



New method to obtain hybrid conducting nanocomposites based on polyaniline and carbon nanotubes

The combination of nanoparticles and conducting polymers, known as *hybrid conducting nanocomposites*, is a new emerging research field. The combination of conductive polymers, such as polyaniline (PANI), with conductive carbon nanotubes (CNTs) has already shown some synergistic properties. Hence, they have a variety of applications, e.g., as sensors, actuators, touch screens, etc. Usually PANI and CNTs are combined by using electrochemical synthesis starting with the monomer aniline. In this work a new method to obtain PANI/CNTs nanocomposite is described, consisting of Electrophoretic co-Deposition of PANI in the polymerised form, and CNTs. The advantages of the new deposition method, with respect to the usual electrochemical synthesis, are shown also in terms of electrochemical properties of the obtained hybrids nanocomposites

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Un nuovo metodo per preparare materiali ibridi nanocompositi a base di polianilina e nanotubi di carbonio

I nanocompositi ibridi conduttori, formati da nanoparticelle e polimeri conduttori, sono una classe emergente di materiali con straordinarie caratteristiche. La combinazione di polimeri conduttori, ad esempio la polianilina (PANI) e di nanotubi di carbonio (CNT) ha dimostrato di avere notevoli proprietà, tanto da renderla adatta alle più svariate applicazioni, ed esempio come sensori, attuatori o touch screen. Usualmente, il nanocomposito formato da PANI e CNT è ottenuto mediante una sintesi elettrochimica operata sul monomero corrispondente, l'anilina. In questo lavoro, è stato descritto un nuovo metodo di elettrodeposizione, basato sulla Deposizione Elettroforetica, in cui si usa la forma già polimerizzata della PANI. I vantaggi del metodo proposto sono illustrati anche attraverso lo studio delle proprietà elettrochimiche dei materiali ottenuti con i due metodi

Introduction

Polymeric nanocomposites consist of nanoparticles imbedded in organic polymers. When *conducting nanoparticles* are inserted in *conducting polymers*,

hybrid conducting nanocomposites are obtained. The properties of these materials are so outstanding that they are attractive for both industry and academia.

Among conducting polymers, polyaniline (PANI) has been one of the most studied because of its facile synthesis, electrical conductivity, low cost and environmental stability [1-2]. It is characterised

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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. Each oxidation state can exist in the form of its base or its protonated form (salt) by treatment of the base with an acid. Depending on the oxidation state and the degree of protonation, PANI can be either an insulator or a conductor with different conductivity [3-4].

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

Finally, PANI is known as having good anticorrosion properties, depending on the oxidation states. 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 affecting PANI's growth and properties. 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 [5-6]. Other suggested the non-conductive state of PANI performed better than the conductive one [7].

Recently, several studies in the fields of new materials have introduced the possibility to use conducting polymers as suitable matrices to disperse nanostructured elements, such as Carbon Nanotubes (CNTs). In particular, it has been shown that the introduction of CNTs into PANI can improve its electrical conductivity and mechanical properties [8-9]. In this work, we introduced CNTs in a PANI matrix in order to obtain a better performance in terms of corrosion protection. Moreover, two different electrosynthesis methods, Electropolymerisation and Electrophoretic Deposition, were used in order to compare the properties of the so obtained hybrid conducting nanocomposites.

Electropolymerisation is typically used for the synthesis of PANI coatings. In general, this method consists in applying an opportune potential to a working electrode immersed in an electrolyte solution (Fig. 1). The monomer is thus electrochemically oxidised and polymerisation occurs at the electrode surface with deposition of the polymer film. The main advantage of this method is an accurate control of the polymerisation rate and of the state of material generated by varying potential values. Moreover, Electropolymerisation is environmentally friendly and polymerisation media can be used repeatedly. However, this method is hardly applicable to large areas, due to problems related to solubility, film quality and coverage. These drawbacks are particularly relevant since relatively large quantities of materials are needed for industrial applications.

Electrophoretic Deposition (EPD) is one of the most outstanding coating techniques based on electrodeposition. It is a traditional method employed to obtain ceramic coatings. Nowadays, due to its wide potential in coating processing technology, it has gained increasing interest both by the academia and industrial communities.

