Poly(3,4-ethylenedioxythiophene) on self-assembled alkanethiol monolayers for corrosion protection

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Self-assembled monolayers (SAMs) of octanethiol and dodecanethiol were used to modify the stainless steel substrates for electrodeposition of poly(3,4-ethylenedioxythiophene) (PEDOT), a well known polyelectrolyte derivative. Although the influence of the alkanethiol monolayers on the morphology and topology of micrometric (thickness: 2.25–2.35 μm) PEDOT films is practically negligible, they increase significantly the ability to store charge and the adherence. In contrast, treated substrates not only enhance the electrochemical properties of ultra-thin PEDOT films (thickness: 150–350 nm) but also affect significantly the thickness, roughness, porosity, morphology and topology. Such changes depend on both the length of the alkyl chain in the alkanethiol and the incubation period used for the preparation of the SAMs. Finally, the protection against corrosion imparted by PEDOT films deposited on treated substrates has been examined and compared with that obtained using PEDOT deposited on bare stainless steel electrodes. Inhibition of the corrosion in a 3.5% NaCl solution was found to be considerably higher when PEDOT is deposited on treated electrodes, which has been attributed, in addition to the barrier effect produced by the SAMs, to the structural changes induced at the first stages of the electropolymerization.

Introduction

Many studies about the preparation and characterization of self-assembled monolayers (SAMs) at solid surfaces to fabricate interfaces with organized structures and well defined composition and thickness have been reported. Self-assembly of molecular monolayers relies on spontaneous adsorption of a functional reagent from solution onto a surface, and microstructural organization of the adsorbates through the hydrophobic effect or van der Waals interactions. In particular, alkanethiols anchored to Au(111) surfaces have attracted considerable attention because of the strong interaction between the SH headgroup and the surface, providing a better understanding of the structural organization and properties of these layers. The electron transfer behavior of SAMs also led to the development of new strategies for modifying electrode surfaces aiming at control of their electrochemical processes. Electrons can be transferred across an alkanethiol monolayer by a tunneling mechanism, which operates up to ~12 carbon atoms in the alkyl chain affording electroactive properties to such monolayers.

A field that has received attention in the last fifteen years is the anodic polymerization of conjugated conducting polymers (CPs) on electrodes modified with SAMs to control surface properties and to form stable surface modifications. Specifically, electrochemical oxidation of the corresponding monomers on polycrystalline platinum or gold electrodes coated with long-chain alkanethiols has been used to prepare, among others, polyaniline and some of its derivatives, poly(3-methylthiophene), poly(3-vinylthiophene), poly(3-methylthiophene) and poly(3-octylthiophene). In general, results indicated that the p-adsorption of alkanethiol monolayers improves the electrochemical and optical properties of the conducting polymers.

Poly(3,4-ethylenedioxythiophene), hereafter abbreviated PEDOT (Scheme 1), is one of the most important CPs due to its high conductivity (up to 500 S cm⁻¹), good environmental and chemical stability, fast doping–dedoping processes and excellent biocompatibility. Moreover, PEDOT presents excellent...
electrochemical properties in terms of electroactivity and electrostability, explaining the high ability of this material to store charge (i.e. electrical energy).\textsuperscript{23–25} In spite of the impressive properties of this CP, to the best of our knowledge, there is a unique study combining both PEDOT and SAMs, even though the latter were not used to modify the electrodes before electro-polymerization but the films once generated.\textsuperscript{26} Specifically, electrochemically grown films of PEDOT and other CPs were treated with alkane- and fluoroalkane-thiols for incubation periods ranging from 1 to 24 h.\textsuperscript{26} Treatment of the investigated CPs resulted in covalent bonding of the thiol groups to the polymer backbone, even though this effect was to a lesser extent in PEDOT than in PPy and PAni. SAMs deposited onto the PEDOT and PPy films induced a reduction in the electroactivity, while coated PAni retained the electroactivity.

The aim of this work is to examine the properties of PEDOT electrodeposited on alkanethiol-coated electrodes. Specifically, the surface of stainless steel substrates, which were successfully used to produce micrometric and nanometric PEDOT films with excellent electrical and electrochemical properties,\textsuperscript{24,25,27} was treated with octanethiol (C\textsubscript{8}SH) and dodecanethiol (C\textsubscript{12}SH). The influence of the two alkanethiols on structural and electro-chemical properties of PEDOT films has been examined in detail using X-ray photoelectron spectroscopy (XPS), atomic force microscopy (AFM), scanning electron microscopy (SEM) and cyclic voltammetry (CV). Furthermore, the impact of the SAMs on the corrosion resistance imparted by PEDOT films has been examined using electrochemical impedance spectroscopy (EIS) and SEM. For this purpose, PEDOT coatings electrodeposited on treated and untreated steel sheets were immersed in 3.5\% NaCl aqueous solution, electrochemical and morphological changes at the surface of the barrier films being analyzed.

