

Unveiling the mass transport dynamics in PEDOT:PSS films: Insights from a probe beam deflection analysis

Daniel R. Santos^a, Jorge F. Zeferino^a, Ana S. Viana^a, K.G.U. Wijayantha^b, Killian Lobato^c,
Jorge P. Correia^{a,*} 

^a Centro de Química Estrutural, Institute of Molecular Sciences, Departamento de Química e Bioquímica, Faculdade de Ciências, Universidade de Lisboa, Campo Grande, 1749-016 Lisboa, Portugal

^b Centre for Renewable and Low Carbon Energy, Cranfield University, Cranfield, Bedford MK43 0AL, United Kingdom

^c Instituto Dom Luiz, Faculdade de Ciências, Universidade de Lisboa, Campo Grande, 1749-016 Lisboa, Portugal

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ABSTRACT

The redox conversion of PEDOT:PSS synthesised potentiostatically and galvanostatically at 0 °C was monitored by *in-situ* Probe Beam Deflection (PBD) in NaClO₄/CH₃CN. The analysis of the redox current and laser beam deflection, as a function of time, is carried out by applying a mathematical treatment based on individual temporal convolutions with specific transfer functions for each species moving between the electrode surface and the solution. A quantitative determination of the extent of the ion transfer involvement in the redox conversion process has been carried out, allowing to dynamically estimate the relative proportion of each species during the oxidation and reduction process of the polymer film through the respective transport numbers. It was confirmed that the conversion process is dominated by the cation, which validates unequivocally the pseudocationic doping of films synthesised galvanostatically at 0 °C (approximately 77% Na⁺ compared to approximately 23% ClO₄⁻). By complementing the information obtained through PBD with the electromicrogravimetric technique, the quantitative contribution of each species involved in the conversion process was determined for the first time, confirming the significant participation of solvent accompanying the charge-transfer-dependent ions.

1. Introduction

Conducting polymers (CPs) are promising materials for energy storage applications due to their specific physicochemical and electrochemical properties [1,2]. One polymer that demonstrates particular desirable characteristics for applications in batteries, such as high stability in the oxidised state, ease of synthesis, excellent electrochemical reversibility and rather high conductivity, is poly(3,4-ethylenedioxythiophene) (PEDOT) [3]. When synthesised with a polyanion, such as sodium poly(4-styrenesulfonate) (NaPSS), it helps stabilise the EDOT monomer in an aqueous medium while also functioning as a counterion [4,5], enabling a conjugated backbone that facilitates electron delocalisation in the π -orbitals [6]. The PEDOT synthesis has also been carried out with other polyelectrolytes, such as poly-(2-acrylamido-2-methyl-1-propanesulfonic acid) (PAMPSA), poly-(4,4'-(2,2'-disulfonic acid)-diphenylene-terephthalamide) (t-PASA), sodium dodecyl sulphate (SDS), among others, as reported elsewhere [7–9]. This particular doping can induce changes in the morphology and electrical conductivity of the film, depending on the ratio

of monomer/polyanion used [10]. Additionally, the combination of PSS with PEDOT can impart a pseudocationic character to the polymer, essential for applying this polymer film as a cathode in metal-ion batteries. Pseudocationic doping is a charge-transfer mechanism that occurs during the redox conversion of the film, governed by the doping polyanions that are immobilised into the polymeric matrix and forcing the charge balance to be carried out by cations that are expelled during oxidation and incorporated back into the film during reduction. This doping mechanism has already been explored with PEDOT by immobilising two types of polyelectrolytes (NaPSS and Dextran Sulphate (DS)), in an organic medium, to evaluate the exchange of Li⁺ [11,12] as well as Mg²⁺ [12]. It has demonstrated its effectiveness in the exchange of the metal ion to some extent, while still confirming the pseudocationic nature of the redox conversion of these polymeric films.

Within a conventional 1:1 electrolyte, the redox process in PEDOT:PSS films may occur through two alternative pathways. Diagram 1 illustrates the two redox processes occurring within the polymeric film during conversion.

* Corresponding author.

E-mail addresses: jorge.correia@fc.ul.pt, jmcorreia@fc.ul.pt (J.P. Correia).

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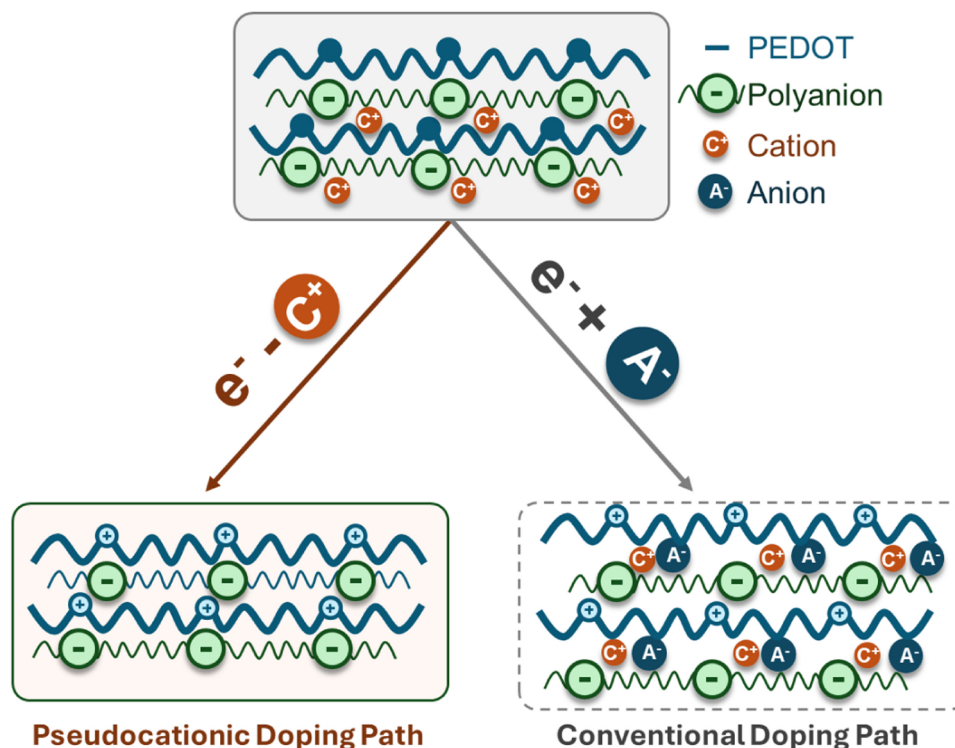


Diagram 1. Possible routes for the oxidation of a PEDOT:PSS film in a 1:1 electrolyte.

