

Electrochromism and conductivity of sulfonated polyaniline films in propylene carbonate

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Abstract: : In this work we compare the spectroelectrochemical response of electrochemically deposited sulfonated polyaniline and polyaniline films. The electrochromic performance of SPAN is slightly superior to that of PANI, showing faster coloring and bleaching and slightly higher electrochromic efficiency than PANI. Furthermore, submitting SPAN to successive voltammetry scans in LiClO₄/propylene carbonate constitutes a simple method to improve SPAN conductivity by a factor 20.

Keywords: sulfonated polyaniline, electrochromism, propylene carbonate, conductivity.

Introduction

Electrochromic materials attract much interest in academia and industry, both for their fascinating spectroelectrochemical properties and for their commercial applications^{1,2}. A large number of electrochromic materials are presently available. Among them, some of the most important are transition metal oxides¹⁻⁷, Prussian blue systems^{2,7-9}, viologens^{2,6-10} and conducting polymers²⁻¹².

In recent years, conducting polymers (CPs) have received a lot of attention for electrochromic display devices due to the fact that CPs are potentially more processable than inorganic materials, offering again the advantage of a high degree of color tailorability¹³⁻¹⁵. Many investigations concerning polyaniline (PANI) and its derivatives have been reported with results attractive for applications in electrochromic displays^{16,17}. PANI and its derivatives show stability in air and high conductivity at ambient temperature¹⁸. PANI films are polyelectrochromic (transparent yellow to green, dark blue and black), the yellow-green transition being durable to repetitive color switching⁷.

Among many derivatives of PANI, self-doped polyanilines possess some distinct properties, making them promising in a potentially broader field of applications. In 1990, Yue and Epstein¹⁹, and Bergeron et al.²⁰ reported the syntheses of self-doped conducting PANI derivatives. Since these reports many articles have been published dealing with synthesis and properties of self-doped conducting polymers²¹⁻²³.

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Sulfonated polyaniline (SPAN) contains in its structure an ionizable, negatively charged functional group ($-\text{SO}_3^-$), which acts as an inner dopant anion, but differently than in conventional PANI, it is bound to the polymer backbone. Thus, no anion exchange between the polymer and surroundings take place during oxidation or reduction. The charge compensation occurs in this case at the expense of a cation (usually a proton) exchange, that occurs very fast and does not limit the rate of the charging process. Another interesting characteristic regards the conductivity, which remains unchanged for $\text{pH} \leq 7.5$, whereas PANI turns insulating for $\text{pH} > 4$ ^{23,24}.

Li and Mu, quantitatively investigating the electrochromic properties of SPAN, observed that in non-aqueous solution it has a good electrochemical activity and fast charge transfer characteristics²⁵, basic requirements for high performance electrochromic displays. In the present work we report the quantitative investigation of the electrochromic properties of sulfonated polyaniline, comparing it to polyaniline, both studied in propylene carbonate.

Results and Discussion

Electrochemical properties of SPAN and PANI modified ITO-electrodes

The selection of a suitable electrolyte is important for the application of conducting polymers (CPs) in electrochromic devices. Non-aqueous electrolytes provide several advantages for such applications, like wider electrochemical windows and absence of release of hydrogen and oxygen in the operating potential range. According to this point of view and because both polymers, SPAN and PANI, are insoluble in this medium, LiClO_4 dissolved in propylene carbonate (LiClO_4/PC) was selected to infer the spectroelectrochemicals properties of SPAN in relation to PANI³⁰. Figure 1 represents the cyclic voltammograms (CVs) of PANI and SPAN in $0.5 \text{ mol dm}^{-3} \text{ LiClO}_4/\text{PC}$ non-aqueous medium. The solid line is the second response for both polymers and the broken line is the response after steady state current achievement (30 cycles for SPAN and 10 cycles for PANI). Both CVs present similar redox peaks after several voltammetry cycles (dashed lines in the figure), showing only slightly displaced potential values. These peaks are attributed to the same redox processes, which is characteristic of the polyanilines. The first one refers to the leucoesmeraldine-esmeraldine interconversion, while the other one is associated to the esmeraldine- pernigraniline interconversion³¹. Comparing both voltammograms, one can observe that SPAN presents slightly near proximity between anodic and cathodic peaks ($\sim 200 \text{ mV}$), than PANI ($\sim 300 \text{ mV}$). The same behavior was observed by MacDiarmid et al³⁰ and was attributed to higher charge compensation diffusibility than PANI. Furthermore, the SPAN redox peaks are displaced to a lower potential, when compared to PANI, a fact that is more pronounced in the second redox pair. Both peaks contribute to an easier neutralization of the oxidation-involved charges in the case of SPAN³².

