



Temperature-dependent electrosynthesis of PEDOT:PSS: Enhanced Na⁺ transfer targeting high-performance Na-ion batteries

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ABSTRACT

Poly(3,4-ethylenedioxythiophene):Poly(sodium 4-styrenesulfonate) (PEDOT:PSS) is a versatile conducting polymer with physicochemical properties favourable for energy storage applications, such as chemical and mechanic stability and flexibility. However, the temperature at which the polymer is synthesised can significantly influence its properties. In this study, a detailed investigation of the effect of temperature on the electroactivity, morphology, optical properties, and ionic/solvent transport during the redox conversion of potentiostatically and galvanostatically synthesised films was conducted. Electrochemical data, supported by ellipsometry, atomic force microscopy, microgravimetry, and probe beam deflection measurements, revealed that films synthesised at lower temperatures (0 °C) were more compact compared to those synthesised at higher temperatures (40 °C). Films synthesised at 0 °C also exhibited near-ideal reversibility, with a Q_O/Q_R ratio of ca. 1. Importantly, the 0 °C films showed a strong pseudocationic doping behaviour, characterised by predominant sodium ion exchange during redox processes. In contrast, films synthesised at 40 °C exhibited mixed ion participation (both sodium and perchlorate), which could negatively impact the performance of electrode material in battery applications. This study demonstrates the potential of PEDOT:PSS as a versatile material for sodium ion cathodes, with properties that can be finely tuned through the synthesis temperature, yielding more compact ion-storage films at lower temperatures.

1. Introduction

Due to their high energy and power density, lithium-ion batteries (LIBs) are the most widely used energy storage systems [1]. However, the high demand for lithium, combined with the fact that many of the existing lithium mines are difficult to exploit, results in high extraction costs [2]. To address this limitation, sodium-ion batteries (SIBs) are emerging as a promising alternative, given that sodium is one of the most abundant elements in the Earth's crust [3]. Despite this advantage, one of the main challenges in the commercialisation of SIBs lies in developing electrode materials that can accommodate the larger size of sodium cations during redox conversion [4].

The difficulty with sodium-ion battery electrodes is designing materials with capacities and potentials similar to those used in lithium-ion battery cathodes. The larger ionic radius of sodium, compared to

lithium, makes it harder to incorporate sodium into the crystal structure of cathode materials designed for lithium-ion batteries [4,5]. Currently, research on cathode materials for sodium-ion batteries is focused on layered transition metal oxides [6,7], polyanion-type compounds [8,9], prussian blue analogues [10,11], and organic materials [12,13]. The combination of the physicochemical properties of organic polymers with the electrical conductivity typical of semiconductors has led to extensive studies of electronically conducting polymers (ECPs) [14,15]. These organic materials consist of alternating σ and π bonds between carbon atoms, where the σ bonds provide structural stability and the π bonds facilitate electron delocalisation, allowing for electronic conductivity [16].

These characteristics of electronically conducting polymers (ECPs) drive their application in various technologies such as solar cells [17], electrochromic devices [18], sensors [19], and energy storage systems

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[20]. Among the various ECPs, Poly(3,4-ethylenedioxythiophene) (PEDOT), a derivative of polythiophene, has garnered significant attention due to its regular molecular structure [21], stability [22], crystallinity [23], and high electrical conductivity [24], making it an excellent candidate for electrochemical applications. Due to the low solubility of 3,4-ethylenedioxythiophene (EDOT) in aqueous solutions, it is necessary to incorporate a polyanion with a long carbon chain to form a stable dispersion of the monomer prior to polymerisation [25]. Most frequently, aqueous dispersions of EDOT are prepared with poly(sodium 4-styrenesulfonate) (PSS) [26]. Notably, this polyanion does not directly contribute to electronic conductivity because the anionic charges remain immobilised in the polymer matrix and should be counterbalanced by electrolyte cations. The sulfonate groups on the molecular structure allow for charge compensation of the oxidised form of the polymer, balancing the positive charges of the thiophene rings [27]. During the oxidation process, cations are expelled from the polymeric matrix, while during reduction, cations are incorporated, in a charge transfer mechanism known as pseudocationic doping. This process, where cations move in and out of the polymer matrix to maintain charge neutrality during redox reactions, is vital for the application of PEDOT:PSS as a cathode material in sodium-ion batteries.

When PEDOT is synthesised electrochemically, either doped or not with a polyanion, the electropolymerisation conditions - such as polymerisation mode and electrochemical settings - significantly affect the properties of the resulting polymeric film [28,29]. Additionally, external factors, such as temperature, influence the polymerisation kinetics as well as the mechanical, morphological, and particularly the conductivity properties of the polymeric film [30,31]. Plesu *et al.* [32] showed that temperature affects the film thickening, electroactivity and electrical properties when polyaniline films are electrochemically synthesised at different temperatures. As a result, temperature can have a crucial effect on the ionic exchanges during the film's redox conversion, as these processes are strongly dependent on the structure of the polymeric matrix.

One commonly used technique to study ion fluxes during film oxidation and reduction is the electrochemical quartz crystal microbalance (EQCM) [33]. However, EQCM measures total mass flow (ions + solvent) but cannot distinguish the nature of the different flows. To solve this issue, a complementary technique is required. Probe beam deflection (PBD) [34], in combination with EQCM, allows for the discrimination of each ionic flux. PBD works by measuring the deviation of a collimated light beam aligned close and parallel to the electrode surface. The beam is refracted according to concentration gradients and corresponding refractive index changes in the solution adjacent to the electrode [35]. When coupled with an electrochemical technique like cyclic voltammetry, PBD can dynamically provide discrete information about ionic exchanges occurring at the electrode/electrolyte interface [36].

In this work, we present a detailed investigation of the temperature effect on the electropolymerisation of PEDOT:PSS films grown by different electrochemical modes. The optical properties and morphology after synthesis were analysed through *ex-situ* ellipsometry and atomic force microscopy (AFM). Additionally, PBD was employed to evaluate the extent of pseudocationic doping, complementing the data gathered by EQCM. *Ex-situ* AFM was also conducted to gain insights into morphological changes during the redox process. The findings from this study demonstrate the significant role that electrosynthesis temperature plays in regulating the physical and electrochemical characteristics of PEDOT:PSS films such as compactness, reversibility, electroactivity and pseudocationic character, which are essential for application as sodium-ion battery cathodes.

2. Methods and materials

2.1. Chemicals

3,4-ethylenedioxythiophene (EDOT, ACROS Organics, 99%), poly

(sodium 4-styrenesulfonate) (PSS, Aldrich, MW ~70,000, p.a), sodium perchlorate (NaClO₄, Acros Organics, p.a) and acetonitrile extra dry (CH₃CN, Acros Organics, 99.9%) were used without further purification. Ultrapure water (18 MΩ·cm at 25 °C) from a MILLI-Q A10 Gradient purification system was used for preparing the monomer solution and for cleaning steps.

2.2. Electrodes

Two types of platinum electrodes were used in this study. For electrochemical measurements, ellipsometry, AFM and PBD, "specpure" platinum disks electrodes with active areas of 0.16 cm² and 0.20 cm² were utilised. Prior to each experiment, these electrodes were polished to a mirror finish using alumina suspensions (Al₂O₃, Buehler) with particle sizes of 5.0 μm, 1.0 μm, and 0.3 μm, and subsequently washed thoroughly with deionised water. For EQCM assays, the working electrode consisted of an 8 MHz AT-cut quartz crystal coated with a 100 nm platinum layer and an active area of 0.29 cm². A saturated calomel electrode (SCE) was used as the reference electrode, and a platinum foil was used as the counter electrode for all *in-situ* experiments. The platinum foil counter electrode was exposed to a butane gas flame before use to remove any organic residues.

2.3. Electropolymerisation of PEDOT

Platinum electrodes were modified with poly(3,4-ethylenedioxythiophene) doped with 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, both for 60 s at different temperatures (0 °C, 25 °C, and 40 °C), using 10 mM EDOT and 0.1 M PSS in aqueous solution, deaerated with N₂ bubbling for 15 min. The monomer-containing solution was stirred for 7 h to obtain a homogeneous dispersion. Electropolymerisation was carried out in a temperature-controlled, jacketed electrochemical cell, using a thermostatic heater/cooler bath (Thermomix BU/Frigomix S, B.Braun). All experiments were performed inside a Faraday cage using a VoltaLab PGZ100 potentiostat/galvanostat (Radiometer Analytical).

For the EQCM experiments, the same conditions were used, but the contacts on the EQCM electrodes were protected with varnish to allow full submersion of the quartz crystal in the temperature-controlled polymerisation solution. The EQCM setup was later used to track mass changes during the redox conversion processes, as discussed in the following sections.

2.4. Film characterisation

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 [37]. After the modification of the platinum electrodes with polymeric films, the refractive index, extinction coefficient, and polymer thickness (*L*) were calculated using a multi-angle approach based on a three-phase isotropic model (air-film-substrate) [37]. The values of *n*, *k*, and *L* for each polymeric film were inferred by minimising the error between the experimental and modelled data.

AFM measurements were performed *ex-situ* under ambient conditions (21 ± 2 °C) using a Multimode 8 HR microscope (Digital Instruments, Bruker) coupled to a Nanoscope V controller. The images were acquired in Peak Force Tapping mode using ScanAsyst (frequency of 2 kHz) with silicon nitride tips (ScanAsyst-Air probes, spring constant ~0.40 N·m⁻¹) at a scan rate of 1 Hz. Morphological data were processed with NanoScope Analysis 1.8 software.