When the polymer is oxidised, two electrochemical processes may ensue. Either cations (C^+) are expelled from the matrix, and electro-neutrality is maintained by the oxidised film and the polyanion (pseudocationic doping – cation transfer), or anions (A^-) are incorporated into the polymer film, and the electroneutrality is ensured by the polymer and polyanion, together with the electrolyte ionic pair (conventional doping – anion transfer). In addition to these processes, solvent fluxes are also involved, which always accompany the ionic flux but do not involve charge transfer. The properties of the conducting polymer, and consequently its doping mechanism, are strongly influenced by its formation conditions, such as the concentration of monomer/dopant agent, solvent, electrochemical growth mode, etc. [13]. One parameter that has not been extensively investigated but has proven to impact the doping mechanism of the polymer matrix significantly is the synthesis temperature. Santos *et al.* [14] discovered that PEDOT:PSS films synthesised either galvanostatically or potentiostatically at 0 °C exhibited significant cation exchange during redox conversion in a solution containing NaClO_4 , making it suitable to analyse the mass transfer dynamics of the ionic flow involved in the electrochemical doping/undoping. In this specific case, both pathways presented in the diagram were evidenced, demonstrating a balance of both redox doping/undoping processes.

In this work, the pseudocationic character of these films is evaluated using probe beam deflection (PBD). This technique is based on the deflection of a light beam aligned parallel and close to the electrode surface. The deflection is caused by concentration gradients formed in the diffusion region (Debye layer), providing information on ion transfer during the redox conversion process [15]. As a result of the electrochemical reaction, a concentration gradient of a given species develops, which translates into a refractive index gradient in the solution, causing the deflection of a light beam passing through this region [16]. By convention, the deflection signal, θ , has the same sign as the concentration gradient, $\partial c/\partial x$, i.e., positive when a species is consumed at the electrode and negative when it is released [17]. This technique is suitable for simultaneous application with electrochemical methods, such as cyclic voltammetry, to obtain a correlation between charge transfer and

ionic flow [16,18]. This instrumental technique can be applied to the study of electrosynthesised films at low temperatures, as these exhibit the greatest potential for use as cathodes in metal-ion batteries, given that they demonstrate the highest cation exchange, particularly sodium ions, during redox conversion [14].

A temporal convolution approach was employed to quantify the mass fluxes associated with the redox conversion of the polymer monitored by PBD. This mathematical tool allows a direct comparison between the current response of the system and the optical deflection signal, assuming, in this particular case, semi-infinite linear diffusion of the ionic species involved [17,19]. Essentially, this operation projects the electrical signal from the point and instant where it is measured (at the electrode, at time t) to the distance where the optical beam is located (distance x from the electrode) at time $t + \Delta t$, where Δt is the time it takes for the species involved in the electrochemical event at the electrode surface at time t to travel the distance x [17]. Thus, this time lag, Δt depends exclusively on the diffusion coefficient of the species involved in the charge transfer process and the distance separating the optical beam from the electrode surface. This time- and space-projected electrical signal can then be converted into a beam deflection signal, accounting for the local refractive index of the solution. When the current signal is convoluted with a characteristic function, it is transduced into a signal representing the ionic fluxes at a given distance from the electrode [20,21]. By comparing this signal with the experimental deflection, it is possible to discriminate and quantify the mass transfer associated with the polymer's redox conversion [22]. It should be noted that the PBD technique is insensitive to the solvent flows between the solution and the modified electrode surface [21]. Therefore, by complementing the responses from the PBD technique with the Electrochemical Quartz Crystal Microbalance (EQCM) measurement [18,23,24] (which provides information about the total mass flux), it becomes possible to access the individual contribution of solvent flow and cation and anion fluxes for the overall mass transport during PEDOT:PSS conversion.

2. . Methods and Materials

2.1. Chemicals

3,4-ethylenedioxythiophene (EDOT, ACROS Organics, 99%), sodium poly(4-styrenesulfonate) MW ~70000 (NaPSS, Aldrich, p.a.), sodium perchlorate anhydrous (NaClO₄, Acros Organics, p.a.) and acetonitrile extra dry (CH₃CN Acros Organics, 99.9%) were used without further purification. Ultrapure water from the MILLI-Q A10 Gradient purification system (18.2 MΩ·cm at 25°C) was used to prepare the monomer solution and cleaning steps.

2.2. Cells and Electrodes

For electrochemical measurements, ellipsometry and PBD, "specpure" platinum disks electrodes with active areas of 0.16 cm² and 0.20 cm² were utilised as working electrodes. Before each experiment, these electrodes were polished with successively finer grades of alumina suspensions (Al₂O₃, Buehler, 5.0 μm, 1.0 μm, and 0.3 μm) and washed thoroughly with deionised water. For EQCM assays, Pt-coated 8 MHz AT-cut quartz crystals were employed, cleaned in a plasma chamber (ZEPTO from diener electronic) for 3 min at 0.3 mbar in air atmosphere. A saturated calomel electrode (SCE) was used as the reference electrode, and all the potential values mentioned in this work were reported. A large area of platinum foil was used as a secondary electrode. A platinum mesh counter electrode was also used for PBD experiments; it was placed far enough from the working electrode so the reactions that occurred in it would not interfere in the deviation of the laser. A glass single compartment thermo-controlled jacketed electrochemical cell and a three-compartment conventional cell were used for the synthesis and electrochemical characterisation, respectively, of the polymer films. A single-compartment Teflon cell was employed for EQCM experiments, exposing a Pt area of 0.29 cm². A 2 cm wide quartz cuvette cell, fixed in an optical bench, was also used for PBD assays.

