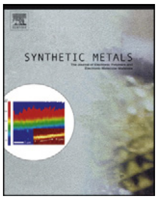
Synthetic Metals 161 (2012) 2718–2726

Contents lists available at SciVerse ScienceDirect

Synthetic Metals

journal homepage: www.elsevier.com/locate/synmet



Development and characterization of poly(3,4-ethylenedioxythiophene)-coated poly(methylene blue)-modified carbon electrodes

Somayeh Kakhki[a,b], Madalina M. Barsan[a], Esmaeil Shams[b], Christopher M.A. Brett[a,*]

[a] *Departamento de Química, Faculdade de Ciências e Tecnologia, Universidade de Coimbra, 3004-535 Coimbra, Portugal*
[b] *Chemistry Department, University of Isfahan, 81746-73441 Isfahan, Iran*

ARTICLE INFO

Article history:
Received 27 July 2011
Received in revised form
27 September 2011
Accepted 7 October 2011
Available online 8 November 2011

Keywords:
Poly(3,4-ethylenedioxythiophene)
Poly(methylene blue)
Conducting polymers
Electropolymerization

ABSTRACT

Poly(3,4-ethylenedioxythiophene) (PEDOT) films have been formed by electropolymerization for the first time on top of poly(methylene blue) (PMB) modified GCE (PMB/GCE), in order to improve PMB modified electrode stability. Experimental conditions, such as electrolyte and fixed potential or potential cycling electrosynthesis have been optimized for PEDOT polymerization on bare GCE. Characterization of PMB modified together with PEDOT/PMB modified and bare GCE was done by cyclic voltammetry and electrochemical impedance spectroscopy (EIS). The operational and storage stability of PEDOT/PMB/GCE was tested. Its good stability and the lack of influence of dissolved oxygen on its electrochemical properties, make it promising for sensor and biosensor applications.

1. Introduction

Organic conducting polymers are described as polymers with spatially extended σ-bonding systems, with broad valence and conduction bands which can be obtained by electropolymerization or chemical oxidation. Over the last 25 years, they have been extensively studied for various technological applications [1–5], such as protective coatings for corrosion control [6,7], chemical sensors [8,9], batteries [10], and electrochromic display devices [11].

Among many applications of conductive polymers, their use in the electrochemical sensor and biosensor area seems to be very promising, and for this purpose phenazine-dye electroactive polymers were introduced in the mid-1990s. The most successful until now were poly(neutral red), poly(methylene blue), poly (methylene green), poly(brilliant cresyl blue) and poly(Nile blue), as recently reviewed in [12].

Methylene blue (MB), or 3,7-bis(dimethylamino)phenothiazine, is an organic dye in the phenothiazine family, which has had widespread application as a redox marker in electrochemical biosensors to detect the DNA hybridization event [13–15], as a sensor for analytes such as ascorbate, epinephrine, dopamine [16], and vitamin B_6 [17], and as an electron transfer mediator in biosensor assembly [18,19] due to its high electron transfer efficiency and low cost [20]. The stability of poly(methylene blue) films formed by electropolymerization on solid substrates is not satisfactory due to polymer hydrophilicity and it has been observed that PMB films can dissolve into electrolyte solution [21]. The aim of this study was to increase the PMB-modified electrode stability, by protecting the PMB polymer with an inert conductive polymer. In this way the operational stability of PMB based sensors and biosensors could be substantially extended and the potential applications of PMB exploited.

Among inert conductive polymers, poly(3,4-ethylenedioxythiophene) (PEDOT) is attractive because of its high conductivity and good stability under ambient conditions [22,23]. On the basis of these properties, PEDOT derivatives are used in a wide range of electronic devices for the fabrication of supercapacitors [24], and have electrochemical and optical applications as electrochromic devices, due to its low-energy band gap (ca. 1.6–1.7 eV) [25–30].

Generally, the electrosynthesis of PEDOT is performed by oxidation of the corresponding monomer, either chemically or electrochemically, films with different morphologies and consequently slightly different physical and chemical properties being obtained [31–33].

EDOT is only slightly soluble in water [34] and water molecules inhibit EDOT polymerization due to their reaction with thienyl cation radicals, which are the initiating species during polymerization [35]. Despite these inconveniences, water is preferred as solvent rather than organic media, which have also been employed for EDOT polymerization [28,36], for economic and environmental reasons. The solubility problem of the monomer can be resolved by

---

[*] Corresponding author. Tel.: +351 239 835295; fax: +351 239 835295.
E-mail address: brett@ci.uc.pt (C.M.A. Brett).

0379-6779/$ – see front matter © 2011 Elsevier B.V. All rights reserved.
doi:10.1016/j.synthmet.2011.10.007

adding chosen surfactants, which can be anionic, such as sodium dodecyl sulfate (SDS) [37,38] or sodium poly(styrene sulphonate) (NaPSS) [39,40], cationic [41] or non-ionic [42,43].

When PEDOT is synthesized electrochemically, the electropolymerization conditions, such as the solvent, the electrode substrate, polymerization potential and technique (either by cycling the potential or applying a fixed potential) play an important role in the properties of the PEDOT films.

In this work, PEDOT was synthesized at fixed potential and by cyclic voltammetry at bare glassy carbon electrodes (GC) and PMB-modified GCE. The influence of the electropolymerization technique and experimental conditions on EDOT polymerization was investigated. The electrochemical properties of the PEDOT modified electrodes were characterized by cyclic voltammetry and electrochemical impedance spectroscopy (EIS). The operational and storage stability of PEDOT/PMB/GCE electrodes were also tested.

2. Experimental

2.1. Reagents and solutions

All chemicals were analytical reagent grade and used as received. The monomers 2,3-dihydrothieno[3,4-b]-1,4-dioxin (EDOT) and methylene blue (MB) were from Aldrich, Germany.

The electrolytes used for the polymerization of EDOT were 0.1 M sodium chloride (NaCl, Riedel-de Haen, Germany) and 0.1 M 4-styrenesulfonic acid sodium salt hydrate (NaPSS, Aldrich, Germany), containing 0.01 M of monomer.

The solution used for the electropolymerization of MB contained 1 mM of monomer dissolved in 0.025 M borate buffer ($Na_2B_4O_7$) with the addition of 0.1 M Na_2SO_4 (both from Merck, Germany) pH 9.25. The electrolyte used for the electrochemical characterization of the modified electrodes was 0.1 M KCl, from Panreac, Spain.

Millipore Milli-Q nanopure water (resistivity ≥ 18 MΩ cm) and analytical reagents were used for the preparation of all solutions. Experiments were performed at room temperature, $25 \pm 1\,^{\circ}C$.

2.2. Instrumentation

All experiments were carried out in a three-electrode cell using a bare or modified glassy carbon electrode as working electrode, a platinum foil as counter electrode and the reference electrode was a saturated calomel electrode (SCE).

Electrochemical measurements were done using a potentiostat/galvanostat Autolab PGSTAT30 connected to a computer with general purpose electrochemical system software (GPES v4.9). Electrochemical impedance spectroscopy (EIS) experiments were carried out by using a PC-controlled Solartron 1250 Frequency Response Analyzer, coupled to a Solartron 1286 Electrochemical Interface (Solartron Analytical, UK), using ZPlot 2.4 software (Scribner Associates Inc., USA) with an rms perturbation of 10 mV applied over the frequency range 65.5 kHz–0.1 Hz, and 10 frequency values per frequency decade. The spectra were recorded at −0.6, −0.3, 0.0 and 0.3 V vs. SCE and were fitted using electrical equivalent circuits with ZView 3.2 software (Scribner Associates Inc., USA).