The polymeric films were characterised electrochemically in organic

medium by cyclic voltammetry at room temperature. The potential window was set between -0.90 V and 0.80 V vs. SCE, with a scan rate of $50 \text{ mV}\cdot\text{s}^{-1}$ for 20 cycles in deaerated acetonitrile solution containing 0.1 M NaClO_4 . Prior to voltammetric assays, the films were fully reduced for 120 s at -0.90 V to guarantee a complete discharged polymer film. Additionally, EQCM experiments were conducted inside a Faraday cage using a CHI420 Electrochemical Analyzer, utilising a one-compartment Teflon cell.

The PBD source used was an Oriel Model 79,2002 mW He-Ne laser, with a $1/e^2$ beam diameter of 0.63 mm . The laser beam was focused by a lens with a 60 mm focal length to the centre of the cell (quartz cuvette). A position detector system, consisting of a double photodiode (spot-2DMI Optilas) with a $10 \text{ }\mu\text{m}$ gap between the two photodiodes, was employed to measure the laser beam deflection. A home-built differential amplifier connected to the photodiodes ensured beam deviation sensitivity of $97 \text{ }\mu\text{rad}\cdot\text{V}^{-1}$. The working electrode was mounted on a translation base, which was connected to a motorised Oriel microcontroller device, allowing vertical and tilt movements. A positive sign of deflection occurs when the laser beam deflects away from the working electrode surface, while a negative sign occurs when the beam deflects towards the electrode. During cyclic voltammetry, the laser beam was aligned parallel to and at a fixed distance of $143 \text{ }\mu\text{m}$ from the electrode surface. A detailed description of the PBD setup and experimental conditions is provided elsewhere [38,39]. The working and reference electrodes were the same as those used in the other assays, while a platinum mesh counter electrode was placed far enough from the working electrode to avoid interference with the concentration gradients created at the modified electrode surface.

3. Results and discussion

3.1. Electropolymerisation

Like most conducting polymers, EDOT can be polymerised through different electrochemical modes [40,41]. In this work, the electrochemical synthesis of PEDOT films doped with PSS was conducted under both potentiostatic and galvanostatic control. The corresponding chronoamperograms and chronopotentiograms are presented in Fig. 1a and 1b, respectively. The polymeric films were synthesised at various temperatures (0°C , 25°C , and 40°C) for 60 s to evaluate the growth conditions influence on the characteristics of PEDOT:PSS. The synthesis at 25°C was used as a reference for comparison with the lower and higher

temperature assays.

For the synthesis under potentiostatic mode, a potential of 0.90 V was chosen based on the cyclic voltammogram recorded over a wide potential range (Fig. S1, Supplementary Material). This potential, slightly above the onset potential of monomer oxidation [42], was expected to allow for the formation of a uniform polymeric film on platinum with reproducible characteristics. The registered chronoamperograms (Fig. 1a) show a current minimum at $\text{ca.} 9 \text{ s}$ for films synthesised at 0°C and at 3 s for those synthesised at 40°C , corresponding to the precipitation of the first polymer segments on the working electrode surface [43]. These oligomers precipitate once they reach a critical size, becoming insoluble and depositing on the electrode, leading to the formation of the initial polymeric nuclei. After the current minimum, nuclei begin to coalesce, and the polymer matrix grows until the process is interrupted. This nucleation process was previously observed by Hillman and Mallen during the potentiostatic synthesis of polythiophenes [44]. At 40°C , the synthesis current continues to rise, indicating continuous agglomeration of polymeric segments, resulting in an increased electroactive area deposited on the electrode surface. As is evidenced in the next section, the formation of a porous material at this temperature is contrasted by the compactness of films generated at lower temperatures, where a reverse tendency of the potential transient is observed. As can be observed from the inset shown in Fig. 1a, the rate of polymer formation is strongly influenced by the synthesis temperature, with the kinetics registered at 0°C three times slower than that recorded at 40°C .

For the galvanostatic synthesis, a current density of $0.75 \text{ mA}\cdot\text{cm}^{-2}$ was selected based on the current values obtained during potentiostatic growth. The objective was to synthesise films that are comparable by having the same growth charge, allowing us to evaluate the differences caused by the varying the deposition temperature (Fig. 1b). The recorded chronopotentiograms show a potential increase at the beginning of the synthesis, which corresponds to the accumulation of charge in the double layer, resulting in an instantaneous rise in overpotential [45]. During this phase, the charge accumulation is associated with the oxidation of monomers adjacent to the working electrode, leading to the formation of radical cations [46] that react with each other. As expected, the film synthesised at 0°C requires more energy (a higher potential) to form the radical cations compared to the film synthesised at 40°C . Indeed, a higher potential is required to counterbalance the temperature decrease, which raises the energy barrier for monomer oxidation [47, 48]. Consequently, a potential peak is recorded, occurring after 4 s for

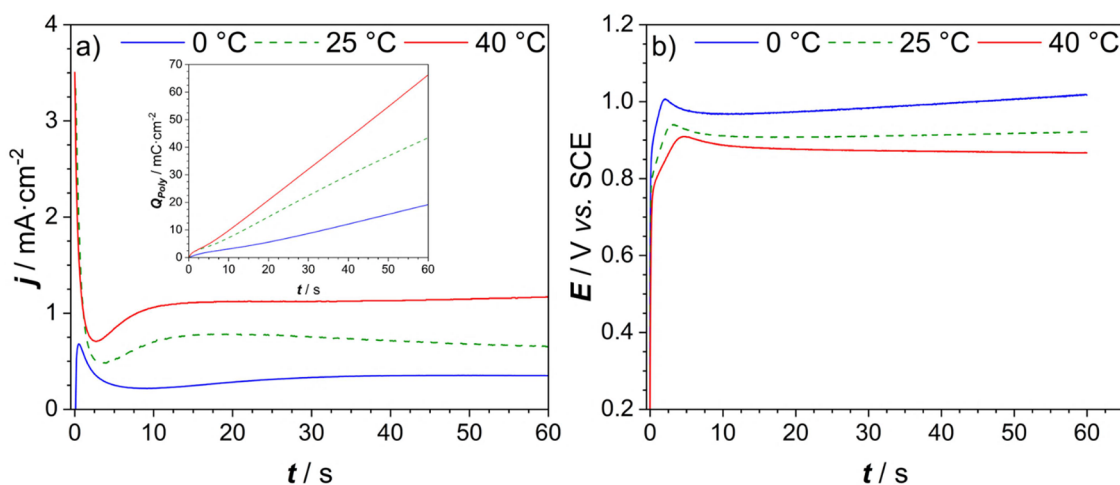


Fig. 1. Current and potential transient registered during electrosynthesis of PEDOT:PSS in a deaerated aqueous solution containing 10 mM EDOT monomer and 0.1 M PSS. (a) Potentiostatic mode growth at a potential of 0.90 V for 60 s at 0°C , 25°C , and 40°C . (b) Galvanostatic mode growth at an anodic current density of $0.75 \text{ mA}\cdot\text{cm}^{-2}$ for 60 s at 0°C , 25°C , and 40°C . Charge transient registered during electrosynthesis of potentiostatically grown films at different temperatures – inset in (a).

the film synthesised at 40 °C, while it occurs after 2 s for the film prepared at 0 °C. After charging the double layer, it begins the formation of solid and discrete polymer nuclei (nucleation step) [49]. They will coalesce until a polymer phase is formed at the electrode surface, corresponding to the potential peak. From there on, we assist to the 3D growth of the polymer matrix [44].

Notably, the nucleation time for the synthesis at 0 °C is half of that of the synthesis at 40 °C. This is likely due to a higher deposition rate (polymer formation), despite the oxidation rate (monomer oxidation, oligomer/polymer formation) being the same, resulting in faster substrate coverage by the polymeric film. This may be attributed to the slower diffusion of soluble oligomers away from the interface at low temperatures, whereas at higher temperatures, more significant mass transfer away from the interface takes place, leading to a lower surface concentration of the polymer constituents. A lower solubility of the oligomers at lower temperatures is also likely, promoting a sooner deposition of the new polymeric phase. Additionally, during the synthesis at 40 °C, the potential stabilizes at approximately 0.87 V, while for the synthesis at 0 °C, the potential continues to rise throughout the experiment, reaching approximately 1.02 V by the end.

3.2. Film characterisation

The films synthesised on the platinum substrate were characterised using multiple surface techniques to study their physicochemical properties. *Ex-situ* ellipsometry was employed to estimate the optical properties (refractive index and extinction coefficient) and the thickness of the polymer matrices under dry conditions [50,51]. Prior to film synthesis, the optical properties of the platinum substrate were measured at two incidence angles ($\varphi = 60^\circ$ and $\varphi = 70^\circ$), providing the necessary substrate parameters for computing the optical properties and thickness of the films after their synthesis (Table S1, Supplementary Material).

After electropolymerisation, the experimental values ($\Psi / ^\circ$ and $\Delta / ^\circ$) were obtained from the modified electrode in triplicate assays (Table S1, Supplementary Material). Table 1 presents the refractive index, extinction coefficient, and film thickness, calculated using an isotropic and homogeneous three-phase model (air/film/platinum) for the two incidence angles aforementioned. The standard deviation for each optical property and thickness is also reported.