2.3. Electrosynthesis and Characterization

Platinum electrodes were modified with PEDOT:PSS. The polymers were grown potentiostatically (E_g) by applying a potential of 0.90 V or galvanostatically (I_g) by applying a current density of 0.75 mA·cm⁻², for 120 and 60 seconds, respectively, at 0°C, using 0.01 M EDOT and 0.1 M NaPSS in aqueous solution, deaerated with N₂ for, at least, 15 minutes. The monomer-containing solution was stirred for 7 h to obtain a homogeneous mixture. A thermostatic heater/cooler bath (Thermomix BU/Frigomix S, B. Braun) circulating a mixture of water:ethylene glycol in the jacketed cell was employed to control the monomer solution temperature. The electropolymerisation assay was performed using a VoltaLab PGZ100 (Radiometer Analytical).

Ellipsometric measurements were carried out *ex-situ*, at 60° and 70° incident angles, using a single-wavelength ellipsometer (SE400, Sentech Instruments GmbH) equipped with a He-Ne laser source (632.8 nm) in a polarizer-sample-analyser (PSA) configuration. The refractive index (*n*) and extinction coefficient (*k*) of the platinum substrate were computed using a two-phase model for the platinum/air interface [14]. After the modification of the platinum electrodes with polymer films, the refractive index, extinction coefficient, and polymer thickness of the film (*L*) were calculated using a multiangle approach based on a three-phase model (air-film-substrate) assuming a homogeneous and isotropic film [14]. These ellipsometric measurements were performed in triplicate with polymers synthesised under the same conditions aforementioned.

Prior to the characterisation, the modified electrodes were voltammetrically cycled at room temperature in the potential range of -0.90 V to 0.80 V vs. SCE at 50 mV·s⁻¹ during 20 cycles in deaerated acetonitrile solution containing 0.1 M NaClO₄. It was then moved to a new electrolyte solution (same composition: 0.1 M NaClO₄/CH₃CN) for characterisation.

2.4. Ion Transfer Analysis

The PBD setup is reported elsewhere [25]. Briefly, the light source was an Oriel Model 79200 2 mW He-Ne laser with a 1/e² beam diameter of 0.63 mm. The laser beam was converged by a lens with a 60 mm focal length to the centre of the cell. A position detector system, consisting of a double photodiode (spot-2DMI Optilas) with a 10 μm gap between the two photodiodes, was employed to measure the laser beam deflection. In this configuration, a home-built differential amplifier connected to the photodiodes ensured beam deviation sensitivity of 97 μrad·V⁻¹ [14]. The working electrode was mounted on a translation base and connected to an Oriel microcontroller device that controls vertical and tilt movements. A positive deflection sign occurs when the laser beam deflects away from the working electrode surface, while a negative sign occurs when the beam deflects towards the electrode. Before the experiments, the laser beam was aligned parallel to the electrode surface at a fixed distance of 143 μm.

The refractive indices of the different concentrations of the supporting electrolyte in the organic media were measured at room temperature with an Abbe Refractometer (NAR-1T Liquid, Atago). Na⁺ and ClO₄ diffusion coefficients were calculated according to the Nernst-Einstein equation [26].

3. . Theory and Calculations

The temporal convolution treatment was carried out according to the model proposed by Vieil and Lopez [17]. With this model, a theoretical approach is made and contrasted to the experimental result to get the data of the ionic transfer taking place during the polymer redox process. In addition, the registered time delay between the electrochemical event and its optical detection due to species diffusion was also considered.

To apply the temporal convolution approach, there are two equations that must be considered. The first one refers to the deflection angle of the collimated beam that, eventually, is the measured deviation of the laser beam,

$$\theta_{\text{exp}}(x, t) = \frac{L}{n} \sum_i \left(\frac{\partial n}{\partial c} \right)_i \frac{\partial c_i(x, t)}{\partial x} \quad (1)$$

where $\theta_{\text{exp}}(x, t)$, (rad), is the deflection angle of the beam at time *t* experimentally measured, that passes through the medium at a distance *x* from the electrode; *L*, (cm), is the spatial length that the light beam travels in the region where the concentration of species *i* is disturbed relative to the bulk of the solution (electrode diameter – 0.45 cm); $(\partial n / \partial c)_i$, (mol⁻¹·cm³), is the refractive index change of the solution caused by the variation in the concentration of species *i*; $\partial c_i(x, t) / \partial x$, (mol·cm⁻²), is the concentration gradient of species *i* perpendicular to the electrode surface.

The second fundamental equation is the one that describes the ionic movement in the Debye layer. This transfer function, assuming semi-infinite linear diffusion of the species involved in the redox process, is represented by

$$\mathcal{F}_i(x, t) = \frac{x}{\sqrt{\pi D_i t^3}} \exp\left(-\frac{x^2}{4D_i t}\right) \quad (2)$$

where $\mathcal{F}_i(x, t)$, (s⁻¹), is the transfer function accounting for the nature and boundary conditions of mass transfer, with *D_i*, (cm²·s⁻¹), the diffusion coefficient of the participating species in the electrochemical event.

The light deviation is ruled by the optical constraints of the perturbed layer of the solution near the electrode, being converted in a scaling factor, *h_i*, described by

$$h_i = \frac{t_i \left(\frac{\partial n}{\partial c} \right)}{n D_i} \cdot \frac{L}{z_i F} \quad (3)$$

Table 1

Refractive index (n), extinction coefficient (k), and thickness (L) of polymer films on modified electrodes under the deposition conditions shown in Fig. S1. Presented as mean values $\pm$ standard deviation.

Growth conditions	n_{film}	k_{film}	$L_{\text{film}} / \text{nm}$
$E_g = 0.90 \text{ V}$; 0°C ; 120 s	1.400 ± 0.002	0.325 ± 0.002	171.2 ± 0.3
$I_g = 0.75 \text{ mA}\cdot\text{cm}^{-2}$; 0°C ; 60 s	1.489 ± 0.003	0.354 ± 0.001	174.7 ± 0.1

where t_i is a coefficient that express the participation of a given species i into the total ionic flow (like a transport number), F is the Faraday constant (ca. $96485 \text{ C}\cdot\text{mol}^{-1}$), and z_i is the charge of the ion i (in this case $z_i = 1$ for both ions).

