Preparation and characterisation of poly(3,4-ethylenedioxythiophene) and poly(3,4-ethylenedioxythiophene)/poly(neutral red) modified carbon film electrodes, and application as sensors for hydrogen peroxide

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ABSTRACT

Poly(3,4-ethylenedioxythiophene) (PEDOT) films have been prepared for the first time on carbon-film electrodes (CFE) in aqueous solution using electropolymerisation by potential cycling, potentiostatically and galavanostatically. Characterisation of the modified electrodes was done by cyclic voltammetry and electrochemical impedance spectroscopy and the stability of the polymer films was probed. The coated electrodes were tested for application as hydrogen peroxide sensors, by oxidation and reduction. A novel polymer film was also formed by modification of CFE by co-electropolymerisation of EDOT and the phenazine dye neutral red (NR) – (PEDOT/PNR) with a view to enhancing the properties for sensor applications. It was found that hydrogen peroxide reduction at the PEDOT/PNR coated electrodes could be carried out at a less negative potential, the sensor performance comparing very favourably with that of other polymer-modified electrodes reported in the literature.

1. Introduction

Conducting polymers have been widely used in order to enhance the speed, sensitivity and versatility of various sensors and biosensors [1–3] and among them, poly(3,4-ethylenedioxythiophene) (PEDOT) has proved to have good stability under ambient conditions and retains its conductivity even after storage at 120 °C for 1000 h [4]. Electropolymerisation has been mainly carried out on platinum electrodes [1,4–7]. Other electrode substrates have been used relatively little, exemplified by gold in an electrochemical quartz–crystal microbalance (ECQM) [8] or glassy carbon [9]; in addition, different assemblies containing PEDOT obtained in combination with carbon nanotubes [10] or carbon nanofibres [11] have also been reported. PEDOT has been applied to the detection of several important chemically and biologically relevant compounds such as hydrogen peroxide [12,13], nitric oxide [14], dopamine [9] and ascorbic acid [15].

Carbon has proved to be successful as an electrode support material due to its good conducting properties, stability and availability in different forms [16]. The enhancement of the performance characteristics of sensors and biosensors, based on carbon electrode substrates, can be achieved through different surface modifica-tion strategies such as the deposition of films of polymeric redox mediators [17], application of nanotubes or the immobilisation of enzymes into polymer matrices [18,19]. Ensuring sensor selectivity towards a given compound is a constant challenge and hydrogen peroxide (H_2O_2), selected in this work, is a compound with important applications in environmental studies, chemical industry, pharmaceutical and industrial research [20,21].

Polyphenazines are also very attractive polymers, acting both as conducting polymers and redox mediators. Neutral red (NR), an acid base indicator with $pK_a \sim 6.8$ from the family of azines, can be electropolymerised and poly(neutral red) (PNR) has already been used as redox mediator in enzyme electrodes [17,22]. The combination of different polymers to obtain composites with better properties than each polymer by itself is of current interest [13]. To our knowledge EDOT and NR have not been previously co-polymerised.

In the present work, we describe, for the first time, the polymerisation of EDOT on carbon film electrodes (CFE) made from carbon film electrical resistors of $2\,\Omega$ [23] that have been used successfully in various sensor and biosensor applications [17,24]. PEDOT modified electrodes were prepared in aqueous solution by potential cycling, potentiostatic and galvanostatic methods. The resulting PEDOT-modified electrodes were characterised by cyclic voltammetry and electrochemical impedance spectroscopy (EIS) in order to evaluate which polymer formation method leads to the best properties for application in sensors. EDOT was also co-polymerised with the azine dye neutral red (NR) to probe any

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synergistic effects between the polymers in coated electrodes. Up until now most hydrogen peroxide sensors have been enzyme-based [12]. Here the development of non-enzymatic sensors for H_2O_2 is described based on the electroanalytical potentialities of PEDOT and PEDOT/PNR modified electrodes.

2. Experimental

2.1. Reagents and solutions

All chemicals were analytical reagent grade, used as received. The monomers 2,3-dihydrothieno[3,4-*b*]-1,4-dioxin (EDOT) and neutral red (NR) were from Aldrich, Germany. Hydrogen peroxide was purchased from José M. Vaz Pereira, Portugal.

The electrolytes used in the polymerisation of EDOT were sodium chloride (NaCl, Riedel-de Haen, Germany) and 4-styrenesulfonic acid sodium salt hydrate (NaPSS, Aldrich, Germany).

For polymerisation of NR alone, or with EDOT, a pH 5.5 buffer solution (0.025 M phosphate buffer + 0.1 M KNO_3) was prepared from di-potassium hydrogenphosphate (K_2HPO_4, Riedel-de Haen, Germany), potassium di-hydrogenphosphate (KH_2PO_4, Fluka) and potassium nitrate (KNO_3, Riedel-de Haen, Germany).

The buffer electrolyte used for hydrogen peroxide measurement was 0.1 M sodium phosphate buffer pH 7.0 prepared from sodium phosphate dibasic dihydrate ($NaH_2PO_4 \cdot 2H_2O$, Sigma, Germany) and sodium dihydrogen phosphate (Na_2HPO_4, Riedel-de Haen, Germany).

Millipore Milli-Q nanopure water (resistivity > 18 MΩ cm) was used for preparation of all solutions. All experiments were performed at $25 \pm 1\,°C$.

2.2. Instrumentation

Electrochemical experiments were done using a potentio-stat/galvanostat (Autolab PGSTAT30) connected to a computer with general purpose electrochemical system software (GPES v4.9) and frequency analysis software (FRA v4.9) from Metrohm-Autolab (Utrecht, The Netherlands).