The main advantages of this technique are high versatility, since it can be used with different materials and their combinations, and cost effective-

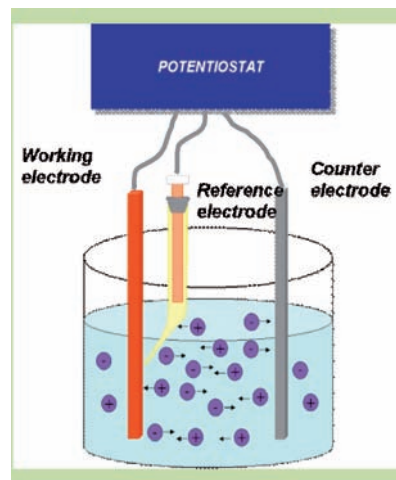


FIGURE 1 Electrolytic cell with the three-electrode configuration

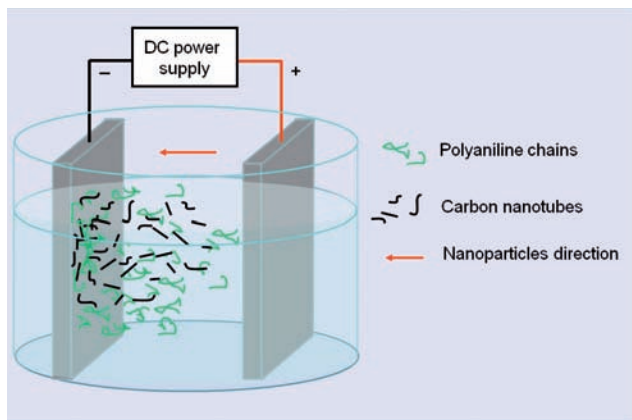


FIGURE 2 Scheme of an electrophoretic cell, with a suspension containing PANI and CNTs

ness, as 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 small scale, to fabricate composite micro- and nanostructures, 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 into 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 the 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 (Fig. 2).

Of course, the process parameters, mainly the formulation of the electrophoretic suspension containing the particles, have to be suitable to coating material and coating application. New EPD application areas are: low-cost fabrication of composite materials including advanced coatings based on nanocomposites, laminate structures, functional graded materials and fibre reinforced ceramics.

In this paper, the synthesis of PANI composite films containing CNTs, performed by ELD and EPD, is described. Since PANI properties, and therefore its performance in several applications, depend on

synthesis parameters – such as the technique of electrosynthesis and the composition of the polymerisation solution – films characterisation was performed in order to investigate electrochemical properties and CNTs influence on the PANI composite coatings.

Experimental details

All analytical-grade chemicals were purchased from Sigma-Aldrich and used as received, including Aniline monomer (analytical-grade), Polyaniline and CNTs. The used CNTs had a 110-170 nm diameter and were 5-9 μm long. By SEM observation, CNTs resulted to be quite straight and similar to hollow ropes with some impurity.

CNTs were purified by boiling in a solution of HNO_3 and HCl (3:1) for 1 hour to dissolve any catalysts. Then, CNTs were washed with deionised water until pH 6 and then dried at about 70°C . Triton X-100 was used as surfactant to disperse CNTs in water, since this prevents them from becoming aggregated for a long period. For the aniline polymerisation and composite formation (ELD process), a conventional three-electrode cell was used where the working electrode was a carbon paper disk, the counter electrode was a Pt wire, and the reference electrode was an Ag/AgCl electrode (AMEL). For the films deposition, a PAR 273A potentiostat (Princeton Applied Research, Oak Ridge, TN) in remote control was used. All the experiments were carried out at room temperature. Deionised water was used for rinsing electrodes and preparing solutions.

In order to deposit PANI and PANI-CNTs films on carbon paper substrates, 0.25 M Aniline solution in 1 M HCl was used. In a typical experiment, CNTs dispersed in Triton X-100 were added to Aniline solutions, varying the content from 0 to 0.3 %v/v (volume percent with respect to Aniline solution). The electrodeposition of PANI/CNTs composite films, hereinafter referred to as ELD PANI/CNTs, was performed by Cyclic Voltammetry between 0.0V and +1.0V vs. Ag/AgCl, at 50mV/s as scan rate.

For Electrophoretic Deposition of PANI-CNTs composite (EPD process), a well dispersed solution containing PANI and CNTs was used. Firstly, 0.2 mg/ml of PANI was mixed with 0.38 mg/ml of dode-

cylbenzenesulfonic acid (DBSA) and dissolved into a chloroform : *m*-cresol solution (9:1 v/v). Then, an opportune aliquot of the aqueous CNTs suspension was added to the PANI solution, so that the CNTs content was varied between 0 and 0.3 %v/v. For EPD of composite films, hereinafter referred to as EPD PANI-CNTs, a voltage supply was used (Keithley 2400). EPD composite films were obtained by applying 25 V for 5 minutes.