Methods

Chemicals

3,4-Ethylenedioxythiophene (EDOT) monomer, C\textsubscript{8}SH, C\textsubscript{12}SH and acetonitrile (analytical reagent grade) were purchased from Aldrich and used as received. LiClO\textsubscript{4} (analytical reagent grade) from Aldrich was stored in an oven at 80\°C before use in the electrochemical trials.

Monolayers formation

Thiol monolayers were prepared by immersing stainless steel electrodes, which were previously cleaned with acetone, into 50 mL of alkanethiol as received from Aldrich for time $\tau=2, 10$ or 24 h. Then, the C\textsubscript{8}SH-steel and C\textsubscript{12}SH-steel modified electrodes were removed from the solutions, rinsed with acetonitrile and dried with nitrogen.

Synthesis

PEDOT was obtained by potentiostatic electropolymerization (chronoamperometry, CA) at 1.40 V (ref. 24) in an acetonitrile solution containing 0.01 M of the corresponding monomer and 0.1 M LiClO\textsubscript{4} using polymerization times ($\theta$) of 10 and 300 s. Polymerizations were carried out in a standard three-electrode two-compartment cell under nitrogen atmosphere (99.995\% in purity) at 25\°C. Steel AISI 316 sheets of 4 cm\textsuperscript{2} area (or 1 cm\textsuperscript{2} for topographic and morphologic analyses; see below) were employed as working and counter electrodes, while the reference electrode was an Ag|AgCl electrode containing a KCl saturated aqueous solution ($E^0 = 0.222\ V$ at 25\°C). In order to avoid interferences during the electrochemical analyses, the working and counter electrodes were cleaned with acetone and dried in an air-flow before each trial. The thickness of PEDOT films produced using $\theta = 10$ and 300 s was determined to be ~150 nm (ref. 28) and 2.25–2.35 $\mu$m (ref. 29), respectively.

Chronoamperometric measurements during the anodic polymerization process were controlled using a VersaStat II potentiostat–galvanostat connected to a computer controlled through a Power Suite Princeton Applied Research program. After electropolymerization, all coated electrodes were cleaned with acetonitrile (generation medium) and dried with nitrogen.

Electrochemical measures

The ability to store charge (electroactivity) and electrochemical stability upon consecutive oxidation–reduction cycles (electro-stability) of PEDOT films grown in untreated-, C\textsubscript{8}SH- and C\textsubscript{12}SH-steel electrodes were determined by CV using an acetonitrile solution with 0.1 M LiClO\textsubscript{4}. The initial and final potentials were $-0.50\ V$, while the reversal potential was 1.60 V. The electroactivity increases with the similarity between the anodic and cathodic areas of the first control voltammogram, whereas the electrostability decreases with the oxidation and reduction areas of consecutive control voltammograms. Accordingly, electroactivity and electrostability were determined through direct measure of the anodic and cathodic areas in the control voltammograms using the Power Suite Princeton Applied Research software. The electrochemical thickness of both nanometric and micrometric PEDOT films was derived from the mass of the polymer deposited in the untreated-, C\textsubscript{8}SH- and C\textsubscript{12}SH-steel electrodes, using a previously described procedure.\textsuperscript{29} EIS measurements were performed using an AUTOLAB PGSTAT 30/FRA 2 system in potentiostatic mode at the open circuit potential (OCP). The amplitude of the EIS perturbation signal was 50 mV, and the studied frequency ranged from $10^3$ to $10^{-3}\ Hz$. Corrosion tests were performed using a 3.5\% NaCl solution. All experiments were carried out in air at 25\°C.

Fourier-transform infrared (FTIR)

Spectra were recorded on an FTIR 4100 Jasco spectrophotometer with a resolution of 4 cm\textsuperscript{-1} in the absorbance mode. The samples were placed in an attenuated total reflection accessory
with thermal control and a diamond crystal (Golden Gate Heated Single Reflection Diamond ATR, Specac-Teknokroma).