All experiments were carried out in a three-electrode cell using a modified or unmodified carbon-film working electrode, a platinum foil as counter electrode and the reference electrode was a saturated calomel electrode (SCE). For impedance experiments a sinusoidal voltage perturbation of 10 mV was applied, scanning from 65,000 Hz to 0.1 Hz, with ten measurement points per frequency decade. The equivalent circuit modelling/fitting was done by ZView 2.4 software (Solartron Analytical, UK)

2.3. Electrode preparation

2.3.1. Carbon film electrode pre-treatment

Carbon film resistors were used to prepare carbon film electrodes with an exposed geometric area of $0.16\,cm^2$ using the procedure described in [23]. All bare electrodes were first pre-treated by cycling the applied potential between 0.0 V and 1.0 V in 0.1 M NaCl (or 0.1 M NaPSS) at a scan rate of $100\,mV\,s^{-1}$ ten times until a stable voltammogram was achieved.

2.3.2. Poly(3,4-ethylenedioxythiophene) electrodeposition

A 0.01 M EDOT solution was prepared by dissolving the appropriate amount of monomer in a chosen volume of electrolyte solution (0.1 M NaCl or 0.1 M NaPSS). Vigorous magnetic stirring for about 30 min followed by 10 s of ultrasonic treatment ensured complete monomer dissolution. One of the following procedures was then applied to electropolymerise the EDOT monomer:

- Potential cycling (CV) from −0.6 V to 1.0 V for ten consecutive cycles at a scan rate of $50\,mV\,s^{-1}$.
- Potentiostatically (Pot), applying a fixed potential of +1.0 V, during 100 s.
- Galvanostatically (Galv), using a fixed current density of $0.2\,mA\,cm^{-2}$ during 110 s.

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

2.3.3. Poly(3,4-ethylenedioxythiophene) and poly neutral red (PNR) electrodeposition

For neutral red polymerisation, a 0.5 mM solution of NR monomer was prepared in pH 5.5 (0.025 M phosphate buffer + 0.1 M KNO_3) and 10 potential cycles were done between −1.0 and +1.0 V vs. SCE at a potential sweep rate of $50\,mV\,s^{-1}$. The same experimental conditions were used for electropolymerisation of EDOT and NR in different molar ratios (EDOT/NR = 10, 6, 2, 1), always with 0.5 mM NR.

3. Results and discussion

3.1. Electrode modification by EDOT polymerisation

Electropolymerisation of EDOT from a solution containing 0.01 M monomer was carried out in three different ways – potential cycling, potentiostatically and galvanostatically – in two electrolyte solutions: 0.1 M NaCl and 0.1 M NaPSS. The electrolyte solution was varied as it plays an important role in both electron transfer rate and in diffusion processes, having a significant effect on the electropolymerisation process and on the properties of the polymer films obtained [27]. Before using the carbon film electrodes, they were subjected to electrochemical pre-treatment by cycling the potential as described in the experimental section. The background current decreases with each cycle due to the decrease of the number of the functional groups on the surface of the carbon film electrode [23].

Electropolymerisation, carried out using the three electrochemical techniques, is shown in Fig. 1: potential cycling in Fig. 1(A), potentiostatically in Fig. 1(B) and galvanostatically in Fig. 1(C). As the polymer film grows, there is a visible change in colour from silver-grey (unmodified carbon film electrode) to opaque dark-blue (electrodeposited PEDOT characteristic colour) [28].

In previous studies, the polymerisation of EDOT by potential cycling was performed in different potential ranges, for example between −1.0 and 1.2 V [29] at a nickel electrode in 0.1 M $LiClO_4$ or between 0.2 and 1.2 or 1.5 V [4] at platinum electrodes in phosphate buffer with NaPSS. Vasantha et al. [30] also reported on the modification of glassy carbon electrodes by PEDOT prepared by potential cycling between −0.6 V and 1.1 V. In order to avoid PEDOT overoxidation which is assumed to occur above 1.1 V according to Du [25], in the present work the potential range was chosen between −0.6 and 1.0 V.

