



**HAL**  
open science

# Switching of the ion exchange behaviour of PEDOT thin films during a potential cycling: an electrochemical atomic force microscopy study

Adrien Mocaër, Françoise Pillier, Alain Pailleret

## ► To cite this version:

Adrien Mocaër, Françoise Pillier, Alain Pailleret. Switching of the ion exchange behaviour of PEDOT thin films during a potential cycling: an electrochemical atomic force microscopy study. *Electrochimica Acta*, 2021, 389, pp.138651. 10.1016/j.electacta.2021.138651 . hal-03234656

**HAL Id: hal-03234656**

**<https://hal.sorbonne-universite.fr/hal-03234656>**

Submitted on 25 May 2021

**HAL** is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

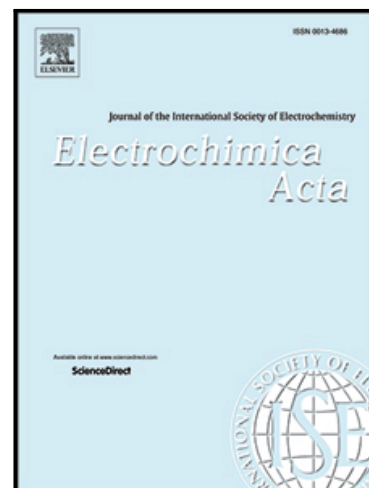
L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

## Journal Pre-proof

Switching of the ion exchange behaviour of PEDOT thin films during a potential cycling: an electrochemical atomic force microscopy study

Adrien Mocaër , Françoise Pillier , Alain Pailleret

PII: S0013-4686(21)00941-5  
DOI: <https://doi.org/10.1016/j.electacta.2021.138651>  
Reference: EA 138651



To appear in: *Electrochimica Acta*

Received date: 10 January 2021  
Revised date: 20 April 2021  
Accepted date: 15 May 2021

Please cite this article as: Adrien Mocaër , Françoise Pillier , Alain Pailleret , Switching of the ion exchange behaviour of PEDOT thin films during a potential cycling: an electrochemical atomic force microscopy study, *Electrochimica Acta* (2021), doi: <https://doi.org/10.1016/j.electacta.2021.138651>

This is a PDF file of an article that has undergone enhancements after acceptance, such as the addition of a cover page and metadata, and formatting for readability, but it is not yet the definitive version of record. This version will undergo additional copyediting, typesetting and review before it is published in its final form, but we are providing this version to give early visibility of the article. Please note that, during the production process, errors may be discovered which could affect the content, and all legal disclaimers that apply to the journal pertain.

© 2021 Published by Elsevier Ltd.

# Switching of the ion exchange behaviour of PEDOT thin films during a potential cycling: an electrochemical atomic force microscopy study

Adrien Mocaër<sup>a</sup>, Françoise Pillier<sup>a</sup>, Alain Pailleret<sup>a,\*</sup>

<sup>a</sup> Sorbonne Université, Faculté de Sciences et Ingénierie, CNRS, Laboratoire Interfaces et Systèmes Electrochimiques (LISE, UMR 8235, case courrier 133), 4 place Jussieu, F-75005, Paris, France

## Abstract

Thickness variations of poly(3,4-ethylenedioxythiophene) (PEDOT) thin films placed under potential conditioning were measured with the help of electrochemical atomic force microscopy (EC-AFM). In this purpose, in-situ AFM operating in the contact mode was coupled with either cyclic voltammetry (CV) or advanced cyclic voltammetry (AdCV). A PEDOT functionalized platinum electrode was used simultaneously as a sample for in-situ AFM measurements and a working electrode in a usual three electrode electrochemical setup. PEDOT films were electrodeposited with the help of the CV technique from lithium perchlorate aqueous solutions. From these EC-AFM investigations, brand new PEDOT films were found to be anion exchangers, in good agreement with conclusions of investigations reported in literature. Unexpectedly, PEDOT films having undergone a comprehensive electrochemical cycling (i.e. an electrochemical aging) in a potential range encompassing narrowly their redox process by using tens of CV or AdCV potential cycles behave as cation exchangers. Such observation strongly suggests that the electrochemo-mechanical and ion exchange behaviours of PEDOT can be both switched by simply using a potential cycling. Interestingly, the initial steps of this switching process were observed on a brand new PEDOT film during 26 consecutive CV scans. In the course of this process still ongoing at the end of the 26<sup>th</sup> cycle, a second swelling peak appears and grows progressively beside the initial

swelling peak attributed to an anion exchange behaviour. This leads to a dual ion exchange behaviour for the resulting PEDOT film within the explored potential range. Indeed, this new swelling peak can be attributed to a cation exchange behaviour from the comparison of the potential dependant chronothicknograms and corresponding voltathicknograms with those obtained previously in this work.

## **Introduction**

Electronically Conducting Polymers (ECPs) keep attracting the attention of numerous research groups worldwide as a consequence of their exciting and interdependent properties among which one can cite their mixed ionic/electronic conductivity, their redox activity, their ion and solvent exchange behaviour, their electrochromic properties and their electrochemo-mechanical behaviour [1,2]. ECPs can be synthesised as powders or thin films, whether these latter are supported or not, using either chemical or electrochemical methods. Moreover, they can be functionnalised using different strategies such as covalent grafting of functional groups on their monomers, electrochemical doping, or insertion of nano-objects (nanoparticles, enzymes, ...) during the synthesis step. All the abovementioned properties of ECPs are electrochemically tunable, which justifies that ECPs are widely involved in a large number of applications, among which one can cite, in a non-exhaustive list, supercapacitors [3-7], batteries [8-11], electrochemical (bio-)sensors [12,13], artificial muscles and ion-selective membranes [14-19], tissue engineering [20], organic electrochemical transistors [21], protection against corrosion [22-23], (photo-)electrocatalysis [24], or electrochromism [11,25-26].

The electrochemo-mechanical behaviour of ECPs has been surprisingly much less investigated than any other of the properties recalled above for this well-known family of insertion materials. It is though well established that ECPs are likely to swell and shrink as a

consequence of ion and solvent exchanges. These latter are known to result from the electrochemically driven switching of the redox state of ECPs and they occur so as to maintain a global electroneutrality in the bulk of these materials. Obviously, in a first step, ions, whether these latter are solvated or not, and free solvent molecules, are transferred at the film/electrolytic solution interface. Nevertheless, they create thickness variations not only in a superficial layer of the thin polymer film but actually throughout its whole bulk as a consequence of diffusion of the inserted species inside the polymer film. One can observe from literature that experimental techniques allowing the in-situ measurement of thickness variations of ECPs placed under electrochemical conditioning are not so numerous [27]. Scanning electron microscopy has been widely used for thickness measurements of ECP thin films placed under vacuum but it does not allow in operando measurements, which severely limits the interest of this technique for this purpose. Raman spectroscopy [28] and Electrochemical Impedance Spectroscopy (EIS) [29-30] are able to provide thickness values when applied on ECPs in-situ but their interpretation is model dependant and they do not offer a time resolution well adapted to this kind of measurements. Ellipsometry could be an interesting technique for this purpose but only in the case of films whose thickness is lower than about 1  $\mu\text{m}$  [31-32]. Scanning ElectroChemical Microscopy (SECM), ElectroChemical Scanning Tunneling Microscopy [27] and Scanning Ion Conductance Microscopy [33] are powerful scanning probe microscopy techniques that allow in-situ measurements of thickness variation of ECPs thin films during electrochemical conditioning with simultaneously very satisfying time and spatial (vertical) resolutions. Unfortunately, they require respectively the use of electroactive doping ions or very specific probes, which limits the expansion of these techniques in this frame. A laser based method recently introduced in literature seems to be promising in spite of a limited spatial resolution [34-36]. On the contrary, ElectroChemical Atomic Force Microscopy (EC-AFM) appears to be fully adapted to the follow-up as a

function of time of thickness variations of ECPs thin films placed under an electrochemical conditioning. This technique offers indeed ideal time and spatial (vertical) resolutions and a very soft and tunable mechanical interaction between the AFM tip and the polymer film. In spite of these obvious advantages, EC-AFM investigations related to thickness variations of ECPs have been reported only in a very limited number of publications. This is even truer if we exclude those addressing more specifically nucleation, growth, morphology, and roughness studies of electrodeposited ECP thin films [27]. Interestingly, they reveal a very large range of values for the thickness variation rate (expressed for example as percentage). Obviously, these latter are likely to depend on the experimental conditions used for the production of the investigated polymer films. For example, Nyffenegger *et al.* demonstrated a clear dependence between thickness variation and the initial anodic charge measured after transfer [37]. Later on, a 35% to 125 % volume expansion was evidenced in the case of dodecylbenzenesulfonate doped polypyrrole patterns as a consequence of solvent uptake or potential conditioning [38-39]. In the case of perchlorate doped poly(3-hexylthiophene) (P3HT) films electrodeposited from propylene carbonate, volume expansion was found to vary in 15-17% to 35-40% ranges [40], whereas, in the case of PANI, it varies from 17.5 % up to 89.8 % as a function of their morphology (films, microtubules or nanowires) [41]. Let us mention also a 950 % volume change that was reported for poly(styrenesulfonate) doped PEDOT films [42]. This range of values is even larger if one takes into account values extracted from other relevant methodologies.