**X-Ray photoelectron spectroscopy**

Measurements were performed using a SPECS system equipped with an Al anode XR50 source operating at 150 W and a Phoibos 150 MCD-9 detector XP. Samples of 1 cm² were fixed into the sample holder using double sided carbon tape. The pass energy was set at 25 eV using 0.1 eV steps. The partial pressure of the argon flood gun was below $1.5 \times 10^{-9}$ mbar. Data acquisition and processing were achieved with the Advantage Software. Spectral calibration was determined by setting the main C1s component at 285 eV.

**Atomic force microscopy**

Topographic images were obtained with a Molecular Imaging PicoSPM using a NanoScope IV controller in ambient conditions. The tapping mode AFM was operated at constant deflections (i.e. vertical constant force with triangular shaped gold-coated silicon nitride). The row scanning frequency was set to 1 Hz and the physical tip–sample motion speed was 10 µm s⁻¹. The root-mean-square (RMS) roughness ($r$) was determined using the statistical application of the Nanoscope software, which calculates the average considering all the values recorded in the topographic image with exception of the maximum and the minimum. The scan window size was 5 x 5 µm² in all cases, a total of 65,536 topographic data being computed in each image. In all images acquired, which are 512 x 512 pixel² maps, differences in height are indicated by a color scale: dark is low and white is high. Significant searches in different areas of the films were performed to find optimum images. Only reproducible images have been reported in this paper.

The thickness of the nanometric PEDOT films generated on the C₈SH- and C₁₂SH-steel electrodes was determined using AFM scratch technique. This method is based on the use of AFM topographic measurements to determine the height at the step defined by the substrate–PEDOT interface of films scratched without penetrating the substrate.

**Scanning electron microscopy**

SEM images were analyzed using a Focused Ion Beam Zeiss Neon40 scanning electron microscope at 3 kV.

**Adherence**

Measurements were based on the standard sellotape test (TESA-4204 BDF), which consists in cutting the film into small squares, sticking the tape and then stripping it. The ratio between the number of adherent film squares remaining and their total number gives the percentage adherence.

**Results and discussion**

**Steel-modified electrodes**

Fig. 1 compares the height images and transversal section profiles determined by AFM for untreated-, C₈SH- and C₁₂SH-steel substrates, the latter two corresponding to an incubation of $\tau = 24$ h in the alkanethiol solution. As it can be seen, the untreated-steel surface is very flat showing a RMS roughness of only $r = 11$ nm. Deposition of alkanethiols produces significant variations in both the roughness, which is 57 and 27 nm for C₈SH- and C₁₂SH-steel, respectively, and topography of the surfaces. Regarding the latter, irregularities are more frequent in C₈SH-steel than in C₁₂SH-steel. SAMs produced using the alkanethiol with the largest hydrocarbon chain are more uniform and show fewer structural defects than those made with the shortest one, which should be attributed to the better packing of the former with respect to the latter. Thus, it is well known that long chain alkanethiols CₙSH with $n \geq 11$ form well-ordered monolayers on surfaces because of the close-packing of the molecules.\textsuperscript{30,31}

To characterize the covalent attachment of the thiols to the surface of stainless steel, XPS analyses were performed. Fig. 2a shows the high resolution spectra of the sulfur 2p region for C₁₂SH-steel prepared using $\tau = 2$ h. The S 2p binding energy ranges from 155 to 168 eV. The component at 162.87 eV (S 2p₃/₂) corresponds to the steel-bound thiolate (S–Fe), whereas the component at 163.90 eV (S 2p₁/₂) can be assigned to unbound thiol (–SH) or disulfide bonds (S–S).\textsuperscript{2a,32,33} The formation of SAMs on steel sheets is schematically depicted in Fig. 3.

**Micrometric PEDOT films**

FTIR analyses (data not shown) indicate that the band centered at 756 cm⁻¹, which corresponds to the C–H out-of-plane bending mode, is detected in the spectrum recorded for the pure
EDOT monomer but not in the spectra of PEDOT films, independently of both the substrate and $\theta$. This feature reflects that in all cases CA provides linear polymer molecules through the formation of $\alpha,\alpha$-linkages. Accordingly, electropolymerization of PEDOT using steel electrodes coated with $\text{C}_n\text{SH}$ was a success in all cases (Fig. 3).