Potential cycling in 0.1 M NaPSS electrolyte, Fig. 1(A) shows a clear increase of current (solid line) with increasing capacitive current. Nevertheless, in 0.1 M NaCl electrolyte solution, there is almost no increase in current with successive cycles. For potentiostatic deposition a potential of +1.0 V was chosen, the same positive limit as in potential cycling, taking into account the studies in [25,26], where it was observed that overoxidation of PEDOT takes place at potentials higher than +1.1 V, and also that at potentials lower than 0.9 V polymerisation does not occur [7]. Electropolymerisation at +1.0 V vs. SCE proceeds well in both electrolyte solutions, Fig. 1(B). In NaCl, as electropolymerisation begins, there is a slight increase in current until a steady state is achieved; for NaPSS electrolyte solution, initial deposition shows an initial spike
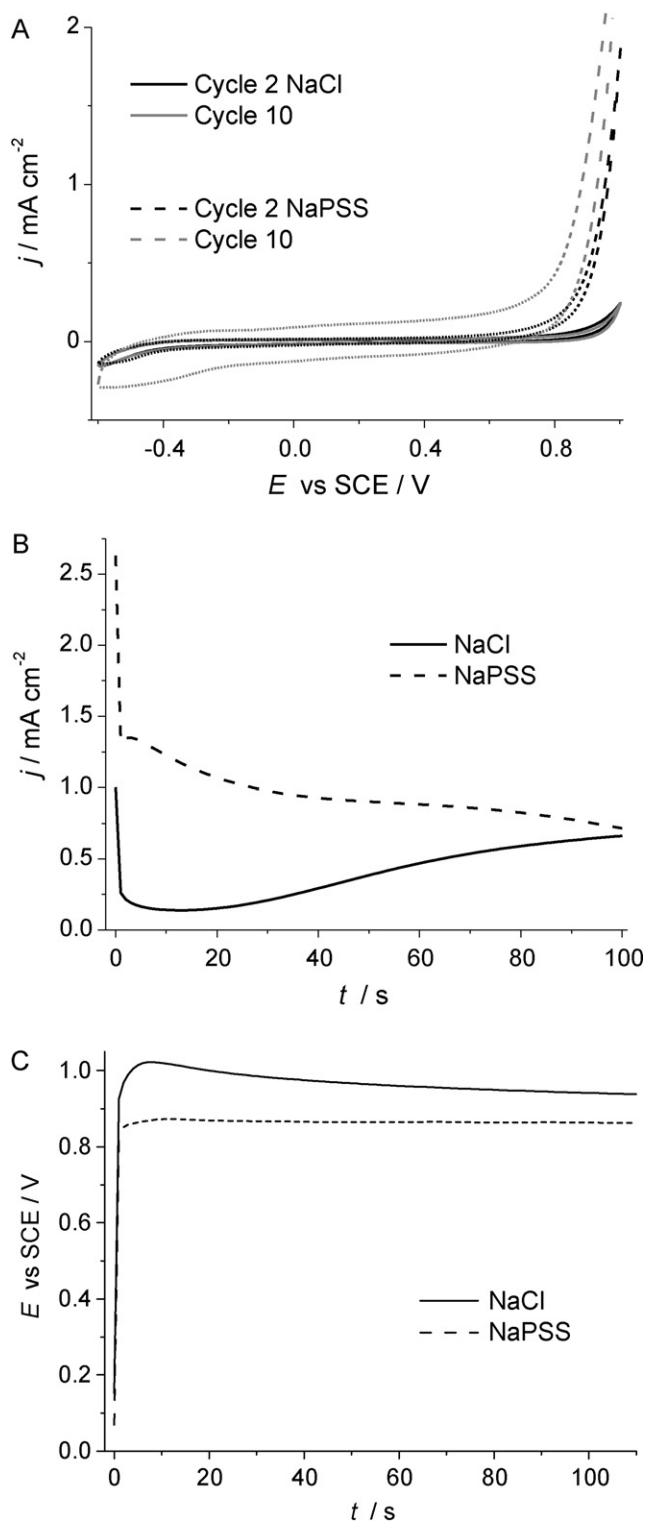
Fig. 1. Electropolymerisation of EDOT by (A) potential cycling; (B) potentiostatically (+1.0 V) and (C) galvanostatically (0.2 mA cm^{-2}) in 0.1 M NaCl (—) and 0.1 M NaPSS (– – –).

and then the current falls. However, at the end of each polymerisation procedure, a maximum current was reached (750 µA cm^{-2}) and the PEDOT characteristic colour was observed on the surface of the carbon-film modified electrodes. Different curve profiles can be related to different polymerisation mechanisms, where a nucleation and growth mechanism are identified by an initial current spike, a falling current to a steady value and a final increase

to a plateau characteristic of application of a constant potential [27].

Finally, electrodeposition at a constant current density of 0.2 mA cm^{-2} was chosen based on the work by Bobacka [5] concerning galvanostatic polymerisation, during 110 s. Fig. 1(C) shows the attainment of a constant potential in both electrolyte solutions: +1.0 V in NaCl solution and +0.85 V in NaPSS solution; hence, a lower potential can be employed for EDOT polymerisation in NaPSS. PEDOT-deposited films become visible as the characteristic colour progressively changes. The difference between the polymerisation potential in the two electrolytes (0.15 V) was also observed under similar conditions on platinum electrode substrates [5].

From the results of the three electropolymerisation techniques used, it can be concluded that the PSS$^-$ anion aids polymer film formation, compared with Cl$^-$, as doping anion, except using fixed potential, where the results are similar. These observations might be explained by a mechanism of strong electrostatic interactions between EDOT radicals and PSS anions, as suggested in [5].

3.2. PEDOT-coated electrode characterisation

Bare and PEDOT-coated carbon-film electrodes were characterised by CV and EIS. It is already well known that the electrolyte used affects conducting polymer properties and thus, this effect was explored, using the same electrolytes as for electropolymerisation.

3.2.1. Cyclic voltammetry

The charge accumulation capacity of each type of PEDOT-coated electrode was calculated by numerical integration from the cyclic voltammograms recorded in the corresponding buffer electrolytes between −0.5 V and +0.5 V vs. SCE at 50 mV s^{-1}, before and after polymerisation. In this potential range, the cyclic voltammograms of the coated electrodes show a capacitive current and do not reveal any well-defined oxidation or reduction peaks. The same observation was made previously by Bobacka [5] and Sundfors [6]. The results are shown in Fig. 2(A) for polymerisation in NaCl and Fig. 2(B) for polymerisation in NaPSS solution.

When polymerisation was performed in 0.1 M NaCl electrolyte solution, Fig. 2(A), the highest charge accumulation was obtained for the polymer formed potentiostatically (9.5 and 11.0 µC in NaCl and NaPSS, respectively); an intermediate value was achieved when the polymer was obtained galvanostatically (6.0 and 6.2 µC in NaCl and NaPSS) and the lowest charge was recorded when potential cycling was used (1.2 and 1.4 µC in NaCl and NaPSS). Potential cycling under these experimental conditions appears to be a relatively ineffective polymerisation procedure. The potentiostatic method is the best choice for electropolymerisation in 0.1 M NaCl electrolyte solution; as it shows a charge ten times that of potential cycling and two times higher than that achieved by the galvanostatic method.