The pH-measurements were done with a CRISON 2001 micro pH-meter.

2.3. Electrode preparation

The GC electrode was successively polished to a mirror finish using Diamond Spray of particle size 6 μm (Kemet International, UK) followed by thoroughly rinsing with Millipore Milli-Q nanopure water. The electrode was pretreated by cycling the potential between −1.0 to +1.0 V vs. SCE at 100 mV s^{-1} in the electrolyte solution used for the polymerization of MB or EDOT, until a stable voltammogram was recorded.

MB was polymerized using the procedure reported in [44] by cycling the potential between −0.65 and +1.0 V vs. SCE at 50 mV s^{-1} for 30 cycles in a solution containing 1 mM MB in 0.25 M borate + 0.1 M Na_2SO_4 pH 9.25. The PMB modified electrodes were allowed to dry in air for 24 h, at room temperature, kept away from light.

For the electropolymerization of EDOT, a 0.01 M monomer solution was prepared by dissolving the appropriate amount of monomer in a chosen electrolyte solution, either 0.1 M NaCl or 0.1 M NaPSS. Vigorous magnetic stirring and heating for about 30 min, followed by 10 s in an ultrasonic bath, ensured complete monomer dissolution.

The electrochemical procedures used for EDOT polymerization were (a) potential cycling from −0.6 up to 1.0, 1.1 or 1.2 V vs. SCE for 10 cycles at a scan rate of 50 mV s^{-1} or (b) fixed potentials of 1.0, 1.1 and 1.2 V vs. SCE during 100 or 200 s.

After PEDOT deposition, the modified electrodes were left in air at ambient temperature, for at least 24 h, before use.

3. Results and discussion

3.1. Optimization of experimental condition for EDOT polymerization

3.1.1. Choosing the electrolyte solution

Electropolymerization of EDOT from solutions containing 0.01 M monomer was carried out in two electrolyte solutions: 0.1 M NaCl and 0.1 M NaPSS. These electrolyte solutions were chosen, since the monomer dissolves differently in each and they also play an important role in both electron transfer rate and in diffusion processes, the anion having a significant effect on the electropolymerization process and on the properties of the polymer films obtained [33]. It was found that the size of the dopant ion affects the oxidation kinetics and the electrical conductivity of the films [45].

As observed in Fig. 1, during the electropolymerization process of EDOT in NaCl solution, there is no significant increase in the oxidation current at 1.0 V, at which potential radical cation species are expected to be formed. On the contrary, in NaPSS solution, the increase in oxidation current at positive potentials demonstrates the formation of cation radicals which initiate the polymerization process. The process begins with the generation of $EDOT^{\bullet+}$ radical cation species, which then polymerize and then the oligomers formed also are being oxidized so that oligomer radical cation species are produced, that interact with other $EDOT^{\bullet+}$, forming the polymer. The deposition of PEDOT polymer at the electrode surface is indicated by the increase in the capacitive current from 1.6 to 24 mF cm^{-2} for the 10th cycle, calculated from the CV-s recorded during polymerization in the capacitive region of the voltammograms (see Fig. 1a).

The monomer is much more soluble in NaPSS solution due to its surfactant and emulsifier properties that facilitate EDOT dissolution [46]. It was also reported in the literature that surfactant molecules, like SDS, exhibit an electrocatalytic effect, characterized by a decrease of the EDOT oxidation potential, which may result from strong electrostatic interactions between the EDOT cation radical ($EDOT^{\bullet+}$) and SDS anions. [37]. In particular, when the polymer is electrosynthesized in the presence of the polyelectrolyte poly(styrene-4-sulfonate) ($(PSS)^{n-}$), a kind of composite can be formed, in which $(PSS)^{n-}$ polyanion is incorporated into the polymer to compensate the positive charge of PEDOT. Such films have high ionic conductivities, good electrochemical stability and

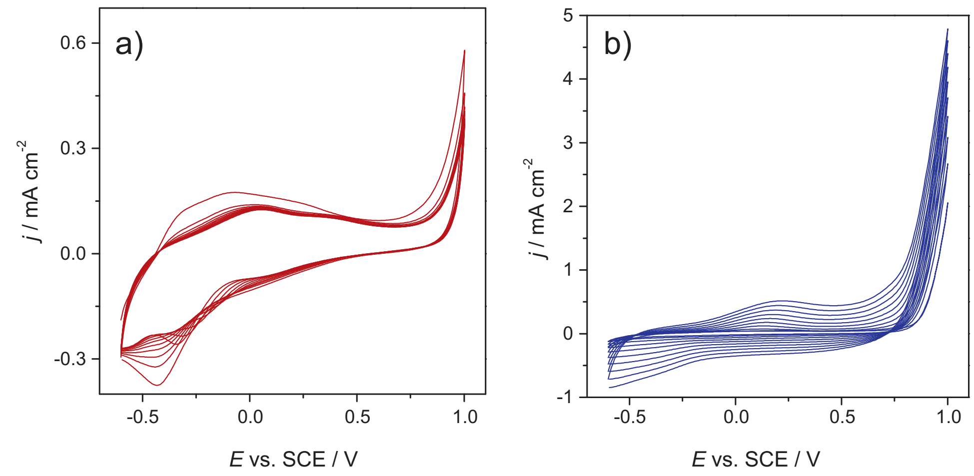


Fig. 1. Cyclic voltammograms recorded during the electropolymerization of EDOT at GCE from a solution containing 0.01 M EDOT monomer in (a) 0.1 M NaCl and (b) 0.1 M NaPSS; $\nu = 50\,\mathrm{mV\,s^{-1}}$, 10 scans between −0.6 and +1.0 V vs. SCE.

a capacitance suitable for practical use in electrochemical supercapacitors [47–49]. Due to all the above-mentioned reasons, NaPSS was chosen as electrolyte for further PEDOT synthesis.

3.1.2. Optimization of the electrochemical techniques for EDOT electropolymerization

3.1.2.1. Potentiostatic polymerization of EDOT. The currents recorded during EDOT polymerization at GCE, at the fixed applied potentials of 1.0, 1.2 and 1.5 V vs. SCE, in the potentiostatic mode, are shown in Fig. 2. As observed by comparing the curves, the plateau region is reached fastest using 1.5 V and takes a longer time to stabilize when the applied potential is 1.2 V vs. SCE. After 50 s, the constant currents reached for both these applied potentials are the same, with a value of $0.25\,\mathrm{mA\,cm^{-2}}$. An increase in the plateau current, up to $1.35\,\mathrm{mA\,cm^{-2}}$, is recorded when 1.0 V potential is applied. It has been reported that if EDOT is polymerized at potentials lower than 1.1 V (at Pt electrodes), overoxidation of PEDOT is negligible, and a higher applied potential leads to an increase in the plateau current values. On the contrary, at potentials higher than 1.1 V, e.g. 1.2 and 1.5 V vs. SCE, as in the present case, both polymerization of EDOT and overoxidation of PEDOT occur, which decreases the plateau current [50].