The morphology and the microstructure of both ELD and EPD composite films were characterised by using a FEG-SEM LEO 1530 microscope and a transmission electron microscope TECNAI G2 F30. ELD and EPD PANI-CNTs films were characterised electrochemically in a 0.5 M H₂SO₄ solution, that was deaerated with Argon gas for 10 min prior to use. In order to study their potential efficiency in corrosion prevention, 10 mM FeSO₄ was added to Sulphuric Acid solution. All experiments were done at room temperature.

Results and discussion

ELD process

As mentioned before, the synthesis of ELD PANI-CNTs composite films was performed via electrochemical co-deposition onto electrode materials, so that CNTs were incorporated in the PANI matrix during the Electropolymerisation process. In other words, the formation of the composite occurred during the electrogeneration-deposition of the polymer just near the electrode surface, in the solution containing both CNTs and Aniline.

Recent studies have shown that the functionalisation of CNTs by means of PANI occurs via formation of donor-acceptor complexes (Fig. 3). In fact CNTs act as good electron acceptors, while PANI is a fairly good electron donor [10]. The π -bonded surface of

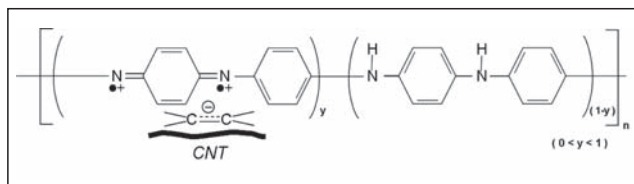


FIGURE 3 Scheme of PANI - CNTs interaction during electropolymerisation

the CNTs interacts strongly with the conjugated structure of PANI, especially through the quinoid ring. Such selective interaction of CNTs with the quinoid ring of PANI was reported in literature [11-12]. 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 [13].

In this work, the formation and deposition of PANI and PANI-CNTs films on carbon paper were obtained by means of 3 consecutive CV scans recorded from 0.0 V to 1.2 V at a scan rate of 20 mV/s. Whereas the aniline solution was uncoloured, the deposited films were green, the typical colour of PANI in the emeraldine salt state, meaning that the polymerisation had occurred.

Figure 4 shows the CVs of the 3 cycles in a 1 M HCl solution containing 0.25 M Aniline and 0% CNTs (a) and 0.3%v/v CNTs (b), respectively. As previously described, in the first positive potential scan, the Aniline is oxidized, exhibiting an irreversible anodic peak. This peak is at 1.1 V in the absence of CNTs, whereas it is shifted at lower anodic potential, i.e., 1.0 V, in the presence of CNTs.

When the Aniline is oxidised, the polymer growth process takes place. Voltammograms recorded during continuous scans showed an increasing current in each successive cycle, meaning the regular growth of the polymer film onto the carbon substrate. From a comparison of the first CV for PANI and PANI with CNTs, it is possible to notice that the voltammogram related to the solution containing CNTs is similar in shape to that recorded from the solution containing only Aniline. However, the curve for ELD PANI-CNTs exhibits a considerable increase in current intensities at the monomer oxidation region. Moreover, the CNTs addition to the Aniline solution favours a catalytic effect towards the monomer oxidation. In fact the Aniline is oxidised more readily in the presence of CNTs (see the peak shifted at less anodic potential), producing a higher current density during the anodic oxidation. This phenomenon was already observed by Wu [14], who reported that the presence of CNTs in an acid Aniline aqueous solution accelerates the growth rate of PANI.