Fig. 2(B) shows the charge accumulation when polymerisation was done in 0.1 M NaPSS solution. The potentiostatic method (12.8 and 13.4 µC In NaCl and NaPSS) is still the best choice, whereas potential cycling (6.0 and 6.2 µC in NaCl and NaPSS) is better than the galvanostatic method (3.0 and 3.2 µC in NaCl and NaPSS, respectively). Thus, the polymer film formed by the potentiostatic method showed the highest charge in both electrolytes, higher when formed in NaPSS. For the other cases, it is not clear which of the electrolytes confers better characteristics but, in general, NaPSS appears to be better. Independent of the electrolyte in which the polymer was formed, higher charges are obtained in NaPSS media. Moreover, the polymer formed in NaCl is more dependent on the anion of the supporting electrolyte, as seen by the accumulated charge in the two electrolytes. This behaviour has already been reported in [5]; however, in that study the PEDOT formed in NaCl presented a higher charge in NaCl solution than in NaPSS, unlike
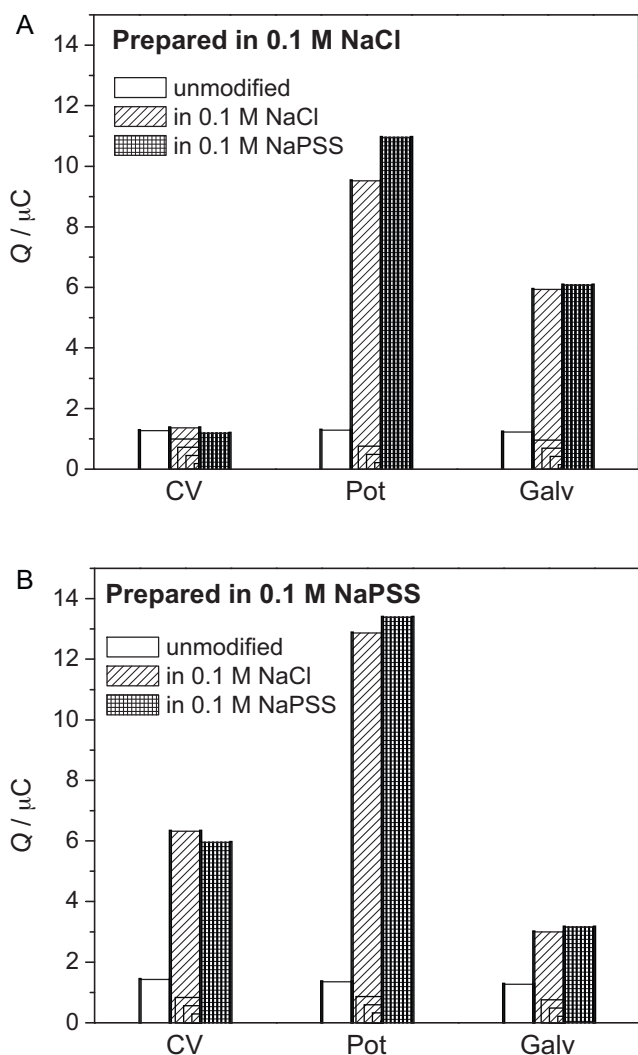
Fig. 2. Charge accumulation of PEDOT-modified electrodes from cyclic voltammograms of films obtained by potential cycling, potentiostatic and galvanostatic methods in (A) 0.1 M NaCl and (B) 0.1 M NaPSS.

here. Thus, the final conclusion is that for both electrolytes used for polymer formation there is anion exchange between the polymer film and solution.

The PEDOT-coated electrode stability was tested through thirty successive potential cycles, at a potential sweep rate of $50\,\text{mV}\,\text{s}^{-1}$ between $-0.5\,\text{V}$ and $+0.5\,\text{V}$ vs. SCE in 0.1 M NaPSS. A change in the capacitive current was observed for each electrode. The percentage charge variation after 30 cycles in relation to the initial value (2nd cycle) was calculated, Table 1. It was found that the loss in charge was between 0% and 15%, these extremes corresponding to electrodes polymerised galvanostatically in NaCl and NaPSS, respectively; for all the others intermediate values were obtained. No particular reasons for these differences can be advanced, except that they reflect variations in the polymer structures formed.

3.2.2. Electrochemical impedance spectroscopy

EIS was used to investigate the interfacial properties of PEDOT films on the carbon film electrode. Studies on the reduction or oxidation of H_2O_2 have been done at potentials ranging from $-0.7\,\text{V}$ to $+0.6\,\text{V}$ vs. SCE [20,31]; the results that are discussed here are those at $-0.4\,\text{V}$ and at $+0.4\,\text{V}$ vs. SCE, being the more relevant for H_2O_2 detection applications. Spectra were recorded in 0.1 M NaPSS electrolyte solution (Fig. 3), since the cyclic voltammetry studies showed this to be better than 0.1 M NaCl. Equivalent electrical circuits were used to model both unmodified and modified electrodes and the fitting results are shown in Table 2.

The circuit used to fit the spectra was the same at both $-0.4\,\text{V}$ and $+0.4\,\text{V}$ for unmodified and PEDOT-modified electrodes (except at $+0.4\,\text{V}$ for PEDOT obtained potentiostatically). This circuit consists of a cell resistance R_Ω and a constant phase element CPE_1 in parallel with a charge transfer resistance R_1; CPE_1 is assumed to be a non-ideal capacitance with roughness factor α, where α is equal to 1 for a perfectly smooth surface and 0.5 for a porous electrode [23]. For the PEDOT-Pot modified electrode at $+0.4\,\text{V}$ a straight line was obtained (Fig. 3(B)), so the circuit was R_Ω in series with a constant phase element, consistent with no electron transfer. Values of R_Ω were around $17\,\Omega\,\text{cm}^2$ in all cases.

For unmodified electrodes, the charge transfer resistance at $-0.4\,\text{V}$ vs. SCE was $4.20\,\text{k}\Omega\,\text{cm}^2$ and the capacitance was $C_1 = 123\,\mu\text{F}\,\text{cm}^{-2}\,\text{s}^{\alpha-1}$. At $+0.4\,\text{V}$, the charge transfer resistance was higher ($75.5\,\text{k}\Omega\,\text{cm}^2$) and the capacity lower ($49.4\,\mu\text{F}\,\text{cm}^{-2}\,\text{s}^{\alpha-1}$).

