodified coating and the epoxy coating modified with inorganic corrosion inhibitors.
	Painting and solvent evaporation	EIS and Tafel polarisation curve in 0.5% NaCl	[52]	PANI fibres having different morphology are prepared in different medium: HCl, HNO ₃ , H ₂ SO ₄ , and H ₃ PO ₄ . H ₃ PO ₄ -doped PANI shows the best protective effect, followed by HNO ₃ -doped PANI, H ₂ SO ₄ -doped PANI, and HCl-doped PANI.
	Film application	EIS in 3.5% NaCl	[55]	EB-PANI is added to the hardener. The coating resistance and the charge transfer resistance are the highest for 2.5wt% PANI-EB, and the lowest for epoxy coating without EB-PANI.
	Painting	EIS in 3.5% NaCl	[53]	Epoxy modified with PANI nanoparticles shows an increase in coating resistance for longer immersion times.
	Dipping	Monitoring OCP and EIS in 3% NaCl	[102]	Epoxy coating with 2.5wt% PANI-ES offers lower corrosion protection than the coating with 2.5wt% PANI+P-PVA.
PANI with epoxy on magnesium alloy	Painting and solvent evaporation	EIS in 3.5% NaCl	[51]	Epoxy containing PANI sulfonated has the best performance in the protection of steel with respect to coatings containing PANI or zinc phosphate.
	Painting	EIS in 3.5% NaCl	[40]	The corrosion protection of PANI coating on AZ91D magnesium alloy is better with respect to the varnish coating but worsens in presence of O ₂ .
PANI+Zn with epoxy on iron	Casting	Tafel polarisation in HCl	[103]	Epoxy is used as an additive. The addition of both Zn particles and epoxy resin in PANI coating improves the overall anticorrosion performance of coating. PANI+Zn+Epoxy nanocomposite coating shows the best anticorrosion performance by the addition of 4wt% Zn particles and 3-7wt% epoxy.
PANI with epoxy and Polyurethane on steel	Painting	Accelerated corrosion in 5% NaCl EIS in 3.5% NaCl	[49]	In epoxy coating, PANI pigments increase the capacitance and decrease the OCP. In Polyurethane coating, PANI has an adverse effect.
PANI with chlorine ether resin on steel	Painting	Tafel polarisation curves in 5% H ₂ SO ₄ , 5% NaOH, 3.5% NaCl	[104]	The best performance of PANI + resin coating is obtained for PANI concentration between 15% and 25%.
PANI+O-MMT with epoxy on	Painting	EIS in 3.5% NaCl	[40]	The corrosion protection of PANI+O-MMT coating on AZ91D magnesium alloy is better than pure PANI coating.

CPs mixed to Epoxy				
Type of polymer coating (s) and Substrate	Method of coating deposition	Method of corrosion tests	REF.	Results
magnesium alloy				
PANI+P-PVA with epoxy on steel	Dipping	Monitoring OCP and EIS in 3% NaCl	[102]	Epoxy coating with 2.5wt% PANI+P-PVA offers higher corrosion protection than the coating with 2.5wt% PANI-ES .
PPy with epoxy on steel	Immersion and solvent evaporation	Immersion in 3.5% NaCl	[54]	The epoxy coating containing PPy (with concentration from 0.3 to 1.5wt%) provides a better corrosion protection with respect to the unmodified epoxy coating, but a worse one with respect to PANI coating with epoxy.

Table 4. Some examples of coatings based on CPs and Epoxy for corrosion protection.

4. Preparation of hybrid conducting nanocomposites based on PANI and CNTs

In this section, two methods successfully used to prepare PANI-CNTs nanocomposite coatings on steel will be described: Electropolymerisation (EP) and Electrophoretic Deposition (EPD) (Figure 9).

Electropolymerisation is the usual method used for the synthesis of PANI coatings. In general, this method consists of applying a potential to a working electrode immersed in an electrolyte solution. As mentioned before, the potential can be applied through CV, potentiostatic, or galvanostatic methods. The EP method used in this work was CV. During the EP process, the monomer is electrochemically oxidised in an acid solution (usually HCl or H₂SO₄) and polymerisation occurs on the electrode surface where the deposition of the polymer film takes place. The main advantage of this method is the accurate control of the polymerisation rate and of the state of material generated by varying potential values. Moreover, EP is environmental friendly and polymerisation media can be used repeatedly. However, this method is not applicable to large areas, due to problems related to solubility, film quality and coverage. Therefore, with a view to industrial applications of CPs coatings, these drawbacks are particularly relevant.

The synthesis of PANI-CNTs nanocomposite films via EP is an electrochemical co-deposition wherein the CNTs are incorporated in the PANI matrix. In other words, the formation of the nanocomposite occurs during the electrogeneration-deposition of the polymer just near the electrode surface, in the solution containing both CNTs and monomer (in this case Aniline). In such a way, CNTs are functionalised by PANI in the solution and then, after being covered by PANI, deposit onto the electrode surface.