AFM and SEM images of micrometric PEDOT films ($\theta = 300\text{ s}$) deposited on untreated- and $\text{C}_8\text{SH}$-steel, where the SAMs of the latter substrate were prepared considering $\tau = 2\text{ h}$, are displayed in Fig. 4. The resemblance between the images obtained for the two systems, which in addition are very similar to those recorded from films deposited on $\text{C}_{12}\text{SH}$-steel and on modified substrates prepared using $\tau = 10$ and $24\text{ h}$ (data not shown), indicates that influence of the SAMs’ interface on the globular morphology is practically negligible when the thickness of the film is within the micrometric scale. Similarly, electrochemical measures indicate that the influence of SAMs on the thickness is negligible, the values obtained for films deposited on $\text{C}_8\text{SH}$- and $\text{C}_{12}\text{SH}$-steel (Fig. 4c) being practically identical to those reported for films on untreated-steel ($2.25–2.35\text{ m}$) and the modified substrate was obtained by immersing the steel electrode into $50\text{ mL}$ of octanethiol by $\tau = 24\text{ h}$.

High resolution XPS spectra of the C 1s, O 1s, S 2p and Cl 2p regions for PEDOT films obtained using untreated- and $\text{C}_{12}\text{SH}$-steel ($\tau = 2\text{ h}$) electrodes were carried out to characterize the structure, counterion bonding and composition. The position of the peaks in the spectra was practically identical for both systems. Analysis of the C 1s region (Fig. 2b) evidences four types of carbon, C=C (285.0 eV), C–S (285.3 eV) in the $\alpha$ position, C=C–O (286.3 eV) in the $\beta$ position, and C–O–C (287.2 eV) in the ethylene bridge, which is in agreement with the values previously reported.\textsuperscript{[14],[35]} The carbon spectra also show an asymmetrical tail that resulted from a combination of $\pi–\pi^*$ shake-up transition
and possibly positively polarized or charged carbon.\textsuperscript{34,36–38} The PEDOT characteristic C–O–C (533.3 eV) bonding is present in the O 1s region (Fig. 2c) as well as a perchorlate (531.9 eV) contribution.\textsuperscript{39} The PEDOT spin–split sulfur coupling, S 2p_{3/2} (164.1 eV) and S 2p_{1/2} (165.3 eV), with a separation of 1.18 eV,\textsuperscript{40} also presents a higher energy broad tail arising from positively charged sulfur within the thiophene ring (Fig. 2d).\textsuperscript{41–43} Another sulfur species observed at 166–167 eV have been attributed to oxidized S species, which may be due to fact that samples were repeatedly exposed to the atmosphere since their generation.\textsuperscript{33}

Fig. 5 compares the control voltammograms of micrometric PEDOT films deposited on untreated-, C\(_8\)SH- and C\(_{12}\)SH-steel, the latter two being prepared considering \(\tau = 2\), 10 and 24 h. As it can be seen, the electroactivity of films obtained using electrodes pre-treated with alkanethiols was significantly higher than that of PEDOT deposited on untreated-steel. Thus, the ability to store charge increases by \(\sim 20\%\) and \(\sim 30\%\) for C\(_8\)SH- and C\(_{12}\)SH-steel, respectively, even though such enhancement is practically independent of \(\tau\). On the other hand, the loss of electroactivity upon 30 consecutive oxidation–reduction cycles is of only 14\% for PEDOT films deposited on untreated-steel, whereas the electro-stability of films on C\(_8\)SH- and C\(_{12}\)SH-steel largely depends on \(\tau\).

![Fig. 5 Control voltammograms for the oxidation of micrometric PEDOT films deposited on untreated- (black line in both (a) and (b)), C\(_8\)SH- (a) and C\(_{12}\)SH-steel (b) substrates, the latter two being prepared considering \(\tau = 2\) h (blue line), 10 h (green line) and 24 h (red line). Voltammograms were recorded using a 4 cm\(^2\) steel electrode in acetonitrile with 0.1 M LiClO\(_4\), at 100 mV s\(^{-1}\) and 25 °C. Initial and final potentials: –0.50 V; reversal potential: 1.60 V. The absence of electrochemical activity of uncoated C\(_8\)SH- and C\(_{12}\)SH-steel substrates (blank samples) is evidenced in the insets of (a) and (b), respectively.](image)

This is reflected in Fig. 6, which displays the variation of the loss of electroactivity against \(\tau\) for the two types of pre-treated substrates. In both cases, the loss of electroactivity increases with \(\tau\), even though films deposited on C\(_{12}\)SH-steel using \(\tau = 2\) and 10 h are more electrostable than those on untreated-steel.