From Table 1, it is evident that the estimated extinction coefficient values for each film reveal an absorbing character, $k > 0.2$, slightly higher than those reported elsewhere [52]. The film with the lowest thickness (synthesised at 0 °C for 60 s in potentiostatic mode) exhibits the lowest extinction coefficient ($k = 0.249$). The refractive index values show that films synthesised at 0 °C for 60 s, whether in potentiostatic or galvanostatic mode, are denser (with refractive indices of 1.46 and 1.49, respectively) and consequently more compact compared to the other films. When contrasting films synthesised for the same duration but under different growth modes and temperatures, films deposited at lower temperatures consistently display higher refractive index values than those deposited at higher temperatures. This indicates that films prepared at lower temperature are more compact and more absorbing compared to those synthesised at 40 °C. This distinction is especially

clear in the galvanostatically prepared films with the same growth charge. In what concern the thickness, film synthesised at 0 °C under galvanostatic control for 60 s is thinner (175 nm) than those synthesised with the same growth charge at higher temperatures (184 nm and 201 nm). It should be noted that the same observations can be made for potentiostatically grown films with approximately the same thickness. Indeed, films electrosynthesised under the same charge conditions, ca. $19 \text{ mC}\cdot\text{cm}^{-2}$, exhibit higher compactness and lower absorbance when prepared at lower temperatures ($E_g = 0.90 \text{ V}$; 0 °C; 60 s) compared with the values computed for the modified electrodes formed at higher temperatures ($E_g = 0.90 \text{ V}$; 40 °C; 20 s), as revealed by their refractive indices and extinction coefficients. This supports the idea that lower temperatures lead to the formation of more compact films, while higher temperatures result in more porous matrices, likely due to increased branching. This difference in polymer structure has a significant impact on mass transfer during redox conversion, as discussed in the following sections.

Based on the refractive index values obtained for each film, it is expected that the polymer films exhibit morphological differences dependent on the growth mode and temperature during synthesis. Fig. 2a-d presents the AFM images of the films immediately after polymer synthesis.

As shown in Fig. 2, AFM characterisation reveals that PEDOT:PSS films grown at 0 °C (Fig. 2a and 2c), regardless the polymerisation mode, display a granular morphology with the presence of donut-like polymeric rings. These rings are likely due to the partial freezing of water molecules retained on the polymer surface during deposition [31]. When the modified electrode is returned to room temperature, the water molecules melt, creating the ring-shaped holes visible in the AFM images. On the other hand, films synthesised at 40 °C (Fig. 2b and 2d) present a cauliflower-like granular topography, which is the typical morphology for PEDOT [53]. Furthermore, films grown at 0 °C exhibit a smaller grain size than the films synthesised at 40 °C and a more compact morphology, especially those grown using the galvanostatic mode.

After synthesis, the polymeric films were voltammetrically stabilised in an organic medium using a deaerated solution of 0.1 M NaClO₄ in acetonitrile, at a scan rate of $50 \text{ mV}\cdot\text{s}^{-1}$ for 20 cycles at room temperature within a potential window of $[-0.90, +0.80] \text{ V}$ (Fig. S2, Supplementary Material). Before performing the cyclic voltammetry, the PEDOT:PSS films were fully reduced for 120 s by applying a potential of -0.90 V to ensure the films were fully discharged. Stabilisation in the organic medium is crucial, as the polymeric films must expel all water present in their matrix to incorporate the supporting electrolyte and organic solvent.

During the first 20 cycles, the polymer undergoes structural rearrangements, stabilising around the thirteenth cycle. After this point, the voltammetric response becomes completely stable in the organic environment and exhibits reproducible redox conversions.

Fig. 3a, b shows the 21st cycle of redox conversion after the polymer stabilisation in a fresh organic electrolyte solution.

All registered voltammograms show a reversible behaviour during the redox conversion of the PEDOT:PSS polymer films, regardless the electropolymerisation mode or the temperature at which they were synthesised. During the oxidation of the films, three anodic bands are observed in all cases. The first band results from localised counterbalancing at the onset of polymer oxidation [54]. These oxidation peaks are primarily due to electronic interactions during the polymer's redox conversion from its neutral state to polaronic and then to bipolaronic states [55]. However, the origin of the current peaks is more complex, as they are also influenced by polymeric local packing [54], such as expansion and contraction of the organic matrices during redox conversion [56], deposition of polymer segments with varying sizes during electropolymerisation [57], and their orientation on the electrode surface [58]. In fact, the occurrence of different intercalation processes of the counterions into the polymer films is likely due to the coexistence of

Table 1

Refractive index (n), extinction coefficient (k), and thickness (L) of polymer films on modified platinum electrodes under the electrosynthesis conditions shown in Fig. 1. Presented as mean values $\pm$ standard deviation.

Growth conditions	n_{film}	k_{film}	$L_{\text{film}} / \text{nm}$
$I_g = 0.75 \text{ mA}\cdot\text{cm}^{-2}$; 0 °C; 60 s	1.489 ± 0.003	0.354 ± 0.001	174.7 ± 0.1
$I_g = 0.75 \text{ mA}\cdot\text{cm}^{-2}$; 25 °C; 60 s	1.384 ± 0.003	0.343 ± 0.003	183.5 ± 0.8
$I_g = 0.75 \text{ mA}\cdot\text{cm}^{-2}$; 40 °C; 60 s	1.232 ± 0.002	0.292 ± 0.002	201.4 ± 0.4
$E_g = 0.90 \text{ V}$; 0 °C; 60 s	1.462 ± 0.001	0.249 ± 0.002	68.1 ± 0.4
$E_g = 0.90 \text{ V}$; 25 °C; 60 s	1.458 ± 0.001	0.348 ± 0.003	209.4 ± 0.4
$E_g = 0.90 \text{ V}$; 40 °C; 60 s	1.417 ± 0.002	0.316 ± 0.001	274.8 ± 0.3
$E_g = 0.90 \text{ V}$; 40 °C; 20 s	1.402 ± 0.001	0.264 ± 0.002	70.1 ± 0.1

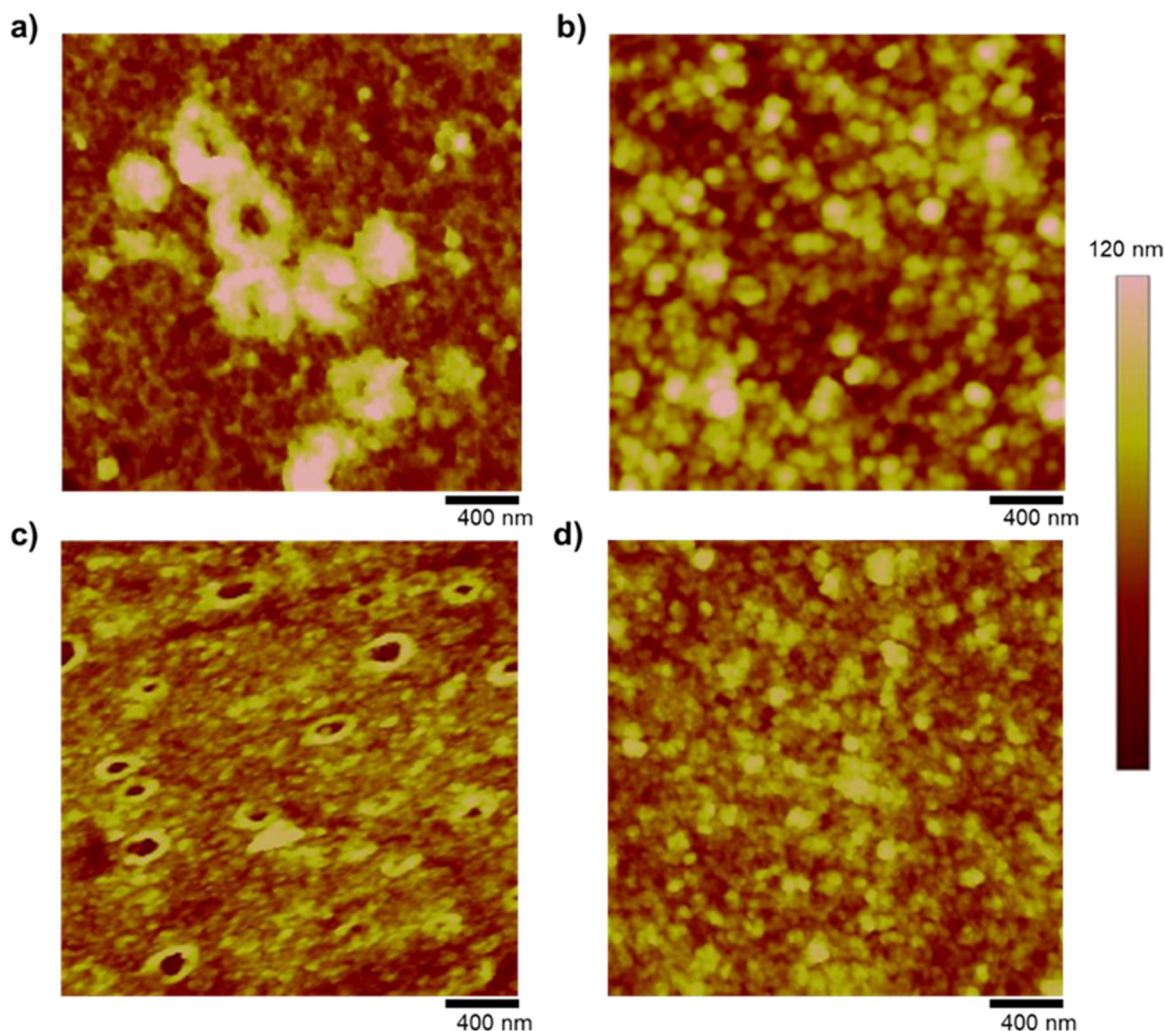


Fig. 2. AFM morphology of platinum electrodes modified with electropolymerised PEDOT:PSS. (a) potentiostatic growth at 0.90 V for 60 s at 0 °C, (b) potentiostatic growth at 0.90 V for 60 s at 40 °C, (c) galvanostatic growth at 0.75 mA·cm⁻² for 60 s at 0 °C, (d) galvanostatic growth at 0.75 mA·cm⁻² for 60 s at 40 °C.