Similar behaviour was observed in CV curves re-

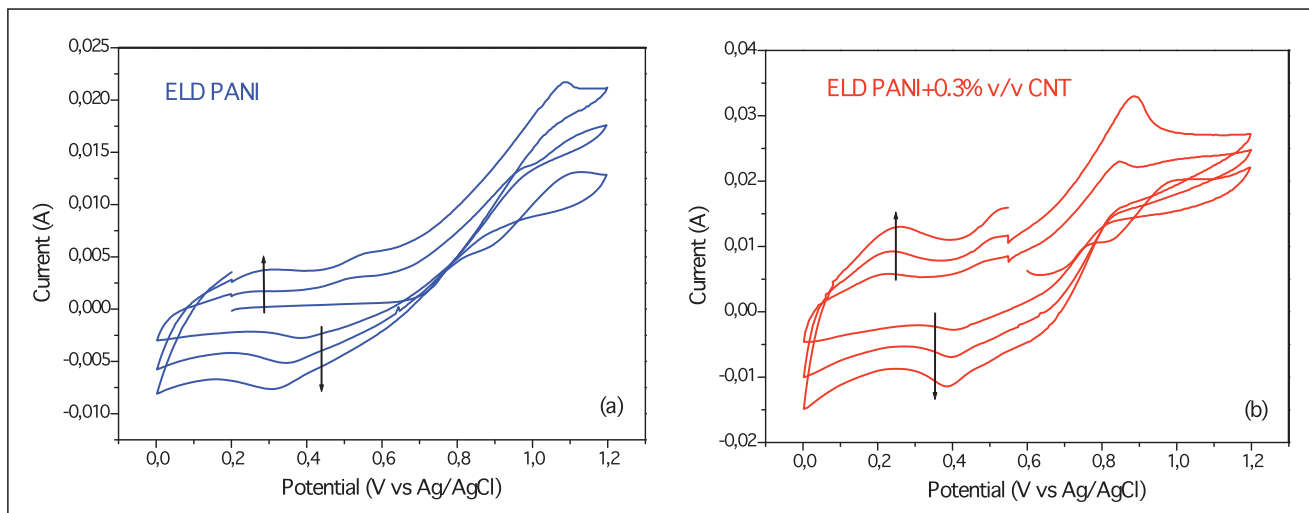


FIGURE 4 CV curves referred to electrodeposition cycles in a 1 M HCl solution containing 0.25 M Aniline and 0% CNTs (a) and 0.3%v/v CNTs (b)

ferring to lower CNTs content (not reported here for sake of brevity). In those curves, a higher current was recorded when the content of CNTs was higher. This effect should be attributed to the dimensional characteristics of CNTs. In fact, in the presence of CNTs, the exposed area available for the PANI electropolymerisation is wide with respect to the surface of a planar working electrode. Therefore, we supposed that an increase in CNTs content in an ANI solution allowed an increase in the amount of electropolymerised PANI.

We also noticed that for CNT-based composites, an anodic peak around 0.2 V appears. This peak can be explained through two mechanistic theories proposed by Huang [15]. One possibility is that CNTs and Aniline undergo strong interactions and lead to charge stabilisation, promoting the protonation of PANI. The other is that CNTs act as condensation nuclei promoting the polymer aggregation.

EPD process

As mentioned before, EPD is a two-step process, consisting in electrophoresis and deposition. Each step requires accurate attention. The main requirement to obtain an efficient EPD process is to use suitable suspensions where particles are well suspended and dispersed into a proper liquid medi-

um. 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 phenomena produce a superficial charge also allowing solids to move in the electric field.

With regard 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 [16]:

$$m = C_s \mu A E t$$

where C_s is the solids' concentration in the suspension; t , the deposition time; μ , the electrophoretic mobility; E , the electric field strength; A , the surface area of the electrode. In this expression, the critical parameter is the electrophoretic mobility, defined as:

$$\mu = \varepsilon \zeta / 4\pi\eta$$

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

For preparing EPD suspensions based on polyani-

line, PANI was dissolved into a mixture of $\text{CHCl}_3/\text{EtOH}$ containing m-cresol and dodecylbenzenesulphonic acid (DBSA). The amphiphile DBSA was 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 [17]. The so prepared suspension was green, indicating the emeraldine salt state of PANI. After addition of some aliquots of CNTs solution, the PANI suspension became darker, tending to black, because of the CNTs colour and the interaction occurring between CNTs and PANI chains. Since PANI was in the protonated state, the possible interactions between PANI and CNTs generation were:

- 1) electrostatic interaction between $-\text{COO}^-$ groups of functionalized CNTs (residual of the purification treatment) and $-\text{NH}^+$ of PANI;
- 2) π -stacking, referring to the attractive no-covalent interaction between aromatic rings of PANI and CNTs;
- 3) hydrogen bonding between $-\text{OH}$ of CNTs and $-\text{NH}$ of PANI.