The adherence was estimated using a normalized sellotape test, which gives a measure ranging from 0 to 100\%. Electrodes modified with SAMs improve the adherence of micrometric PEDOT films. Thus, adherence of PEDOT to the untreated-steel surface is 68\% ± 1%, while that of films deposited on C\(_8\)SH- and C\(_{12}\)SH-steel is 75\% ± 1% and 83\% ± 2%, respectively, independent of \(\tau\).

Nanometric PEDOT films

AFM images of nanometric PEDOT films (\(\theta = 10\) s) deposited on untreated, C\(_8\)SH- and C\(_{12}\)SH-steel (both \(\tau = 2\) and 24 h) are compared in Fig. 7, while the roughness and the thickness of the films are listed in Table 1. As it can be seen, ultra-thin PEDOT films are significantly affected by the pre-treatment of the substrate, the thickness increasing with both the length of the alkyl chain in alkanethiol and \(\tau\). Specifically, comparison with the film deposited in untreated-steel indicates that the thickness increases from 16\% to 54\% and from 74\% to 114\% when the steel electrode is incubated in C\(_8\)SH and C\(_{12}\)SH solutions, respectively, for \(\tau\) values ranging from 2 to 24 h.

The influence of the two alkanethiols on both the roughness and the topology is apparently different. Thus, although \(\tau\) affects considerably both the roughness and topology of the films deposited on C\(_8\)SH-steel, this effect is less pronounced (topology) or almost inexistent (roughness) in films deposited on C\(_{12}\)SH-steel. The high density of small aggregates detected on porous films deposited on untreated-steel transforms into a distribution involving a few compact aggregates upon the pretreatment of the substrate. The dimension (both height and diameter) and the density of such aggregates increases and decreases, respectively, with the size of the alkanethiol and, in the case of the C\(_8\)SH-steel electrode, with \(\tau\). This behavior should be attributed to the fact that SAMs of C\(_{12}\)SH are more regular and well-packed than those of C\(_8\)SH, the influence of the incubation time \(\tau\) on the structure being much less relevant in the former than in the latter.
Similar features are evidenced in Fig. 8, which shows high- and low-resolution images of PEDOT films deposited on untreated-, C₈SH- and C₁₂SH-steel substrates. Films were prepared considering a polymerization time of 10 s. Pre-treated substrates were obtained by immersing the steel electrodes into 50 mL of alkanethiol by \( \tau = 2 \) and 24 h.

### Table 1

<table>
<thead>
<tr>
<th>Substrate</th>
<th>( \tau )</th>
<th>( l )</th>
<th>( r )</th>
<th>( l/r )</th>
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<tr>
<td>Steel</td>
<td>—</td>
<td>153 ± 12</td>
<td>67</td>
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<td>178 ± 23</td>
<td>78</td>
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<td>10 h</td>
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<td></td>
<td>24 h</td>
<td>236 ± 19</td>
<td>87</td>
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<tr>
<td>Steel-C₁₂SH 2 h</td>
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<td>267 ± 31</td>
<td>100</td>
<td>2.7</td>
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<tr>
<td></td>
<td>10 h</td>
<td>308 ± 20</td>
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<td>3.4</td>
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<td></td>
<td>24 h</td>
<td>343 ± 18</td>
<td>93</td>
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### Table 2

<table>
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<th>Electrostability</th>
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<td>39</td>
<td>8</td>
</tr>
<tr>
<td></td>
<td>10 h</td>
<td>36</td>
<td>8</td>
</tr>
<tr>
<td></td>
<td>24 h</td>
<td>35</td>
<td>9</td>
</tr>
<tr>
<td>Steel-C₁₂SH</td>
<td>2 h</td>
<td>45</td>
<td>6</td>
</tr>
<tr>
<td></td>
<td>10 h</td>
<td>43</td>
<td>7</td>
</tr>
<tr>
<td></td>
<td>24 h</td>
<td>41</td>
<td>7</td>
</tr>
</tbody>
</table>

Fig. 8 High- and low-resolution SEM micrographs (left and right, respectively) of PEDOT films deposited untreated-, C₈SH- and C₁₂SH-steel substrates. Films were prepared considering a polymerization time of 10 s. Pre-treated substrates were obtained by immersing the steel electrodes into 50 mL of octanethiol by \( \tau = 2 \) h.
Corrosion protection