On our side, we reported previously ac-electrogravimetry and electrochemical atomic force microscopy (EC-AFM) investigations performed in parallel on sulfonated calix[6]arene (C6S) doped polypyrrole films [43-44]. C6Ss were chosen in these studies because they are bulky polyacidic organic molecules that provide bulky polyanionic species upon deprotonation in aqueous solutions. As a consequence of their anionic character, they will be

irreversibly trapped in the polypyrrole matrix during the electropolymerisation step of pyrrole, leading then to C6S doped PPy films that will behave as cation exchangers. Such hypothesis was confirmed with the help of the results provided by both techniques. Indeed, ac-electrogravimetry experiments performed in  $\text{KNO}_3$  aqueous solutions confirmed that the ions exchanged during the potential cycling of C6S doped PPy films were mainly cations, either  $\text{K}^+$  or  $\text{H}_3\text{O}^+$  cations depending on the investigated potential range. In parallel, electrochemical atomic force microscopy revealed that PPy-C6S films swell during insertion of cations and shrink during their expulsion out of the polymer film. Such a strong correlation between ion exchange phenomena and thickness variations was even better shown from the very similar shape observed for cyclic voltammograms and cyclic voltathicknograms. These latter show respectively the variations of the mass and the thickness of the polymer film as a function of the applied potential (see Figures 2b and 9 in [44]). In the course of these past investigations, it was nevertheless evidenced that under a potential conditioning involving potential steps instead of potential ramps, correlations between mass and thickness variations may disappear at least partially. Such experiments indeed allowed us to observe so-called relaxation steps [18] during which there is no correlation between the thickness variation and the applied potential [43]. In such situation, a fast and intense thickness variation was detected during the potential switching followed by a soft (slow and small) thickness variation in the opposite direction on the potential plateau. Various phenomena such as the memory effect [45-46], the electrochemically stimulated conformational relaxation (ESCR) [47] and electro-osmosis [48], were suggested to justify thickness variations observed in ECPs as a consequence of their electrochemical conditioning.

In this work, ECAFM experiments were performed on electrodeposited perchlorate doped PEDOT thin films having undergone different electrochemical ageing processes. PEDOT is possibly one of the most investigated ECPs and was suggested for a large number

of applications [49-51]. Interestingly, PEDOT thin films can be electrogenerated by using the electropolymerisation technique from either aqueous [52-56], organic [57] or room temperature ionic liquids (RTILs) [58-61] based electrolytic solutions. Let us emphasize that the poor solubility of EDOT monomer in aqueous electrolytic solutions led to the use of micellar aqueous electrolytic solutions prepared from ionic surfactants. Micelles formed in such solutions were shown to favour the solubilisation of EDOT and thus to enhance its electropolymerisation rate. On the other hand, anionic surfactants are often bulky enough to be irreversibly trapped in ECPs during their electrodeposition step (like C6S anions mentioned above), which is known to lead to a cation exchange behaviour for the resulting polymers. In order to avoid any competition with the perchlorate anions in the doping process of PEDOT films during the electropolymerisation step, anionic surfactants were not used in the course of the investigations reported hereafter.

### **Experimental part**

Electrodeposition and storage of PEDOT films: thin PEDOT films were electrodeposited on a platinum disc electrode (2 mm diameter) from aqueous electrolytic solutions containing  $\text{LiClO}_4$  (0.1 M) and EDOT (10 mM) using 10 cyclic voltammetry scans between -0.9 V and +0.85 V vs. Ag at a  $100 \text{ mV}\cdot\text{s}^{-1}$  scan rate. For such experiments, a silver wire and a platinum grid were used as reference and auxiliary electrodes respectively. As already reported by several authors in literature, the EDOT monomer appears to solubilise very slowly in water in the absence of surfactants. As a consequence, aqueous electrolytic solutions used for the electrodeposition of PEDOT were left for two days in a closed flask on the bench in order to maximise the solubilisation of EDOT. The resulting perchlorate doped PEDOT films were dried in air and then imaged using a Ultra 55 FEG-SEM (Zeiss).



EC-AFM experiments: Thickness variations of electrodeposited perchlorate doped PEDOT films were measured using the contact mode of atomic force microscopy during the potential conditioning performed with either cyclic (CV) or advanced cyclic voltammetry (AdCV). The latter technique differs from the former one by the presence of potential plateaus situated at the inversion potentials existing in usual cyclic voltammetry. The duration of these potential plateaus is an experimental parameter to be added to scan rate and inversion (or plateau) potential values. Throughout our experiments, PEDOT films were cycled between -0.65 V and 0.35 V vs. Ag at different scan rates in a transfer aqueous electrolytic solution containing lithium perchlorate (0.1 M). According to a methodology previously reported in literature [43-44], the AFM tip acts in such measurements as a profilometer at a fixed position in the x-y plane of the sample. As a consequence, only its vertical position varies as a function of the potential applied on the PEDOT films.

## Results and discussion

The electropolymerisation reaction of EDOT occurring in the presence of a 1-1 symmetrical electrolyte, i.e. LiClO<sub>4</sub> in our experimental conditions (see Figure 1) can be written as follows:



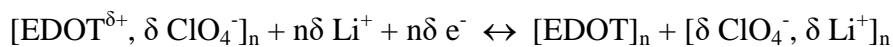
In this reaction,  $n$  is the number of monomer units involved in the polymer growth and  $\delta$  is the doping rate, i.e. the number of cationic charge per monomer unit. This equation indicates that the PEDOT film grows in its cationic form, which necessitates the insertion of anions from the electrolytic solution in order to insure electroneutrality in the resulting polymer film whose composition is therefore  $[\text{EDOT}^{\delta+}, \delta \text{ ClO}_4^-]_n$ . The ion exchange behaviour of the resulting polymer film will then be the consequence of the size of the inserted anions. In our experimental conditions, as perchlorate anions have a rather small ionic radius, i.e. 2.25 Å

[62], the resulting PEDOT-ClO<sub>4</sub><sup>-</sup> films are likely to behave as anion exchangers, and this was actually confirmed using ac-electrogravimetry experiments [63]. They show also a granular morphology, as observed on FEG-SEM images (see Figure 1), as well as a high compacity that is required to allow an easy interpretation of thickness variations measured during EC-AFM experiments.

The ion exchange behaviour of these PEDOT-ClO<sub>4</sub><sup>-</sup> films was further investigated in this work thanks to measurements of thickness variations. Figure 2 shows a first set of EC-AFM experiments resulting from the use of the coupling of cyclic voltammetry with contact mode atomic force microscopy (CV-AFM) on a brand new PEDOT film electrodeposited on a platinum working electrode. On Figure 2A, the red and black curves show respectively the applied potential and the thickness variation of this PEDOT film as a function of time. In the course of this experiment, the PEDOT film underwent 6 CV scans at 50 mV/s, 6 CV scans at 10 mV/s, and finally 6 CV scans at 100 mV/s. Whatever the scan rate, the black curve shown on Figure 2A reveals that the PEDOT film swells during anodic scans and shrinks during cathodic scans. In other words, the anodic inversion potential, i.e. 0.35 V vs. Ag, and the swelling peak maximum are reached almost simultaneously. Similarly, the shrinking peak minimum is observed almost exactly by the time the cathodic inversion potential, i.e. -0.65 V vs. Ag, is reached. This is particularly obvious for high scan rate values (50 and 100 mV/s). For a 10 mV/s scan rate, the same trend is globally observed, i.e. this PEDOT film still swells during anodic scans and shrinks during cathodic scans. Actually, one can clearly observe that it starts swelling just before the cathodic inversion potential, i.e. over several tens of millivolts before -0.65 V vs. Ag and then mainly during the first fourth of the duration of the anodic potential scan, i.e. from -0.65 V to -0.3 V vs. Ag. Its thickness is then approximately unchanged until it starts swelling again at the very end of the anodic potential scan, i.e. from 0.25 to 0.35 V vs. Ag whereas it keeps shrinking almost all along the cathodic scan.