Meanly, all these interactions did not neutralize the

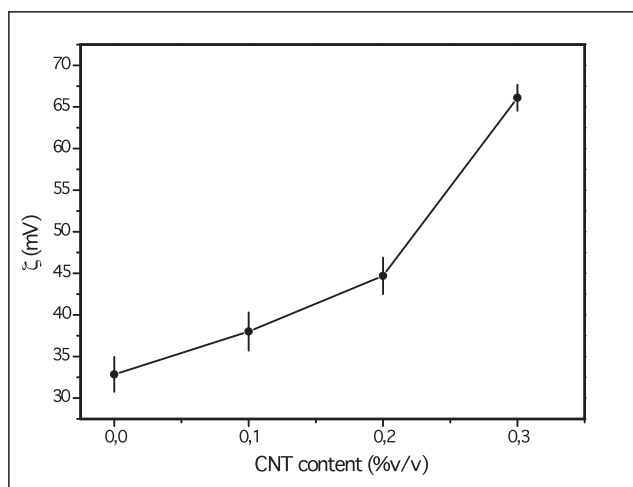


FIGURE 5 Zeta potential of EPD PANI-CNT suspension as a function of the CNTs content

total positive charge of PANI chains, since the amount of CNTs in the PANI suspension was quite low. This affirmation was confirmed by measurements of zeta potential. In Fig. 5, the zeta potential values are reported as a function of the CNTs content. One can notice that PANI is effectively positively charged. After adding CNTs to PANI suspension, the zeta potential increased in positive correlation with the CNTs content, meaning that the CNTs in suspension contributed to improve the efficiency of the EPD process.

Morphological characterisation

After electrochemical and electrophoretic deposition, the surface of all PANI-based films were examined by SEM. Figure 6 shows SEM images of the surface of pure PANI and ELD PANI-CNTs, deposited on carbon paper, when CNTs at the maximum concentration were present in the Aniline solution. The morphology of PANI deposit (Fig. 6a) is porous and appears composed of nano-fibrils. When CNTs are present in PANI, the morphology of ELD PANI-CNTs composites appears modified with respect to pure PANI, as shown in Fig. 6b.

The diameter and the length of the fibrils in composite films are similar to those of individual CNTs, but PANI fibrils are more straightened and with their ends chopped, thus reminding the CNT shape. This means that PANI covered each CNT in a thin layer, acting as a backbone for building the polymer. TEM images (inset) evidence a different structure of PANI-CNTs with respect to pure PANI. The presence of CNTs seems to have made the polymer structure denser, whereas in the pristine form it is characterised by a low degree of order. These results confirm that the interaction between CNTs and PANI produced a PANI coating on each CNT or CNTs wisp.

In the case of EPD PANI-CNTs composites, the presence of CNTs is more evident. In Fig. 7, the EPD PANI shows a structure similar to that of ELD PANI, with the characteristic fibrils having a dimension mainly comparable to ELD PANI's. When CNTs were present in EPD PANI solution, the deposited film appears formed by longer and thinner structures, together to some others with globular shape.

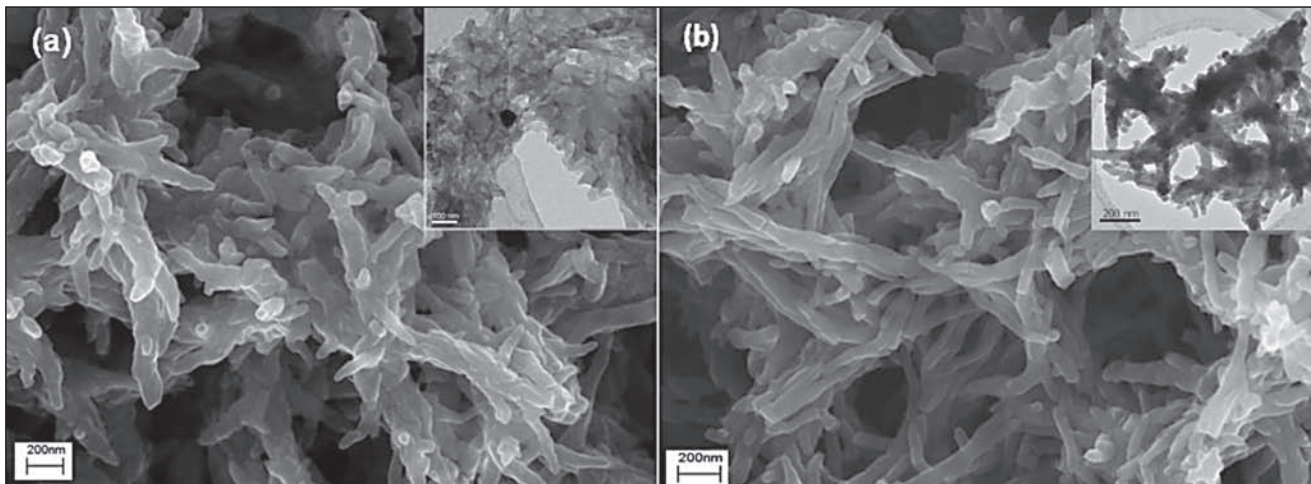


FIGURE 6 SEM and TEM images of ELD PANI without (a) and with CNTs 0.3% v/v (b)