Hybrid conducting nanocomposites based on CPs				
Type of polymer coating (s) and Substrate	Method of coating deposition	Method of corrosion tests	REF.	Results
PANI+graphene on steel	Casting	Tafel polarisation in 3.5% NaCl	[57]	The corrosion current on steel coated by PANI +graphene coating is better than both on the uncoated and on PANI coated steel.
PEDOT+graphene on ITO	Casting	EIS in 2M HCl and 2M H ₂ SO ₄	[110]	(Study of capacitive/supercapacitive properties).
	Cyclic voltammetry	EIS and Cyclic voltammetry in 0.1M H ₂ SO ₄	[86]	(Study of capacitive/supercapacitive properties).
PANI+CNTs on platinum	Cyclic voltammetry	EIS and Cyclic voltammetry in 0.1M H ₂ SO ₄	[87]	(Study of capacitive/supercapacitive properties).
	Cyclic voltammetry	EIS in 0.5M H ₂ SO ₄	[59]	(Study of capacitive/supercapacitive properties).
PANI+CNTs on steel	Potentiostatic deposition	Potentiodynamic polarisation in 3% NaCl	[70]	The corrosion rate of steel coated by PANI+CNTs coating is better than both on the uncoated and on PANI coated steel.
	Cyclic voltammetry	Potentiodynamic polarisation in 3.5% NaCl	Current work	PANI+CNTs nanocomposite coating deposited on steel shows the same corrosion potential of PANI on steel.
	EPD	Potentiodynamic polarisation in 3.5% NaCl	Current work	PANI+CNTs nanocomposite coating shows a more positive corrosion potential than that PANI coating obtained in the same deposition conditions.
PANI on CNTs on steel	Cyclic voltammetry	Potentiodynamic polarisation in 3.5% NaCl	Current work	PANI coating on CNTs shows a more positive corrosion potential than that PANI coating obtained in the same deposition conditions.
	EPD	Potentiodynamic polarisation in 3.5% NaCl	Current work	PANI coating deposited on CNTs on steel shows the same corrosion potential of PANI on steel.
PoPD+CNTs on steel	Cyclic voltammetry	Monitoring OCP	[64]	The OCP remains stable for longer time when CNTs were added to PoPD.

Table 5. Some examples of hybrid conducting nanocomposites coatings based on CPs for corrosion protection.

Recent studies have shown that the functionalisation of CNTs by means of PANI occurs via formation of donor-acceptor complexes. In fact CNTs act as good electron acceptors, while PANI is a fairly good electron donor [66]. The π -bonded surface of the CNTs interacts strongly with the conjugated structure of PANI, especially through the quinoid ring. Such a selective interaction of the CNTs with the quinoid ring of PANI has been reported in literature [67-68]. Moreover, the presence of functional groups on the CNTs surface can favour a chemical interaction of both the monomer and the polymer during its generation [69].

Analysing the cyclic voltammograms acquired from EP PANI in H₂SO₄, it can be observed that, at the anodic potential sweep on the anodic branch of the voltammograms, three anodic oxidation peaks appear and the correspondent three reduction cathodic peaks appear at the

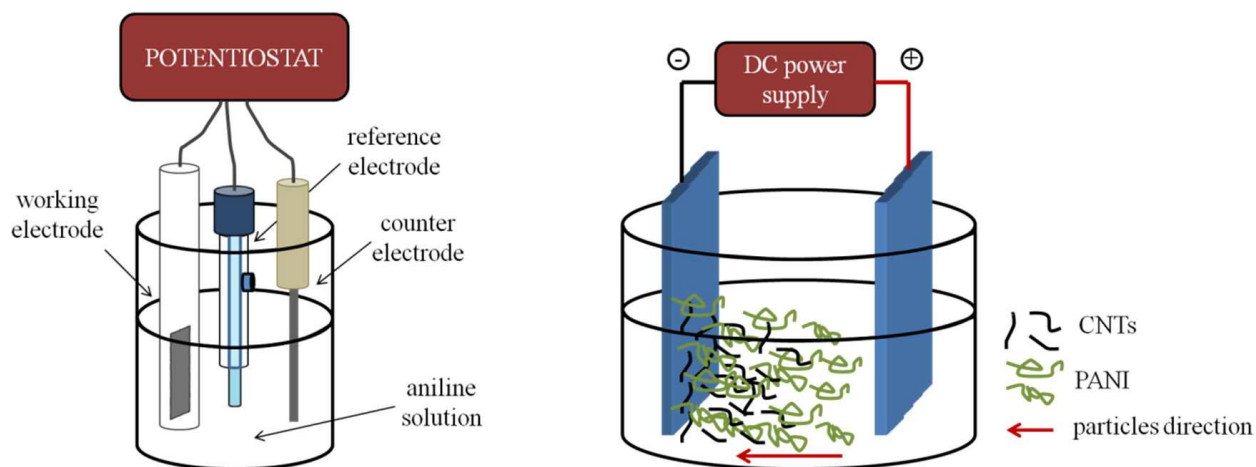


Figure 9. Scheme of an EP (on the left) and an EPD (on the right) cell.

reverse potential sweep, on the cathodic branch of the voltammograms (Figure 10). This fact points to the existence of three redox processes, which take place in the PANI film on different potential ranges. The first redox peak is commonly assumed to correspond to the electron transfer from/to the PANI film. In order to compensate the charge of the PANI film, anion doping/dedoping of the PANI film occurs. The peak in the potential range of 700÷900 mV is probably due to a side reaction in the PANI film, whereas the third redox peak corresponds to deprotonation and protonation process.