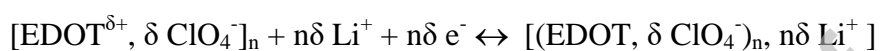
Consecutive voltathicknograms shown on Figures 2B and 2D for high scan rates (50 and 100 mV/s respectively) confirm those trends. Both of them show that our PEDOT film is thicker in the more positive potential range than in the negative potential range. This is a strong indication in favour of an anion exchange behaviour. Indeed, voltathicknograms showing the opposite tilt, i.e. a higher thickness at cathodic potentials rather than at anodic potentials, were clearly attributed to a cation exchange behaviour. This correlation was indeed clearly evidenced on the basis of cyclic electrogravimetry and ac-electrogravimetry results in the case of hexasulfonated calix[6]arenes doped polypyrrole films [43-44]. Voltathicknograms obtained for a 10 mV/s scan rate (see Figure 2C) are somewhat different as they do not show an obvious tilt over the same potential range. They are constituted of two loops, one of which shows a much larger amplitude, and extends over a much larger potential range, than the other one. This observation is interesting because it reveals that the electrochemo-mechanical (ECM) behaviour of PEDOT can be reversibly tailored using the potential scan rate in a cyclic voltammetry experiment. In our experiments, the ECM behaviour observed for a 50 mV/s scan rate was temporarily modified using a 10 mV/s scan rate before it was observed again at 100 mV/s. A closer comparison of Figures 2B-D suggests that thickness variations increase with the scan rate. One can indeed observe that the thickness of the PEDOT film varies over approximately a 400 nm range at 10 mV/s and over a 800 nm range at 100 mV/s when the electrochemical conditioning is applied over a 1 V wide potential range (from -0.65 V up to 0.35 V vs. Ag). It is important to notice that none of these thickness variations was predictable on the basis of the analysis of the cyclic voltammograms (see Figure 2E). These latter are all almost perfectly rectangular and they show a very good stability during potential cycling for a given scan rate, as well as the well-established linear dependence of current with the potential scan rate. This latter was actually expected for a redox couple immobilised on an electrode surface. Moreover, these CVs do not provide any significant or useful information in view of

the identification of the anion exchange behaviour of PEDOT films. Such behaviour can be illustrated using the following redox reaction in the case of p-(un)doping :



On the other hand, this latter does not show the well-established exchange of free solvent molecules according to quartz crystal microbalance or ac-electrogravimetry investigations reported in literature in the case of conducting polymer films [43,63-64]. This first set of experiments confirms therefore that brand new electrodeposited perchlorate doped PEDOT films are mainly anion exchangers, as predicted from the small size of  $\text{ClO}_4^-$  anions. In the next series of experiments, it has been possible for us to demonstrate that aged PEDOT- $\text{ClO}_4^-$  thin films behave mainly as cation exchangers. For this purpose, EC-AFM experiments were performed by coupling advanced cyclic voltammetry with contact mode AFM (AdCV-AFM) on electrodeposited PEDOT- $\text{ClO}_4^-$  thin films having undergone previously 200 potential cycles between -0.65 V and +0.35 V vs. Ag (see Figure 3). In Figure 3A, the polychromic and red curves show respectively thickness variation and potential conditioning of the aged PEDOT- $\text{ClO}_4^-$  thin film. One can observe a striking difference between Figure 3A and Figure 2A : Figure 3A shows that the film is thicker for the lowest potential values, unlike Figure 2A. Indeed, whatever the scan rate (50, 10 or 250 mV/s in a chronological order), the polymer film clearly swells during cathodic potential scans and shrinks during anodic potential scans, although a small increase of the thickness can be observed over several tens of millivolts at the end of each anodic scan (see black portions of the polychromic curve). Interestingly, AdCV allows potential plateaus to be applied between potential scans. During anodic potential plateaus, the polymer film swells slowly (see green portions on polychromic curve in Figure 3A). This swelling step follows a swelling process of small amplitude that starts at the end of the anodic scan and that comes after a shrinking step of large amplitude occurring during the major portion of this same anodic scan. During cathodic potential plateaus, the

polymer film shrinks slowly (see blue portions on polychromic curve in Figure 3A), whereas it swelled during the whole previous cathodic scan, which possibly corresponds to relaxation phenomena previously reported in literature for other conducting polymer films [43,47]. This electrochemo-mechanical behaviour is exactly the opposite of the one shown in Figure 2, which strongly suggests that aged PEDOT-ClO<sub>4</sub><sup>-</sup> films are mainly cation exchangers. Such behaviour can be illustrated using the following redox reaction in the case of p-(un)doping in a LiClO<sub>4</sub> aqueous solution:



This is actually confirmed from the analysis of consecutive voltammograms deduced from Figure 3A (see Figures 3B-D). Whatever the scan rate, these latter all show thickness values that are higher for cathodic potentials than for anodic potentials, as already observed for well-established cation exchangers (see Figure 9 in [44]). Surprisingly, one can also notice that the thickness variation range is not influenced anymore by the scan rate, as it seems to be about 1 μm wide over a 1 V potential window, whatever the scan rate. Again, consecutive cyclic voltammograms shown on Figure 3E are not helpful to predict thickness variation. One can simply notice that they are not as rectangular as those shown on Figure 2E. One can indeed distinguish poorly intense anodic and cathodic peaks observed respectively at 0.1 V and -0.4 V vs. Ag and known to correspond more specifically to cation exchanges, as already shown in literature [63].

At this stage of our investigations, it was difficult to explain this obvious switching of the ion exchange behaviour of our PEDOT-ClO<sub>4</sub><sup>-</sup> film. Could it be a consequence of the specific ageing process used to produce the second PEDOT sample, i.e. the 200 consecutive cyclic potential scans between -0.35 V and 0.65 V vs. Ag ? In order to assess this question, a third set of EC-AFM experiments was performed on another ClO<sub>4</sub><sup>-</sup> doped PEDOT film aged with

the help of a different ageing procedure (see Figure 4). This time, the investigated PEDOT film underwent 15 cyclic voltammetry scans, and then 27 advanced cyclic voltammetry scans, all between -0.35 V and 0.65 V vs. Ag. As already observed in Figure 3A, Figure 4A shows a situation where the potential conditioning and the thickness vary in opposite directions. As the potential is scanned from negative to positive potentials, thickness of the PEDOT film decreases very fast over the first half of the scanned potential range, i.e. from -0.65 V to -0.15 V vs. Ag and then much more slowly over the second half, i.e. from -0.15 to 0.35 V vs. Ag. On the other hand, the thickness increases slowly from 0.35 V to -0.15 V vs. Ag, and then much faster from -0.15 V to -0.65 V vs. Ag, i.e. when the potential is scanned from positive to negative potentials. Such behaviour is observed whatever the scan rate (50, 10 or 100  $\text{mV}\cdot\text{s}^{-1}$ ). This is confirmed from the comparison of the voltathicknograms shown on Figures 4B-D with those reported in Figures 3B-D. Those six voltathicknograms all correspond to PEDOT thin films whose thickness is higher at negative potentials than at positive potentials. Among them, the one shown on Figure 4D possesses a distinctive feature, as it is the only one that reveals a crossing of forward and backward scans at about -0.3 V vs. Ag. The cyclic voltammograms obtained in the course of these experiments for the three different scan rates are shown in Figure 4E. Unlike Figure 2E corresponding to a brand new PEDOT film, and like Figure 3E obtained with an aged PEDOT film, Figure 4E shows poorly intense oxidation and reduction peaks whose peak potential values are 0.1 V and -0.4 V vs. Ag respectively. Such peaks may constitute a fragile proof of the cation exchange behaviour of those films. As already observed in this work, cyclic voltammograms reveal a fairly stable electroactivity that can be correlated with the very reproducible electrochemo-mechanical behaviour observed on Figure 4A, whether the thickness variation rate or range are considered.