At a higher magnification, the morphology of the surface of the long structures and that of the globular ones is similar, appearing quite rough. We attributed this morphology to the polymer that was able to cover the CNTs. Nevertheless, probably the action of *m*-cresol in straightening the PANI chains was not completely efficient, so that some globular aggregate remained in solution and therefore also in the deposited film. TEM observations (inset of Fig 7b) confirmed the presence of PANI around the CNTs.

Electrochemical characterisation

Electrochemical characterisation of PANI and PANI-CNTs films was carried out by CV in 0.5 M H₂SO₄, in presence of Argon gas. Figure 8 shows the last of 10 voltammograms acquired on three coatings of each type of PANI-CNTs composites (ELD and EPD), containing 0, 0.1%v/v and 0.3%v/v of CNTs, respectively.

For ELD PANI-CNTs, the peak structure conforms to that already proven in literature [18]. The anodic peak A at about 0.25 V represents the transition

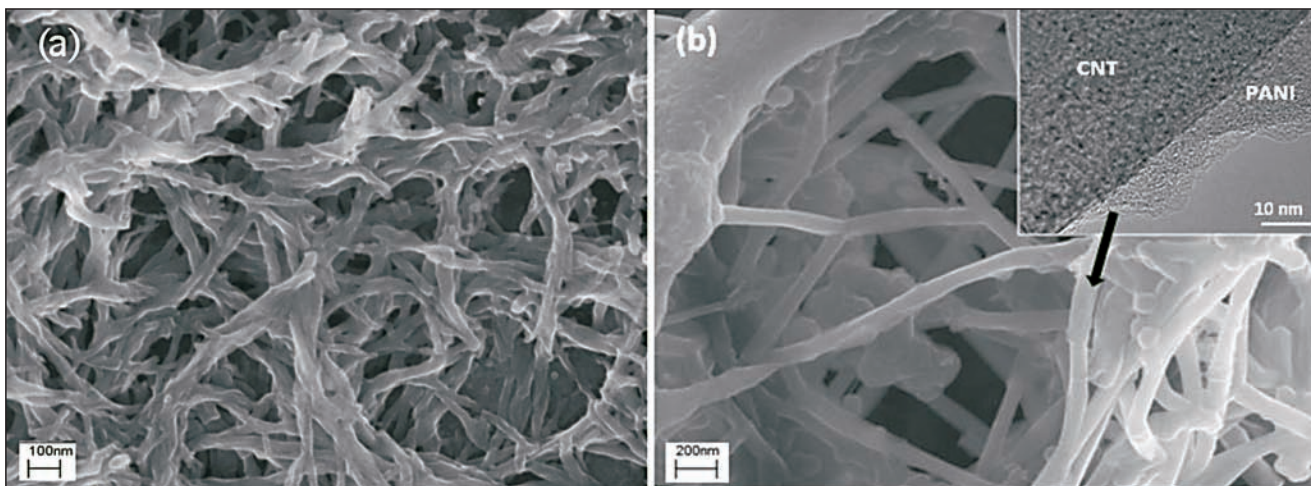


FIGURE 7 SEM and TEM (inset) images of EPD PANI without (a) and with CNTs 0.3% v/v (b)