Figure 1 shows that the initial values were significantly lower for SPAN and that after successive scans (30 for SPAN and 10 for PANI) both polymers achieved steady-state conditions, the current values for both polymers being quite similar. The increasing peak height on subsequent scans was also reported in the case of polyaniline-poly(p-styrenesulfonic acid) composite (PANI-PSS) that showed morphological modifications after successive voltammeteries³³. This fact was attributed to the increase in the amount of electroactive PANI-PSS composite on the electrode: the surface is initially densely packed, this

densely packed state relaxes and the electrolyte solution penetrates the composite film with continuous potential scanning.

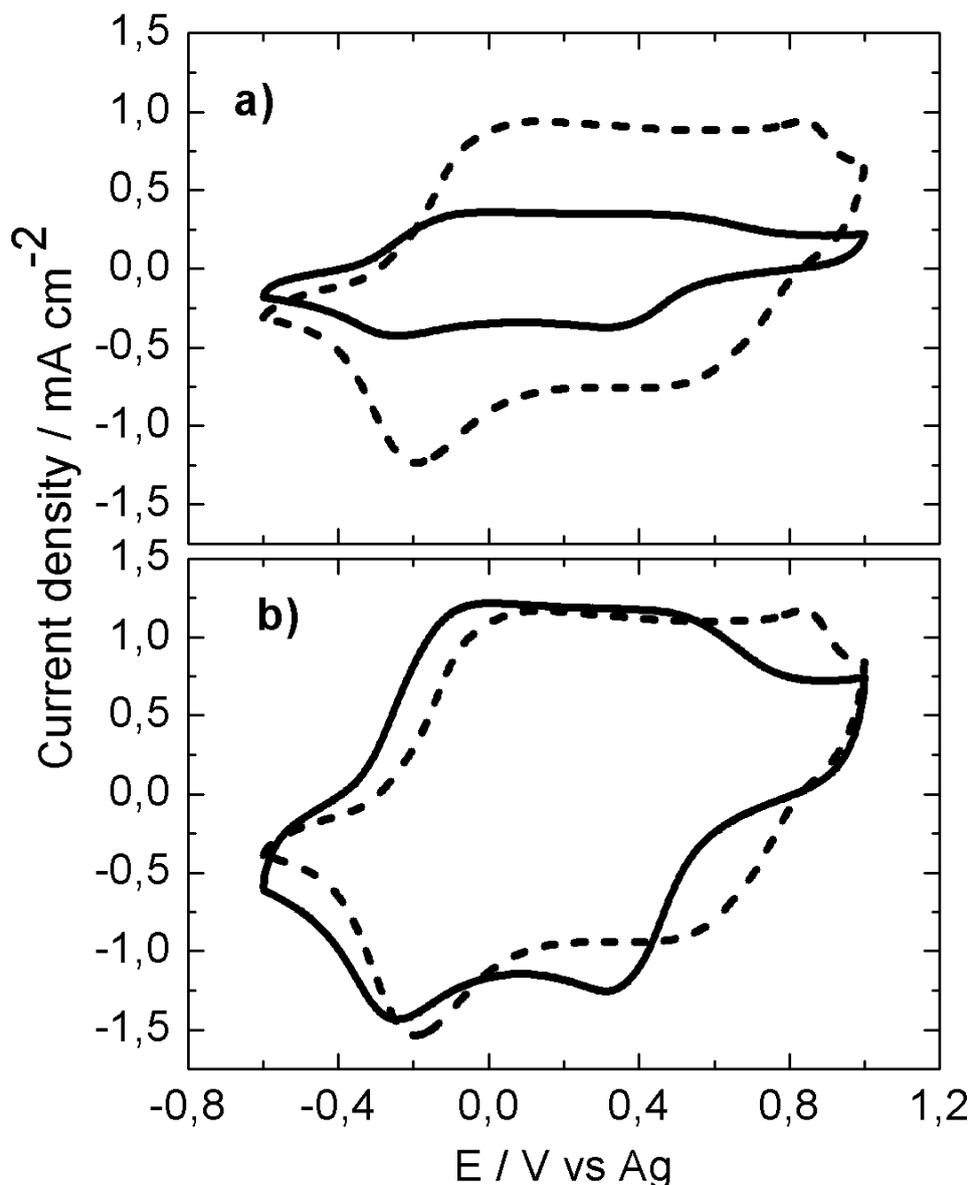


Figure 1: Cyclic voltammograms of SPAN- (a) and PANI- (b) modified ITO-electrode in propylene carbonate solution containing $0.5 \text{ mol dm}^{-3} \text{ LiClO}_4$. The solid line corresponds to the second response and the broken line corresponds to the response after 30 cycles for SPAN and 10 cycles for PANI. Potential scan rate = 100 mV/s .