It appears therefore at this stage that the anion exchange behaviour of brand new PEDOT films can be switched into a cation exchange behaviour using different ageing procedures,

such as a potential cycling for example. One can also suggest that potential plateaus applied in the course of the potential conditioning of the PEDOT film investigated in Figure 4 do not influence the switching mechanism of the ion exchange behaviour of our PEDOT films. Indeed, the EC-AFM results reported above indicate that ageing procedures involving either the CV or AdCV techniques both lead to the same result (see Figures 3 and 4). Although potential cycling seems to allow a switching of the ion exchange behaviour of our PEDOT films, one can hardly predict the influence or the need of potential plateaus involved only in AdCV experiments, as well as that of different scan rates or of the cycle number. Interestingly, Figure 5 shows an example of an ongoing electrochemical ageing process that was observed during 26 consecutive potential cycles using a 50 mV/s scan rate. It allows following most of the evolution of the electrochemo-mechanical behaviour of a brand new PEDOT film. In Figure 5A, initial potential cycles show a single swelling peak whose maximum is slightly shifted beyond the anodic inversion potential, even if one can already observe a small shoulder on its left hand side. This situation is in full agreement with the one observed on Figure 2. After the fourth potential cycle, this asymmetric swelling peak is less and less intense as the number of cycles increases. In parallel, one can clearly observe that the shoulder initially observed becomes also less and less intense and more and more well separated from the initial swelling peak, as a consequence of a progressive shift towards more cathodic potentials. From the tenth cycle, this shoulder has become an individual peak that is more and more distinct from the initial swelling peak, and also more and more intense, as the number of cycles keeps increasing. The value of the corresponding potential is almost exactly equal to the cathodic inversion potential. This new swelling peak rather reminds us the one observed on Figure 4A. Over the last potential cycles shown on Figure 5A, two well defined swelling peaks coexist. Their potential values measured at their highest thickness values are very close to those of the anodic and cathodic inversion potentials and their respective

intensities vary in opposite directions as a function of the number of potential cycles. The corresponding PEDOT film is therefore losing progressively its anion exchange behaviour in favour of a cation exchange behaviour [64]. Although this switching is clearly underway in Figure 5, it is still not fully completed yet. Figure 4 indeed shows that the swelling peak corresponding to anion exchange can disappear completely, on condition that a comprehensive and well-adapted potential conditioning is used for the electrochemical ageing of the PEDOT film, which is clearly not the case yet in Figure 5. This ongoing transition can also be observed on the consecutive voltathicknograms shown on Figure 5B. The first one corresponding to the first potential cycle (see green line on Figure 5B) is rather similar to those obtained during the potential cycling of a brand new PEDOT film (see Figures 2B,D for comparison) whereas the last one (see red line on Figure 5B) shows completely different features. This latter is indeed made of two horizontal loops. It shows therefore an intermediate ion exchange behaviour, by comparison with the one observed on Figure 2 on one side and the one observed on Figures 3 and 4 on the other side.

A further information can be extracted from Figure 5, beyond those already mentioned above, by comparison with Figure 2. One can notice first that i) the five initial cycles lead to highly similar thickness variations in Figures 2 and 5, ii) the ion exchange behaviour of the PEDOT film is not significantly altered after the 18th cycle in Figure 2 as shown by the strong similarities of Figures 2B and 2D, iii) the ion exchange behaviour of the PEDOT film is significantly altered after the 26th cycle in Figure 5 as shown by the strong differences between the first cyclic voltathicknogram (see cycle plotted in green in Figure 5B) and the last one (see cycle plotted in red in Figure 5B). This observation strongly suggests that the scan rate used during the electrochemical ageing step strongly influences the consequences of this latter. It seems indeed that the 10 mV/s scan rate used in Figure 2 did not produce or even better prevent a switching of the ion exchange behaviour of the PEDOT film whereas the 50



mV/s scan rate used constantly in Figure 5 during 26 cycles does lead to a progressive switching of the ion exchange behaviour of the PEDOT film. This latter could hardly be predicted or further interpreted on the basis of corresponding consecutive cyclic voltammograms (see Figure 5C) as these latter show a negligible evolution with the number of cycles.

## Conclusion

This contribution was aimed at characterizing and comparing the ion exchange behaviour of perchlorate doped PEDOT films having undergone various electrochemical ageing procedures through thickness variation measurements. For that purpose, a methodology based on EC-AFM, i.e. the coupling of in-situ atomic force microscopy with various electrochemical techniques (either cyclic voltammetry or advanced cyclic voltammetry) was exploited. In the course of these studies, several identical PEDOT-ClO<sub>4</sub><sup>-</sup> films were electrodeposited using the same experimental parameters. In agreement with literature, we confirmed in a first part of this work that a brand new perchlorate doped PEDOT film behaves as an anion exchanger. In a second step, we demonstrated that such films become cation exchangers as a consequence of two heavy electrochemical ageing procedures that were substantially different. In a first conclusion, we can therefore claim that the switching from an anion exchange behaviour to a cation exchange behaviour occurred in a reproducible manner in the case of our PEDOT-ClO<sub>4</sub><sup>-</sup> thin films on condition that a heavy electrochemical ageing step was applied on a brand new PEDOT film. In a last part of this work, two short electrochemical ageing procedures were compared. The only difference between them stands in the potential scan rate values that were used during the successive potential cyclings and only one of them did not alter the ion exchange behaviour of our PEDOT-ClO<sub>4</sub><sup>-</sup> thin films. This observation strongly suggests that a faster scan rate led to a progressive and partial switching of the ion exchange behaviour of the PEDOT film whereas a slow scan rate did not produce or even better prevent a switching of

this latter. If confirmed in the frame of more comprehensive studies, this important conclusion may contribute to the opening of new roads in the search of efficient and simple means to control the stability of the ion exchange behaviour of ECPs.

These conclusions allowed us to reach three objectives. The first one was to convince the reader that EC-AFM is a powerful and still under-exploited methodology for the quantitative determination and/or the intimate follow-up of thickness variations of a conducting polymer as a function of an electrochemical conditioning. By exposing and developing this methodology with the help of a well-known system (model) such as a perchlorate doped PEDOT film, we want to convince the reader of the deep interest of this methodology. Simultaneously, we developed this latter for example by plotting and exploiting voltathicknograms. We show in particular how useful they are to understand the mechanism and to identify the influencing parameters of the switching process of an ion exchange behaviour. These steps are necessary before we address more original electroactive insertion materials inside or beyond the family of electronically conducting polymers.

Our second objective was to show that there is a close correlation between thickness variations and the ion exchange behaviour of a conducting polymer film, in spite of the simultaneous exchange of free water molecules that has already been reported in the case of many conducting polymers, whatever their identity, the solvent, the electrolyte, or the synthesis method. We think it is interesting and original to tackle this issue through thickness variations rather than through mass variations measurements or electrochemical data for example.

Thirdly, we believe it was necessary to keep bringing further evidence of the possible switching of the ion exchange behaviour of conducting polymers as a consequence of an electrochemical aging procedure, because this issue is still highly debated in literature

nowadays, and we do it in an original manner in this manuscript through the in-situ measurement of thickness variations.

Finally, we believe that this manuscript, in addition with previous publications of ours, does lay a solid foundation for more in-depth studies aimed at understanding the evolution mechanism of the evolution of the ion exchange behaviour of various electroactive insertion materials. On the other hand, beside further methodological developments, we also want to focus in the near future on the most interesting and the most innovative electroactive insertion materials, whether they belong to the family of conducting polymers or to another, so as to help solving the hottest questions that are related to their ion exchange behaviour and/or to their electrochemically-driven thickness variations.

## Acknowledgements

A. Mocaër acknowledges the Doctoral School “Physical Chemistry and Analytical Chemistry of Paris Centre” (ED388, Sorbonne Université) for a Ph.D. grant.