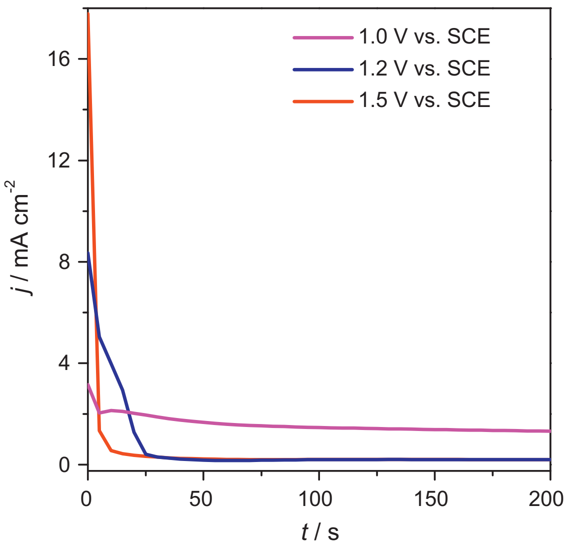


Fig. 2. Electropolymerization of EDOT at GCE from a solution containing 0.01 M EDOT monomer in 0.1 M NaPSS in potentiostatic mode at +1.0, +1.2 and +1.5 V vs. SCE for 200 s.

The capacitive currents recorded at all three PEDOT modified electrodes in 0.1 M KCl at $50\,\mathrm{mV\,s^{-1}}$ were a factor of two higher for PEDOT deposited at 1.2 V than at 1.0 V, $5\,\mathrm{mF\,cm^{-2}}$, even though the plateau current is lower. This was in agreement with what was observed by visual inspection of the electrodes, the blackest color, characteristic of the PEDOT polymer, corresponding to this modified electrode. It has been concluded that a potential of 1.2 V is necessary to generate a sufficient amount of cation radicals, in order to synthesize a uniform, intact layer of polymer.

3.1.2.2. Electropolymerization of EDOT by potential cycling. Fig. 3a_1, a_2 and a_3 shows cyclic voltammograms recorded during the polymerization of EDOT, recorded in different potential ranges: from −0.6 V up to 1.0, 1.2 and 1.5 V vs. SCE. As observed, all three CV plots are characterized by oxidation currents at positive potentials higher than 0.8 V, corresponding to oxidation of the monomer and formation of radical cation species, $\mathrm{EDOT}^{\bullet+}$, and an increase in the capacitive current values during the polymerization process, a characteristic of conductive polymers.

When the positive limit is 1.0 V, there is an increase of a factor of two in the oxidation current corresponding to the cation radical formation, from the first up to the last cycle, but the maximum charge was only 0.8 compared with $4\,\mathrm{mC\,cm^{-2}}$, when the potential was cycled up to 1.2 V vs. SCE, demonstrating that more polymer was deposited in the latter case. This is due to the formation of more radical cation species at 1.2 V, which can subsequently form a thicker PEDOT film, demonstrated by the values of the oxidation current being double those obtained for a positive potential limit of 1.0 V vs. SCE.

When the potential is cycled up to 1.5 V vs. SCE, the first cycle shows a crossover of the reverse negative scan over the positive one, also called “nucleation loop”. This can be due to both the polymer nucleation effect [35,51] and homogeneous reaction between the oligomeric species and the monomer [52]. Since in this case the loop occurs only in the first cycle, it is probably related to the latter phenomenon.

The oxidation current at 1.5 V increases during the second cycle and then drastically decreases, disappearing by the last polymerization cycles. This can indicate that radical cations are generated only at the beginning of the polymerization process. During the first 3 cycles, two oxidation peaks can be observed, the first at around 1.2 V, attributed to EDOT oxidation, and the second, at ≈1.4 V vs. SCE, correlated with the oxidation of PEDOT. After this, only one

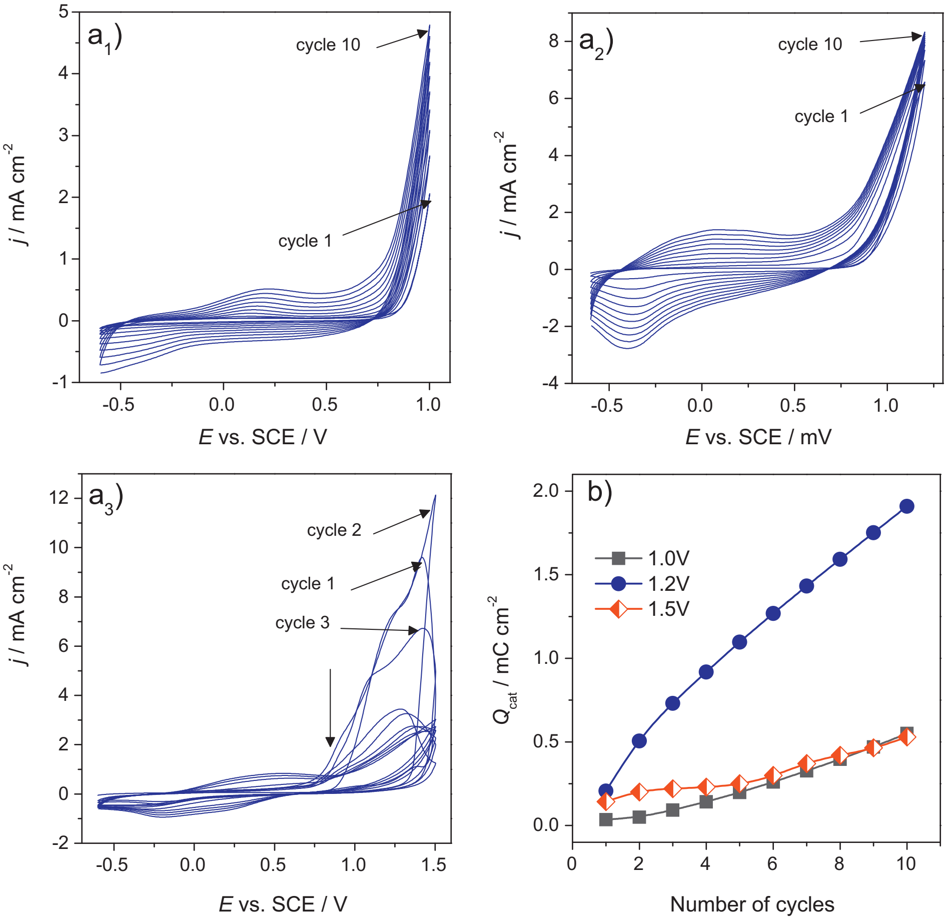


Fig. 3. Cyclic voltammograms recorded during the electropolymerization of EDOT at GCE from a solution containing 0.01 M EDOT monomer in 0.1 M NaPSS; $\nu = 50\,\mathrm{mV\,s^{-1}}$, 10 scans between −0.6 and (a_1) +1.0 V, (a_2) +1.2 V and (a_3) +1.5 V vs. SCE and (b) variation of the cathodic charge corresponding to the undoping process of the formed polymer with each cycle during polymerization.

peak appears at an intermediate potential around 1.3 V, with a continuous decrease in height, until it disappears after a further 3–4 cycles. This can indicate that the electroactivity of PEDOT is first lowered, and then lost, due to its overoxidation at potentials higher than 1.2 V vs. SCE [50].

Fig. 3b shows the variation of cathodic charge corresponding to the undoping process of the deposited polymer with each polymerization cycle, carried out in the three potential ranges investigated. As observed in all cases, there is an increase in the cathodic charge during polymerization, indicating that PEDOT polymer is formed at GCE electrodes. Nevertheless, when polymerization is performed between −0.6 and 1.2 V vs. SCE, significantly higher cathodic charges are recorded, indicating that this is the optimal potential range. It was thus chosen for further EDOT polymerization studies. Moreover, polymerization by potential cycling leads to the deposition of thicker PEDOT films, compared with those obtained at fixed potential, demonstrated by the significantly higher capacitive currents of PEDOT modified electrodes obtained by cycling.