In order to verify if a similar behavior occurs in the case of SPAN, we compared the SPAN and PANI films before and after the cyclic voltammetry procedures. The corresponding micrographs can be shown in Fig. 2. An alteration can be observed only in the PANI films leading to the disregardment of the hypothesis that the penetration of the electrolyte would relax densely packed electroactive states.

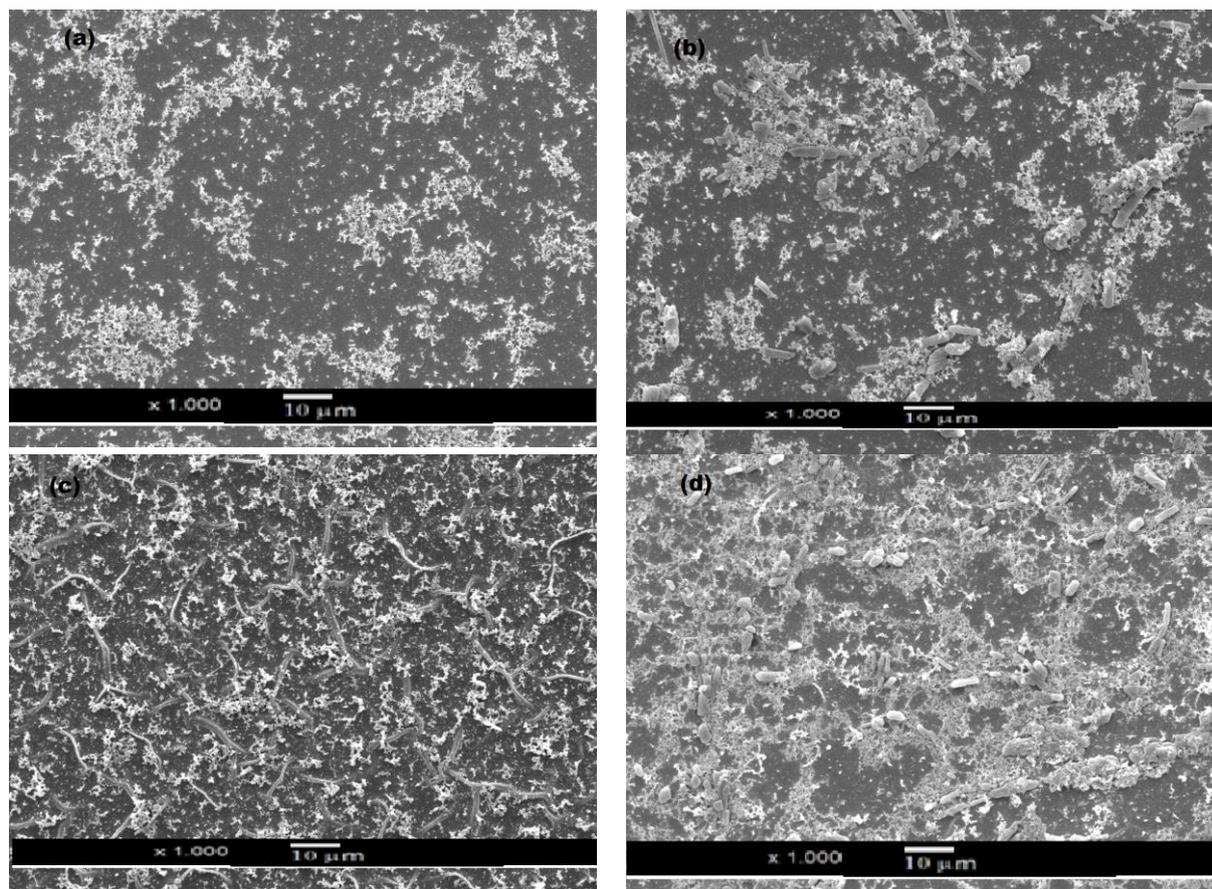


Figure 2: Scanning electron micrographs of the SPAN (a and b) and PANI (c and d) fresh synthesized films (a and c) and after achieving the steady-state (b and d). Extra High Tension = 15 kV.