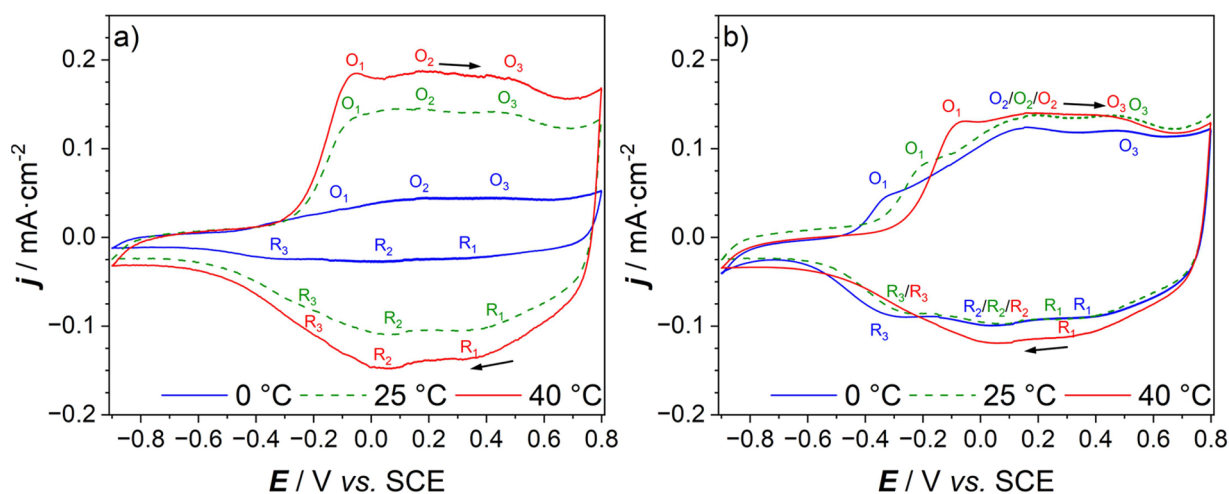


Fig. 3. Cyclic voltammograms recorded at room temperature with a scan rate of 50 mV·s⁻¹ for platinum electrodes modified with electropolymerised PEDOT. (a) by potentiostatic growth and (b) galvanostatic growth at 0 °C, 25 °C, and 40 °C in deaerated acetonitrile containing 0.1 M NaClO₄.

morphological domains with different packing densities of the chains. Skompska *et al.* monitored the swelling of P(3-hexylthiophene) films during charging and observed a two-step process, attributed to a

compact structure and spatial constraints [59]. Furthermore, Abrantes *et al.* demonstrated through *in-situ* ellipsometry that the first reduction peak corresponds to an incomplete discharge of the film, as it becomes

more compact as the potential decreases [60]. The remaining reduction bands are associated with further discharge processes, also influenced by polymeric conformations. When comparing the polymer films synthesised under the same mode, it is evident that the most electroactive films are those deposited at higher temperatures, which tend to be thicker. In order to a better appraisal of the potentiostatically prepared films with different growth charge, the recorded voltammograms (Fig. 3a) were normalised dividing the current density by the deposition charge (Fig. S3, Supplementary Material), displaying the same generic features as those registered galvanostatically grown ones. The characteristics of the redox conversion are summarised in Table 2. It is worth noting that the results presented in Table 2 are based on several replicates, which confirmed the accuracy of the values shown.

The Q_O/Q_R indicates that the films synthesised potentiostatically at 0 °C exhibit poorer reversibility compared to those synthesised at 40 °C. This is due to the fact that the charge produced during the film's oxidation is not fully utilised for the reduction of the polymeric matrix within the experimental timeframe. It is important to note that the redox electric charges for the polymers synthesised under galvanostatic control are relatively similar, despite the films having different thicknesses. This suggests that approximately the same amount of electroactive material was created, but it is confined to films of varying thickness, resulting in different charge and mass transport properties. In the case of the galvanostatically synthesised films at 0 °C and 40 °C with the same charge, they exhibit nearly ideal reversibility, which is a positive indicator for their potential application as battery cathodes when synthesised under these conditions. The value of Q_O/Q_R ratio obtained for the film synthesised galvanostatically at room temperature, despite being abnormal compared with the other temperatures probed in this work, was repeatedly obtained.

As shown in Fig. 2, the electrosynthesis growth modes used to modify the platinum substrates affect the PEDOT:PSS films morphology. However, the most noticeable impact on the polymer morphology comes from the temperature of the monomer containing solution used during the deposition process. After the redox conversion of the films in the organic medium, the morphology of the polymer films synthesised via galvanostatic mode was characterised after being submitted for 120 s to potentials of −0.9 V or 0.8 V in deaerated acetonitrile containing 0.1 M NaClO₄, to reach their reduced or oxidised conditions, respectively (Fig. 4a–d).

The AFM images show that morphological rearrangements occur in films upon potential cycling in the organic medium. These topographic changes are more pronounced for the polymers grown at higher temperatures. For the film synthesised at 0 °C (Fig. 4a, b), an overall smooth and compact morphology is observed, with granular features of varying sizes. The presence of polymeric rings is also noted, but in smaller amounts compared to the film that was not stabilised in the organic solution (Fig. 2), with polymer granules located in the centre of the rings. When this film is oxidised, the polymeric rings disappear, but the underlying morphology remains practically unchanged at this scale. In contrast, the film synthesised at 40 °C (Fig. 4c, d) shows more significant morphological rearrangements, including increased porosity, after cycling in the organic medium, in comparison to the more compact film synthesised at 0 °C. After reduction in the organic medium, the modified electrode exhibits a fibrillar-like structure across its entire surface. This

fibrillar morphology has previously been reported in films synthesised potentiostatically in organic solution using TBAClO₄ as supporting electrolyte [53]. Upon oxidation, the fibrils aggregate, forming a more heterogeneous surface. These morphological differences between the two films are linked to the expansion and contraction that occurs during redox conversion, as further discussed through the analysis of EQCM and PBD experimental data.

The electrochemical characterisation of PEDOT:PSS films synthesised at different temperatures and using different growth modes in an organic medium was monitored by EQCM to track the total mass flow (including cations, anions, and solvent) during the redox conversion process. Fig. 5a and 5b display the mass variations of the modified electrode after film stabilisation in the organic medium (after 20 potential cycles). The Sauerbrey equation [61] was applied to the frequency data to calculate the mass variation, assuming that the polymer films behave as rigid structures [62].

Regardless of the growth mode and the temperature at which the films were synthesised, both films show an increase in mass during oxidation, likely due to the influx of ions and solvent into the polymer matrix. Conversely, a decrease in mass is observed during reduction, possibly as a result of the expulsion of ions and solvent in this potential range. In Fig. 5a, it can be seen that the film synthesised potentiostatically at 40 °C exhibits a greater amplitude of mass transfer during redox conversion compared to the film synthesised at 0 °C. This larger mass transfer is associated with a greater influx and outflow of solvent and ions, which is consistent with the thicknesses obtained by *ex-situ* ellipsometry, approximately 275 nm and 68 nm, respectively, as well as on the porosity. For the films synthesised under current control at different temperatures (Fig. 5b), the mass changes during oxidation and reduction of both films are quite similar, reflecting the comparable thicknesses of the polymers obtained at 0 °C and 40 °C, approximately 174 nm and 201 nm, respectively. The results obtained by EQCM generally confirm that there is an increase in mass during the anodic potential scan, followed by a decrease in mass during the cathodic sweep. Previous studies have reported significant solvent flow during the redox conversion of PEDOT films doped with other counterions, where solvent is incorporated during oxidation and expelled during reduction [60]. This solvent flow may contribute to additional mass variations during the redox process, potentially masking the movement of counter ions.

Since the data collected by EQCM can be influenced by the incorporation or expulsion of solvent, which may mask the mass transfer of ions during charge counterbalance, the mirage effect technique was employed to verify the nature of the mass flows observed through electromicrogravimetry (which considers the contributions of cations, anions, and solvent). The mirage effect technique has the advantage of being insensitive to solvent flow [35]. Fig. 6a–d shows the deflectograms recorded during the redox conversion of PEDOT:PSS films synthesised potentiostatically and galvanostatically at different temperatures.

For the analysis of the deflectograms recorded during the polymer's redox process, it is essential to understand that oxidation of the polymer matrix involves either the incorporation of anions (resulting in positive deflection) or the expulsion of cations (negative deflection) to maintain the polymer's electroneutrality. Conversely, during reduction, there will be either an outflow of anions (negative deflection) or an inflow of

Table 2

Summary of oxidation and reduction peak potentials, oxidation and reduction charges, and the reversibility parameter during the redox process.