3.2. *Preparation of PEDOT modified PMB/GCE*

3.2.1. *Polymerization of MB at GCE*

The electropolymerization of MB was carried out by cycling the potential between −0.65 V and +1.0 V vs. SCE at $50\,\mathrm{mV\,s^{-1}}$ in a solution containing 1 mM monomer in 0.025 M $Na_2B_4O_7$ + 0.1 M Na_2SO_4, pH 9.25. Cyclic voltammograms recorded during electropolymerization are presented in Fig. 4.

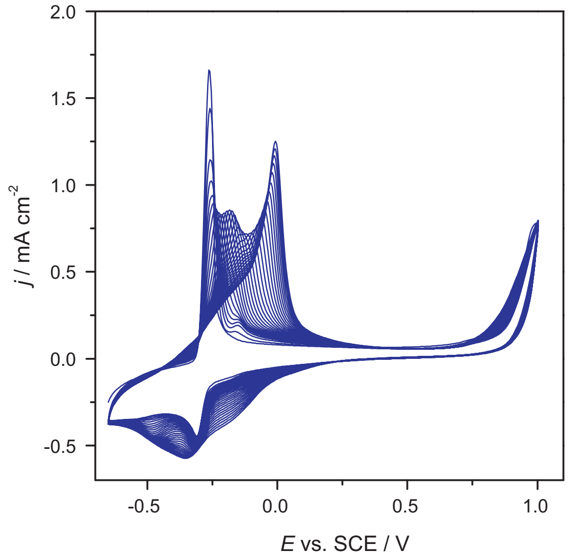


Fig. 4. Electropolymerization of MB from a solution containing 1 mM MB monomer in 0.025 M Na borate + 0.1 M Na_2SO_4 pH 9.25; $\nu = 50\,\mathrm{mV\,s^{-1}}$, 30 scans between −0.65 and +1.0 V vs. SCE at GCE.

The electropolymerization process begins with the adsorption of monomer at the electrode surface and formation of the cation-radical species at high positive potentials, around 1.0 V vs. SCE. MB monomer contains two tertiary amino groups and the

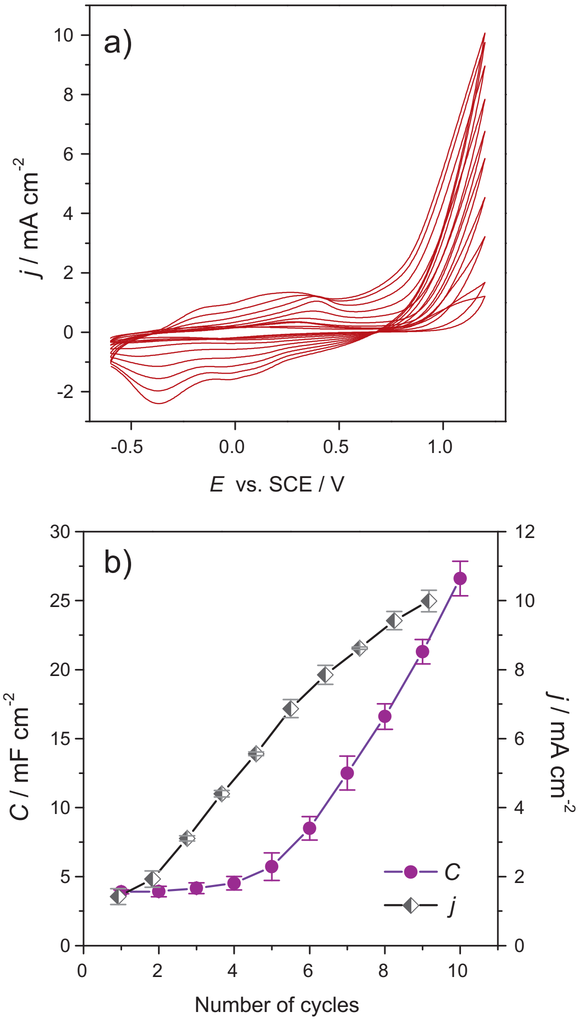


Fig. 5. (a) Cyclic voltammograms recorded during the electropolymerization of EDOT at PMB/GCE from a solution containing 0.01 M EDOT monomer in 0.1 M NaPSS; $v = 50\,\mathrm{mV\,s^{-1}}$, 10 scans between −0.6 and +1.2 V vs. SCE; (b) the variation of the capacitance values and oxidation currents corresponding to the radical cation formation with each cycle during polymerization.

cation-radical species are formed at positive potentials near the potential corresponding to oxygen evolution [44].

During the polymerization process, the oxidation currents of $\approx 1.7\,\mathrm{mA\,cm^{-2}}$, due to the redox activity of the monomer, decrease and, while polymer is formed, the oxidation currents shift towards more positive potentials, and increase up to the final, 30th cycle, reaching a value of $1.3\,\mathrm{mA\,cm^{-2}}$.

3.2.2. Polymerization of EDOT at PMB/GCE

Fig. 5a shows cyclic voltammograms recorded during the polymerization of EDOT at a PMB-modified GCE from a solution containing 0.01 M EDOT monomer in 0.1 M NaPSS. The CVs recorded during polymerization are very similar to those observed during polymerization of EDOT, under the same experimental conditions, at bare GCE, with the difference that, at the bare electrode the current at 1.2 V remains constant at $\approx 8\,\mathrm{mA\,cm^{-2}}$, whereas there is a constant increase in the oxidation current at PMB-modified electrodes, from 1.2 up to $10\,\mathrm{mA\,cm^{-2}}$. This indicates that an increasing amount of radical cation species are generated in each polymerization cycle.

The peaks of PMB are not visible since the currents are 10 times lower than those due to the PEDOT polymer.

As occurs for the polymerization of EDOT at bare electrodes, there is an increase in the capacitive current with each cycle, see Fig. 5b, which indicates the deposition of PEDOT. The capacitive current calculated for the last cycle of EDOT polymerization was $\approx 25\,\mathrm{mF\,cm^{-2}}$.

3.3. Characterization of PMB/GCE, PEDOT/PMB/GCE and PEDOT/GCE electrodes

3.3.1. Cyclic voltammetry

PMB/GCE, PEDOT/PMB/GCE and PEDOT/GCE electrodes were characterized by cyclic voltammetry in 0.1 M KCl. Cyclic voltammograms at different scan rates, from 10 to $200\,\mathrm{mV\,s^{-1}}$, were recorded and are shown in Fig. 6. Both PMB/GCE and PEDOT/PMB/GCE showed a linear dependence of peak current on square root of scan rate (Fig. 6a_2 and b_2), indicating that the overall electrochemical process is diffusion-controlled. A typical PMB redox response is observed in Fig. 6a_1, with an anodic peak at −0.1 V and a cathodic one at −0.36 V vs. SCE. At PEDOT/PMB/GCE, the currents are approximately 10 times greater, as expected due to the capacitive currents exhibited by PEDOT, and the higher slopes of peak current vs. square root of the scan rate also indicate higher diffusion rates. When both PMB and PEDOT are immobilized at GCE, two oxidation and reduction processes can be observed, for oxidation one less apparent at −0.1 V, at the same potential where PMB oxidation occurs, and a second, more evident at +0.3 V vs. SCE, that can also be observed during the last 5 cycles of EDOT polymerization at PMB/GCE, and which is slightly visible in CV-s recorded at PEDOT/GCE (Fig. 6c), so that this process is probably correlated with the electroactivity of PEDOT polymer.