Table 1
Charge variation of PEDOT-modified electrodes obtained by different methods in 0.1 M NaCl and in 0.1 M NaPSS obtained by comparing the second and thirtieth cyclic voltammograms recorded in 0.1 M NaPSS.

PEDOT formation method + electrolyte	Initial charge (μC)	Final charge (μC)	Charge loss (%)
CV (NaCl)	2.12	2.04	3.7
Pot (NaCl)	8.85	8.00	9.7
Galv (NaCl)	7.97	7.97	0.1
CV (NaPSS)	18.1	16.3	9.9
Pot (NaPSS)	25.2	22.4	11
Galv (NaPSS)	4.47	3.80	15

Table 2
Equivalent circuit parameters from impedance spectra of PEDOT and PEDOT/PNR modified electrodes obtained by different methods recorded in 0.1 M NaPSS.

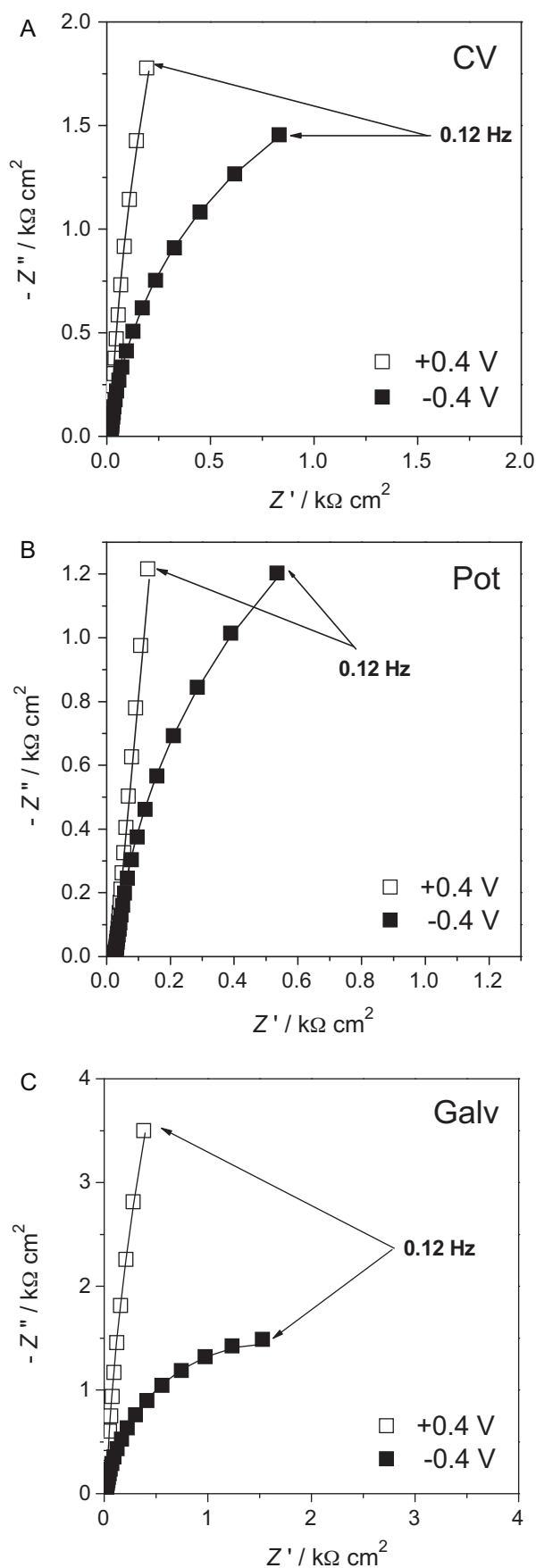| Potential vs. SCE/V	Electrode coating	R_1 (kΩ cm^2)	C_1 (μF cm^{-2} s$^{\alpha-1}$)	α_1
−0.4	Bare electrode	4.2	123	0.84
	PEDOT-CV	3.9	662	0.95
	PEDOT-Pot	4.0	894	0.95
	PEDOT-Galv	3.2	404	0.94
	PEDOT/PNR-CV	5.7	138	0.76
+0.4	Bare electrode	75.5	50	0.88
	PEDOT-CV	26.1	709	0.98
	PEDOT-Pot	–	837	0.95
	PEDOT-Galv	52.7	358	0.97
	PEDOT/PNR-CV	253	31.3	0.89

Data from Figs. 3 and 6.

Fig. 3. Complex plane impedance spectra of PEDOT-coated electrodes in 0.1 M NaPSS at +0.4 and −0.4 V vs SCE, for each polymerisation procedure (A) CV; (B) Pot and (C) Galv. The lines show equivalent circuit fitting.

The values of R_1 at −0.4 V for the PEDOT-modified electrodes and bare electrodes are almost the same, showing that the polymer is not undergoing any redox process at this potential. For PEDOT-CV and PEDOT-Galv modified electrodes at +0.4 V, the curvature in the complex plane spectra and thence the necessity of the resistance R_1 might be explained by the fact that polymer film does not completely cover and block access to the carbon film electrode substrate surface, hence the behaviour shows some similarities to the bare carbon film electrode. The values of the α exponent increase at both potentials (from 0.84–0.87 to 0.94–0.98) showing a decrease in non-uniformity with modification of the electrodes by the polymer film. The values of capacitance increase significantly for all modified electrodes, being the highest in the case of PEDOT-Pot modified electrodes. These results are consistent with potential cycling where it was also observed that charge accumulation was the highest in the case of the PEDOT-coated electrode modified potentiostatically.

3.3. Determination of H_2O_2 with PEDOT-modified electrodes

To investigate the possibility of H_2O_2 oxidation or reduction at the PEDOT-modified electrodes, CVs, between −0.6 V and +0.8 V vs. SCE, were recorded in phosphate buffer solution pH 7.0 in the absence and in the presence of 1 mM and 2 mM H_2O_2. A small increase in the cathodic current after addition of H_2O_2 was found at around −0.50 V and also an increase in the oxidation current at around +0.55 V vs. SCE (not shown).