## Bibliography

- [1] J. Heinze, B.A. Frontana-uribe, S. Ludwigs, Electrochemistry of Conducting Polymers Persistent Models and New concepts, *Chem. Rev.* 110 (2010) 4724–4771.
- [2] X. Guo, A. Facchetti, The journey of conducting polymers from discovery to application, *Nature Materials*, 19 (2020) 922–928.
- [3] R. Kötz, M. Carlen, Principles and applications of electrochemical capacitors, *Electrochim. Acta.* 45 (2000) 2483–2498.
- [4] G.A. Snook, P. Kao, A.S. Best, Conducting-polymer-based supercapacitor devices and electrodes, *J. Power Sources*, 196 (2011) 1–12.
- [5] N. Kurra, Q. Jiang, A. Syed, C. Xia, H.N. Alshareef, Micro-Pseudocapacitors with Electroactive Polymer Electrodes: Toward AC-Line Filtering Applications, *ACS Appl. Mater. Interfaces* 8 (2016) 12748–12755.
- [6] L. Benhaddad, J. Gamby, L. Makhloufi, A. Pailleret, F. Pillier, H. Takenouti, Improvement of capacitive performances of symmetric carbon/carbon supercapacitors by addition of nanostructured polypyrrole powder, *J. Power Sources.* 307 (2016) 297–307.
- [7] Y.-Z. Long, M.-M. Li, C. Gu, M. Wan, J.-L. Duvail, Z. Liu, Z. Fan, Recent advances in synthesis, physical properties and applications of conducting polymer nanotubes and nanofibers, *Prog. Polym. Sci.* 36 (2011) 1415–1442.

- [8] Y. Xuan, M. Sandberg, M. Berggren, X. Crispin, An all-polymer-air PEDOT battery, *Org. Electron.* 13 (2012) 632-637.
- [9] R. Holze, Y.P. Wu, Intrinsically conducting polymers in electrochemical energy technology: Trends and progress, 122 (2014) 93-107.
- [10] J. Kim, J. Lee, J. You, M.S. Park, M.S. Al Hossain, Y. Yamauchi, J.H. Kim, Conductive polymers for next-generation energy storage systems: recent progress and new functions, *Mat. Horiz.* 3 (2016) 517.
- [11] F. Wolfart, B.M. Hryniewicz, M.S. Góes, C.M. Corrêa, R. Torresi, M.A.O. S. Minadeo, S.I. Córdoba de Torresi, R.D. Oliveira, L.F. Marchesi, M. Vidotti, Conducting polymers revisited: applications in energy, electrochromism and molecular recognition, *J Solid State Electrochem* 21 (2017) 2489–2515.
- [12] S. Cosnier, A. Karyakin, *Electropolymerization, Concepts, Materials and Applications*, Wiley-VCH, Weinheim, 2010.
- [13] A. Ion, I. Ion, J.C. Moutet, A. Pailleret, A. Popescu, E. Saint-Aman, E. Ungureanu, E. Siebert, R. Ziessel, Electrochemical recognition of metal cations by redox-active receptors in homogeneous solution and in polymer films: some relevant examples, *Sensors and actuators B-Chem.*, (1999), 59, 118.
- [14] T.F. Otero, J.G. Martinez, Physical and chemical awareness from sensing polymeric artificial muscles. Experiments and modeling, *Prog. Polym. Sci.* 44 (2015) 62-78.
- [15] T.F. Otero, J.G. Martinez, J. Arias-Pardilla, Biomimetic electrochemistry from conducting polymers. A review. Artificial muscles, smart membranes, smart drug delivery and computer/neuron interfaces, *Electrochim. Acta* 84 (2012) 112-128.
- [16] T.F. Otero, Biomimetic Conducting Polymers: Synthesis, Materials, Properties, Functions, and Devices, *Polym. Rev.* 53 (2013) 311-351.
- [17] T.F. Otero, M. Alfaro, V. Martinez, M.A. Perez, J.G. Martinez, Biomimetic Structural Electrochemistry from Conducting Polymers: Processes, Charges, and Energies. Coulovoltammetric Results from Films on Metals Revisited, *Adv. Funct. Mat.* 23 (2013) 3929-3940.
- [18] T.F. Otero, J.G. Martinez, Ionic exchanges, structural movements and driven reactions in conducting polymers from bending artificial muscles, *Sens. Actuators, B* 199 (2014) 27-30.
- [19] T.F. Otero, J.G. Martinez, Artificial Muscles: A Tool to quantify Exchanged Solvent during Biomimetic Reactions, *Chem. Mater.* 24 (2012) 4093-4099.
- [20] R. Balint, N.J. Cassidy, S.H. Cartmell, Conductive polymers: towards a smart biomaterial for tissue engineering, *Acta Biomater.* 10 (2014) 2341-2353.
- [21] S. Inal, J. Rivnay, A.I. Hofmann, I. Uguz, M. Mumtaz, D. Katsigiannopoulos, C. Brochon, E. Cloutet, G. Hadziioannou, G.G. Malliaras, Organic Electrochemical Transistors Based on PEDOT with Different Anionic Polyelectrolyte Dopants, *J. Polym. Sci., Part B: Polym. Phys.* 54 (2016) 147-151.
- [22] P.P. Deshpande, D. Sazou, *Corrosion protection of metals by Intrinsically Conducting Polymers*, CRC Press, Boca Raton, 2015.
- [23] A. Pailleret, N.T.L. Hien, D.T.M. Thanh, C. Deslouis, Surface reactivity of polypyrrole/iron oxide nanoparticles: Electrochemical and CS-AFM investigations, *J. Solid State Electrochem.*, 11 (2007) 1013-1021.
- [24] C. Janáky, K. Rajeshwar, Progress in Polymer Science The role of ( photo ) electrochemistry in the rational design of hybrid conducting polymer / semiconductor assemblies : From fundamental concepts to practical applications, *Prog. Polym. Sci.* 43 (2015) 96–135.
- [25] W.T. Neo, Q. Y, S.-J. Chua, J. Xu, Conjugated polymer-based electrochromics : materials, devices fabrication and application prospects, *J. Mater. Chem. C*, 4 (2016) 7364-7376.

- [26] H. Wang, M. Barrett, B. Duane, J. Gu, F. Zenhausern, Materials and processing of polymer-based electrochromic devices, *Mat. Sci. Engin. B* 228 (2018) 167-174.
- [27] A. Pailleret, O.A. Semnikhin, Nanoscale Inhomogeneity of Conducting Polymer Based Materials, in: A. Eftekhari (Eds), *Nanostructured Conducting Polymers*, Ch. 3, Wiley, Amsterdam, 2010, p. 99-159.
- [28] X. Wang, M.C. Bernard, C. Deslouis, S. Joiret, P. Rousseau, Kinetic reactions in thin polyaniline films revisited through Raman-impedance dynamic coupling, *Electrochim. Acta*, 56 (2011) 3485-3493.
- [29] C. Deslouis, T. El Moustafid, M.M. Musiani, B. Tribollet, Mixed ionic-electronic conduction of a conducting polymer film. Ac impedance study of polypyrrole, *Electrochim. Acta* 41 (1996) 1343-1349.
- [30] M.A. Vorotyntsev, J.-P. Badiali, G. Inzelt, Electrochemical impedance spectroscopy of thin films with two mobile charge carriers : effects of the interfacial charging, *J. Electroanal. Chem.* 472 (1999) 7-19.
- [31] 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.
- [32] W. Ogieglo, H. Wormeester, K.-J. Eichhorn, M. Wessling, N.E. Benes, In situ ellipsometry studies on swelling of thin polymer films : a review, *Prog. Polym. Sci.*, 42 (2015) 42-78.
- [33] C. Laslau, D.E. Williams, B.E. Wright, J. Travas-Sejdic, Measuring the Ionic Flux of an Electrochemically Actuated Conducting Polymer Using Modified Scanning Ion Conductance Microscopy, *J. Am. Chem. Soc.* 133 (2011) 5748-5751.
- [34] D. Melling, S.A. Wilson, E.W.H. Jager, Controlling the electro-mechanical performance of polypyrrole through 3- and 3,4-methyl substituted copolymers, *RSC Adv.* 5 (2015) 84153-84163.
- [35] D. Melling, S.A. Wilson, E.W.H. Jager, The effect of film thickness on polypyrrole actuation assessed using novel non-contact strain measurements, *Smart Mater. Struct.* 22 (2013) 104021 (10pp).
- [36] T.F. Otero, Coulovoltammetric and Dynamovoltammetric Responses from conducting Polymers and Bilayer Muscles as tools to identify Reaction-driven Structural Changes. A review, *Electrochim. Acta* 212 (2016) 440-457.
- [37] R. Nyffenegger, E. Ammann, H. Siegenthaler, R. Kotz, and O. Haas, *Electrochimica Acta*, 40, 1995, 1411-1415.
- [38] E. Smela, N. Gadegaard, Volume change in polypyrrole studied by atomic force microscopy, *J. Phys. Chem. B*, 105 (2001) 9395-9405.
- [39] E. Smela, N. Gadegaard, Surprising volume change in PPy (DBS): an atomic force microscopy study, *Adv. Mater.* 11 (1999) 953-957.
- [40] 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 LiClO<sub>4</sub>, *Langmuir* 19 (2003) 2318-2324.
- [41] P.R. Singh, S. Mahajan, S. Rajwade, A.Q. Contractor, EC-AFM investigation of reversible volume changes with electrode potential in polyaniline, *J. Electroanal. Chem.* 625 (2009) 16–26.
- [42] D.S.H. Charrier, R.A.J. Janssen, M. Kemerink, Large Electrically Induced Height and Volume Changes in Poly(3,4-ethylenedioxythiophene)/Poly(styrenesulfonate) Thin Films, *Chem. Mater.* 22 (2010) 3670-3677.
- [43] L.T.T. Kim, C. Gabrielli, A. Pailleret, H. Perrot, Ions/Solvent Exchanges and Electromechanical Processes in Hexasulfonated Calix[6]Arene Doped Polypyrrole Films: Towards a Relaxation Mechanism, *Electrochem. Solid State Lett.* 14 (2011) F9–F11.