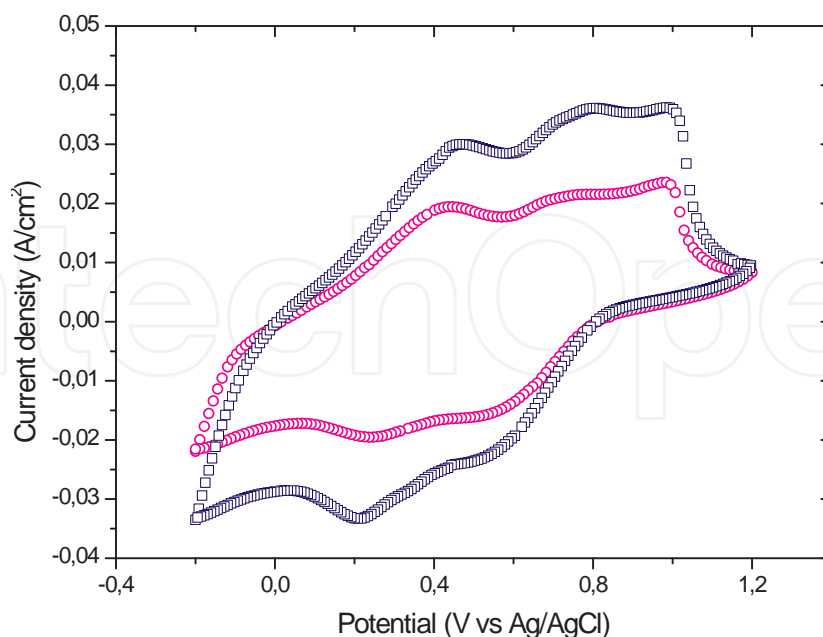


Figure 10. Cyclic voltammetric curve in 0.5 M H₂SO₄ relative to PANI (magenta circles) and PANI+CNTs (blue squares) obtained by EP.

The same peaks are present in voltammograms acquired on PANI-CNTs composite films. The difference is in the recorded current, higher when CNTs are present in aniline solution, due to the effect of CNTs acting as condensation nuclei and therefore allowing an increase of the amount of electropolymerised PANI. This consideration has been also reported by other authors for PANI [70], PPy [71], and PoPD [64].

As an alternative deposition method, EPD has been used to obtain PANI-CNTs nanocomposite coatings. EPD is one of the most outstanding coating techniques based on electrodeposition. It is a traditional method employed to obtain ceramic coatings. Nowadays, increasing interest has been shown both by academics and industrialists, due to its wide potential in coating processing technology, as described, for example, in references [72-74].

The main advantages of this technique are high versatility, since it can be used with different materials and their combinations, and cost effectiveness, because it requires simple and cheap equipment. Moreover, it can be used both on a large scale also when coating objects with a complex geometrical form, and on a smaller scale, to fabricate composite micro- and nano-structures, as well as near net-shape objects having accurate dimensions (micro- and nano-manufacturing).

EPD is a two-step process. In the first step, charged particles, suspended in a liquid medium, move towards the oppositely charged electrode under the effect of an externally applied electric field (electrophoresis). In the second step, the particles deposit on the electrode forming a more or less thick film, depending on process conditions (concentration of particles in solution, applied electric field, time). The substrate acts as an electrode and the deposit of particles is the coating (Figure 9).

Of course, the process parameters, mainly the formulation of the electrophoretic suspension containing the particles, have to be suitable in relation to the coating material and the coating application.

Each of the two steps mentioned above requires special attention. The main requirement to obtain an efficient EPD process is to use suitable suspensions where particles are well suspended and dispersed in a proper liquid medium. The stability of a suspension is essentially due to two possible phenomena occurring at the surface of solids in suspension: the dissociation of functional groups in ionic charges (electrostatic stability), or the adsorbing of ionic surfactants (steric or electrosteric stability). Both the phenomena produce a superficial charge that also allows the movement of solids in the electric field.

With regards to the second step of EPD, the deposition, the deposited mass per area unit in a cell with planar geometry is given by the expression [75]:

$$m = C_s \mu A E t \quad (2)$$

where C_s , solids concentration in the suspension; t , deposition time; μ , electrophoretic mobility; E , electric field strength; A , surface area of the electrode. In this expression, the critical parameter is the electrophoretic mobility, defined as:

$$\mu = \frac{\varepsilon\zeta}{4\pi\eta} \quad (3)$$

where ε , dielectric constant; ζ , zeta potential; η , viscosity of the liquid medium. It is evident that a particle has a good mobility, if the zeta potential is high. As a consequence, the efficiency of the deposition process can be evaluated through zeta potential measurements.

Recently the EPD process has been applied to suspension containing polymers both in the form of small solid particles and as more or less long chains [58,76]. For preparing EPD suspensions based on Polyaniline, PANI is dissolved in a mixture of $\text{CHCl}_3/\text{EtOH}$ containing *m*-cresol and dodecylbenzenesulfonic acid (DBSA). DBSA is used because it increases significantly the mean molecular area, provided the sub-phase is maintained sufficiently acidic to keep the PANI protonated and the DBSA negatively charged. The addition of *m*-cresol as a co-solvent is believed to straighten the PANI chains and is therefore responsible for increasing the mean molecular area per PANI unit [77]. Since PANI is in the protonated state, the possible interactions between PANI and CNTs are:

- electrostatic interaction between negative functional (usually $-\text{COO}^-$ or $-\text{SO}_4^{2-}$) groups of CNTs (residual of the purification treatment) and $-\text{NH}^+$ of PANI;
- π -stacking, referring to the attractive no-covalent interaction between aromatic rings of PANI and CNTs;
- hydrogen bonding between $-\text{NH}$ of PANI and $-\text{OH}$ of CNTs (deriving from functionalising medium).