Combining Eqs. 2 and 4 results in a function which, when multiplied by the current density at time t , $j(t)$, provides the theoretical deviation that the laser beam should undergo, considering the process carried out by species i (as described in Eq. 4).

$$\theta_i(x, t) = h_i \cdot \mathcal{F}_i(x, t) \cdot j(t) \quad (4)$$

The salt diffusion coefficient values were obtained from conductivity measurements of the electrolytic solution. The NaClO_4 molar conductivity was related to the ionic conductivities by the Nernst-Einstein equation. Since there are no values reported for these ions in this organic medium and for this concentration, it was assumed that the ratio between the individual coefficients reported in water at infinite dilution would be the same as those in acetonitrile at the current concentration. In this way, the values of $0.938 \times 10^{-5} \text{ cm}^2\cdot\text{s}^{-1}$ and $1.260 \times 10^{-5} \text{ cm}^2\cdot\text{s}^{-1}$ were obtained as diffusion coefficients of sodium and perchlorate ions, respectively. These values should be compared with 1.334×10^{-5} and $1.792 \times 10^{-5} \text{ cm}^2\cdot\text{s}^{-1}$ in water [26], or 2.050×10^{-5} and $2.759 \times 10^{-5} \text{ cm}^2\cdot\text{s}^{-1}$ in acetonitrile [27], at infinite dilution at 25°C , for Na^+ and ClO_4^- , respectively. With these computed values and the distance of the beam to the electrode surface ($143 \mu\text{m}$), one can establish the corresponding transfer functions (Eq. 2) for the sodium and perchlorate ions.

To calculate the contribution of each ion involved in the redox process, the following mathematical expression was used:

$$\theta_{\text{exp}}(x, t) = (\theta_{\text{cation}} \times t^+ + \theta_{\text{anion}} \times t^-) \quad (5)$$

where t^+ and t^- are the so-called transport numbers related to the individual participation of the anion and the cation for the overall redox conversion. Thus, the electric current is convoluted with the scaling factors, h_i , and the specific transfer function of each species, $\mathcal{F}_i(x, t)$, involved in the redox conversion process (sodium ion; perchlorate ion), considering that the charge balance is achieved exclusively by each of the ions; This results in θ_{cation} and θ_{anion} deduction. Since the contribution of both ions totals 100% of the ionic flux inherent to charge compensation ($t^+ + t^- = 1$), it is thus possible to calculate the extent to

which each species contributes to the experimentally observed deflection (Eq. 5).

4. Results and Discussion

Films of PEDOT doped with PSS⁻ were electrosynthesised at 0°C under potentiostatic and galvanostatic control, with different deposition times, to produce polymers with approximately the same thickness, allowing for direct comparison of the ionic transfer occurring during their redox conversion process (growth current/potential transients shown in Fig. S1, Supplementary Material). The establishment of the synthesis conditions (E_g at 0.90 V and I_g at $0.75 \text{ mA}\cdot\text{cm}^{-2}$) was based on those previously used at 25°C , which resulted in an equivalent process kinetics [14]. Under those conditions (at 25°C), no signs of over-oxidation were observed for galvanostatically grown polymer films (e.g. a rise in potential over the course of the synthesis; normally the potential should monotonically decrease [28]), whereas such signs were apparently present when the film was formed potentiostatically. In the latter case, a decay in the current value was observed from the moment the substrate surface became fully covered with film ($\approx 15 \text{ s}$), which could suggest some degree of polymer overoxidation. However, ellipsometric analysis reveals that the film electrosynthesised potentiostatically is significantly denser (higher refractive index) than its galvanostatically grown counterpart, which would inhibit the kinetics of polymer deposition. This means that the signs of polymer overoxidation, though apparent, may in fact be masked by an increased kinetic hindrance caused by the film greater compactness. In the films synthesised in the present work at 0°C , the same operational conditions did not lead to comparable deposition rates, and signs of overoxidation appear to be present during film formation via both growth modes. These, as previously discussed, may simply result from the mechanical characteristics of the polymers, particularly their density and morphology. However, some degree of inherent overoxidation in these films cannot be ruled out, although this does not compromise their applicability.

For thickness control, *ex-situ* ellipsometry was employed, which allowed for the estimation of not only the film thickness but also their optical properties (refractive index and extinction coefficient) [14]. Prior to the film synthesis, the optical properties of the platinum substrate were measured at two angles of incidence ($\varphi = 60^\circ$ and $\varphi = 70^\circ$), providing the substrate parameters necessary to calculate both the optical properties and the thickness of the films using a multiangle approach (Table S1, Supplementary Material). Table 1 presents the refractive index (n), extinction coefficient (k), and thickness of the selected films, calculated according to an isotropic and homogeneous three-phase model (air/film/substrate) for the two aforementioned incident angles. As expected, the films exhibit high refractive index values (indicating dense films), particularly the polymer synthesised

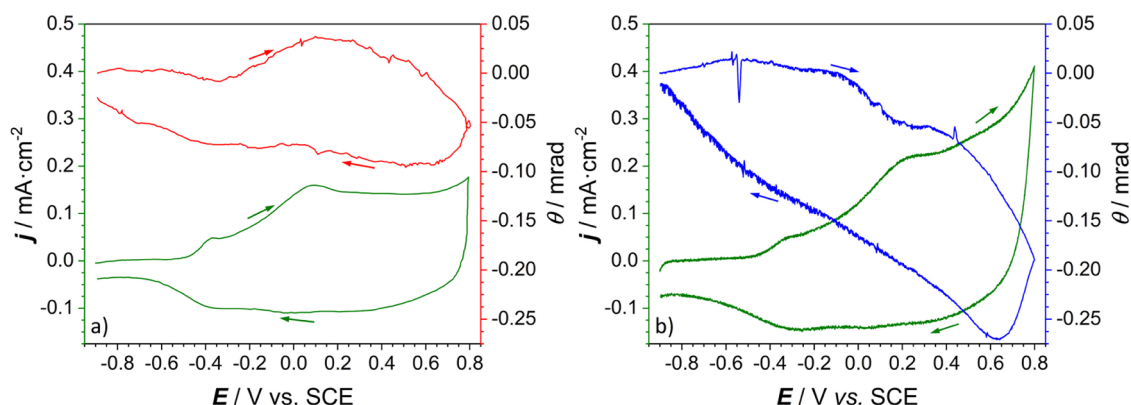


Fig. 1. Current and laser deflection signals recorded during cyclic voltammetry, at room temperature with $\nu = 50 \text{ mV}\cdot\text{s}^{-1}$, of platinum electrodes modified with electropolymerised PEDOT:PSS, a) via potentiostatic growth and b) via galvanostatic growth at 0°C , in deaerated acetonitrile containing 0.1 M NaClO_4 .