Amperometric experiments at a constant potential of −0.50 V and +0.55 V were conducted with each type of coated electrode. Thus, after baseline stabilisation, known aliquots of hydrogen peroxide were added to buffer solution and the change of the current was recorded. Calibration curves were plotted and from their linear regression analysis sensor performance characteristics were determined (Table 3).

Regarding the oxidation of H_2O_2, similar sensitivities were obtained for the three types of electrode, a little higher for the polymer formed by the galvanostatic method. Despite the higher detection limit, the polymer obtained by potentiostatic method shows a much wider linear range, whilst the other two exhibited similar detection limits and linear ranges. For the reduction of H_2O_2 the detection limits do not vary as much as for oxidation. The narrower linear range was obtained for the polymer formed by potential cycling, which also shows the lowest sensitivity. In addition, the linear range of potentiostatically and galvanostatically formed modified electrodes was two times higher and sensitivity about three and four times higher, respectively. The linear range obtained with the proposed modified electrodes is comparable to that reported in [12], where a PEDOT/PSS matrix was used to modify indium–tin–oxide electrodes; the sensitivity they obtained of 0.544 $\mu A\,cm^{-2}\,mmol^{-1}\,dm^3$, is also due to the fact that the determination of hydrogen peroxide was enhanced by using horseradish peroxidase (HRP). Thus, carbon film electrodes modified with PEDOT films proved to be effective candidates for the determination of H_2O_2 by both oxidation and reduction.

3.4. PEDOT/PNR electrode modification

It has been shown previously that phenazine dyes are successful redox mediators [17]. Thus, seeking to enhance PEDOT coated electrode performance characteristics, a combination of different molar ratios of EDOT and NR monomers was used (EDOT/NR = 10, 6, 2, 1) to make polymer films. For comparison, NR by itself was also polymerised on CFE. Carbon film electrodes were modified by potential cycling for 10 cycles in 0.025 M K_2HPO_4 + KH_2PO_4 (pH 5.5) containing 0.1 M KNO_3. This buffer was chosen because it has been shown that NR film growth is strongly dependent on the acid-

Table 3
The performance of the PEDOT-electrodes towards the oxidation and reduction of H_2O_2 in phosphate buffer solution.

Applied potential vs. SCE/V	Electrode coating	Upper linear range (mmol dm^{-3})	Sensitivity (μA cm^{-2} mmol^{-1} dm^3)	LOD (μmol dm^{-3})
+0.55 (oxidation)	PEDOT-CV	0.54	0.56	28
	PEDOT-Pot	1.60	0.57	67
	PEDOT-Galv	0.30	0.93	36
−0.50 (reduction)	PEDOT-CV	0.50	−3.12	42
	PEDOT-Pot	1.00	−8.94	62
	PEDOT-Galv	0.94	−12.8	52
−0.36 (reduction)	PNR-CV	0.46	−1.42	48
	PEDOT/PNR-CV	0.46	−0.92	80

ity of the solution and a similar polymerisation procedure of NR films onto carbon film electrodes has already been tested [17] – for EDOT polymerisation it was observed that the differences in the films obtained are not significant when prepared at different pH values. Potential cycling was preferred to potentiostatic because NR polymerises more efficiently this way, as observed in separate experiments. However, since PEDOT by itself was better formed at fixed potential, polymerisation at +1.0 V for 100 s with both monomers was also performed and the resulting modifier films compared.

During the polymerisation process of NR by CV, an irreversible oxidation peak appears at around 1.0 V (Fig. 4(A)) corresponding to monomer oxidation leading to cation radical formation and two redox couples also appear: one at about −0.55 V ascribed to monomer/polymer oxidation/reduction and the other around +0.25 V corresponding to doping/de-doping of the polymer [17]. The height of the oxidation peak at −0.5 V increases with the number of cycles, demonstrating PNR polymer growth. The size of this oxidation peak was used as a control parameter to monitor the growth of the polymer mixture and to choose the best electrode for use in further studies. It was observed that each EDOT/NR ratio led to a different voltammetric profile (data not shown) and the highest increase was obtained for a ratio of EDOT/NR = 2 (Fig. 4(B)). At fixed potential it was observed that the current density reached in the EDOT/NR polymerisation is 15.2 μA cm^{-2}, about half that found when forming PNR alone and 50 times less than that with EDOT alone.

3.5. PEDOT/PNR characterisation

The PEDOT/PNR films obtained by potential cycling and potentiostatically were compared using cyclic voltammetry. The CV profiles show characteristics of both PEDOT and PNR, mainly of the latter, and the response was much higher (∼30%) for the potentiodynamically obtained copolymer (Fig. 5(A)). Hence, this type of polymer-modified electrode was chosen for further studies.

A more detailed characterisation of PEDOT/PNR modified electrodes was carried out by cyclic voltammetry and impedance spectroscopy. CVs were recorded in different electrolytes including 0.1 M KCl, 0.1 M NaCl, 0.1 M NaPSS, 0.1 M sodium phosphate and 0.025 M potassium phosphate buffer pH 5.5 with and without 0.1 M KNO₃. In NaCl and KCl the response is similar, slightly higher in NaCl. In NaPSS the peaks were not well defined (probably due to the high pH value, around 10). The higher response in sodium phosphate buffer than in potassium phosphate, can also be due to the different buffer concentrations. In potassium phosphate buffer in the presence of KNO₃ the response was higher by 13%, suggesting that nitrate anions play an important role in the polymer mixture doping. The PEDOT/PNR films appear to be more selective to anions when the largest anions are present in solution, perhaps due to a shielding effect that makes the participation of cations difficult, especially potassium cations. So both cations and anions

participate as counterions during charge compensation processes in PEDOT/PNR films, as observed before for PNR [32].