Growth conditions	E_p^{O1} /V vs. SCE	E_p^{O2} /V vs. SCE	E_p^{O3} /V vs. SCE	E_p^{R1} /V vs. SCE	E_p^{R2} /V vs. SCE	E_p^{R3} /V vs. SCE	Q_O /mC·cm ^{−2}	Q_R /mC·cm ^{−2}	Q_O/Q_R
$E_g=0.90$ V; 0 °C 60 s	−0.11	0.17	0.45	0.31	0.02	−0.36	0.96	0.65	1.48
$E_g=0.90$ V; 25 °C 60 s	−0.08	0.08	0.45	0.34	0.08	−0.28	2.82	2.34	1.21
$E_g=0.90$ V; 40 °C 60 s	−0.06	0.17	0.47	0.36	0.03	−0.19	3.61	3.11	1.16
$I_g=0.75$ mA cm ^{−2} 0 °C; 60 s	−0.33	0.16	0.48	0.38	0.04	−0.31	2.45	2.42	1.01
$I_g=0.75$ mA cm ^{−2} 25 °C; 60 s	−0.20	0.16	0.47	0.32	0.06	−0.28	2.76	2.19	1.26
$I_g=0.75$ mA cm ^{−2} 40 °C; 60 s	−0.08	0.16	0.43	0.35	0.06	−0.24	2.66	2.63	1.01

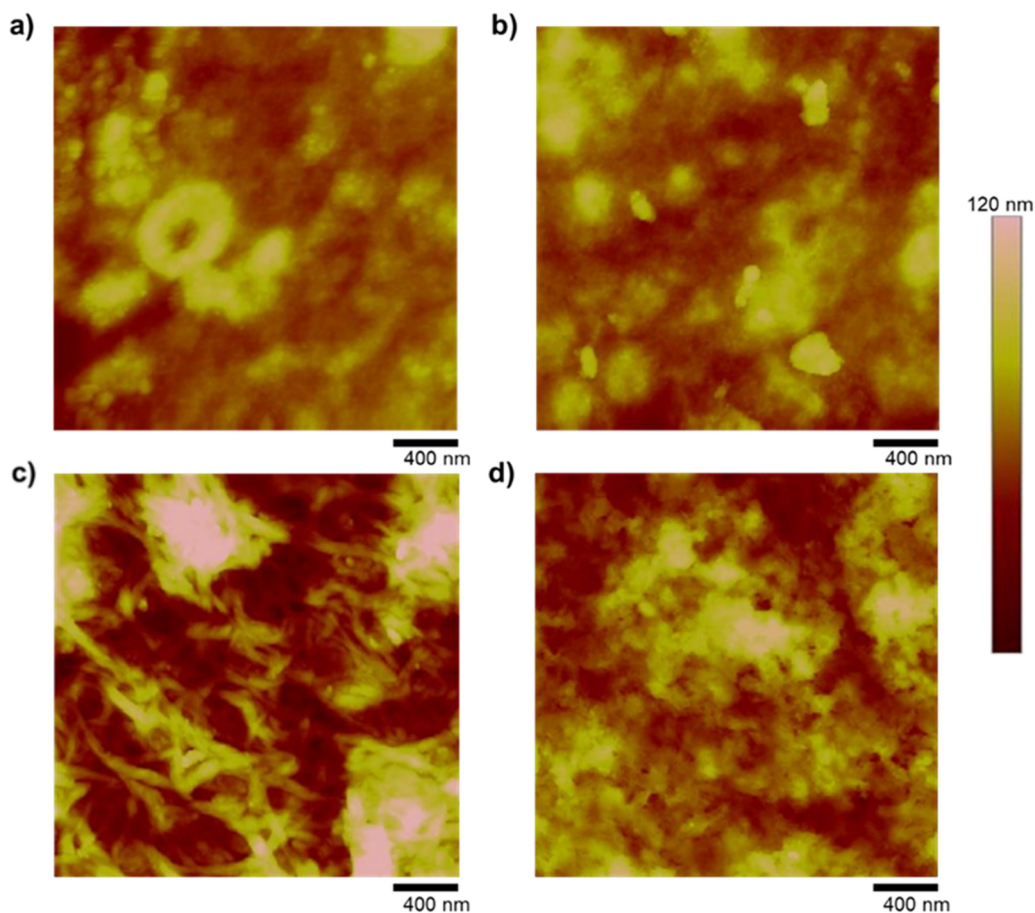


Fig. 4. *Ex-situ* AFM topographic images of platinum electrodes modified with electropolymerised PEDOT:PSS grown galvanostatically at $0.75 \text{ mA}\cdot\text{cm}^{-2}$ for 60 s (a) and (b) at 0°C and (c) and (d) at 40°C , of stabilised films over 20 potential cycles, $[-0.90, +0.80] \text{ V}$, in deaerated acetonitrile containing 0.1 M NaClO_4 at room temperature: (a) and (c) after 120 s at -0.9 V , (b) and (d) after 120 s at 0.8 V .

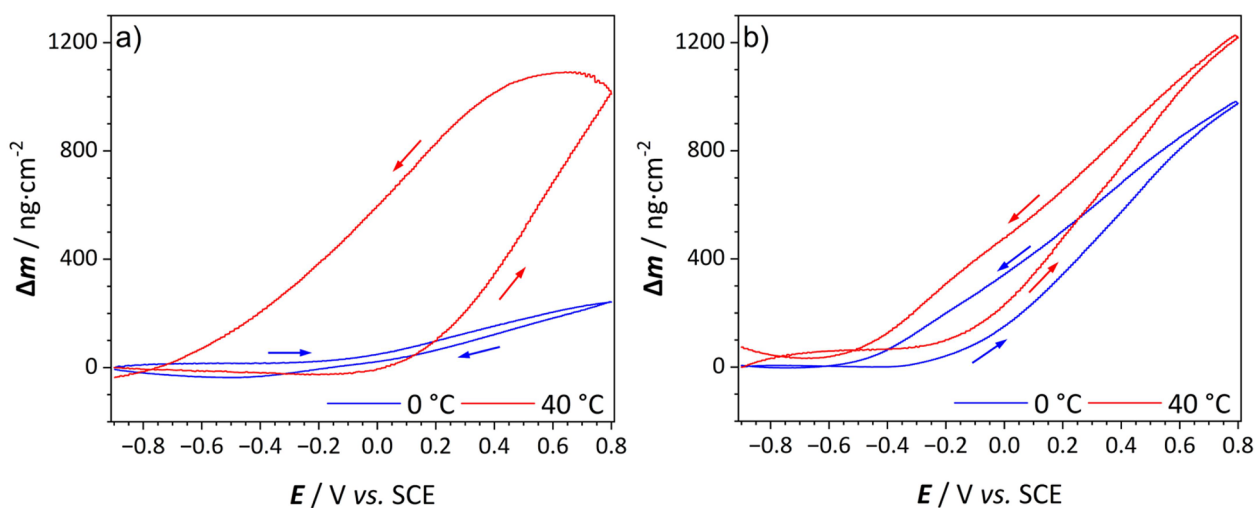


Fig. 5. Mass variation during cyclic voltammetry recorded at room temperature with a scan rate of $50 \text{ mV}\cdot\text{s}^{-1}$ for platinum electrodes modified with electro-synthesised PEDOT:PSS. (a) potentiostatically growth and (b) galvanostatically growth at 0°C and 40°C in deaerated acetonitrile containing 0.1 M NaClO_4 .

cations (positive deflection).

The film synthesised potentiostatically at 0°C (Fig. 6a) exhibits a negative deflection, indicating an expulsion of cations, followed by a positive deflection during oxidation indicating an incorporation of perchlorate ions. After this first oxidation phase, the deflection becomes negative again, corresponding to the continued expulsion of sodium ions

until the potential of 0.60 V in the cathodic scan. During the reduction phase, the deflection remains constant until 0.10 V , with only a positive deflection observed, indicating a dominance of cationic flow. This suggests that the film synthesised at 0°C exhibits pseudocationic doping, a crucial feature for conductive polymers used as cathode materials in Na-ion batteries. This behaviour, where both cations and anions participate