SAMs derived from alkanethiols were successfully applied to inhibit the corrosion of iron and other metallic substrates.\textsuperscript{44,45} Thus, the formed stable hydrophobic films depressed significantly the metal dissolution of the underlying substrate. On the other hand, PEDOT has been found to impart protection against corrosion when it is used as an anticorrosive additive in the formulation of conventional epoxy paints,\textsuperscript{46,47} whereas the protective effect of PEDOT films directly deposited on the metal substrate was very slight.\textsuperscript{48} In this section, we examine the benefits of the alkanethiols in the protective effects of PEDOT films.

The EIS plots obtained for PEDOT films ($\theta = 300 \text{ s}$) deposited on untreated- and C$_8$SH-steel ($\tau = 2 \text{ h}$) after 24, 168 and 480 h of immersion in a 3.5% NaCl solution are provided in Fig. 9. The EIS diagrams obtained for the films deposited on C$_6$SH- and C$_{14}$SH-steel were very similar and, therefore, the latter are not reported here for the sake of simplicity. In all cases, spectra show three well-characterized regions. At high frequencies ($f > 25 \text{ Hz}$), a capacitive semi-circle related with the polymer–electrolyte interface is observed, its diameter determining the charge transfer resistance ($R_{CT}$) in parallel with the double layer capacitance ($C_{DL}$). At intermediate frequencies ($25 \text{ Hz} < f < 1.5 \text{ Hz}$), the spectra show a linear line with a slope around 45°, which corresponds to a Warburg diffusion region and should be attributed to the semi-infinite diffusion of protons at the polymer–electrolyte interface. Finally, at the low frequency range ($f < 1 \text{ Hz}$), a nearly vertical line is found due to the faradaic pseudocapacitance of the PEDOT film, as previously described.\textsuperscript{39,50} Thus, at higher frequencies the process is charge-transfer controlled while at lower frequencies the diffusion of charges in the CP film determines the impedance response. According to Hunter et al.,\textsuperscript{51} the frequency range of the diffusion behavior is controlled by the diffusion coefficient and the film thickness. Thus, thick films show diffusion over a large frequency range while no diffusion region is detected in ultra-thin films.

EIS diagrams were analyzed using the equivalent circuit (EC) displayed in Fig. 9c, which was previously proposed for CP coatings.\textsuperscript{50,52} The proposed EC is given by $R_s[CPE_{DL}(R_{CT}W)]$ $CPE_{PC}$, where $R_s$ is the ohmic resistance between the working and the reference electrodes; $CPE_{DL}$ is the double layer capacitance; $R_{CT}$ is the charge-transfer resistance in serial connection with a Warburg element, W, that accounts for diffusion; and $CPE_{PC}$ is the pseudo-capacitance at lower frequencies. The capacitances were replaced by a constant phase element (CPE) that describes a non-ideal capacitor when the phase angle is different from −90°. The CPE impedance is attributed to the distributed surface reactivity, surface heterogeneity, and roughness of the current and potential distribution, which are, in turn, related with the electrode geometry and the electrode porosity.\textsuperscript{53} It should be noted that elements associated with the proposed EC, which was selected considering software limitations and the minimum number of circuit elements, are probably involved on both treated and untreated metal surface. The fitting with experimental data provided error percentage smaller than 5% for each circuit component, indicating a satisfactory behavior.

Table 3 shows the simulated values derived from the fitting of the EIS plots represented in Fig. 9a and b to the EC displayed in Fig. 9c. As it can be seen, the impedance is larger for samples deposited on the C$_8$SH-steel than for those generated on untreated steel. The observed increase of the $R_{CT}$ values at the
Table 3  Fitting parameters used to simulate the EIS data obtained for the systems studied in this work