This observation suggests that the current increase during the successive cyclic voltammetry procedure is due to the increase in the conductivity of the SPAN. UV-VIS-NIR *ex-situ* measurements were also performed before and after the successive voltammetries (see Figure 3). It can be clearly observed that the peaks were displaced. Polyaniline salt doped with CSA and dissolved in appropriate organic reagents (*m*-cresol) has been demonstrated to cause a conformational transition of PANI chains from a “compact coil” to an “expanded coil”, leading to a concomitant increase in conductivity by up to several orders of magnitude. MacDiarmid and Epstein explained this conformational change as the “*secondary doping effect*”, characterized by the presence of a free tail at wavelengths higher than 700 nm. The presence of this free tail in the NIR region for the PANI doped with CSA and PSS films indicates the lowering of the PANI band gap, consequently resulting in high conductivity³⁰⁻³⁵. For SPAN, fresh synthesized films present bands at 850 nm, whereas the corresponding for cycled films is located at 1100 nm. Furthermore, a new band at 650 nm appeared, indicating that the film tends to oxidize when exposed to air. For the PANI, a displacement of the peak at 1100 nm to 950 nm of the fresh synthesized film occurs. Following the previous reasoning, it corresponds to a reduction in the band gap of SPAN and an increase in the band gap of PANI after successive cyclic voltammetries, which is consistent with the changes in the conductivities of the polymers.

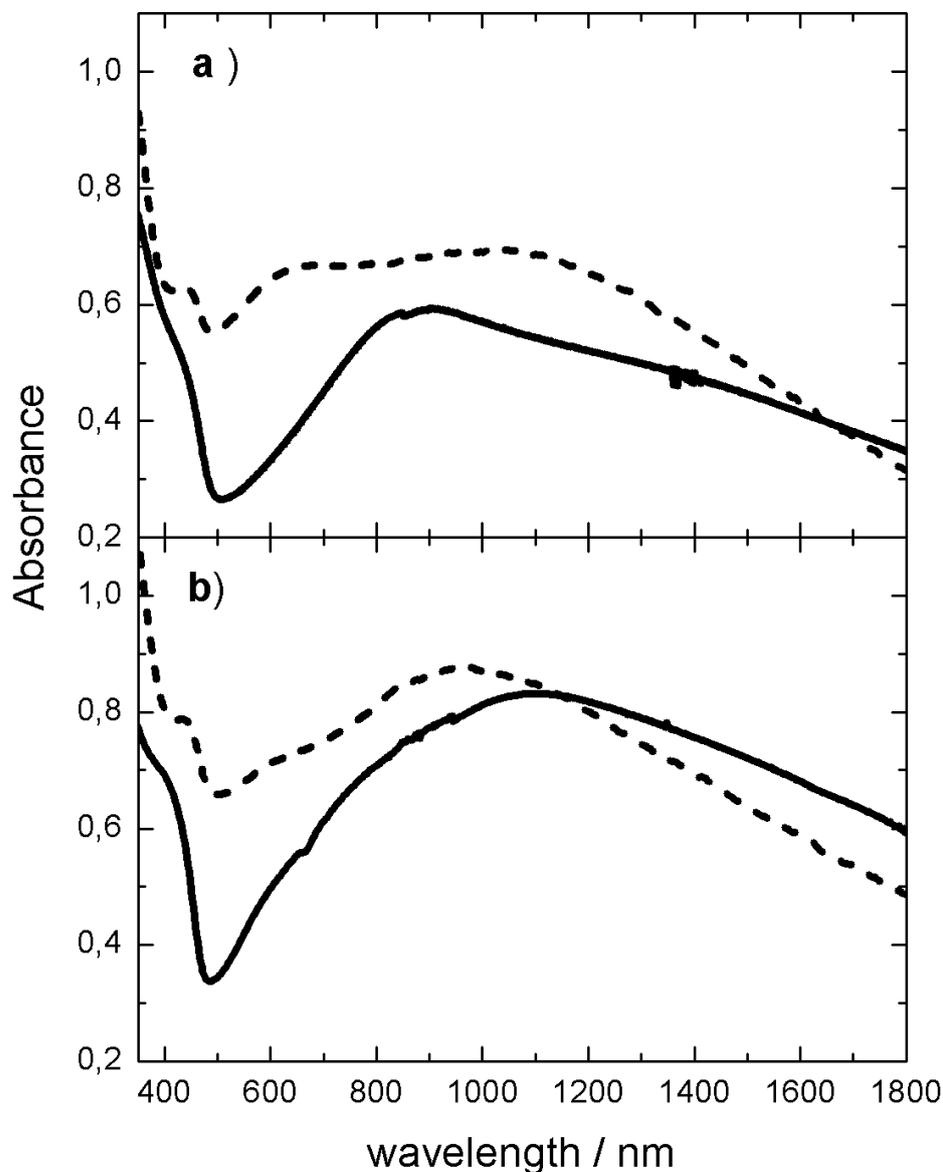


Figure 3: Absorbance spectra of ITO/SPAN (a) and ITO/PANI (b) fresh synthesized films (solid line); and after achieving the steady-state (broken line).