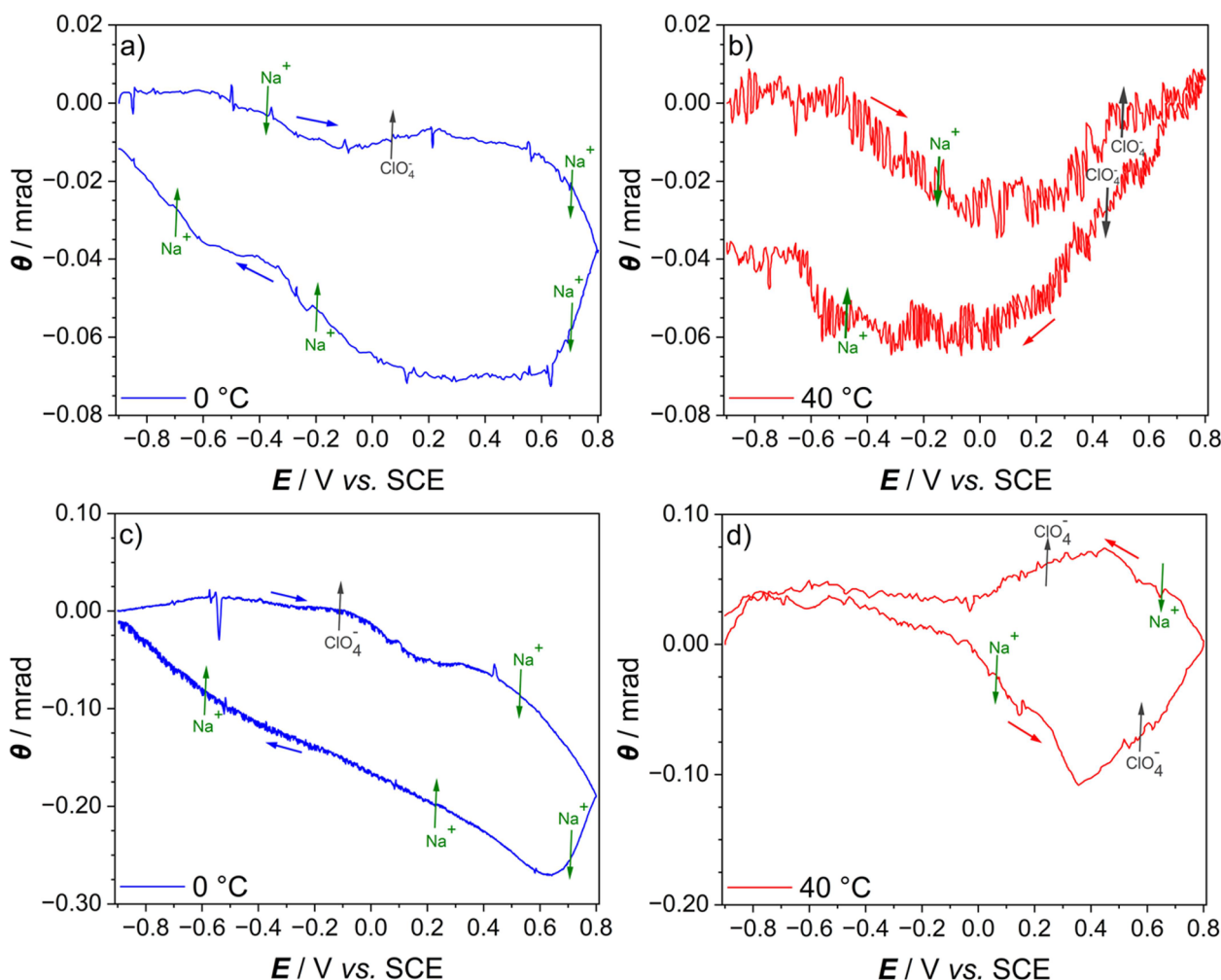


Fig. 6. Laser deflection recorded during cyclic voltammetry, at room temperature with $\nu = 50 \text{ mV} \cdot \text{s}^{-1}$, of platinum electrodes modified with electropolymerised PEDOT:PSS, a) and b) via potentiostatic growth and (c) and (d) via galvanostatic growth at (a) and (c) 0°C and (b) and (d) 40°C , in deaerated acetonitrile containing 0.1 M NaClO_4 . The arrows indicate the predominant ion flow; upwards: ion inlet; downwards: ion outlet.

in the doping/undoping process, has been observed in other conducting polymers using this technique [37]. For the film synthesised potentiostatically at 40°C (Fig. 6b), an initial negative deflection is observed during the anodic scan, indicating the expulsion of sodium ions. This is followed by a positive deflection, corresponding to the incorporation of perchlorate anions into the polymer matrix during oxidation. During the reduction phase, a negative (larger) deflection is observed again, signalling the expulsion of anions from the polymer. This is followed by a positive deflection as cations re-enter the polymer from the solution.

The film synthesised galvanostatically at 0°C (Fig. 6c) shows a continuous negative deflection during oxidation, which corresponds to a flow dominated by the expulsion of sodium ions from the polymer matrix. This cation outlet seems to continue even after the beginning of the cathodic scan. This lag between the electrochemical event and the ion flow detection is due to the diffusion of species in the Debye layer, where species generated (and electrochemically recorded) at a given time are detected later by the light probe (located at a 143 mm from the electrode surface), being the time lapse dependent on their diffusion coefficient. During the reduction, cationic flow from the electrolyte dominates as it compensates for the excess negative charge of the polyanion immobilised in the polymer matrix to maintain electroneutrality. Notably, the deflection magnitude is higher for the film synthesised galvanostatically at 0°C compared to the other films synthesised by either electrochemical method. In contrast, the film synthesised galvanostatically at 40°C (Fig. 6d), shows a negative deflection until approximately 0.4 V

during oxidation, followed by a positive deflection, indicating the incorporation of anions to maintain the polymer's electroneutrality. The positive deflection persists at the beginning of the cathodic scan but turns negative when the potential becomes more negative than approximately 0.5 V .

Based on the mirage effect results, the film synthesised under galvanostatic control at 0°C shows a dominant expulsion of sodium ions during oxidation, as these ions leave the polymer to maintain its electroneutrality. During reduction, the ionic flow reverses, with sodium cations being primarily incorporated into the polymer film to compensate for the excess negative charge of the immobilised counterions within the film. This electrochemical behaviour aligns with a pseudocationic doping process, where the true dopant ion is the immobilised PSS in the polymer matrix, and electroneutrality is maintained predominantly through cation exchange during redox transformations. However, while sodium cations dominate the ionic flow during the redox conversion of the PEDOT:PSS polymer film, the participation of perchlorate ions should not be overlooked. Their involvement could potentially hinder the performance of the material as a cathode in Na-ion batteries, which requires a dedicated separate study to quantify its impact.

4. Conclusions

This study investigated the temperature effect of the electrosynthesis

of PEDOT:PSS films under both potentiostatic and galvanostatic modes in aqueous solution, focusing on comparing their morphological, optical, and electrochemical properties. Films synthesised at lower temperatures were found to be more compact, as indicated by their higher refractive index compared to those synthesised at higher temperatures. Even though films grown at low temperature with the same charge (in galvanostatic mode) were thinner than those obtained at higher temperatures, their electroactivity was only slightly lower. This finding reinforces the notion that compact films produced at lower temperatures have distinct advantages in regulating mass transfer processes. High-resolution microscopy further revealed that these compact films exhibit less granular morphology and the presence of polymeric rings, in contrast to the films synthesised at higher temperatures.

By coupling cyclic voltammetry with gravimetric measurements, we were able to track the mass exchanges during the oxidation and reduction processes, capturing the participation of ions alongside solvent flow. As the polymer matrix undergoes redox conversion, it incorporates and expels supporting electrolytes and solvent, alongside individual ions to maintain electroneutrality. Across all experimental conditions and growth modes tested, an increase in mass was observed during oxidation, followed by a mass decrease during reduction. However, the mirage effect provided additional insights, showing that films synthesised at lower temperatures predominantly expel sodium cations during oxidation. During reduction, this behaviour reverses, with sodium ion incorporation driving the mass flow, thereby demonstrating the pseudocationic doping nature of this material. This behaviour is particularly relevant for the film grown galvanostatically at 0 °C, where large amounts of cations are exchanged, revealing its high potential towards the accumulation of sodium ions in energy storage devices.

CRediT authorship contribution statement

Daniel R. Santos: Writing – review & editing, Writing – original draft, Validation, Methodology, Investigation, Formal analysis, Conceptualization. **Jorge F. Zeferino:** Validation, Methodology, Investigation. **Ana S. Viana:** Writing – review & editing, Investigation, Formal analysis. **K.G.U. Wijayantha:** Writing – review & editing, Supervision, Formal analysis, Conceptualization. **Killian Lobato:** Writing – review & editing, Supervision, Formal analysis, Conceptualization. **Jorge P. Correia:** Writing – review & editing, Supervision, Resources, 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.2025.145760](https://doi.org/10.1016/j.electacta.2025.145760).

Data availability

Data will be made available on request.