On average, all these interactions do not neutralise the total positive charge of PANI chains, since the amount of CNTs in the PANI suspension is quite low. This affirmation is confirmed by measuring the zeta potential. In effect, after adding CNTs to the PANI suspension, the zeta potential increases in positive correlation with the CNTs content, meaning that CNTs in suspension contribute to the improvement of the efficiency of the EPD process, through an increased conductivity of the electrophoretic suspension. This consideration is in agreement with some results obtained by Dhand et al. [78-79].

Voltammograms acquired on EPD PANI in the same conditions of EP PANI show similar peaks both in anodic and in cathodic scans, but the recorded current is significantly lower in EPD PANI than in EP PANI (Figure 11). Moreover, a shift of about 200 mV towards more cathodic potentials is revealed with respect EP PANI. The position of EPD PANI peaks is almost the same as chemically synthesised PANI reported in [80]. On the other hand, PANI used for the preparation of EPD suspension is a purchased chemical and presumably it has been chemically synthesised.

It is worth to note that, similarly to PANI-CNTs composite obtained by EP, the recorded current in EPD PANI-CNTs film is higher than in PANI film. This increase of the current could be indicative of fast charge transport in parallel paths to surface of PANI-CNTs film.

In reality, only a few authors have published referring to EPD of PANI [81-84]. In references [82-85] PANI, also containing CNTs, has been electrophoretically deposited, to obtain sensors and biosensors. EPD films based on PANI and CNTs are produced by starting with a suspension containing PANI in ES form and CNTs functionalised by $-\text{COO}^-$ groups, dissolved in formic acid and acetonitrile. Investigations by FT-IR and UV-visible spectra acquired on PANI-CNTs films evidence a doped state of PANI induced by the interaction between imine sites of PANI and carboxyl groups in CNTs. Moreover, from EIS investigation it results that the charge transfer resistance for ES-CNTs composite film is much lower than that of the ES film.

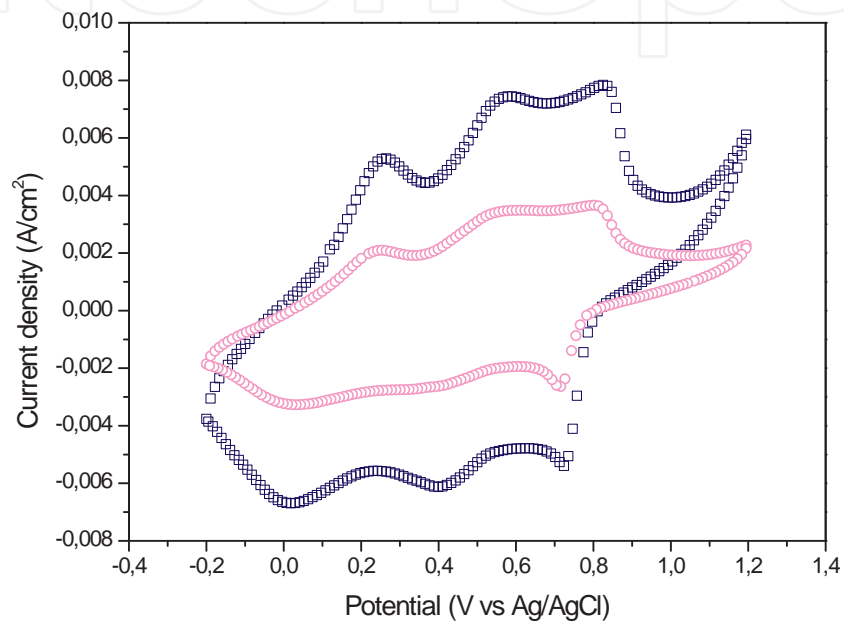


Figure 11. Cyclic voltammetric curve in 0.5 M H_2SO_4 relative to PANI (magenta circles) and PANI+CNTs (blue squares) obtained by EPD.

The enhanced charge transfer is attributed to grain-to-grain wiring of the PANI chains with the uniformly distributed CNTs in the film. Besides this, the presence of CNTs provides “conducting bridges” between ES conducting domains and functions such as charged “jumping centres” facilitating a fast charge transfer via electrons from one polymer chain to another, and finally to the electrode surface. This hypothesis does not disagree with the interaction mechanisms supposed above between PANI chains and CNTs and with the increased electroactivity evaluated through voltammograms.