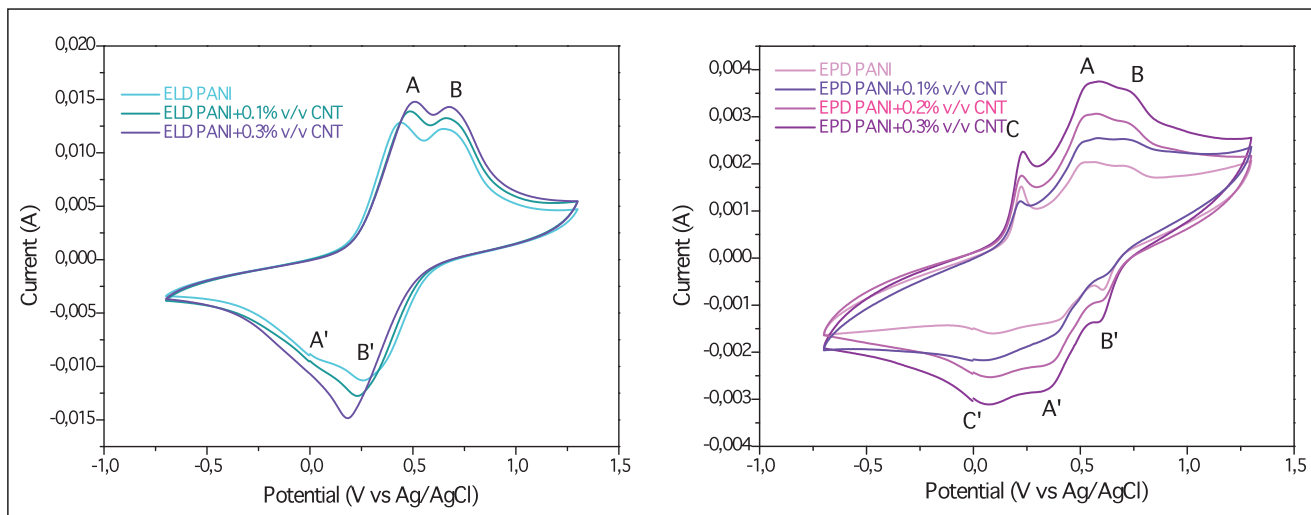


FIGURE 8 CV in H_2SO_4 of ELD PANI-CNTs (a) and EPD PANI-CNTs (b) (the CV referring to 0.2% v/v CNT of ELD composites was omitted for better clarity of the graph)

from leucoemeraldine to protonated emeraldine, which is the most conductive form of PANI. Peak B at about 0.75 V corresponds to the most oxidised state of PANI, concerning the oxidation of emeraldine to pernigraniline. The peaks A' and B' during the cathodic scan correspond to the reversal process.

No additional peaks can be observed due to the CNTs presence in the CV curves, indicating the absence of electrochemical activity of CNTs. However, when compared with PANI, the peak intensities for PANI-CNTs films are higher. This result is in line with the hypothesis that the amount of electrodeposited PANI increases when CNTs are present in the solution. This could allow to have an improved electrochemical activity of the composite films, if compared with the pristine PANI.

For EPD PANI-CNTs, peaks A and B are again present but so close as to form a broad peak. A new peak C is recognizable, corresponding to the generation of radical cations [18]. So, the EPD process seems to produce a more electroactive form of PANI. For both deposition processes, an anodic shift was recorded in the anodic peaks and a cathodic shift in the cathodic peaks, correlated with the CNTs concentration. The shift in the redox peaks can be explained in terms of the effect on the CNTs

addition to the electronic structure of PANI. We suppose that the created interaction between CNTs and ELD PANI during polymerisation, such as that represented in Fig. 4, inhibits the total PANI protonation in the H^+ ions presence, thus making it more possible to block the transition of quinonoid imine ($=N^-$) to benzenoid amine ($-NH^-$).

In Fig. 9. the CVs recorded after $FeSO_4$ injection into the H_2SO_4 solution are reported for ELD PANI-CNTs (Fig. 9a) and for EPD PANI-CNTs (Fig. 9b). By comparing these curves with the CV acquired in H_2SO_4 , it is possible to notice that the injection of $FeSO_4$ gave rise to an evident change in the voltammetric behaviour. For ELD PANI-CNTs, the A- and B- type peaks were progressively shifted and their relative intensities were changed. This result can be related to the competition between Fe^{2+} and H^+ for protonation sites and gives information on the ion-exchange capability of PANI. Ion-exchange behaviour of PANI has been identified as the main explanation of the corrosion protection of ferrous alloys by PANI layers [19-20]. As a consequence, the enhancement of the peak shift brought about by the incorporation of CNTs into PANI layers suggests that CNTs favour the interaction of Fe^{2+} with the modified PANI film, possibly leading to an improved blocking of the products of the corrosion reaction.