The reduction reactions at PEDOT/PMB/GCE are located at significantly more positive potentials, at 0.0 and 0.4 V vs. SCE, in comparison with −0.36 V for PMB/GCE and ≈−0.4 V at PEDOT/GCE. The electroactivity of PEDOT/PMB/GCE at potentials very close to 0.0 V vs. SCE, indicates that they can mediate electron transfers in this potential region, which is excellent for biosensor applications, due to the fact that the responses of possible interfering compounds are significantly smaller around this potential.

3.3.2. Stability of the PEDOT/PMB/GCE

The stability of a chemically modified electrode is very important for practical applications, so the stability of the PEDOT/PMB/GCE was tested by cyclic voltammetry in two ways. The operational stability was examined by recording 100 successive CV-s at PEDOT/PMB/GCE in 0.1 M KCl solution and a decrease to ≈50% of the initial anodic and cathodic peak currents characteristic to PEDOT/PMB/GCE (see Fig. 6b_1) was observed after 60 cycles, afterwards remaining constant. Additionally, a PEDOT/PMB/GCE was tested during 30 days, recording 10 successive CV-s in 0.1 M KCl once every 5 days. When not in use, the modified electrode was stored at room temperature, away from direct contact with UV light. Results are shown in Fig. 7, where both anodic and cathodic peak currents of PEDOT/PMB/GCE modified electrodes are plotted versus time, and it can be seen that there is a sharp decrease of both currents after 15 days, but then they reach a plateau, remaining almost constant. Thus, the stability of PEDOT/PMB/GCE is very good, taking into account that PMB, which usually dissolves relatively easily in aqueous media, is made much more stable by the deposition of PEDOT on top, due to the insolubility of the PEDOT film in aqueous media.

3.3.3. EIS

Electrochemical impedance spectroscopy (EIS) was used to characterize the physical and interfacial properties of the PMB/GCE, PEDOT/PMB/GCE and PEDOT/GCE modified electrodes. Spectra were recorded in 0.1 M KCl, at applied potentials of −0.3, 0.0 and

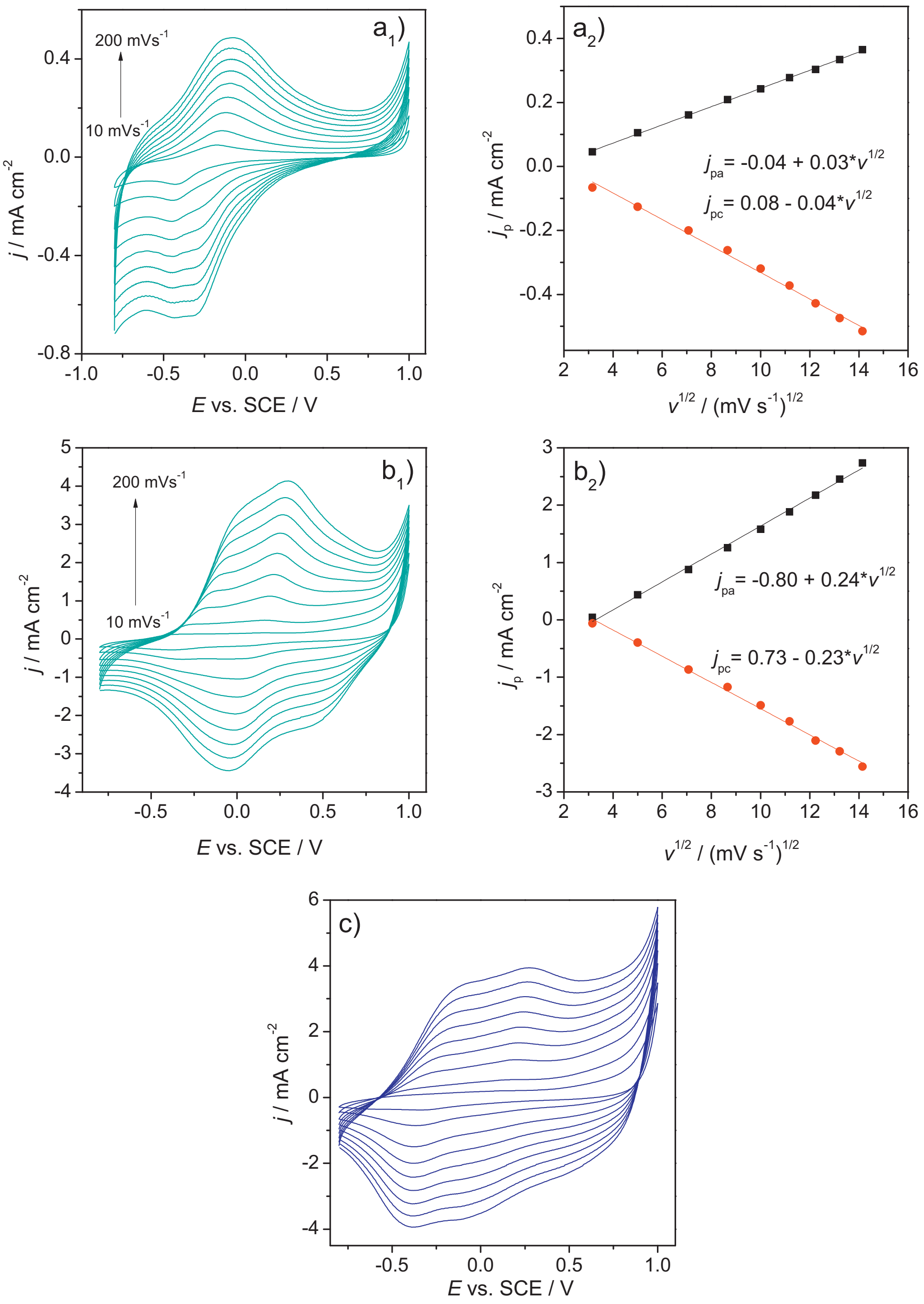


Fig. 6. Cyclic voltammograms recorded at (a) PMB/GCE and (b) PEDOT/PMB/GCE and (c) PEDOT/GCE in 0.1 M KCl solution at different scan rates, from 10 to 200 mV s^{-1} and the corresponding plots of peak vs. square root of scan rate.

+0.3 V vs. SCE, chosen inside and outside of the region where oxidation and reduction of PMB occurs, and are shown in the complex plane plots of Fig. 8. Experiments were done in the presence and absence of oxygen, to evaluate if it has an influence on film properties.

In the case of PMB/GCE, Fig. 8a, the spectra recorded at all potentials have a semicircle profile, with the highest impedance values observed at +0.3 V vs. SCE, as expected, since this potential is the most distant from the midpoint potential of the PMB redox process (see Fig. 4a).

It can be observed in Fig. 8b and c, that spectra recorded at PEDOT/PMB/GCE are very similar to those corresponding to PEDOT/GCE, which indicates that PEDOT has a greater influence on the electrochemical properties of PEDOT/PMB/GCE. The imaginary part of the impedance is ≈20 times lower at these electrodes compared with that of PMB/GCE, which clearly indicates higher capacitance values of PEDOT-modified electrodes, in agreement with cyclic voltammetry. The capacitive lines, with angles very close to 90°, extending down to 0.1 Hz, are characteristic of PEDOT [47,53,54]. In the higher frequency region the spectra present a semicircle with a very small diameter, which means that charge transfer at the electrode/polymer film/solution interface and charge transport through the polymers are both very fast.

The impedance spectra were fitted by using the equivalent circuits presented in Fig. 9. In the case of PMB/GCE, a Randles circuit (Fig. 9a) was used, comprising the cell resistance, R_Ω, of around

Table 1

Resistance (R), constant phase element (CPE), α and capacitance (C) values obtained by fitting the EIS spectra with the equivalent circuits shown in Fig. 8, corresponding to (a) PMB/GCE, (b) PEDOT/PMB/GCE and (c) PEDOT/GCE electrodes in the presence and absence of oxygen in solution.