References

- [1] M.J. Lain, J. Brandon, E. Kendrick, Design strategies for high power vs. High energy lithium ion cells, *Batteries* 5 (2019) 64, <https://doi.org/10.3390/batteries5040064>. -Basel.
- [2] C.Q. Hu, Y.F. He, D.F. Liu, S.Y. Sun, D.Q. Li, Q.S. Zhu, J.G. Yu, Advances in mineral processing technologies related to iron, magnesium, and lithium, *Rev. Chem. Eng.* 36 (2020) 107–146, <https://doi.org/10.1515/revce-2017-0053>.
- [3] A. El Kharbachi, O. Zavorotynska, M. Latroche, F. Cuevas, V. Yartys, M. Fichtner, Exploits, advances and challenges benefiting beyond Li-ion battery technologies, *J. Alloys Compd.* 817 (2020) 153261, <https://doi.org/10.1016/j.jallcom.2019.153261>.
- [4] Q. Zhao, Y. Lu, J. Chen, Advanced organic electrode materials for rechargeable sodium-ion batteries, *Adv. Energy Mater.* 7 (2017) 1601792, <https://doi.org/10.1002/aenm.201601792>.
- [5] K. Matsumoto, J. Hwang, S. Kaushik, C.Y. Chen, R. Hagiwara, Advances in sodium secondary batteries utilizing ionic liquid electrolytes, *Energy Environ. Sci.* 12 (2019) 3247–3287, <https://doi.org/10.1039/c9ee02041a>.
- [6] S.Y. Zhao, Q.-H. Shi, R.J. Qi, X.L. Zou, J. Wang, W.L. Feng, Y. Liu, X.G. Lu, J. Zhang, X.X. Yang, Y.F. Zhao, NaTi₂(PO₄)₃ modified O3-type NaNi_{1/3}Fe_{1/3}Mn_{1/3}O₂ as high rate and air stable cathode for sodium-ion batteries, *Electrochim. Acta* 441 (2023) 141859, <https://doi.org/10.1016/j.electacta.2023.141859>.
- [7] G.Q. Su, H.Q. Zheng, H. Chen, S. Bao, Ca/Mg dual-doping P2-type Na_{0.67}Ni_{0.17}Co_{0.17}Mn_{0.66}O₂ cathode material for sodium ion batteries, *Mater. Lett.* 331 (2023) 133425, <https://doi.org/10.1016/j.matlet.2022.133425>.
- [8] Y. Gao, H. Zhang, X.H. Liu, Z. Yang, X.X. He, Y. Qiao, S.L. Chou, Low-cost polyanion-type sulfate cathode for sodium-ion battery. 11 (2021) 2101751. [10.1002/aenm.202101751](https://doi.org/10.1002/aenm.202101751).
- [9] N. Zhao, T. Zhang, H.L. Zhao, Y.L. Hou, Polyanion-type electrode materials for advanced sodium-ion batteries, *Mater. Today Nano* 10 (2020) 100072, <https://doi.org/10.1016/j.mtnano.2020.100072>.
- [10] X.M. Yan, Y. Yang, E.S. Liu, L.Q. Sun, H. Wang, X.Z. Liao, Y.S. He, Z.F. Ma, Improved cycling performance of prussian blue cathode for sodium ion batteries by controlling operation voltage range, *Electrochim. Acta* 225 (2017) 235–242, <https://doi.org/10.1016/j.electacta.2016.12.121>.
- [11] C.X. Yan, A. Zhao, F.P. Zhong, X.M. Feng, W.H. Chen, J.F. Qian, X.P. Ai, H.X. Yang, Y.L. Cao, A low-defect and Na-enriched Prussian blue lattice with ultralong cycle life for sodium-ion battery cathode, *Electrochim. Acta* 332 (2020) 135533, <https://doi.org/10.1016/j.electacta.2019.135533>.
- [12] Y.J. Sun, J.F. Zheng, Y. Yang, J.H. Zhao, J.H. Rong, H.Y. Li, L. Niu, Design advanced porous polyaniline-PEDOT:PSS composite as high performance cathode for sodium ion batteries, *Compos. Commun.* 24 (2021) 100674, <https://doi.org/10.1016/j.coco.2021.100674>.
- [13] X.P. Yin, S. Sarkar, S.S. Shi, Q.A. Huang, H.B. Zhao, L.M. Yan, Y.F. Zhao, J. Zhang, Recent progress in advanced organic electrode materials for sodium-ion batteries: synthesis, mechanisms, challenges and perspectives, *Adv. Funct. Mater.* 30 (2020) 1908445, <https://doi.org/10.1002/adfm.201908445>.
- [14] K. Namsheer, C.S. Rout, Conducting polymers: a comprehensive review on recent advances in synthesis, properties and applications, *RSC Adv.* 11 (2021) 5659–5697, <https://doi.org/10.1039/d0ra07800j>.
- [15] G.C.M. Wessler, T.L. Wang, J.P. Sun, Y.H. Liao, M.C. Fischer, V. Blum, D.B. Mitzi, Structural, optical, and electronic properties of two quaternary chalcogenide semiconductors: Ag₂SrSiS₄ and Ag₂SrGeS₄, *Inorg. Chem.* 60 (2021) 12206–12217, <https://doi.org/10.1021/acs.inorgchem.1c01416>.
- [16] J.L. Bredas, G.B. Street, Polarons, bipolarons, and solitons in conducting polymers, *Acc. Chem. Res.* 18 (1985) 309–315, <https://doi.org/10.1021/ar00118a005>.
- [17] S.Y. Heo, J.K. Koh, J.K. Kim, C.S. Lee, J.H. Kim, Three-dimensional conducting polymer films for Pt-free counter electrodes in quasi-solid-state dye-sensitized solar cells, *Electrochim. Acta* 137 (2014) 34–40, <https://doi.org/10.1016/j.electacta.2014.05.134>.
- [18] M. Ouyang, G.H. Wang, C. Zhang, A novel electrochromic polymer containing triphenylamine derivative and pyrrole, *Electrochim. Acta* 56 (2011) 4645–4649, <https://doi.org/10.1016/j.electacta.2011.02.103>.
- [19] A. Ramanavicius, A. Ramanaviciene, A. Malinauskas, Electrochemical sensors based on conducting polymer- polypyrrole, *Electrochim. Acta* 51 (2006) 6025–6037, <https://doi.org/10.1016/j.electacta.2005.11.052>.
- [20] H. Teng, J.Y. Song, G.Y. Xu, F.X. Gao, X.L. Luo, Nitrogen-doped graphene and conducting polymer PEDOT hybrids for flexible supercapacitor and electrochemical sensor, *Electrochim. Acta* 355 (2020) 136772, <https://doi.org/10.1016/j.electacta.2020.136772>.
- [21] J. Roncali, P. Blanchard, P. Frère, 3,4-Ethylenedioxythiophene (EDOT) as a versatile building block for advanced functional π -conjugated systems, *J. Mater. Chem.* 15 (2005) 1589–1610, <https://doi.org/10.1039/b415481a7>.