<table>
<thead>
<tr>
<th>Substrate</th>
<th>Immersion time/h</th>
<th>$R_g/\Omega\text{ cm}^2$</th>
<th>$CPE_{DL}/\mu\text{F cm}^{-2}\text{ s}^{-1}$</th>
<th>$n$</th>
<th>$R_{CT}/\Omega\text{ cm}^2$</th>
<th>Width/$\Omega\text{ cm}^2$</th>
<th>$CPE_{PC}/\text{mF cm}^{-2}\text{ s}^{-1}$</th>
<th>$n$</th>
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<tbody>
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<td>Untreated-steel</td>
<td>24</td>
<td>7.02</td>
<td>15.40</td>
<td>0.94</td>
<td>33.6</td>
<td>22.02</td>
<td>6.17</td>
<td>0.80</td>
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<td></td>
<td>168</td>
<td>9.14</td>
<td>20.39</td>
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<td>21.05</td>
<td>20.72</td>
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<tr>
<td></td>
<td>480</td>
<td>10.41</td>
<td>21.73</td>
<td>0.86</td>
<td>104.4</td>
<td>20.53</td>
<td>21.05</td>
<td>0.95</td>
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<tr>
<td>C_8SH-steel</td>
<td>24</td>
<td>7.96</td>
<td>16.81</td>
<td>0.91</td>
<td>102.1</td>
<td>22.17</td>
<td>6.17</td>
<td>0.80</td>
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<td></td>
<td>168</td>
<td>8.16</td>
<td>14.70</td>
<td>0.88</td>
<td>172.9</td>
<td>33.26</td>
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<td>480</td>
<td>11.02</td>
<td>19.26</td>
<td>0.96</td>
<td>240.7</td>
<td>45.51</td>
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</table>

This effect, which produces a reduction of the porosity in the internal side of the films, together with the intrinsic barrier properties of alkanethiol SAMs is responsible for the significant improvement of the abilities of this CP to inhibit corrosion. Thus, EIS experiments showed that PEDOT films deposited on C_8SH- and C_12SH-steel protect the metallic substrate against thiol modified samples was associated with the inhibition effect of thiol layer, decreasing the metal dissolution rate. Moreover, the capacitance associated with this feature ($CPE_{DL}$) is lower than that of the sample deposited on untreated-steel, remaining practically unchanged during the immersion time, probably due to surface smoothing. The Warburg impedance increases with the immersion time, assuming higher values at the samples deposited on C_8SH-steel. Additionally, the pores and/or defects of the CP coating can be blocked by corrosion products, making diffusion more difficult and hindering the access of the aggressive electrolyte to the metal surface, which led to an increase of the overall resistance.

![Fig. 10a](image-url)  
**Fig. 10a** SEM micrographs of the PEDOT film deposited on C_8SH-steel after 168 h of immersion in a 3.5% NaCl solution. As it can be seen, aggregates tend to fill the pores at the surface of the CP, making the access of the anions to the substrate difficult. However, the same protection mechanism was also observed in PEDOT films generated on untreated-steel (data not shown).

![Fig. 10b](image-url)  
**Fig. 10b** SEM micrographs of the PEDOT film deposited on C_8SH-steel after 480 h of exposure to the 3.5% NaCl solution. The film was washed with distilled water before to obtain the SEM micrographs. As it can be seen, the NaCl does not affect the morphology of the internal side, which is more compact than that of the external side. This observation is consistent with the results obtained for PEDOT films with nanometric thickness (Fig. 7 and 8). Accordingly, the corrosion protection showed by EIS diagrams (Fig. 9) should be attributed not only to the barrier effect produced by the SAMs of alkanethiol but also to their influence on morphology of the CP at the first stages of the electropolymerization process.

**Conclusions**

SAMs of C_8SH and C_12SH have been anchored to stainless steel substrates through C–S covalent bonds. A comparison of PEDOT films deposited on untreated-, C_8SH- and C_12SH-steel reveals that SAMs may affect the structural and electrochemical properties of the CP, even though the scale of such effects depends on the thickness of the films. Specifically, the topology and morphology at the surface of PEDOT films obtained using $\theta = 300$ s, which present thickness larger than 2 μm, are not affected by alkanethiols. However, SAMs promote both the electroactivity and the adherence of micrometric films, such enhancements increasing with the length of alkyl chain of the alkanethiol. In contrast, the influence of SAMs in nanometric PEDOT films, produced using $\theta = 10$ s, is more drastic, affecting the topology, morphology and electrochemical properties of the CP. The extension of such effects depends on the alkanethiol and, in some cases, also on the incubation period $\tau$. Furthermore, SAMs promote the formation of compact molecular aggregates in the first stages of the electropolymerization of PEDOT films. This effect, which produces a reduction of the porosity in the internal side of the films, together with the intrinsic barrier properties of alkanethiol SAMs is responsible for the significant improvement of the abilities of this CP to inhibit corrosion.
corrosion, whereas the protective effect of PEDOT deposited on untreated-steel is considerably lower.

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