A third kind of nanocomposite material based on PANI and CNTs has been prepared by using EP and EPD to deposit PANI on a EPD deposit of CNTs. In other words, firstly CNTs have been deposited by EPD on an electrode and then a PANI film has been deposited on CNTs by EP or by EPD. In such a way two other types of samples have been produced. In these cases, the interactions between ANI (in EP process) or PANI (in EPD process) and CNTs are different in respect to those occurring when CNTs are present in an ANI or a PANI solution. Similarly to other PANI-CNTs nanocomposites, voltammograms (Figure 12) show redox peaks relative to the oxidation states of PANI at the same potentials recorded for EP PANI and EPD PANI,

respectively. The recorded current is higher for EP PANI than for EPD PANI. In Figure 13 it is reported a scheme of the three different kinds of CP based nanocomposites considered in this discussion.

At the best knowledge of the authors, only one paper reports on PANI deposited onto CNTs [86]. In that case, a CNTs solution was cast on the surface of an electrode that was dried at room temperature. Then PANI was deposited on CNTs by a conventional CV electropolymerisation. Only capacitive characteristics of this kind of layered material were studied.

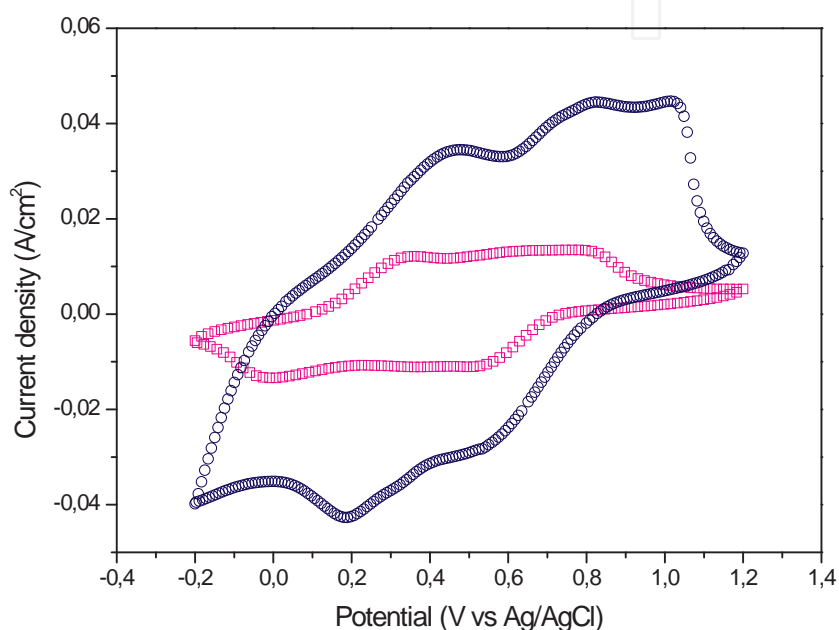


Figure 12. Cyclic voltammetric curve in 0.5 M H_2SO_4 relative to EPD PANI (magenta squares) and EP PANI (blue circles) deposited on CNTs.

5. Anticorrosion behaviour of hybrid conducting nanocomposites based on PANI and CNTs

In order to investigate the anodic performance of the PANI-CNTs nanocomposites, potentiodynamic scans have been acquired in a NaCl solution (Figure 14). The potentiodynamic curves relative to PANI and PANI-CNTs obtained by EP are overlapping, meaning that only PANI is active towards electrolytic species in the test solution. As mentioned before, CNTs are completely coated by PANI during the EP process and therefore their surface is not exposed to electrolytic solution. Moreover, this means PANI is very efficient in blocking the aggressive species, as no evidence of a contribution of CNTs to corrosion protection is observed. From a corrosion point of view, the highest amount of PANI electropolymerised in the presence of CNTs in solution does not influence the protective effect of the coating.