- [44] L.T.T. Kim, C. Gabrielli, A. Pailleret, H. Perrot, Correlation between ion-exchange properties and swelling/shrinking processes in hexasulfonated calix[6]arene doped polypyrrole films: Ac-electrogravimetry and electrochemical atomic force microscopy investigations, *Electrochim. Acta* 56 (2011) 3516–3525.
- [45] B. J. West, T.F. Otero, B. Shapiro, E. Smela, Chronoamperometric Study of Conformational Relaxation in PPy(DBS), *J. Phys. Chem. C* 113 (2009) 1277-1293.
- [46] H. Randriamahazaka, Master curve for analyzing the electrochemical ageing and memory effects of poly(3,4-ethylenedioxythiophene), *Smart Mater. Struct.* 20 (2011) 124010 (6pp) .
- [47] T.F. Otero, Reactions drive conformations. Biomimetic properties and devices, theoretical description, *J. Mater. Chem. B*, 1 (2013) 3754-3767.
- [48] L. Bay, T. Jacobsen, S. Skaarup, Mechanism of Actuation in Conducting Polymers: Osmotic Expansion, *J. Phys. Chem. B* 105 (2001) 8492-8497.
- [49] 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.
- [50] S. Kirchmeyer, K. Reuter, Scientific importance, properties and growing applications of poly(3,4-ethylenedioxythiophene), *J. Mater. Chem.* 15 (2005) 2077-2088.
- [51] D. Mantione, I. del Agua, A. Sanchez-Sanchez, D. Mecerreyes, Poly(3,4-ethylenedioxythiophene) (PEDOT) Derivatives : Innovative Conductive Polymers for Bioelectronics, *Polym.* 9 (2017) 354-374.
- [52] Z.A. King, C.M. Shaw, S.A. Spanninga, D.C. Martin, Structural, chemical and electrochemical characterization of poly(3,4-Ethylenedioxythiophene) (PEDOT) prepared with various counter-ions and heat treatments, *Polym.* 52 (2011) 1302-1308.
- [53] C. Li, T. Imae, Electrochemical and Optical Properties of the Poly(3,4-ethylenedioxythiophene) Film Electropolymerized in an Aqueous Sodium Dodecyl Sulfate and Lithium Tetrafluoroborate Medium, *Macromol.* 37 (2004) 2411-2416.
- [54] R. Schweiss, J.F. Lübben, D. Johannsmann, W. Knoll, Electropolymerization of ethylene dioxythiophene (EDOT) in micellar aqueous solutions studied by electrochemical quartz crystal microbalance and surface plasmon resonance, *Electrochim. Acta* 50 (2005) 2849-2856.
- [55] N. Sakmeche, S. Aeiyaeh, J.-J. Aaron, M. Jouini, J.-C. Lacroix, P.-C. Lacaze, Improvement of the Electrosynthesis and Physicochemical Properties of Poly(3,4-ethylenedioxythiophene) using a Sodium Dodecyl Sulfate Micellar Aqueous Medium, *Langmuir* 15 (1999) 2566-2574.
- [56] V. Lyutov, I. Efimov, A. Bund, V. Tsakova, Electrochemical polymerization of 3,4-ethylenedioxythiophene in the presence of dodecylsulfate and polysulfonic anions-An acoustic impedance study, *Electrochim. Acta* 190 (2016) 285-293.
- [57] H. Randriamahazaka, V. Noël, C. Chevrot, Nucleation and growth of poly(3,4-ethylenedioxythiophene) in acetonitrile on platinum under potentiostatic conditions, *J. Electroanal. Chem.* 472 (1999) 103-111.
- [58] H. Randriamahazaka, T. Bonnotte, V. Noël, P. Martin, J. Ghilane, K. Asaka, J.-C. Lacroix, Medium Effects on the Nucleation and Growth Mechanisms during the Redox Switching Dynamics of Conducting Polymers: Case of Poly(3,4-ethylenedioxythiophene), *J. Phys. Chem. B* 115 (2011) 205-216.
- [59] T. Schoetz, C. Ponce de Leon, A. Bund, M. Ueda, Electro-polymerisation and characterisation of PEDOT in Lewis basic, neutral and acidic EMImCl-AlCl<sub>3</sub> ionic liquid, *Electrochim. Acta* 263 (2018) 176-183.
- [60] H. Randriamahazaka, C. Plesse, D. Teyssié, C. Chevrot, Electrochemical behaviour of poly(3,4-ethylenedioxythiophene) in a room-temperature ionic liquid, *Electrochem. Commun.* 5 (2003) 613-617.

- [61] H. Randriamahazaka, C. Plesse, D. Teyssié, C. Chevrot, Ions transfer mechanisms during the electrochemical oxidation of poly(3,4-ethylenedioxythiophene) in 1-ethyl-3-methylimidazolium bis((trifluoromethyl)sulfonyl)amide ionic liquid, *Electrochem. Commun.* 6 (2004) 299-305.
- [62] E. Kumar, A. Bhatnagar, W. Hogland, M. Marques, M. Sillanpää, Interaction of inorganic anions with iron-mineral adsorbents in aqueous media — A review, *Adv. Colloid Interface Sci.* 203 (2014) 11–21.
- [63] J. Agrisuelas, C. Gabrielli, J.J. Garcia-Jareno, H. Perrot, O. Sel, F. Vicente, Electrochemically induced free solvent transfer in thin poly(3,4-ethylenedioxythiophene) films, *Electrochim. Acta*, 164 (2015) 21-30.
- [64] W. Gao, O. Sel, H. Perrot, Electrochemical and viscoelastic evolution of dodecyl sulfate-doped polypyrrole films during electrochemical cycling, *Electrochim. Acta*, 233 (2017) 262-273.

Journal Pre-proof

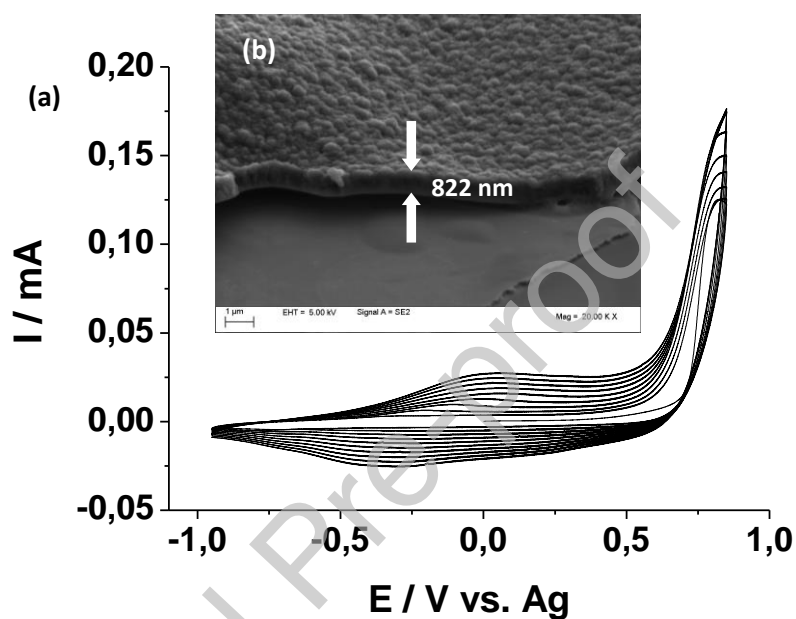


Figure 1 : a) Consecutive cyclic voltammograms (10 consecutive cycles between -0.9 V and +0.85 V vs. Ag) allowing the electrodeposition of a PEDOT film on a platinum working electrode from an aqueous electrolytic solution containing EDOT ( $10^{-2}$  M) and  $\text{LiClO}_4$  (0.1 M). The potential was initially swept from 0 V vs. Ag towards more anodic potentials. b) FEG-SEM image of an electrodeposited perchlorate doped PEDOT film whose thickness is 822 nm in the vacuum conditions of the FEG-SEM chamber.