	E_{ap} (V) vs. SCE	R_1 (kΩ cm^2)	CPE$_1$ (mF cm^{-2} s$^{\alpha-1}$)	α
(a)				
	−0.3	4.6	1.6	0.75
	0.0	3.5	1.0	0.74
	+0.3	23.4	0.4	0.83
No O_2	−0.3	24.5	1.2	0.73
	0.0	21.6	0.5	0.81
	+0.3	29.2	0.4	0.84

	E_{ap} (V) vs. SCE	R_1 (kΩ cm^2)	CPE$_1$ (mF cm^{-2} s$^{\alpha-1}$)	α_1	R_2 (kΩ cm^2)	CPE$_2$ (mF cm^{-2} s$^{\alpha-1}$)	α_2
(b)							
	−0.3	0.12	1.1	0.70	0.92	8.7	0.98
	0.0	0.01	0.9	0.71	–	9.7	0.93
	+0.3	0.001	0.6	0.72	–	8.7	0.95
No O_2	−0.3	0.13	1.0	0.71	1.39	8.8	0.97
	0.0	0.01	1.1	0.68	–	10.2	0.93
	+0.3	0.009	1.4	0.58	–	9.2	0.96

	E_{ap} (V) vs. SCE	R_1 (Ω cm^2)	C_1 (mF cm^{-2})	CPE$_2$ (mF cm^{-2} s$^{\alpha-1}$)	α
(c)					
	−0.3	3.0	3.5	8.8	0.88
	0.0	–	–	10.2	0.95
	+0.3	–	–	9.8	0.97
No O_2	−0.3	3.0	6.4	9.2	0.92
	0.0	–	–	9.7	0.96
	+0.3	–	–	9.7	0.98

15 Ω cm^2, in series with the charge transfer resistance R_1, in parallel with a constant phase element, CPE$_1$, where CPE = $\{(C\,i\omega)^{\alpha}\}^{-1}$, representing the interfacial charge separation, modelled as a non-ideal capacitor, owing to the porosity of the polymer film, the α exponent having values between 0.73 and 0.84. The calculated values of both R_1 and CPE parameters are given in Table 1a. As mentioned above, the charge transfer resistance values are higher at +0.3 V, which is the most distant from the midpoint potential of PMB. Removing oxygen from solution leads to an increase of charge transfer resistance at the PMB modified electrodes, so that they are better for use in oxygenated media, also reported in [44], To fit the spectra at PEDOT/PMB/GCE, two equivalent circuits were used, see Fig. 9b. The spectrum at −0.3 V is different from the others, with a larger diameter semicircle, which indicates that at this potential the modified film is more resistive. In this case, the equivalent circuit contained, beside the solution resistance, two resistance–capacitance combinations, R_1 plus CPE$_1$ and R_2 plus CPE$_2$ corresponding to PMB and PEDOT layers respectively. Constant phase elements were needed, due to polymer porosity and surface non-homogeneity. As observed in Table 1b, which contains the resistance and CPE values, R_1 is smaller than R_2 indicating that charge transfer at PEDOT is lower than at PMB, at this potential. Nevertheless, R_1 has lower values than those corresponding to PMB/GCE, which indicates that PEDOT modification of PMB/GCE improves the charge transfer at PMB interfaces.

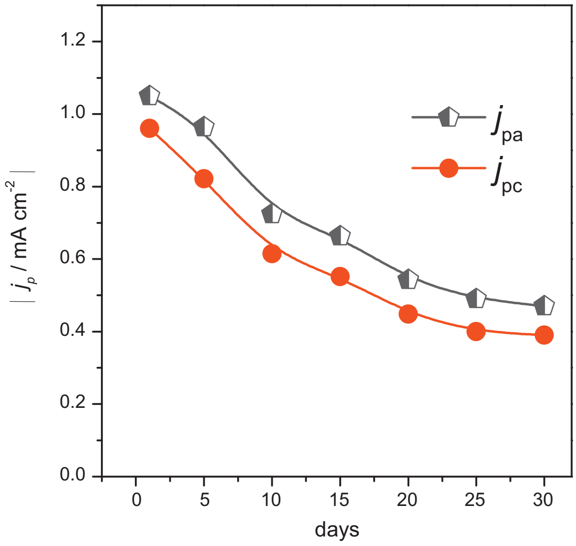


Fig. 7. Storage stability of PEDOT/PMB/GCE electrodes: variation of anodic and cathodic peak currents of PPEDOT/PMB/GCE electrodes, observed in Fig. 6b$_1$.

For applied potentials of 0.0 and +0.3 V, the value of R_1 decreases dramatically, down to 1 Ω cm^2, and R_2 is removed from the equivalent circuit (Fig. 9b). As expected, CPE$_2$ values, which correspond to PEDOT, are 8–10 times higher than CPE$_1$, which have similar values to those recorded at PMB/GCE. The α_2 values are higher than α_1, being very close to 1.0, showing that PEDOT has an almost pure capacitor-like behaviour and also, more importantly, indicates that the PEDOT surface is smoother and more uniform than that of PMB.

Oxygen has little influence on the PEDOT/PMB/GCE properties, only a small increase in both CPE$_1$ and CPE$_2$ values being observed (see Table 1b), an advantage for applications of these PEDOT/PMB/GCE compared to PMB/GCE, since they can be equally used in both oxygenated and deoxygenated media.

The equivalent circuits for PEDOT/GCE are shown in Fig. 9c. All circuits have the cell resistance, R_Ω in series with a CPE, with α values very close to 1.0, indicating that PEDOT-modified GCE acts similarly to a pure capacitor. At −0.3 V vs. SCE, it was necessary to use a charge transfer resistance, R_1, in parallel with a pure capacitance, C_1, to model the high frequency region. The very small charge transfer resistance, of 3 Ω cm^2, underlines the high ionic and electronic conductivity of PEDOT. CPE$_2$ values are around 10 mF cm^{-2} s$^{\alpha-1}$, and are very similar to CPE$_2$ corresponding to the PEDOT/PMB/GCE electrode, attributed to PEDOT polymer on top of