- [22] K.S. Ryu, Y.G. Lee, Y.S. Hong, Y.J. Park, X. Wu, K.M. Kim, M.G. Kang, N.G. Park, S. H. Chang, Poly(ethylenedioxythiophene) (PEDOT) as polymer electrode in redox supercapacitor, *Electrochim. Acta* 50 (2004) 843–847, <https://doi.org/10.1016/j.electacta.2004.02.055>.
- [23] A.I. Melato, M.H. Mendonça, L.M. Abrantes, Effect of the electropolymerization conditions on the electrochemical, morphological and structural properties of PEDOT films, *J. Solid State Electrochem.* 13 (2009) 417–426, <https://doi.org/10.1007/s10008-008-0522-6>.
- [24] L. Groenendaal, F. Jonas, D. Freitag, H. Pielartzik, J.R. Reynolds, Poly(3,4-ethylenedioxythiophene) and Its Derivatives: past, Present, and Future, *Adv. Mater.* 12 (2000) 481–494, [https://doi.org/10.1002/\(SICI\)1521-4095\(200004\)12:7<481::AID-ADMA481>3.0.CO;2-C](https://doi.org/10.1002/(SICI)1521-4095(200004)12:7<481::AID-ADMA481>3.0.CO;2-C).
- [25] Y. Li, M.Y. Liu, Y. Li, K. Yuan, L.J. Xu, W. Yu, R.F. Chen, X.Q. Qiu, H.L. Yip, Poly(3,4-Ethylenedioxythiophene): methylnaphthalene sulfonate formaldehyde condensate: the effect of work function and structural homogeneity on hole injection/extraction properties, *Adv. Energy Mater.* 7 (2017) 1601499, <https://doi.org/10.1002/aenm.201601499>.
- [26] K. Jain, A.Y. Mehandzhyski, I. Zozoulenko, L. Wågberg, PEDOT:PSS nano-particles in aqueous media: a comparative experimental and molecular dynamics study of particle size, morphology and z-potential, *J. Colloid Interface Sci.* 584 (2021) 57–66, <https://doi.org/10.1016/j.jcis.2020.09.070>.
- [27] H. Zhang, S.R. Wang, H.H. Yao, Z.Y. Tang, L.M. Ding, F. Hao, Tuning the phase separation of PEDOT:PSS affords efficient lead-free perovskite solar cells, *Chem. Commun.* 50 (2023) 2251–2254, <https://doi.org/10.1039/d2cc07021a>.
- [28] E. Tamburri, S. Orlanducci, F. Toschi, M.L. Terranova, D. Passeri, Growth mechanisms, morphology, and electroactivity of PEDOT layers produced by electrochemical routes in aqueous medium, *Synth. Met.* 159 (2009) 406–414, <https://doi.org/10.1016/j.synthmet.2008.10.014>.
- [29] X. Du, Z. Wang, Effects of polymerization potential on the properties of electrosynthesised PEDOT films, *Electrochim. Acta* 48 (2003) 1713–1717, [https://doi.org/10.1016/S0013-4686\(03\)00143-9](https://doi.org/10.1016/S0013-4686(03)00143-9).
- [30] S. Sadki, P. Schottland, N. Brodie, G. Sabouraud, The mechanisms of pyrrole electropolymerization, *Chem. Soc. Rev.* 29 (2000) 283–293, <https://doi.org/10.1039/A807124A>.
- [31] J. Zhou, D.H. Anjum, L. Chen, X.Z. Xu, I.A. Ventura, L. Jiang, G. Lubineau, The temperature-dependent microstructure of PEDOT/PSS films: insights from morphological, mechanical and electrical analyses, *J. Mater. Chem. C* 2 (2014) 9903–9910, <https://doi.org/10.1039/C4TC01593B>.
- [32] N. Plesu, A. Kellenberger, M. Mihali, N. Vaszilcsin, Effect of temperature on the electrochemical synthesis and properties of polyaniline films, *J. Non Cryst. Solids* 356 (2010) 1081–1088, <https://doi.org/10.1016/j.jnoncrysol.2010.01.011>.
- [33] C. Visy, J. Kankare, E. Kriván, EQCM and *in situ* conductance studies on the polymerisation and redox features of thiophene co-polymers, *Electrochim. Acta* 45 (2000) 3851–3964, [https://doi.org/10.1016/S0013-4686\(00\)00456-4](https://doi.org/10.1016/S0013-4686(00)00456-4).
- [34] C.A. Barbero, Ion exchange at the electrode/electrolyte interface studied by probe beam deflection techniques, *Phys. Chem. Phys.* 7 (2005) 1885–1899, <https://doi.org/10.1039/b419382b>.
- [35] E. Vieil, K. Meerholz, T. Matencio, J. Heinze, Mass transfer and convolution: part II. *In situ* optical beam deflection study of ionic exchanges between polyphenylene films and a 1:1 electrolyte, *J. Electroanal. Chem.* 368 (1994) 183–191, [https://doi.org/10.1016/0022-0728\(93\)03110-B](https://doi.org/10.1016/0022-0728(93)03110-B).
- [36] E. Vieil, C. Lopez, Quantitative discrimination of mass fluxes at electrochemical interfaces by optical beam deflection, *J. Electroanal. Chem.* 466 (1999) 218–233, [https://doi.org/10.1016/S0022-0728\(99\)00153-9](https://doi.org/10.1016/S0022-0728(99)00153-9).
- [37] L. Almeida, R. Correia, A. Marta, G. Squillaci, A. Morana, F. La Cara, J. Correia, A. Viana, Electrosynthesis of polydopamine films - tailored matrices for laccase-based biosensors, *Appl. Surf. Sci.* 480 (2019) 979–989, <https://doi.org/10.1016/j.apsusc.2019.03.015>.
- [38] L.M. Abrantes, J.P. Correia, On the initiation and growth of polymer films onto electrode surfaces, *Electrochim. Acta* 44 (1999) 1901–1910, [https://doi.org/10.1016/S0013-4686\(98\)00299-0](https://doi.org/10.1016/S0013-4686(98)00299-0).
- [39] J.P. Correia, E. Vieil, L.M. Abrantes, Electropolymerization of 3-methylthiophene studied by multilayer convolution, *J. Electroanal. Chem.* 573 (2004) 299–306, <https://doi.org/10.1016/j.jelechem.2004.06.036>.
- [40] F. Blanchard, B. Carré, F. Bonhomme, P. Biensan, H. Pagès, D. Lemordant, Study of poly(3,4-ethylenedioxythiophene) films prepared in propylene carbonate solutions containing different lithium salts, *J. Electroanal. Chem.* 569 (2004) 203–210, <https://doi.org/10.1016/j.jelechem.2004.03.002>.
- [41] D.X. Han, G.F. Yang, J.X. Song, Niu L., A. Ivaska, Morphology of electrodeposited poly(3,4-ethylenedioxythiophene)/poly(4-styrene sulfonate) films, *J. Electroanal. Chem.* 602 (2007) 24–28, <https://doi.org/10.1016/j.jelechem.2006.11.027>.
- [42] F. Li, W.J. Albery, A novel mechanism of electrochemical deposition of conducting polymers: two-dimensional layer-by-layer nucleation and growth observed for poly(thiophene-3-acetic acid), *Electrochim. Acta* 37 (2010) 393–401, [https://doi.org/10.1016/0013-4686\(92\)87027-W](https://doi.org/10.1016/0013-4686(92)87027-W).
- [43] F. Chao, M. Costa, C. Tian, Different steps in electrodeposition of poly(3-methylthiophene) films on platinum electrodes studied by ellipsometry, SEM and AFM techniques, *Synth. Met.* 53 (1993) 127–147, [https://doi.org/10.1016/0379-6779\(93\)90885-Z](https://doi.org/10.1016/0379-6779(93)90885-Z).
- [44] A.R. Hillman, E.F. Mallen, Nucleation and growth of polythiophene films on gold electrodes, *J. Electroanal. Chem. Interfacial Electrochem.* 220 (1987) 351–367, [https://doi.org/10.1016/0022-0728\(87\)85121-5](https://doi.org/10.1016/0022-0728(87)85121-5).
- [45] V.A. Isaev, O.V. Grishenkova, Galvanostatic nucleation and growth under diffusion control, *J. Solid State Electrochem.* 17 (2013) 1505–1508, <https://doi.org/10.1007/s10008-013-2119-y>.
- [46] P. Sakunpongtiporn, K. Phasuksom, N. Paradee, A. Sirivat, Facile synthesis of highly conductive PEDOT:PSS via surfactant templates, *RSC Adv.* 9 (2019) 6363–6378, <https://doi.org/10.1039/C8RA08801B>.
- [47] C. Gainaru, R. Kumar, I. Popov, M.A. Rahman, M. Lehmann, E. Stacy, V. Bocharova, B.G. Sumpter, T. Saito, K.S. Schweizer, A.P. Sokolov, Mechanisms controlling the energy barrier for ion hopping in polymer electrolytes, *Macromolecules* 56 (2023) 6051–6059, <https://doi.org/10.1021/acs.macromol.3c00879>.
- [48] S. Kang, G. Snyder, Charge-transport model for conducting polymers, *Nat. Mater.* 16 (2017) 252–257, <https://doi.org/10.1038/nmat4784>.
- [49] C. Tian, G. Jin, F. Chao, M. Costa, J.P. Roger, Optical spectra of a conducting polymer (polymethyl-3-thiophene) at several stages of the electrodeposition process, *Thin Solid Films* 233 (1993) 91–95, [https://doi.org/10.1016/0040-6090\(93\)90068-Z](https://doi.org/10.1016/0040-6090(93)90068-Z).
- [50] L.M. Abrantes, J.P. Correia, G. Jin, The heterogeneous growth of P(3MeTh)—An ellipsometric study, *Electrochim. Acta* 46 (2001) 3993–3999, [https://doi.org/10.1016/S0013-4686\(01\)00706-X](https://doi.org/10.1016/S0013-4686(01)00706-X).
- [51] L.C. Almeida, R.D. Correia, B. Palys, J.P. Correia, A.S. Viana, Comprehensive study of the electrochemical growth and physicochemical properties of polycatecholamines and polycatechol, *Electrochim. Acta* 386 (2021) 138515, <https://doi.org/10.1016/j.electacta.2021.138515>.
- [52] L.A.A. Pettersson, S. Ghosh, O. Inganäs, Optical anisotropy in thin films of poly(3,4-ethylenedioxythiophene)-poly(4-styrenesulfonate), *Org. Electron.* 3 (2002) 143–148, [https://doi.org/10.1016/S1566-1199\(02\)00051-4](https://doi.org/10.1016/S1566-1199(02)00051-4).
- [53] A.I. Melato, A.S. Viana, L.M. Abrantes, Influence of the electropolymerization mode on PEDOT films morphology and redox behaviour—An AFM investigation, *J. Solid State Electrochem.* 14 (2010) 523–530, <https://doi.org/10.1007/s10008-008-0684-2>.
- [54] M.A. Vorotyntsev, M. Skompska, E. Pousson, J. Goux, C. Moise, Memory effects in functionalized conducting polymer films: titanocene derivatized polypyrrole in contact with THF solutions, *J. Electroanal. Chem.* 552 (2003) 307–317, [https://doi.org/10.1016/S0022-0728\(03\)00038-X](https://doi.org/10.1016/S0022-0728(03)00038-X).
- [55] R.E. Padilla-Hernandez, J. Barroso-Flores, A.R. Hernandez-Martinez, Exploring polaron formation in PEDOT oligomers through Advanced DFT analysis, *Comput. Theor. Chem.* 1229 (2023) 114348, <https://doi.org/10.1016/j.comptc.2023.114348>.
- [56] M. Skompska, A. Szkurlat, The influence of the structural defects and microscopic aggregation of poly(3-alkylthiophenes) on electrochemical and optical properties of the polymer films: discussion of an origin of redox peaks in the cyclic voltammograms, *Electrochim. Acta* 46 (2001) 4007–4015, [https://doi.org/10.1016/S0013-4686\(01\)00710-1](https://doi.org/10.1016/S0013-4686(01)00710-1).
- [57] M. Skompska, Alternative explanation of asymmetry in cyclic voltammograms for redox reaction of poly(3-methylthiophene) films in acetonitrile solutions, *Electrochim. Acta* 44 (1998) 357–362, [https://doi.org/10.1016/S0013-4686\(98\)00058-9](https://doi.org/10.1016/S0013-4686(98)00058-9).
- [58] C. Yang, F.P. Orfino, S. Holdcroft, A phenomenological model for predicting thermochromism of regioregular and nonregioregular poly(3-alkylthiophenes), *Macromolecules* 29 (1996) 6510–6517, <https://doi.org/10.1021/ma9604799>.
- [59] M. Skompska, A. Szkurlat, A. Kowal, M. Szklarczyk, Spectroelectrochemical and AFM studies of doping - undoping of poly(3-hexylthiophene) films in propylene carbonate and aqueous solutions of LiClO₄, *Langmuir* 19 (2003) 2318–2324, <https://doi.org/10.1021/la0261850>.
- [60] L.M. Abrantes, J.P. Correia, A.I. Melato, An ellipsometric study of poly(3,4-ethylenedioxythiophene) electrosynthesis – from the initial stages to thick layers formation, *J. Electroanal. Chem.* 646 (2010) 75–84, <https://doi.org/10.1016/j.jelechem.2010.02.025>.
- [61] G. Sauerbrey, Use of the vibrating quartz for film weighing and microweighing, *Z. Fur Phys.* 155 (1959) 206–222, <https://doi.org/10.1007/BF01337937>.
- [62] C. Weidlich, K.M. Mangold, K. Jüttner, EQCM study of the ion exchange behaviour of polypyrrole with different counterions in different electrolytes, *Electrochim. Acta* 50 (2005) 1547–1552, <https://doi.org/10.1016/j.electacta.2004.10.032>.



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