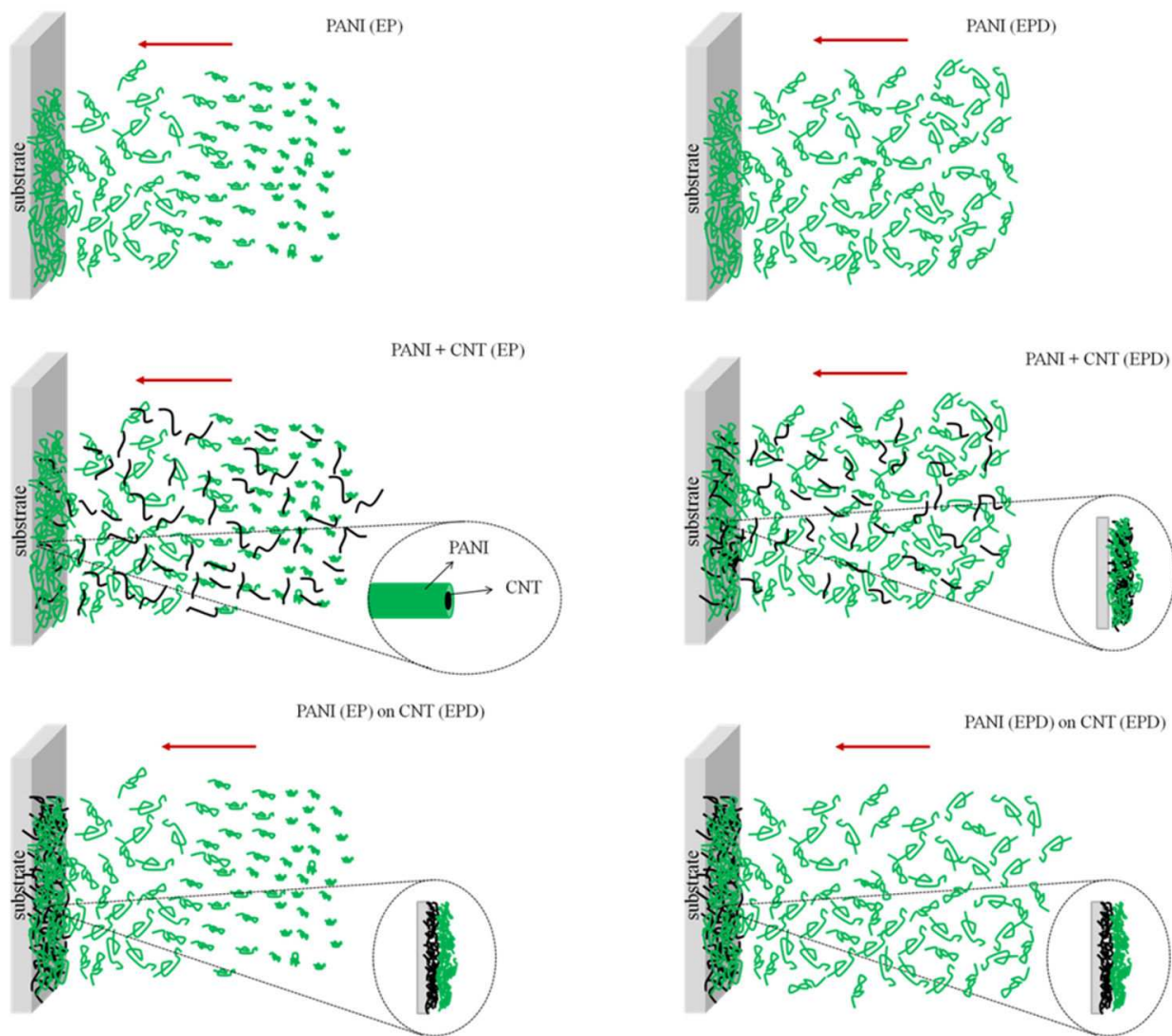


Figure 13. Scheme of the PANI-CNTs based samples. The arrow shows the direction of the polymer chains or the CNTs movement, from the solution towards the electrode by effect of the electric field.

On the contrary, corrosion potential is shifted towards more positive values when PANI is deposited on previously electrophoretically deposited CNTs. In this case, the exposed area is wider than a flat substrate, and therefore the amount of PANI electropolymerised is higher. It is reasonable to suppose that the increased deposited amount of conducting polymer causes the improved corrosion protection of PANI deposited on CNTs and therefore the corrosion potential results nobler.

In [87], EIS measurements on composites containing PANI and functionalised CNTs, deposited by EP, are reported. The aim of that work was to investigate the capacitance of PANI-CNTs composites and therefore the results there described are devoted to the understanding of the behaviour of the composite in consideration to this application. It is reported the real impedance at low frequencies, where the capacitive behaviour dominates, is an indication of the combined resistance of the electrolyte and the film including both electronic and ionic

contributions. The values of the real impedance at 0.01 Hz of the PANI-functionalised CNTs films are significantly lower in resistance than PANI films. This result is attributed both to higher overall conductivity offered by PANI-functionalised CNTs than the PANI film, and to the increased porosity of composite material, that improves ionic accessibility. Moreover, it is suggested that the embedded CNTs provide interconnected pathways for electrons through the CNTs and for ions through the pore network or the direct interaction between the delocalised electrons on polymer chains and the CNTs. In principle, these hypotheses are prejudicial to corrosion protection because of the favourite access of aggressive species to coating-electrode interface.

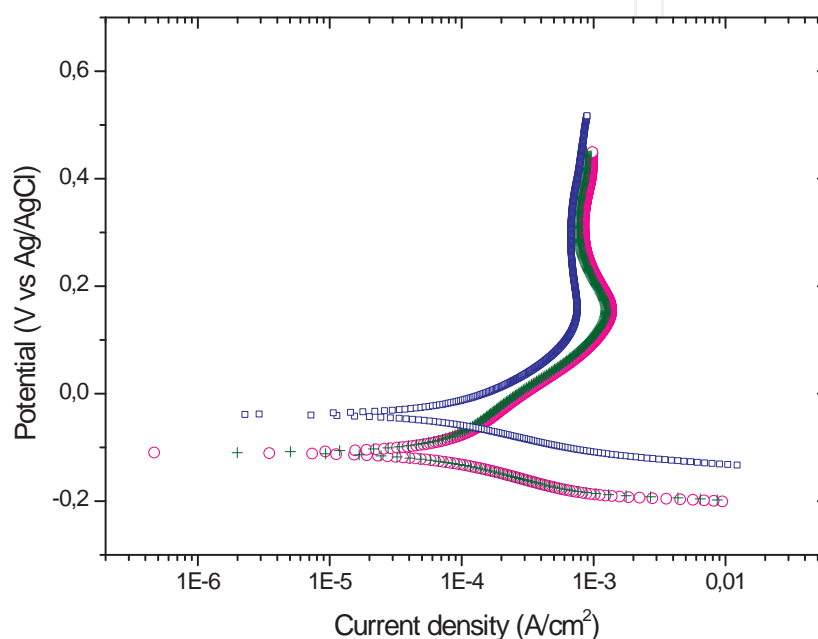


Figure 14. Potentiodynamic curves acquired in 3.5 % NaCl relative to EP PANI (green crosses), EP PANI-CNTs nanocomposite composite (magenta circles), and EP PANI on CNTs (blue squares)