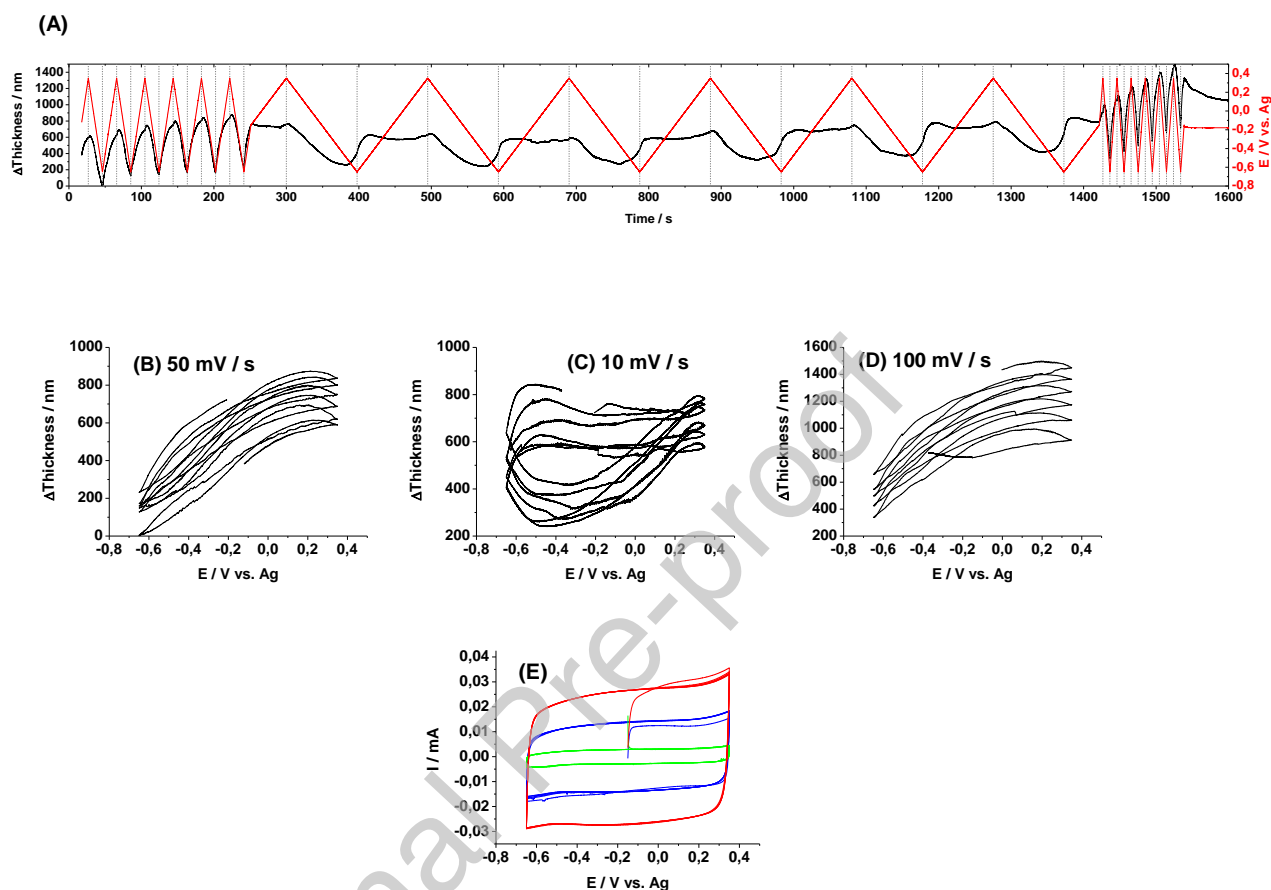


Figure 2 : A) EC-AFM data showing the thickness variation (black curve) of a brand new PEDOT film and its potential conditioning (red curve) performed with the help of cyclic voltammetry, both as a function of time. The potential was swept from -0.15 V vs. Ag towards more anodic potentials. B-D) consecutive cyclic voltathicknograms obtained at B) 50  $\text{mV} \cdot \text{s}^{-1}$ , C) 10  $\text{mV} \cdot \text{s}^{-1}$ , D) 100  $\text{mV} \cdot \text{s}^{-1}$  (6 scans each), and E) consecutive cyclic voltammograms obtained at 50  $\text{mV} \cdot \text{s}^{-1}$  (blue curve), 10  $\text{mV} \cdot \text{s}^{-1}$  (green curve) and 100  $\text{mV} \cdot \text{s}^{-1}$  (red curve) (6 scans each).

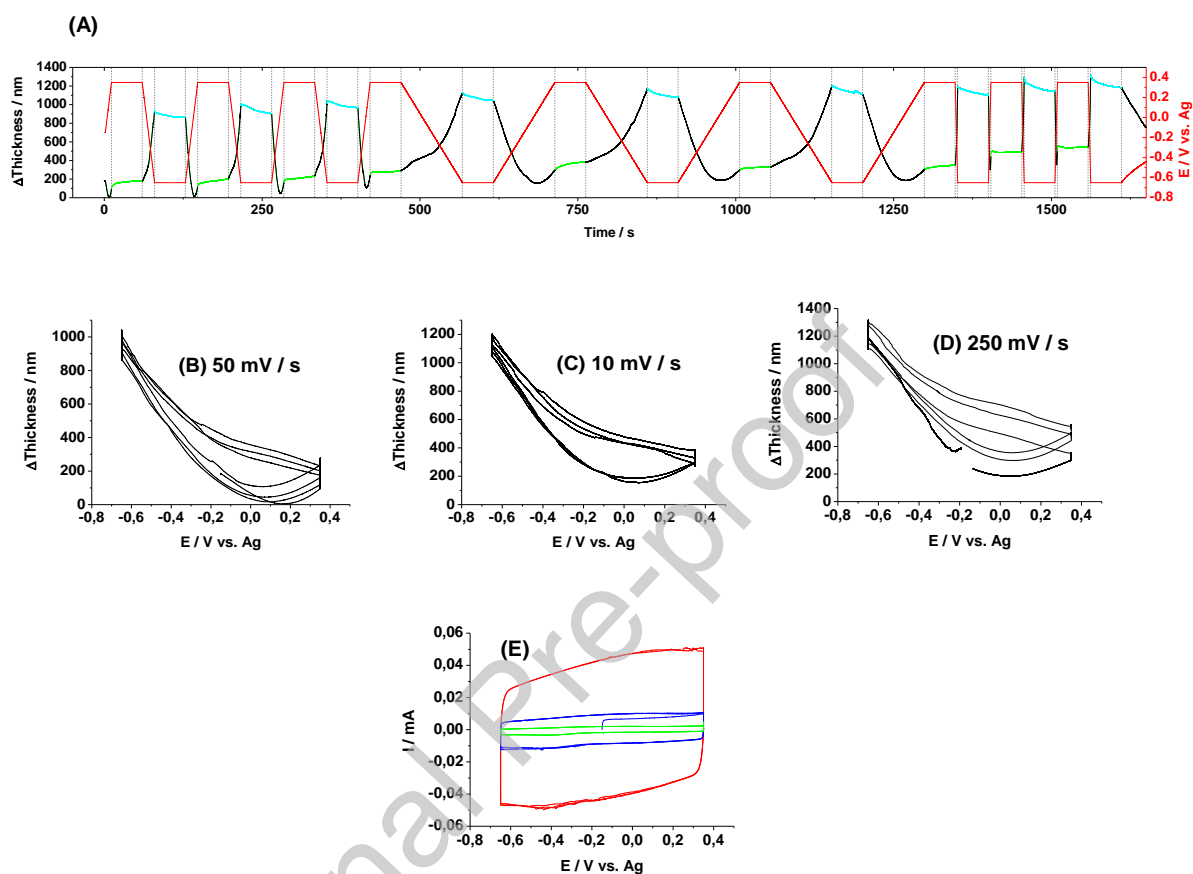


Figure 3 : A) EC-AFM data showing the thickness variation (polychromic curve) of a PEDOT film having undergone previously 200 potential cycles between  $-0.65$  V and  $+0.35$  V vs. Ag, and its potential conditioning (red curve) performed with the help of advanced cyclic voltammetry, both as a function of time. The potential was swept from  $-0.15$  V vs. Ag towards more anodic potentials. B-D) consecutive cyclic voltathicknograms obtained at B)  $50 \text{ mV}\cdot\text{s}^{-1}$ , C)  $10 \text{ mV}\cdot\text{s}^{-1}$ , D)  $250 \text{ mV}\cdot\text{s}^{-1}$  (3 scans each), and E) consecutive cyclic voltammograms obtained at  $50 \text{ mV}\cdot\text{s}^{-1}$  (blue curve),  $10 \text{ mV}\cdot\text{s}^{-1}$  (green curve) and  $250 \text{ mV}\cdot\text{s}^{-1}$  (red curve) (3 scans each).