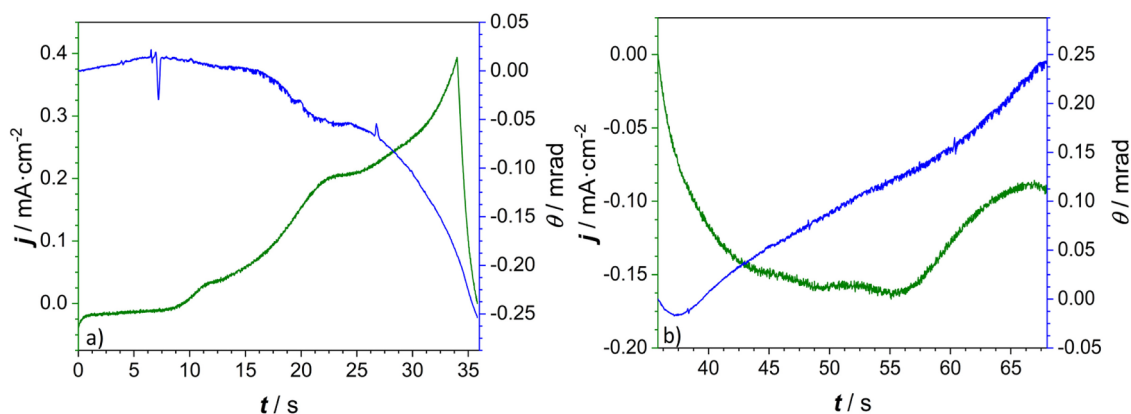


Fig. 2. Deflectogram and voltammogram as a function of time of the redox conversion process at room temperature with $\nu = 50 \text{ mV}\cdot\text{s}^{-1}$ of a PEDOT:PSS film grown galvanostatically by applying a current density of $0.75 \text{ mA}\cdot\text{cm}^{-2}$ for 60 s at 0°C . a) oxidative scan, b) reductive scan.

galvanostatically. The continuous increase in potential observed during synthesis may therefore be associated with a possible overoxidation of the material, an increased kinetic hindrance to growth, or a combination of both phenomena. It is also worth noting - also anticipated, as it is typical of these materials - that the film grown potentiostatically for 120 s is optically less dense than the one produced under the same conditions for 60 s [14]. This indicates that, when interpreted in light of the same physical model (homogeneous and isotropic film), the inner layers of the film are more compact than the outermost phase, which appears to be more porous, possibly more branched showing signs of some overoxidation. This observation further highlights the high compactness achieved with the galvanostatically grown film, whose thickness is comparable to that of the polymer synthesised under constant potential.

Table 1 shows that the films exhibit a similar thickness despite their different optical properties, as noted. The film synthesised galvanostatically shows a higher refractive index than the film synthesised potentiostatically, indicating greater compactness. Furthermore, its extinction coefficient is higher, indicating that this film exhibits greater optical absorption than the one synthesised potentiostatically. These distinct optical properties demonstrate that, although the films have approximately the same thickness, the polymer structure differs, which may highlight dissimilarities in ionic transfer during the redox conversion. Indeed, the differences observed in the n and k values exhibited by the films are significant and meaningful. They reflect variations in the nature of films grown under different modes [29], as well as the structural and morphological diversity of PEDOT:PSS synthesised under various conditions (mode, temperature, thickness) [14].

Probe beam deflection was employed to evaluate the occurrence of pseudocationic doping. Fig. 1 shows the deflectograms and the cyclic voltammograms simultaneously recorded during the redox conversion of PEDOT:PSS films grown potentiostatically and galvanostatically at 0°C .

The electrochemical behaviour exhibited by the polymers is described in [14]. For the analysis of the deflectograms recorded during the polymer's redox process, it is essential to understand that the oxidation of the polymer may involve either the expulsion of cations (negative deflection) or the incorporation of anions (positive deflection) to maintain the electroneutrality of the film. Similarly, cation entry results in a positive deflection during reduction, while anion expulsion is associated with a negative deflection. It is worth noting that the terms 'positive deflection' and 'negative deflection' actually refer to deflection towards more positive and negative values, respectively, rather than the sign of the measured deflection at a given moment. They should thus be interpreted as the value of the first-time derivative that the deflection signal takes at a given moment.

Fig. 1 shows a time lag between the electrochemical event and the ion flow detection. This is due to the displacement of species in the

diffusion layer, where species generated in a given moment are detected later by the light probe, located, in this work, at $143 \mu\text{m}$ from the electrode surface, being the time-lapse dependent on the ion diffusion coefficient.

Despite being more compact, this feature does not appear to hinder the redox activity of the galvanostatically generated film. Being denser and of similar thickness, it would naturally consist of a greater amount of electroactive material - which is indeed observed. In fact, the oxidation charge involved in the redox transformation is $4.33 \text{ mC}\cdot\text{cm}^{-2}$, while for the potentiostatically grown counterpart it is $3.07 \text{ mC}\cdot\text{cm}^{-2}$ ($Q_{\text{ox}}/Q_{\text{red}} = 1.02$ and 1.14 for the films synthesised under constant current and constant potential, respectively). In addition to the differing extent of the redox conversion process, greater redox activity is observed for the I_g film at the anodic end of the potential window, accompanied by an increase in ionic flux. This observation considerably reduces the likelihood of the material being heavily overoxidised, as it retains a high specific electroactivity. The film synthesised potentiostatically at 0°C (Fig. 1a) exhibits a positive deflection during oxidation, indicating an incorporation of perchlorate ions, followed by a negative deflection, indicating an expulsion of cations, until the potential of 0.62 V in the cathodic scan. During the reduction phase, a positive deflection is visible, indicating a dominance of cationic flow. This indicates that the film synthesised at 0°C exhibits pseudocationic doping to some extent. The film synthesised galvanostatically at 0°C (Fig. 1b) shows a negative deflection during oxidation, corresponding to a flow that mainly expels sodium ions from the polymer matrix. During the reduction, a cationic flow from the electrolyte dominates, compensating for the excess negative charge of the polyanion immobilised in the polymer matrix to maintain electro-neutrality [14].