Cyclic voltammetry was performed in sodium phosphate buffer at different scan rates (Fig. 5(B)) and it was observed that there is an increase of current with increase in scan rate linearly dependent on the square root of scan rate, consistent with a diffusion-controlled process. The linear regression curves obtained were: j_{pa} (μA cm^{-2}) = −7.7 + 277$v^{1/2}$ and j_{pc} (μA cm^{-2}) = −20 − 290$v^{1/2}$, the slope of the reduction peak being a bit higher, meaning that this process occurs at a higher rate. Since counterion diffusion through
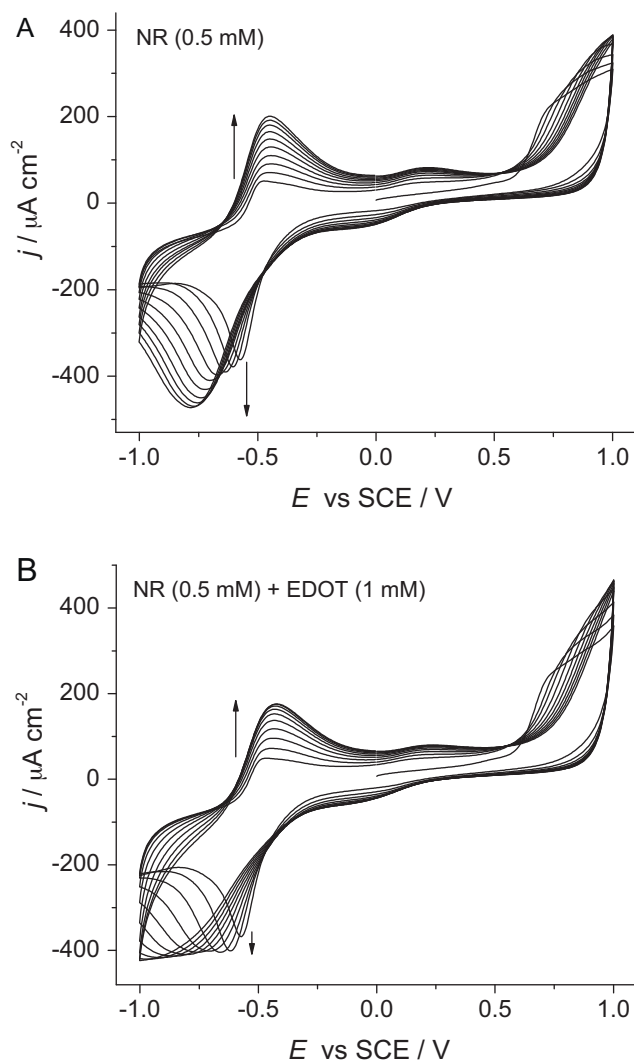

Fig. 4. CVs showing polymerisation in phosphate buffer (pH 5.5) between −1.0 V and 1.0 V vs. SCE for (A) 0.5 mM NR and (B) mixture of 1.0 mM EDOT and 0.5 mM NR. Scan rate 50 mV s^{-1}.
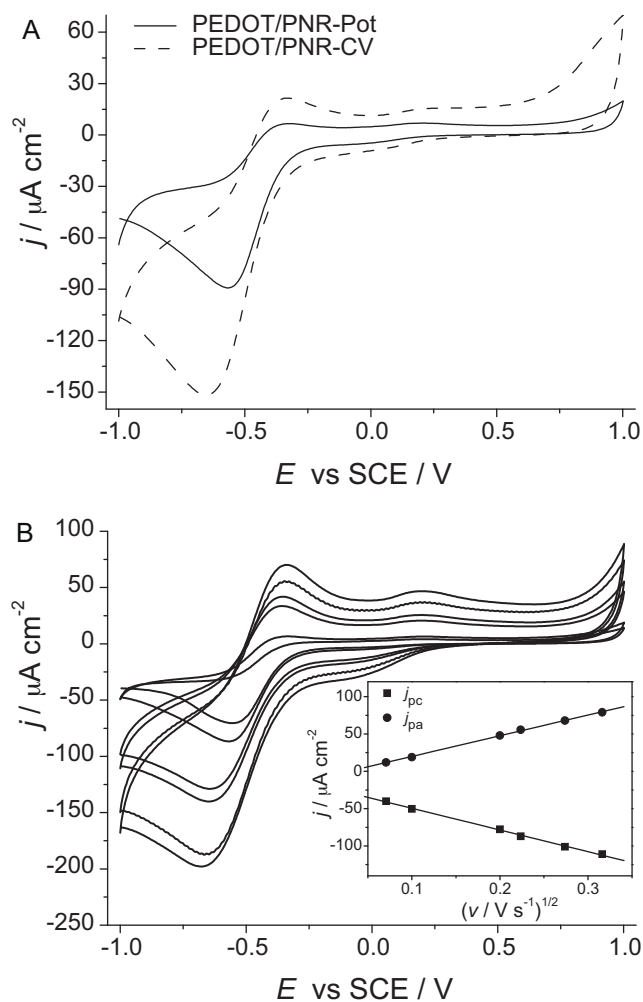
Fig. 5. CV in phosphate buffer (pH 5.0) of PEDOT/PNR obtained (A) by CV and Pot methods; scan rate 50 mV s^{-1} and (B) by CV at different scan rates. Inset shows the plot of current peak dependence on the square root of scan rate.
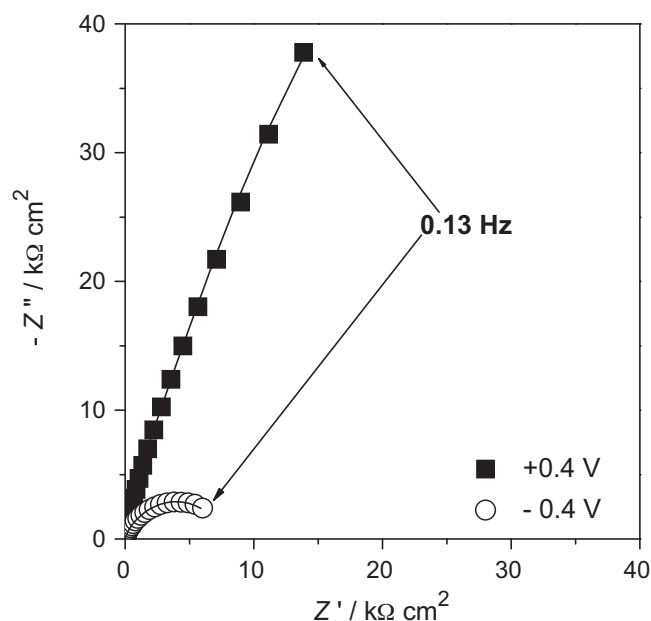