In order to verify if the conductivity changes, it was estimated using sandwich-like devices (area = 1.0 mm²) measuring the current-voltage characteristics at two terminals. Table 1 shows the conductivity values for SPAN and PANI films just after preparation and for films submitted to successive cyclic voltammetries. This data evidences an increase of the conductivity of the SPAN films submitted to successive cyclic voltammetries by a factor 20, whereas the PANI films showed a slight conductivity decrease after the same procedure. Furthermore, the strong thickness and variation observed in the case of PANI (~120% and ~)

when compared to SPAN (~14%) indicates a stronger participation of the electrolyte ions in the redox process of the former.

Table 1: Conductivities of synthesized SPAN- and PANI-films.

Polymer	Conductivity / $10^{-3} \text{ S.cm}^{-1}$	Thickness / nm	Average roughness / nm
PANI (fresh synthesized)	2.2 ± 0.2	414	92
PANI (steady state)	1.7 ± 0.2	926	373
SPAN (fresh synthesized)	0.11 ± 0.01	380	46
SPAN (steady state)	2.6 ± 0.3	435	57

Spectral properties of SPAN and PANI modified ITO-electrodes

Several UV-VIS *in situ* investigations of PANI were reported so far. Stilwell and Park³⁵ showed that there are four different optically active species in PANI films, which are directly dependent on the applied potential: one leuco-form, absorbing at 320 nm, one cation radical form absorbing at 440 nm, delocalized free electron states absorbing at ~800 nm, and a quinoid form absorbing at ~650 nm. There is less available information for SPAN than for PANI, but it is known that the sulfonic group influences sterically and electronically the molecular backbone³⁰, resulting in a hypsochromic displacement of the bands. In the case of polyaniline, the transition between leucoemeraldine and emeraldine is reversible, but the transition from pernigraniline occurs concomitantly with the polymer degradation in aqueous media. In non-aqueous organic media, one intermediate stable oxidized blue form can be obtained before the irreversible formation of pernigraniline³⁶⁻³⁹. To investigate the transition from the leucoemeraldine to this blue form and the related spectral variations due to the different oxidation states of PANI and SPAN, electronic absorption spectra of PANI- and SPAN-coated ITO samples were measured *in situ* at various applied potentials ($-0.6 \text{ V} < E < +1.0 \text{ V}$ versus silver wire).

Figure 4 shows the electronic absorption spectra at different potentials. It can be observed that the spectral behaviour of both polymers is qualitatively similar, without significant displacements of the absorption bands, as observed in aqueous media. It can also be noted that 600 mV is the lowest potential at which both polymers show bluish. For a more detailed analysis of electrochromic properties of SPAN and PANI, characteristics like response time, electrochromic efficiency (η) and coulombic efficiency (CE) were evaluated¹¹.