Same authors investigated a similar composite material based on PANI and CNTs functionalised by Poly(m-aminobenzenesulfonic acid) (PABS) [70]. Differently from our case, they found that PANI-PABS-CNTs composite has a better anticorrosion behaviour than PANI. In fact, CNTs functionalisation highly influences the interaction with PANI and, as a consequence, the electrochemical behaviour of PANI-CNTs nanocomposite is modified. As an evidence of this affirmation, the authors observed that in CV performed on PANI electropolymerised with CNTs functionalised by COO^- and SO_4^{2-} group, the recorded current in the case of CNTs functionalised by SO_4^{2-} is almost three times higher than that of CNTs functionalised by COO^- group (Figure 15). In reference [87] it is shown that also the morphology of PANI-CNTs films is modified by the different functionalisation of CNTs.

The nanocomposite coatings based on PANI and CNTs prepared by EPD have an absolutely dissimilar behaviour. Both PANI films deposited on the bare electrode and on the modified electrode by CNTs have a similar E_{corr} and I_{corr} , whereas the nanocomposite film formed by

CNTs co-deposited with PANI has the best anticorrosive behaviour. The difference is attributed to a different interaction between CNTs and PANI (Figure 16).

In the EPD process, when PANI chains, more or less entangled, arrive at the electrode, they can coagulate and deposit onto it as a result of van der Waals attractive forces conveying at close distance [72]. As these forces are accomplished by any strong chemical bond, there is no difference if the electrode is bare or modified by CNTs previously deposited on it. Moreover, the PANI surface exposed to electrolyte solution does not show morphological differences with respect to PANI covering the modified electrode by CNTs (Figure 17).

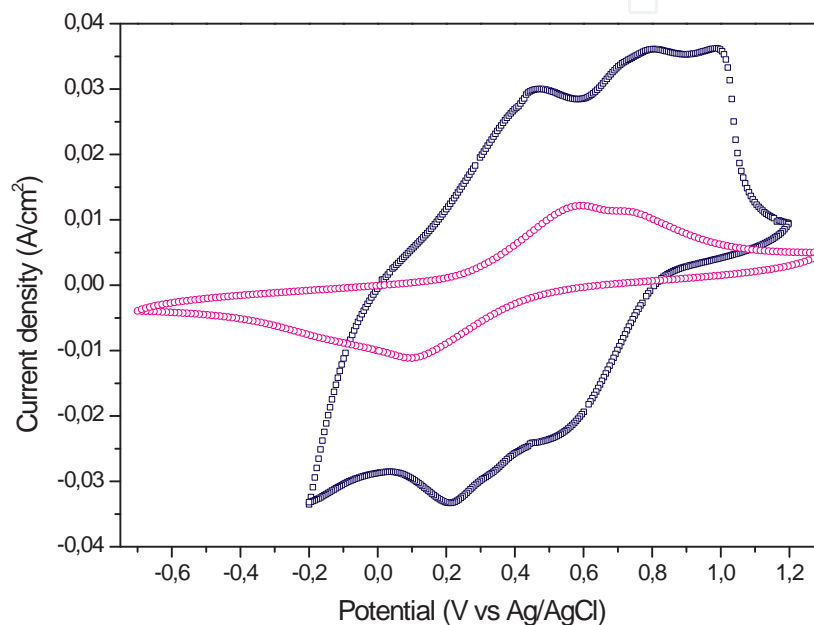


Figure 15. Cyclic voltammetric curve in 0.5 M H_2SO_4 relative to EP PANI-CNTs nanocomposite. CNTs were treated with H_2SO_4 (blue squares) or HNO_3 (magenta circles).

On the contrary, when CNTs and PANI chains are in the electrophoretic suspension, chemical interactions occur, as depicted before. This fact entails two effects. The first one is an increased mass deposited by EPD, as demonstrated by the increased zeta potential and by CV acquired on PANI in the presence of CNTs. This result can be explained considering that a single CNT manages to catch a certain number of PANI chains, which are dragged towards the electrode during electrophoresis. The second effect consists of an increased electroactivity of PANI chains functionalising the CNTs surface, due to a faster charge transport in the composite film than in the PANI film, as emphasised before. For both these reasons, the corrosion potential relative to the PANI-CNTs coating is shifted towards less negative potentials. Definitely, the addition of CNTs to PANI is advantageous for the anticorrosion properties of the PANI based coating. In fact, CNTs allow to increase the amount of PANI deposited both in electropolymerisation and in electrophoretic co-deposition, and moreover, in the case of EPD process, improve the electroactivity of the nanocomposite coating.