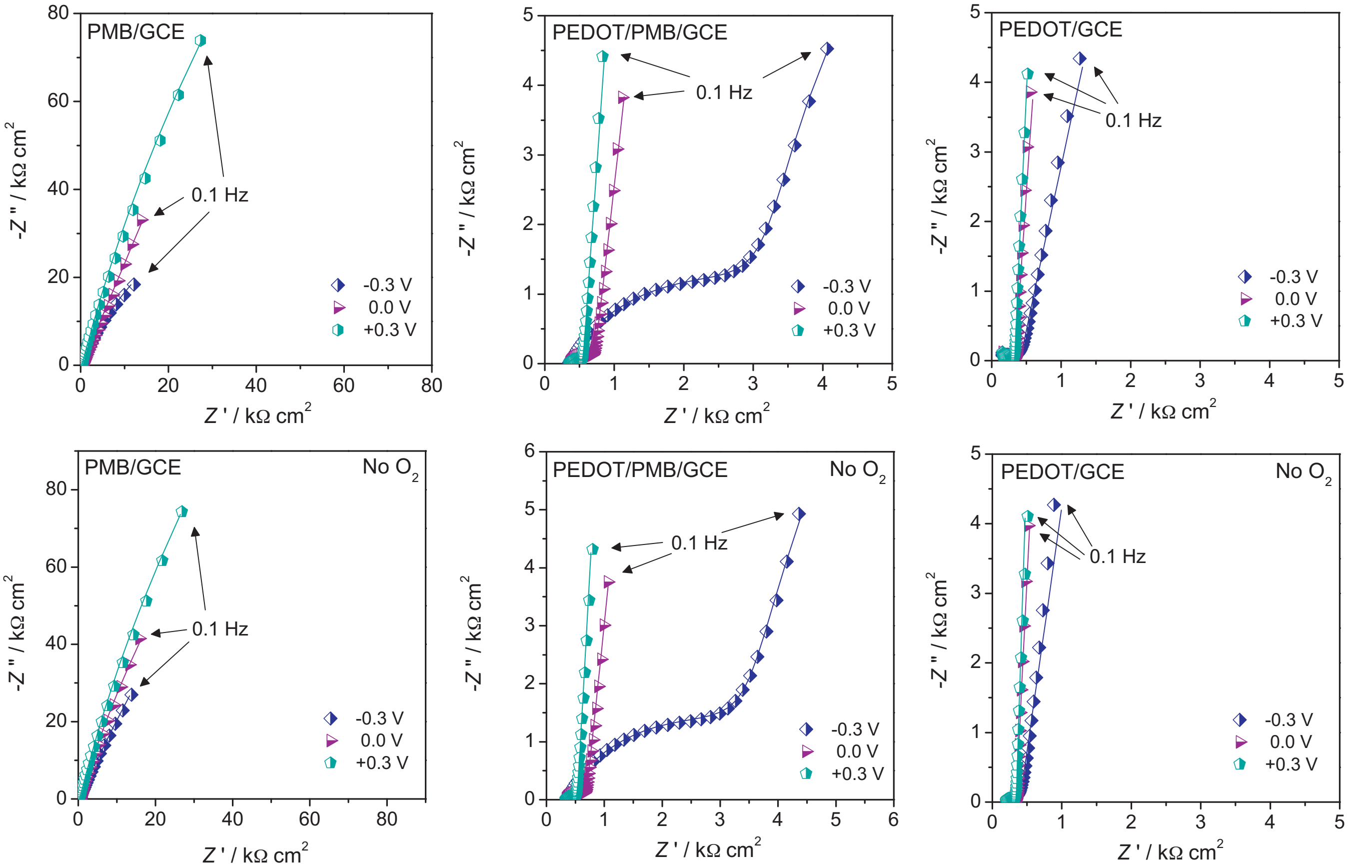


Fig. 8. Complex plane impedance plots recorded in 0.1 M KCl at −0.3, 0.0 and +0.3 V vs. SCE at PMB/GCE, PEDOT/PMB/GCE and PEDOT/GCE in the presence and absence of oxygen in solution. The lines show equivalent circuit fittings.

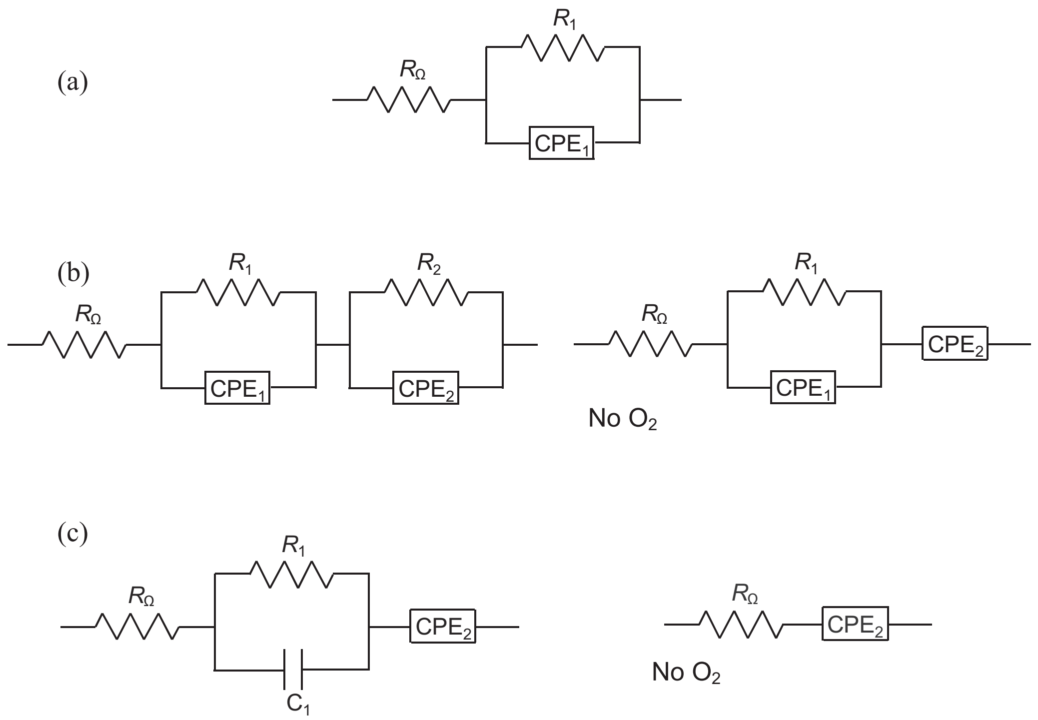


Fig. 9. Equivalent circuits used to fit the impedance spectra recorded at (a) PMB/GCE, (b) PEDOT/PMB/GCE and (c) PEDOT/GCE in the presence and absence of oxygen in solution.

PMB. This, together with the similarities in α values, implies that the substrate on top of which EDOT is polymerized does not affect the properties of the deposited film.

4. Conclusions

PEDOT has been successfully polymerized at GCE, thicker films being deposited by potential cycling. The positive potential limit is important in the polymerization mechanism, since it dictates the generation of $EDOT^{\bullet +}$ radical cations, which initiate polymer formation. A value of +1.2 V vs. SCE was optimal for EDOT polymerization, at which the highest capacitance values were recorded, with a continuous increase during the polymerization process. EDOT polymerizes better on PMB-modified GCE electrodes, more cation radicals being formed and a thicker film of PEDOT being deposited, reflected in higher capacitance currents. Cyclic voltammetry and EIS results indicate that PEDOT is the film component that dominates the electrochemical properties of PEDOT/PMB/GCE, exhibiting a very similar behaviour to that of PEDOT/GCE. The charge transfer resistance at PMB interface is lowered when PEDOT is deposited on top of PMB/GCE and CPE values of PEDOT are 8–10 times higher than of PMB, with α values very close to 1.0, underlining PEDOT's capacitor character and the smoothness and uniformity of the PEDOT surface. The lack of influence of oxygen on the PEDOT/PMB/GCE properties, and their good storage and operational stability demonstrate the improvement of PMB modified electrode characteristics, which make them more suitable for application in sensor or biosensor construction.

Acknowledgements

SK thanks the Ministry of Research Science and Technology of Iran for financial support. Financial support from Fundação para a Ciência e a Tecnologia (FCT), Portugal PTDC/QUI/65732/2006 and PTDC/QUI-QUI/116091/2009, POCI 2010 and COMPETE (co-financed by the European Community Fund FEDER) and CEMUC® (Research Unit 285), Portugal, is gratefully acknowledged. MMB thanks FCT for postdoctoral grant SFRH/BPD/72656/2010.