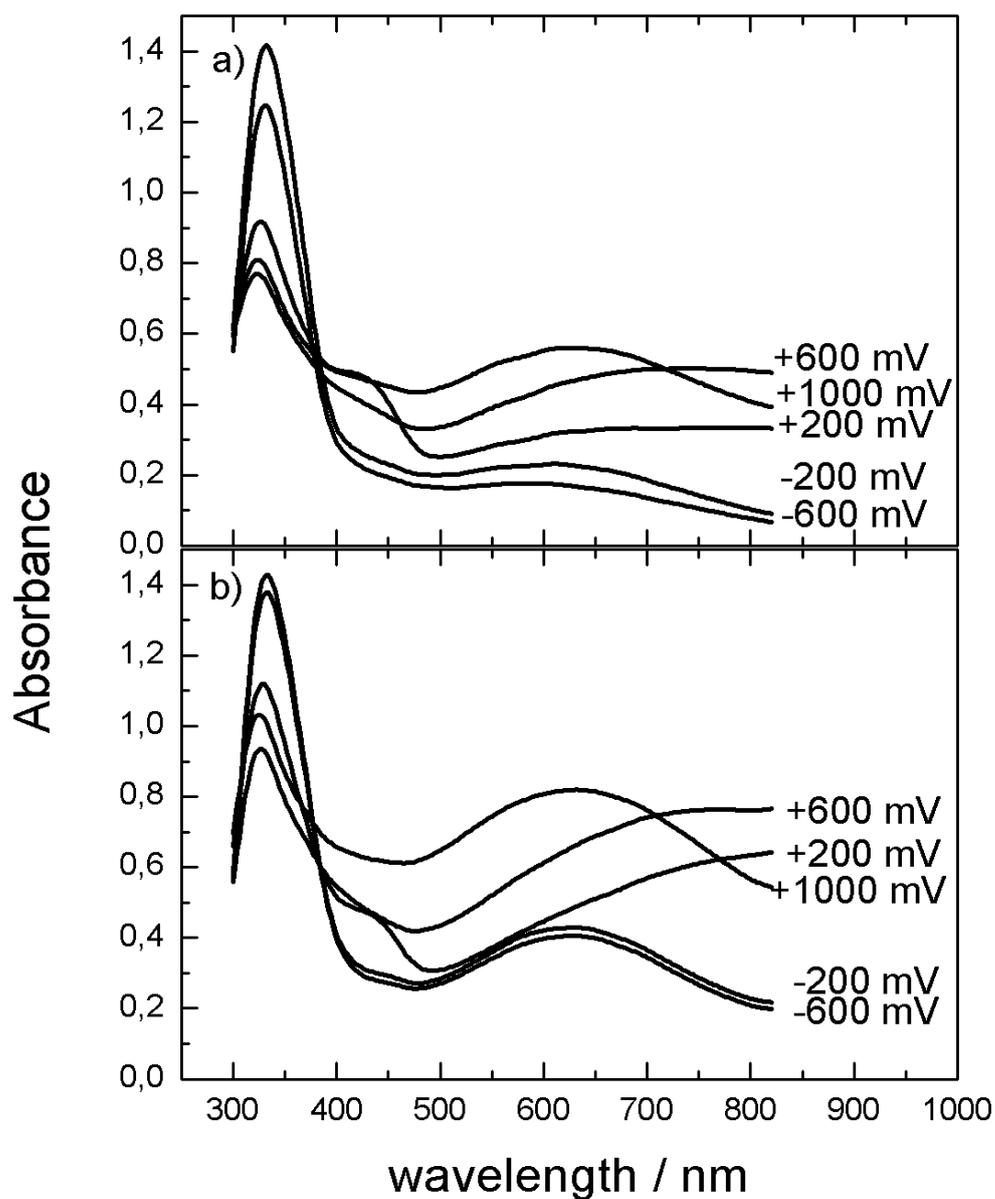


Figure 4: Absorbance spectra of the ITO/SPAN (a) and ITO/PANI (b) equilibrated in $0.5 \text{ mol dm}^{-3} \text{ LiClO}_4/\text{PC}$ at different applied potentials vs. silver wire.

Response time of SPAN and PANI films

The coloration (bleaching) time, defined as the time taken for the transmittance to decrease (increase) by two-thirds of the difference between the steady-state transmittances in the

bleached (colored) and colored (bleached) states⁴⁰ was measured. A double potential step chronoamperometry was performed to estimate the response time. Potentials were stepped between -0.5 V and +0.6 V with a residence time of 60 s. As can be seen from Fig. 5, the bleaching time is about 1.5 s in case of SPAN and 4.0 s for PANI; and the coloring time is about 3.0 s for SPAN and 4.0 s for PANI, indicating a faster response in the case of SPAN, especially regarding the bleaching process. This characteristic is consistent with the charge compensation and cation exchange mechanism cited before.