It is worth noting that, unlike the behaviour exhibited by the film grown under potentiostatic conditions, where regions with a prevalence of anionic exchange were observed, the galvanostatically generated film displays fluxes dominated by cationic exchanges throughout the entire voltammogram. Moreover, the film synthesised under galvanostatic control exhibits a deflection amplitude - and consequently an extent of cationic exchanges - significantly larger than that potentiostatically grown. It should be mentioned that the overall deflection amplitude is also significantly higher than those recorded at higher temperatures [14] and during the exchange of other cations [11,12]. This reveals the particular suitability of the sodium ion for the pseudocationic doping mechanism of PEDOT:PSS films, which is expressively improved by the low synthesis temperature of the polymeric matrices.

As the aim of this work is not to compare how the synthesis conditions determine the nature of the ionic exchange processes occurring during the redox conversion of the polymers, but rather to select the one that exhibits the highest ionic exchange, the galvanostatically synthesised film is naturally defined as the material of interest for

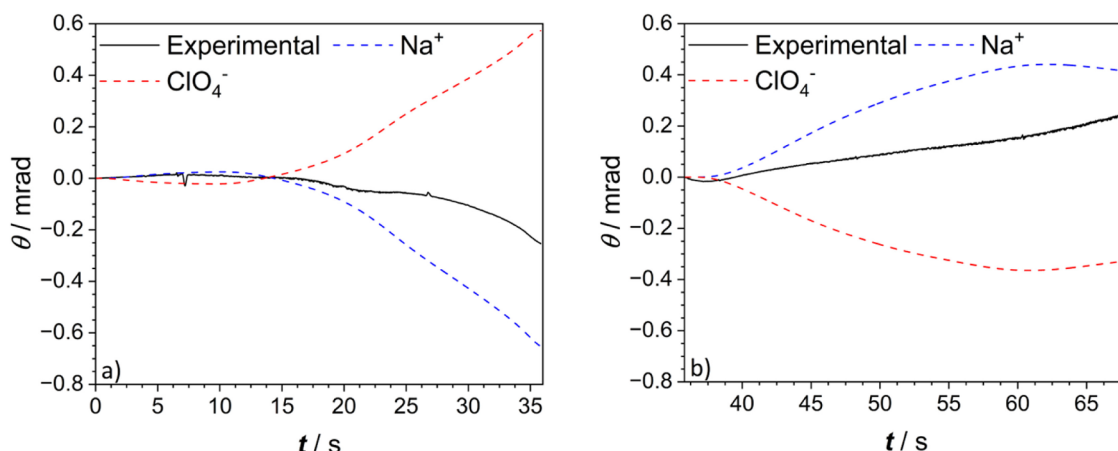


Fig. 3. Beam deflection computed by the temporal convolution of the electric current, considering exclusively the anion or cation transfer during redox conversion for a galvanostatically grown film. a) oxidative scan, b) reductive scan.

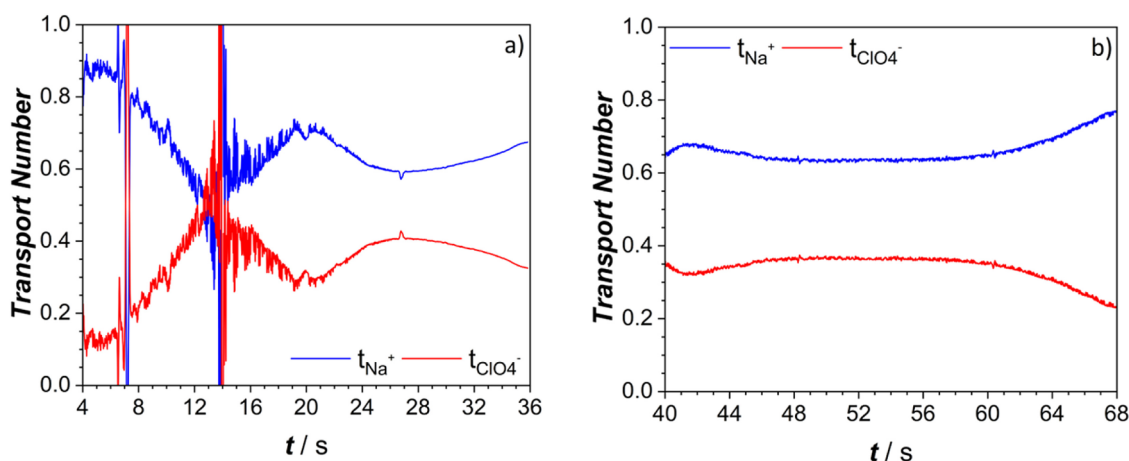


Fig. 4. Dynamic transfer numbers of the sodium and perchlorate ions obtained by the temporal convolution computation for a galvanostatically grown film. a) oxidative scan, b) reductive scan.

quantifying the pseudocationic behaviour. This behaviour highlights a strongly pseudocationic character of the polymer, justifying its quantification through a mathematical treatment by temporal convolution of the electrochemical records obtained during the PBD assay. However, although the positive ion dominates the ionic flow during the redox conversion of the PEDOT:PSS polymeric film, the participation of the perchlorate anion should not be overlooked as it can penalise the cathode's performance when applied in a metal-ion battery.

To convolute the current signal to be compatible with the experimental deflectogram, both records must be normalised (concerning the oxidation and reduction charges and initial beam deviation) and represented as a function of time, for each segment (Fig. 2).

As shown in Fig. 2a, the negative deflection corresponds to the expulsion of sodium ions during polymer oxidation. On the other hand, during the reduction process, in Fig. 2b, there is a positive deflection corresponding to the incorporation of sodium ions.