Fig. 6. Complex plane impedance spectra of PEDOT/PNR-coated electrodes in 0.1 M NaPSS at +0.4 and −0.4 V vs SCE. The lines show equivalent circuit fitting.

the polymer film is the rate determining step of the redox process, this can be explained by diffusion-controlled expulsion of the counterion which occurs during oxidation being slower than its diffusion-controlled insertion. The behaviour is similar to that observed for PNR/CFE [33]. In order to elucidate whether some fragments of oligomers of the two polymers are present on the electrode surface, an experiment was performed by dipping the modified electrodes in buffer overnight. After 48 h no colouration of the buffer solution occurs, meaning that the presence of short-chain oligomers in the polymer film can be excluded.

Characterisation by electrochemical impedance spectroscopy was also carried out. The measurements were performed in both NaPSS and phosphate buffer and the shape of the spectra were similar. To enable comparison with PEDOT, the results to be discussed here are those obtained in the same electrolyte, namely NaPSS – see Fig. 6 and Table 2. Two different circuits were used to fit the spectra: at +0.4 V the circuit consisted in the cell resistance in series with a parallel combination containing a constant phase element (CPE$_1$) and a resistance (R_1), a simplified version of the circuit used in [34] for the fitting of PNR-ITO modified electrodes and the same as that used previously for PEDOT-modified electrodes. Although the R_1 value is much higher, the value of C_1 is much lower. At −0.4 V a second parallel combination of constant phase element (CPE$_2$) and resistance (R_2) was necessary to adjust the experimental data. At this potential, close to the redox couple of PNR, the polymer

combination seems to behave as distinct layers: electron transfer can occur at the interface of one polymer with solution and at the interface between the two polymers.

3.6. Determination of H$_2$O$_2$ at PEDOT/PNR modified electrode

The PNR peak position and height depends on pH [35] and it was also reported that PNR acts better as mediator in acidic media. Thus, studies with H$_2$O$_2$ were performed in phosphate buffer pH 5.5. First, CV analysis was performed with PNR and PEDOT/PNR modified electrodes before and after the addition of aliquots of H$_2$O$_2$; in both cases the voltammograms exhibited a decrease in the oxidation current at −0.36 V and a increase in the reduction current around −0.75 V (not shown). Following this, amperometry at fixed potential (−0.36 V) was then carried out and the performance characteristics were calculated, showing a sensitivity of 0.92 μA cm^{-2} μmol^{-1} dm^3 and a detection limit of 80 μmol dm^{-3} (Table 3).

Importantly, using this combination of monomers (EDOT/NR = 2) to form the PEDOT/PNR film, hydrogen peroxide can be determined at a less negative potential (−0.36 V) than when using just PEDOT (−0.50 V). Additionally, the PEDOT/PNR combination gives a robust modifier film.

In the literature, a combination of EDOT with (4-vinylpyridine/PSS) [13] has been used to detect H$_2$O$_2$ and the analytical parameters (linear range 0–30 μmol dm^{-3}; sensitivity 0.130 μA cm^{-2} μmol^{-1} dm^3) are less than in the present work and HRP enzyme was used by them to amplify the signal. In another study [36] with the polymer 5,2′:5′,2″-terthiophene-3′-carboxylic acid polymer (TCAP), also with HRP, hydrogen peroxide reduction was measured at −0.2 V vs. Ag/AgCl and the response was more sensitive (0.48 μA cm^{-2} mmol^{-1} dm^3), with a wider linear range (up to 1.5 mmol dm^{-3}) but the detection limit of 0.2 mmol dm^{-3}) was higher than in the present work. There are very few reports in the literature concerning the determination of hydrogen peroxide without enzyme amplification at electrodes modified with conducting polymers [37] or composites containing polymer [38]; hence the method proposed in this work presents an important advantage for wider application. More detailed studies concerning performance as a sensor for various analytes are under way.

4. Conclusions

Modification of carbon electrodes by PEDOT has been successfully achieved by electropolymerisation of EDOT monomer, by applying potential cycling, potentiostatic and galvanostatic methods in aqueous electrolytes. These polymer films have a charge accumulation capacity that is dependent on the electropolymerisation procedure as well as the electrolyte in which polymerisation occurs. The PEDOT coated electrodes were successfully applied to both oxidation and reduction of hydrogen peroxide. Copolymerisation of EDOT and NR led to a polymer film (PEDOT/PNR) which exhibited characteristics of both polymers. Use of the PEDOT/PNR-modified electrode led to a decrease in the stabilisation time of the hydrogen peroxide sensor and to a less negative detection potential, besides giving a more robust modifier film than poly(neutral red) or PEDOT alone. The analytical parameters obtained were similar to those in the literature. Future work will include the testing of other polymer combinations or possibly immobilisation of horseradish peroxidase enzyme to further improve the sensitivity.

Acknowledgements

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