References

[1] M. Trojanowicz, Microchim. Acta 143 (2003) 75–91.
[2] V. Singh, S. Mohan, G. Singh, P.C. Pandey, R. Prakash, Sens. Actuators B 132 (2008) 99–136.
[3] A.G. Macdiarmid, Synth. Met. 125 (2002) 11–22.
[4] A. Pron, P. Rannou, Prog. Polym. Sci. 27 (2002) 135–190.
[5] P. Zarras, N. Anderson, C. Webber, D.J. Irvin, J.A. Irvin, A. Guenthner, D.J. Stenger-Smith, Radiat. Phys. Chem. 68 (2003) 387–394.
[6] A.J. Dominis, G.M. Spinks, G.G. Wallace, Prog. Org. Coat. 48 (2003) 43–49.
[7] G. Anitha, E. Subramanian, Sens. Actuators B: Chem. 92 (2003) 49–59.
[8] K. Gurunathan, D.P. Amalnerkar, D.C. Trivedi, Mater. Lett. 57 (2003) 1642–1648.
[9] P.C. Pandey, R. Prakash, J. Electrochem. Soc. 45 (1998) 999–1003.
[10] G. Illing, K. Hellgardt, M. Schonert, R.J. Wakeman, A. Jungbauner, J. Membr. Sci. 253 (2005) 199–208.
[11] A. Malinauskas, Bioelectrochemistry at surface modified carbon electrodes, in: A. Hubbard (Ed.), Encyclopedia of Surface and Colloid Science, Marcel Dekker, New York, 2002, pp. 753–773.
[12] R. Pauliukaite, M.E. Ghica, M.M. Barsan, C.M.A. Brett, Anal. Lett. 43 (2010) 1588–1608.
[13] P. Kara, K. Kerman, D. Ozkan, B. Meric, A. Erdem, Z. Ozkan, M. Ozoz, Electrochem. Commun. 4 (2002) 705–709.
[14] D. Ozkan, P. Kara, K. Kerman, B. Meric, A. Erdem, F. Jelen, P.E. Nielsen, M. Ozsoz, Bioelectrochemistry 58 (2002) 119–126.
[15] B. Meric, K. Kerman, D. Ozkan, P. Kara, S. Erensoy, U.S. Akarca, M. Mascini, M. Ozsos, Talanta 56 (2002) 837–846.
[16] U. Yogeswaran, S.M. Chen, Sens. Actuators B 130 (2008) 739–749.
[17] L. Tan, Q. Xie, S. Yao, Electroanalysis 16 (2004) 1592–1597.
[18] A. Silber, N. Hampp, W. Schuhmann, Biosens. Bioelectron. 11 (1996) 215–223.
[19] N. Zhu, A. Zhang, Q. Wang, P. He, Y. Fang, Anal. Chim. Acta 510 (2004) 163–168.
[20] A. Salimi, A. Noorbakhs, S. Soltanian, Electroanalysis 18 (2006) 703–711.
[21] M.M. Barsan, E.M. Pinto, C.M.A. Brett, Phys. Chem. Chem. Phys. 13 (2011) 5462–5471.
[22] X. Crispin, F.L.E. Jakobsson, A. Crispin, P.C.M. Grim, P. Andersson, A. Volodin, C. van Haesendonck, M. van der Auweraer, W.R. Salaneck, M. Berggren, Chem. Mater. 18 (2006) 4354–4360.
[23] D.W. Breiby, L.B. Samuelsen, B. Groenedaal, B. Struth, J. Polym. Sci. Polym. Phys. 41 (2003) 945–952.
[24] J.C. Carlberg, O. Inganaes, J. Electrochem. Soc. 144 (1997) L61–L64.
[25] M. Dietrich, J. Heinze, G. Heywang, F. Jonas, J. Electroanal. Chem. 369 (1994) 87–92.
[26] B.L. Groenendaal, F. Jonas, D. Freitag, H. Pielartzik, J.R. Reynolds, Adv. Mater. 12 (2000) 481–494.
[27] Q.B. Pei, G. Zuccarello, M. Ahlskog, O. Inganaes, Polymer 35 (1994) 1347–1351.
[28] G.A. Sotzing, J.L. Reddinger, J.R. Reynolds, P.J. Steel, Synth. Met. 84 (1997) 199–201.
[29] C. Carlberg, X.W. Chen, O. Inganaes, Solid State Ionics 85 (1996) 73–78.
[30] J.C. Gustafsson, B. Liedberg, O. Inganaes, Solid State Ionics 69 (1994) 145–152.
[31] K.I. Seo, I.J. Chung, Polymer 41 (2000) 4491–4499.
[32] Y. Yagci, S. Jockush, N.J. Turro, Macromolecules 40 (2007) 4481–4485.
[33] G.M. Abou-Elenien, A.A. El-Maghraby, G.M. El-Abdallah, Synth. Met. 146 (2004) 109–119.
[34] Z.G. Qi, P.G. Pickup, Chem. Commun. 21 (1998) 2299–2300.
[35] A.J. Downard, D.J. Pletcher, J. Electroanal. Chem. 206 (1986) 139–145.
[36] H. Randriamahazaka, V. Noe, C. Chevrot, J. Electroanal. Chem. 472 (1999) 103–111.
[37] N. Sakmeche, S. Aeiyach, J.J. Aaron, M. Jouini, J.C. Lacroix, P.C. Lacaze, Langmuir 15 (1999) 2566–2574.
[38] Y. Kudoh, K. Akami, Y. Matauya, Synth. Met. 98 (1998) 65–70.
[39] E. Tamburri, S. Orlanducci, F. Toschi, M.L. Terranova, D. Passeri, Synth. Met. 159 (2009) 406–414.
[40] A.R. Gonçalves, M.E. Ghica, C.M.A. Brett, Electrochim. Acta 56 (2011) 3685–3692.
[41] P. Manisankar, C. Vedhi, G. Selvanathan, H. Gurumallesh Prabu, J. Appl. Polym. Sci. 104 (2007) 3285–3291.
[42] V. Tsakova, S. Winkels, J.W. Schultze, Electrochim. Acta 46 (2000) 759–768.
[43] S. Zhang, J. Hou, R. Zhang, J. Xu, G. Nie, S. Pu, Eur. Polym. J. 42 (2006) 149–160.
[44] M.M. Barsan, E.M. Pinto, C.M.A. Brett, Electrochim. Acta 53 (2008) 3973–3982.
[45] F. Pern, A.J. Frank, J. Electrochem. Soc. 137 (1990) 2769–2777.
[46] E. Tamburr, S. Sarti, S. Orlanducci, M.L. Terranova, M. Ross, Mater. Chem. Phys. 125 (2011) 397–404.
[47] J. Bobacka, A. Lewenstam, A. Ivaska, J. Electroanal. Chem. 489 (2000) 17–27.
[48] A. Lisowska-Oleksiak, A. Kupniewska, Solid State Ionics 157 (2003) 241–248.
[49] D. Han, G. Yang, J. Song, L. Niu, A. Ivaska, J. Electroanal. Chem. 602 (2007) 24–28.
[50] X. Du, Z. Wang, Electrochim. Acta 48 (2003) 1713–1717.
[51] P. Chandrasekhar (Ed.), Conducting Polymers, Fundamentals and Applications, Kluwer Academic Publishers, Boston, MA, 1999.
[52] J. Heinze, A. Rasche, M. Pagels, B. Geschke, J. Phys. Chem. B 111 (2007) 989–997.
[53] Z. Mousavi, T. Alaviuhkola, J. Bobacka, R.-M. Latonen, J. Pursiainen, A. Ivaska, Electrochim. Acta 53 (2008) 3755–3762.
[54] B. Bezgin, A. Yagan, A.M. Onal, J. Electroanal. Chem. 632 (2009) 143–148.