For the temporal convolution treatment, particularly for the scaling factor h_i (Eq. 3), it is necessary to determine the ratio $\partial n / \partial c$, the medium refraction index and the species' diffusion coefficients. The value of $\partial n / \partial c$ ($14.171 \text{ mol}^{-1} \cdot \text{cm}^3$) was obtained through linear regression of the refraction indices values measured as a function of the NaClO_4 concentration in organic media, Fig. S2 (Supplementary Material). The refractive index of 0.1 M NaClO_4 organic solution was measured to be 1.3448. To calculate the diffusion coefficient of sodium and perchlorate ions, the value of the conductivity, $8.45 \text{ mS} \cdot \text{cm}^{-1}$, was measured for 0.1

M $\text{NaClO}_4 / \text{CH}_3\text{CN}$ solution; the values of molar conductivity at infinite dilution of Na^+ and ClO_4^- ions in water were also considered [26]. Applying the Nernst-Einstein relation, a diffusion coefficient of $9.376 \times 10^{-6} \text{ cm}^2 \cdot \text{s}^{-1}$ was obtained for sodium ion and $1.260 \times 10^{-5} \text{ cm}^2 \cdot \text{s}^{-1}$ for perchlorate ion. This mathematical step is aforementioned in theory and calculations.

As mentioned in section 3, using the calculated diffusion coefficients and the distance between the light beam and the electrode surface ($143 \mu\text{m}$), the transfer functions for each ionic species were established, assuming a semi-infinite linear diffusion of the species, Fig. S3 (Supplementary Material). The values of x and D_i are responsible for the shape of the transfer function during the convolution process of the species (see Eq. 2), translating the extent at each instant of the flow of these species and their contribution to the total flow. Furthermore, as the diffusion coefficient of the species and the distance of the light beam to the electrode surface remain the same, the transfer functions will be the same for both the oxidation and reduction processes. Considering exclusively a cationic or anionic exchange during oxidation and reduction, the ionic scale factors were determined to be $h_{\text{Na}^+} = 5.82$ for the sodium ion and $h_{\text{ClO}_4^-} = 4.34$ for the perchlorate ion.

With the transfer functions for each ion established and their respective scaling factors determined, the temporal convolution procedure was applied to the anodic and cathodic current signals (see Eq. 4) to obtain the projected deflection signal, assuming that the electro-neutrality of the polymeric matrix is maintained exclusively by the

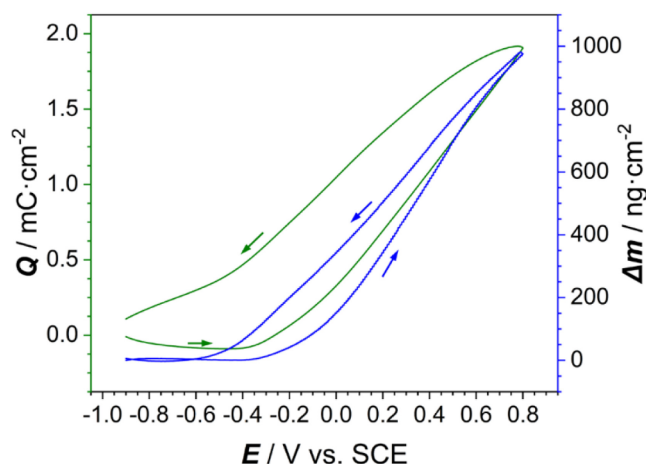


Fig. 5. Registered charge density and mass variation recorded simultaneously by EQCM during the redox conversion process of the film grown galvanostatically ($0.75 \text{ mA}\cdot\text{cm}^{-2}$ for 60 s at 0°C). This assay was recorded at room temperature with $\nu = 50 \text{ mV}\cdot\text{s}^{-1}$ in deaerated acetonitrile solution containing 0.1 M NaClO_4 .

cation (pseudocationic doping) or the anion (conventional doping). The result of this mathematical treatment is shown in Fig. 3 for the oxidative (Fig. 3a) and reductive (Fig. 3b) sweeps. These representations also include the corresponding deflection signals recorded experimentally.

During redox conversion, as shown in Fig. 3a and Fig. 3b, the experimental beam deviation is not decoded by a single and exclusive flow associated with the cation or anion but rather a mixed stream of both ionic species. Furthermore, it is denoted that a dominant contribution of cation compared to the anion is very likely, since the signal of the convoluted current associated with the sodium ion is closer to the experimental mirage signal, both in the oxidation, Fig. 3a, and in the reduction process, Fig. 3b.

To clarify the relative participation of each ionic species throughout the redox process, the dynamic transport numbers during oxidation and reduction were calculated according to Eq. 5, represented in Fig. 4. This figure was obtained by adapting the theoretical calculus by Vieil and Lopez [17]. In the transport number calculations and to circumvent the noise created in the initial moments (of both scans), the first 4 seconds of the oxidation process and the first 4 seconds of the reduction process were not represented since they correspond to the beginning of the

electrochemical process, and the convoluted signals have approximately the same values as the experimental signal.

In Fig. 4a, the cation contribution decreases until ca. 14 seconds, corresponding to a slight positive deflection associated with the sodium ions expelled from the polymer matrix. It should be noted, however, that the current values at this stage are quite small, and therefore, the extent of mass transfer is negligible. At this moment, there is an equilibrium between anionic species and cationic species flow ($t_{\text{Na}^+} = 50\%$; $t_{\text{ClO}_4^-} = 50\%$); from this moment on, the contribution of cation increases and at the end of the oxidation process, its participation is ca. 67%. In comparison, the anion contribution is 33%. As shown in Fig. 4b, the cation remains the dominant contributor during the reduction phase. In this stage, sodium ions are incorporated into the polymer up to the end of the reduction process, with their participation being approximately 77%, while perchlorate ions account for only 23%. It should be noted that these ion exchange values are unlikely to be significantly affected by the concentration of the doping agent (PSS). Indeed, studies dedicated to the effect of different polyelectrolyte concentrations have shown that the charge carrier density generated by the film oxidation is not sensitive to the different EDOT/PSS ratios used in the synthesis, while electrical conductivity decreases with increasing PSS content. This suggests a percolation behaviour between highly conductive PEDOT:PSS complexes and a low-conductivity PSS matrix [30].