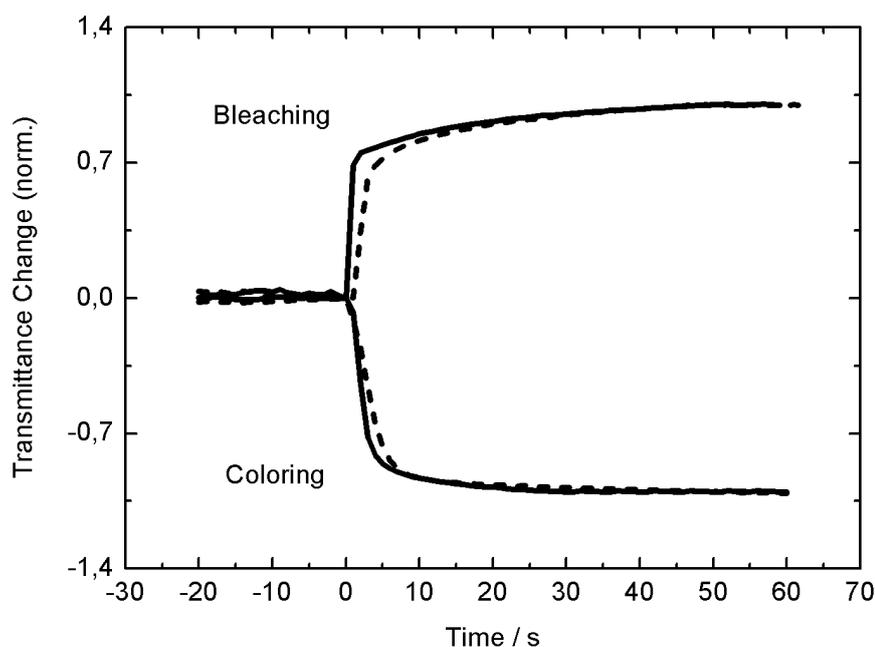


Figure 5: Transient optical transmission at 620 nm of SPAN (solid line) and PANI (broken line) films following applications of - 0.5 V (bleaching) and + 0.6 V (coloring) during 60s.

Transmittance response and electrochromic efficiency of SPAN and PANI modified ITO-electrodes

Electrochromic efficiency (η), also called coloration efficiency, is a parameter widely used for electrochromism quantification, defined as the product of the injected/ejected charge per electrode area (Q_d) and the change in optical density, ΔOD , at a specific wavelength (λ_{max}).

$$\eta = \Delta OD(\lambda) / Q_d \quad (1)$$

where $\Delta OD = \log[T_{ox}/T_{red}]$ for bleaching and $\Delta OD = \log[T_{red}/T_{ox}]$ for coloring⁴⁰. A good electrochromic material presents larger optical changes for a small amount of consumed charge.

A double potential step chronoamperometry was performed to estimate the response time and its stability during 500 consecutive scans. The potential was stepped between - 0.5 V and + 0.6 V with a residence time of 20 s, recording the electrical and optical response simultaneously, as shown in Fig. 6. The analysis of these data indicates that SPAN presents superior optical stability (see $\Delta T\%$ in Table 2), but there is a degradation of these values with time evolution, like in case of PANI. However, differently than PANI, the SPAN does not

tend to exhibit higher absorbance values, a characteristic that may be relevant when device applications are considered. The electrochemical stability of both polymers is similar, but since the $\Delta T\%$ values of SPAN are higher, it would in principle show higher electrochromic efficiency. Table 2 e 3 quantify the electrochromic performance of both polymers, demonstrating that SPAN has not larger electrochromic efficiency. This fact is related to the lower charge values involved in the PANI redox process, which then leads to an apparent increase in the electrochromic efficiency of PANI due to a lower denominator in Eq. (1). In addition, PANI has coulombic efficiency ($CE = Q_{ox}/Q_{red}$)^{11,40} higher than 100%. This fact is simply a consequence of the oxidation charge being larger than the reduction one, a common situation in environments containing oxygen. Differently than PANI, SPAN has coulombic efficiency quite near to the ideal value of 100%. These characteristics make SPAN a promising candidate for working electrodes in electrochromic devices.