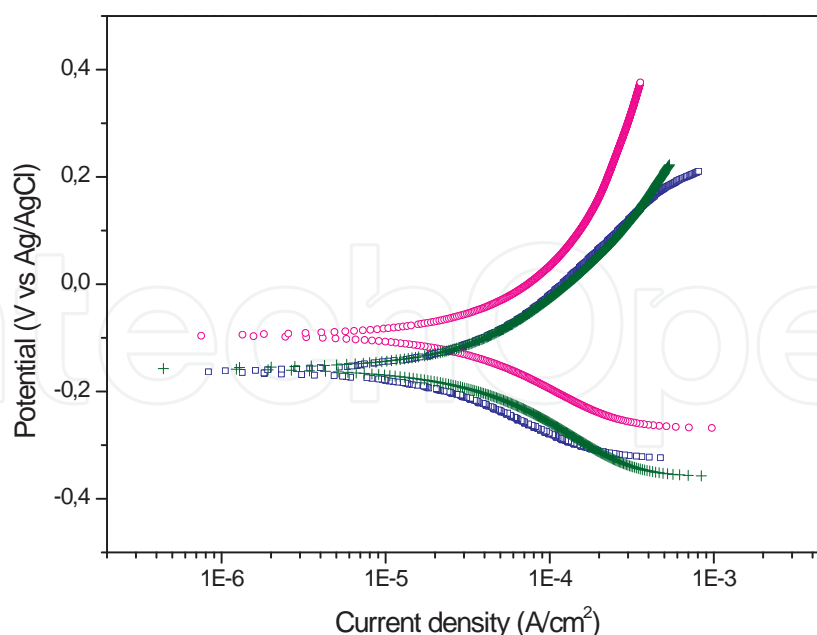


Figure 16. Potentiodynamic curves acquired in 3.5 % NaCl relative to EPD PANI (green crosses), EPD PANI-CNT nano-composite (magenta circles), and EPD PANI on CNTs (blue squares).

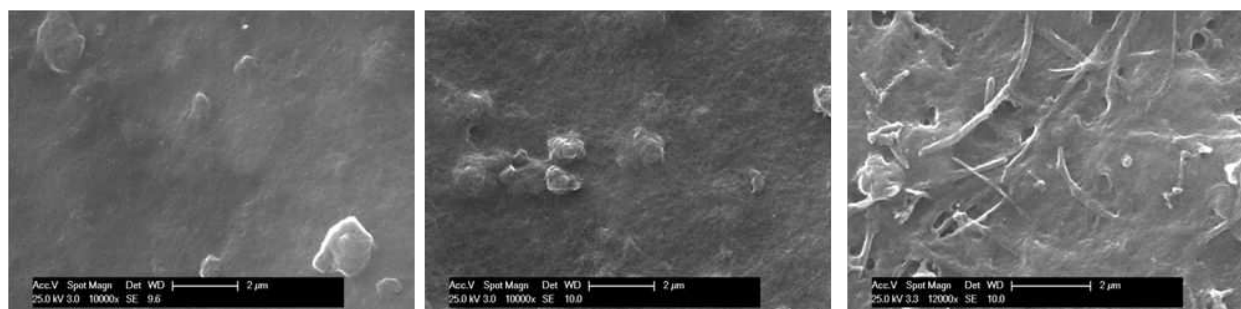


Figure 17. SEM images of the surface of EPD PANI (on the left), EPD PANI on CNTs (in the middle), and EPD PANI+CNTs (on the right).

6. Conclusions

The use of CPs as corrosion protection layers is partly motivated by the desire to replace coatings that are hazardous to the environment and to human health. Since the equilibrium potentials of several CPs are positive relative to those of iron and aluminum, they should provide anodic protection effects comparable to those provided by chromate (VI) or similar inorganic systems.

Either electropolymerisation or chemical oxidation of the respective monomer can be used to form the coating. Cheap and effective polymers, such as PANI, PPy, PEDOT, and PoPD (and their derivatives), have mostly been used to protect steel, aluminum, and copper, but the

provided efficiency and the mechanism of the corrosion protection are not yet fully clarified. Several authors have discussed anodic protection on iron, others have proposed that the passivation is achieved because the doped emeraldine salt form of PANI keeps the potential of the underlying stainless steel in the passive region. However, other authors claim that the mechanism by which PANI protects the underlying metal surface from corrosion is independent of the doping level. Due to the redox processes taking place, more or less thick layers of iron oxide are formed and are stabilised against dissolution and reduction. Inhibition is also reasonable due to physical blocking and reduction of the active surface.

Another strategy for corrosion prevention using CPs is to incorporate inhibitor anions into the polymer coatings. CPs have been also used as primary films under an epoxy layer or additive in paint coatings. Very often it has been referred to the healing effect of CPs upon surface passivation along a defect or scratches. Most recent approaches consider the use of composite coatings based on CPs, containing nanoparticles or carbon nanostructures. CNTs have been incorporated in CPs matrices (PPY, PoPD, and PANI) but the principal characteristic studied has been the capacitive behaviour. Nevertheless, PANI-CNTs nanocomposites have demonstrated to have good corrosion protection properties, although the results are not fully concordant. The use of EPD allows us to produce PANI-CNTs nanocomposite coatings, with characteristics comparable with those of analogous nanocomposites obtained by conventional electrochemical methods.

All considerations reported above and the extensive literature related to this subject induce to conclude that the potential of conducting polymer coatings for corrosion protection is wide but also controversial. In general, the efficacy of CPs very much depends on how they are applied and on the conditions of the corrosion experiment. Therefore many efforts still have to be made in investigations and comprehensions of protective mechanisms in CPs and in hybrid conductive nanocomposites coatings.

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