As previously mentioned, the PBD technique is insensitive to the solvent involvement in the redox conversion of the polymer. Thus, by complementing the information provided by this optical technique with the data gathered microgravimetrically (EQCM), it is possible to assess the real magnitude of the involvement of all species participating in the polymer redox conversion, namely the anion, cation and solvent. In Fig. 5 is depicted both the electric charge variation as well as the electrode mass change during the polymer redox conversion in the same potential window used for PBD experiments.

The amount of cations and anions involved in the mass transfer can be established by operating the charge recorded during the microgravimetric experiment and the transference number determined previously. To bypass the aforementioned noise during the initial stages (when the mass transfer is negligible), a value of 0.50 was assumed for the contribution of both the cation and the anion, for the first 4 seconds in each sweep. The mass registered in the EQCM experiment, subtracted by the contribution of the mass assigned to anions and cations (either positive or negative), represents, naturally, the mass of solvent that is incorporated or expelled by the polymer matrix.

Using these computed values, alongside with the molar masses of

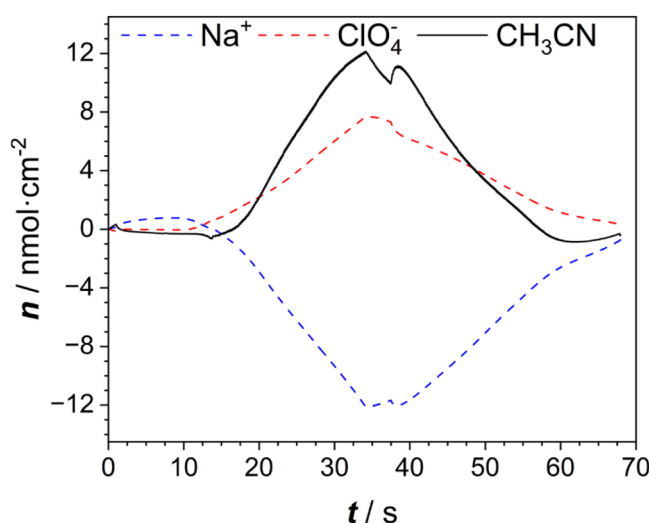


Fig. 6. Molar amount of species involved in the mass transfer process during redox conversion at room temperature with $\nu = 50 \text{ mV}\cdot\text{s}^{-1}$ of PEDOT:PSS film grown galvanostatically applying a current density of $0.75 \text{ mA}\cdot\text{cm}^{-2}$ for 60 s at 0°C .

sodium ($M_{\text{Na}^+} = 22.99 \text{ g}\cdot\text{mol}^{-1}$), perchlorate ions ($M_{\text{ClO}_4^-} = 99.45 \text{ g}\cdot\text{mol}^{-1}$) and acetonitrile ($M_{\text{CH}_3\text{CN}} = 41.05 \text{ g}\cdot\text{mol}^{-1}$), the number of moles of sodium, perchlorate and solvent molecules, taking part in the mass transfer process during the redox conversion of PEDOT:PSS galvanostatically synthesised at 0°C , were determined - Fig. 6.

Fig. 6 clearly shows that sodium ion and acetonitrile fluxes are the dominant processes during the redox conversion of the polymer. Conversely, the contribution of the perchlorate ion to the polymer conversion is much less significant than the other fluxes. This corroborates the findings reported in Santos *et al.* [14], which confirmed the existence of pseudocationic doping for the film synthesised galvanostatically at 0°C . It is also clear that the solvent flux completely masks the ionic flux during the redox conversion.

5. . Conclusion

Coupling the PBD technique with cyclic voltammetry made it possible to confirm which ion was the most dominant in the charge transfer process. This analysis was carried out by comparing the experimental deflection signal with the convoluted current one. The application of the mathematical tool of temporal convolution, assuming the exclusive participation of each ion, elucidated that the redox conversion is a mixed process involving both anions and cations, with a dominant contribution from sodium ions during the electrochemical doping and undoping of the film. It was possible to resolve the dynamic individual contributions as transference numbers at each instant. It was denoted that during oxidation, the relative proportion of the cation increases along the time/potential presenting, at the end of the segment, a participation of *ca.* 67%. During the reduction process, the sodium ion contribution reaches approximately 77%, clearly demonstrating pseudocationic doping. Furthermore, complementing the PBD technique with EQCM revealed that acetonitrile also plays a significant role in mass transfer during the redox conversion process, contributing at a level comparable to that of the cation, albeit in the opposite direction. This significant cation dominance highlights the polymer's strong pseudocationic character, making it a promising material for applications such as metal-ion batteries, where efficient cation transport is critical. The quantified contributions also provide valuable insights for optimizing material performance in energy storage systems, revealing that the PBD technique is an invaluable method for comprehensively characterising mass transfer phenomena during redox reactions. It is also now clear that the solvent flow in and out of the modified electrode masks the ionic flux occurring during the redox event of the matrix when the analysis is based solely on electrochemical and microgravimetric assays.

CRedit authorship contribution statement

Daniel R. Santos: Writing – review & editing, Writing – original draft, Validation, Methodology, Investigation, Formal analysis, Conceptualization. **Jorge F. Zeferino:** Validation, Methodology. **Ana S. Viana:** Writing – review & editing, Investigation, Formal analysis. **K.G. U. Wijayantha:** Supervision, Formal analysis, Conceptualization. **Killian Lobato:** Writing – review & editing, Supervision, Formal analysis, Conceptualization. **Jorge P. Correia:** Writing – review & editing, Supervision, Resources, Methodology, Funding acquisition, Formal analysis, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Supplementary materials

Supplementary material associated with this article can be found, in the online version, at [doi:10.1016/j.electacta.2025.146343](https://doi.org/10.1016/j.electacta.2025.146343).

Data availability

Data will be made available on request.

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Unveiling the mass transport dynamics in PEDOT:PSS films: insights from a probe beam deflection analysis

Santos, Daniel R.; Zeferino, Jorge F.; Viana, Ana S.; Wijayantha, Upul K. G.; Lobato, Killian ...

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