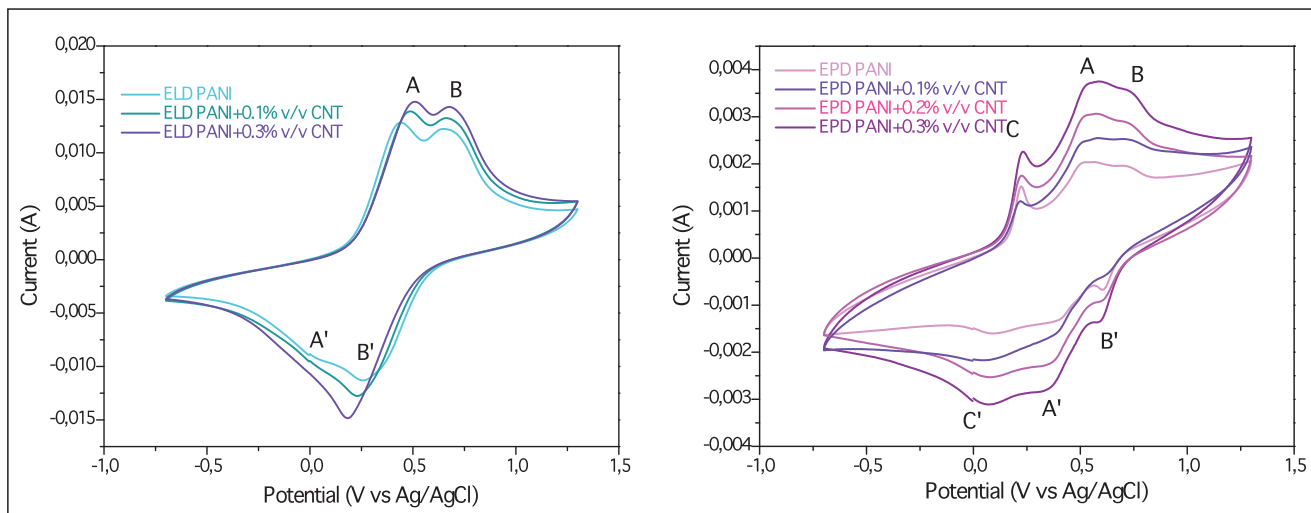


FIGURE 9 CV in H_2SO_4 after injection of FeSO_4 of ELD PANI-CNTs (a) and EPD PANI-CNTs (b)

For EPD PANI-CNTs, after FeSO_4 injection, a shift and a reduction of intensity of the C-type peak was recorded in the anodic scan, whereas a suppression was observed in the cathodic scan. We suppose that this effect was related to the fixing of the Fe^{2+} radicals in the protonated form of PANI. Also the A- and B-type peaks were modified by the FeSO_4 injection, but less evidently with respect to ELD composites. In general, it is possible to notice that the difference between the current intensity of all the peaks, recorded in both the absence and presence of CNTs, was higher for EPD PANI-CNTs than ELD PANI-CNTs.

From the electrochemical characterisation in H_2SO_4 and FeSO_4 , it is possible to conclude that the hybrid composite material based on PANI and CNTs demonstrated the capability to interact with Fe^{2+} , so showing the film potential to block the corrosion products of ferrous alloys. Moreover, PANI deposited by EPD showed more states than that obtained by ELD, also when CNTs were present in PANI matrix. By comparing the two composites, EPD PANI-CNTs demonstrated a better response to the iron ions with respect to ELD PANI-CNTs, in terms of difference between current intensities.

Conclusions

In this work, PANI was modified by introducing CNTs in order to obtain a hybrid conducting nanocomposite. Two different electrosynthesis methods, Electropolymerisation and Electrophoretic Deposition, were used and a comparison between them and the properties of the so obtained materials was made. In the following, the advantages of each method/material are listed.

- ELD technique uses few chemicals and allows to control the oxidation state of PANI. It is a well-known process and the incorporation of CNTs in the PANI matrix is simple. The process is highly reproducible but not applicable on large areas. During electropolymerisation, CNTs acted as a backbone for PANI, so they were completely covered by the polymer. The ELD PANI-CNTs composites showed a good potential in corrosion protection of ferrous alloys, since the interaction of Fe^{2+} with PANI was favoured by the CNTs presence, even if it is scarcely sensible to their amount.
- EPD technique uses more chemicals than ELD, but it is a process easily applicable to large areas, even for simplicity of the deposition apparatus. Nevertheless, it is not simple to control the

oxidation state of deposited PANI, the EPD PANI-CNTs showed to have a better capability to block the corrosion products than the pristine PANI. Moreover, this capability is positively correlated to the amount of CNTs in the PANI matrix.

In conclusion, PANI-CNTs composite material deposited by ELD demonstrated to have better anti-corrosion properties than PANI, which makes it

suitable as a protective coating, for example on electrodes or in electronic devices. Moreover, EPD was successfully used as an alternative method to ELD.

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