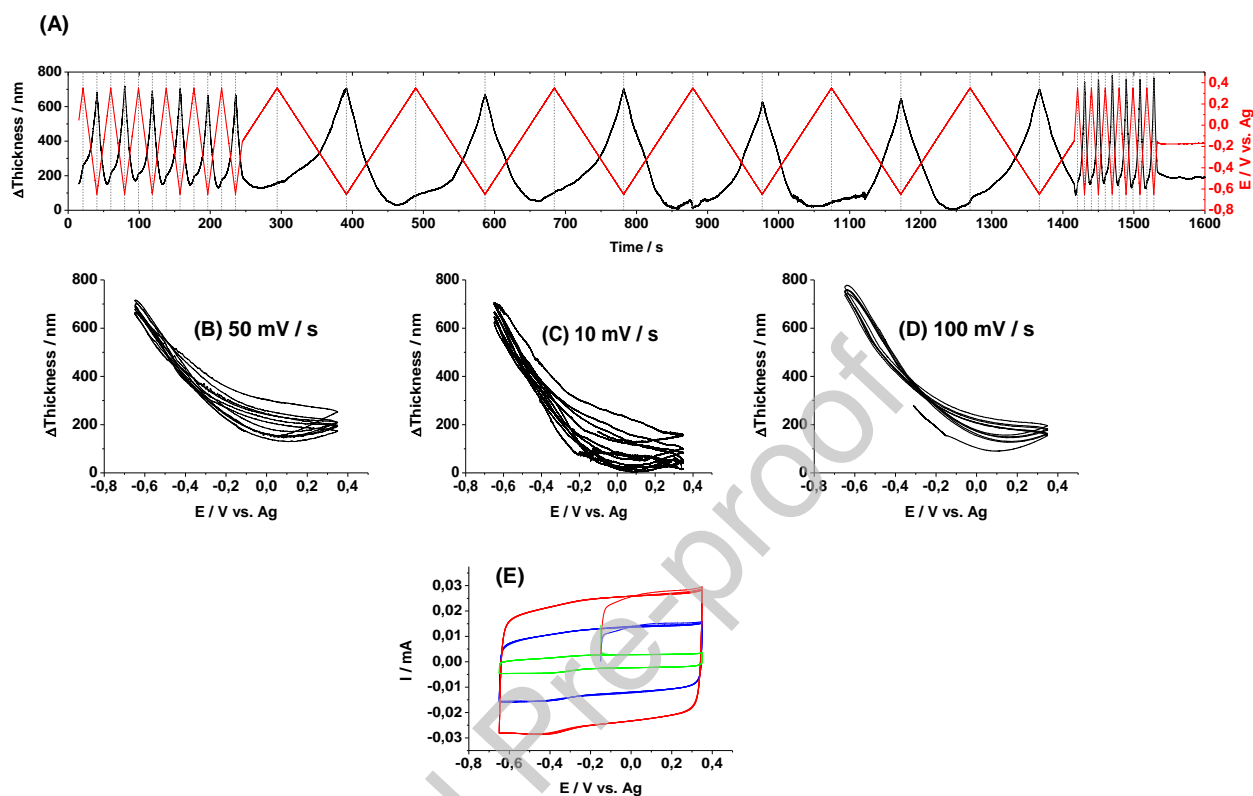


Figure 4 : A) EC-AFM data showing the thickness variation (black curve) of a PEDOT film having undergone previously 15 potential cycles (CV) as well as 27 potential cycles (AdCV) between -0.65 V and +0.35 V vs. Ag, and its potential conditioning (red curve) performed with the help of cyclic voltammetry, both as a function of time. The potential was swept from -0.15 V vs. Ag towards more anodic potentials. B-D) consecutive cyclic voltathicknograms obtained at B) 50 mV.s<sup>-1</sup>, C) 10 mV.s<sup>-1</sup>, D) 100 mV.s<sup>-1</sup> (6 scans each), and E) consecutive cyclic voltammograms obtained at 50 mV.s<sup>-1</sup> (blue curve), 10 mV.s<sup>-1</sup> (green curve) and 100 mV.s<sup>-1</sup> (red curve) (6 scans each).

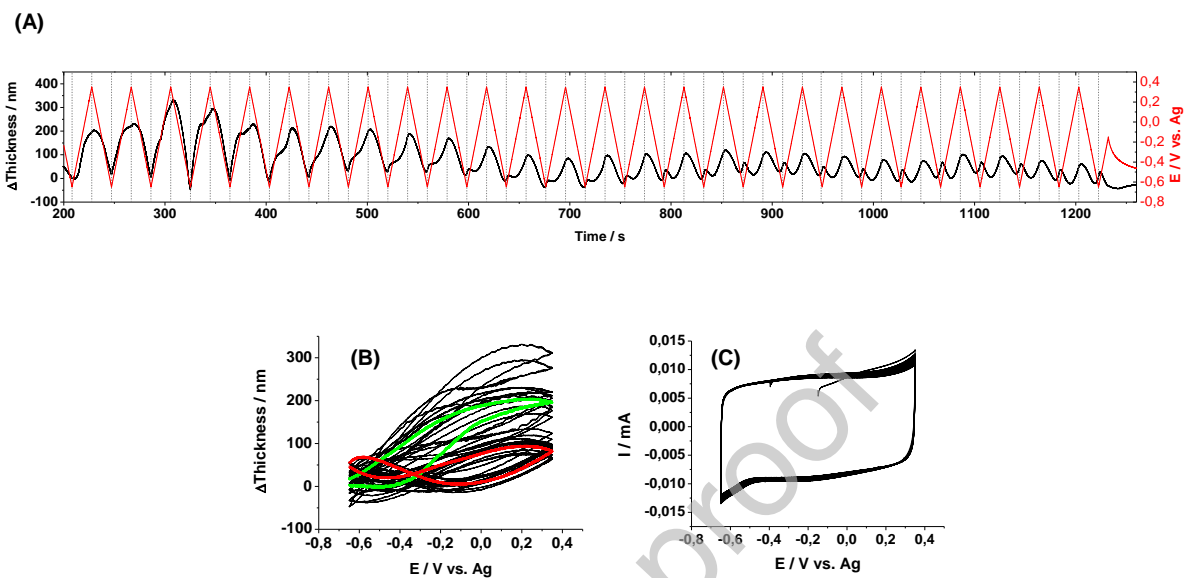


Figure 5 : A) EC-AFM data showing the thickness variation (black curve) of a brand new PEDOT film and its potential conditioning (red curve) performed with the help of cyclic voltammetry, both as a function of time. The potential was swept from -0.15 V vs. Ag towards more anodic potentials B) consecutive cyclic voltathicknograms obtained at 50 mV.s<sup>-1</sup> (26 cycles, 1<sup>st</sup> and last cycles plotted in green and in red respectively) and C) consecutive cyclic voltammograms obtained at 50 mV.s<sup>-1</sup> (26 cycles).

## CRediT authorship contribution statement

**Adrien Mocaër:** Data curation, Investigation, Methodology, Validation, Visualization, Formal analysis. **Françoise Pillier:** Investigation, Formal analysis, Validation, Visualization, **Alain Pailleret:** Conceptualization, Methodology, Validation, Funding acquisition, Writing - review & editing, Supervision

## Declaration of interests

- 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.
- The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

Journal Pre-proof