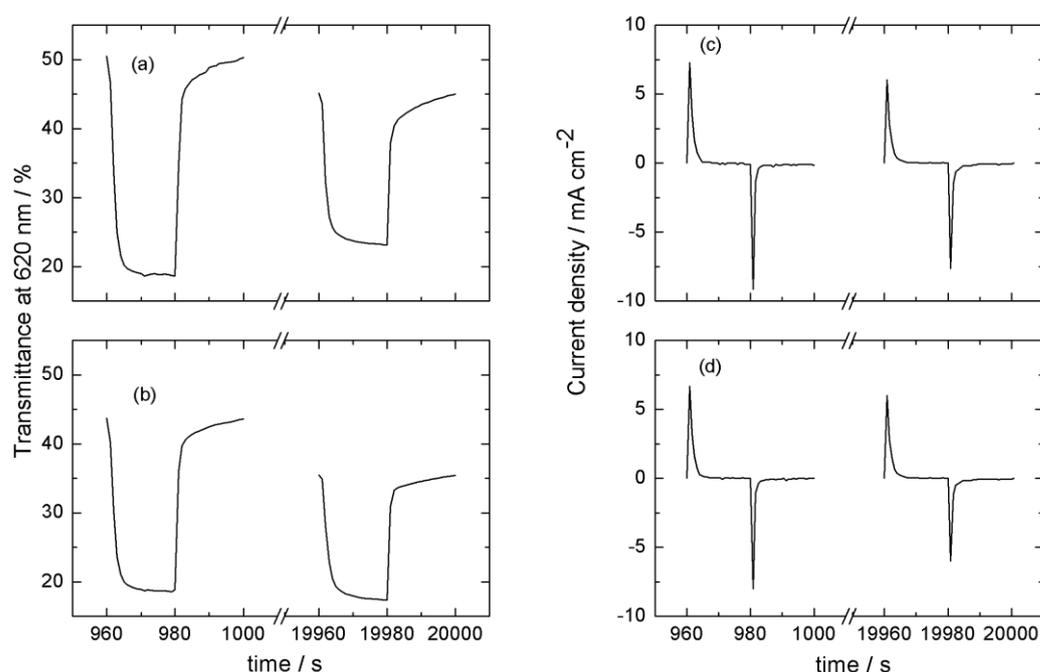


Figure 6: Optical response of SPAN (a) and PANI (b) and Electrical response of SPAN (c) and PANI (d) in a $0.5 \text{ mol dm}^{-3} \text{ LiClO}_4$ solution in propylene carbonate during 500 double step chronoamperometry. Only the 25th and the 500th are shown, for clarity. The applied potentials were + 0.6 V and – 0.5 V, during 20 s in each case.

Table 2: Double potential step results for the SPAN-films.

Cycle Number	Q_{ox} (mC cm^{-2})	Q_{red} (mC cm^{-2})	$\%T_{ox}$	$\%T_{red}$	$\Delta\%T_{620\text{nm}}$	η_{ox} ($\text{cm}^2 \text{C}^{-1}$)	η_{red} ($\text{cm}^2 \text{C}^{-1}$)	CE (%)
1	11.9	11.9	52.0	19.3	32.7	36.2	36.2	100.0
25	10.9	11.0	50.5	18.6	31.9	39.9	39.4	99.1
200	10.6	10.7	47.7	21.4	26.3	32.8	32.5	99.1
500	9.8	10.0	45.2	23.1	22.1	29.7	29.1	98.0

Q_{ox} , Q_{red} = oxidation and reduction charges. $\Delta\%T_{620\text{nm}}$ = optical contrast at 620 nm. η_{ox} , η_{red} = electrochromic efficiency for coloring and bleaching processes. CE = coulombic efficiency.

Table 3: Double potential step results for the PANi-films.

Cycle Number	Q_{ox} (mC cm ⁻²)	Q_{red} (mC cm ⁻²)	% T_{ox}	% T_{red}	$\Delta\%T_{620nm}$	η_{ox} (cm ² C ⁻¹)	η_{red} (cm ² C ⁻¹)	CE (%)
1	15.1	9.7	52.4	20.3	32.1	27.2	42.3	155.7
25	10.7	8.5	43.7	18.8	24.9	34.2	42.9	125.9
200	10.5	8.3	40.2	18.2	22.0	32.8	41.5	126.5
500	9.7	7.9	35.5	17.3	18.2	32.0	39.6	122.8

Q_{ox} , Q_{red} = oxidation and reduction charges. $\Delta\%T_{620nm}$ = optical contrast at 620 nm. η_{ox} , η_{red} = electrochromic efficiency for coloring and bleaching processes. CE = coulombic efficiency.

Conclusion

Comparative *in situ* spectroelectrochemical studies have been carried out on sulfonated polyaniline (SPAN) and polyaniline (PANI) films in 0.5 mol/L LiClO₄ propylene carbonate. The results indicate that SPAN shows a better optical response than PANI, but a worse electrical behavior, resulting electrochromic efficiency only slightly higher than that of PANI. Furthermore, submitting SPAN to successive voltammetry scans in LiClO₄/propylene carbonate constitutes a simple method to improve SPAN conductivity by a factor 20.

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Experimental Section

A conventional three-electrode electrochemical cell was used for the preparation of PANI and SPAN films. The film deposition was carried out in aqueous medium (0.3 mol dm⁻³ perchloric acid) in a one-compartment cell containing 0.12 mol dm⁻³ aniline for PANI synthesis and 0.02 mol dm⁻³ aniline + 0.10 mol dm⁻³ metanilic acid for SPAN synthesis. The electrochemical polymerization of metanilic acid in the absence of aniline results in the formation of soluble oligomers without formation of an adhered film on the electrode^{26,27}. An ITO-coated glass (Delta Technologies, $R \leq 20 \Omega$ per square) was used as the working electrode (electrode area: 2.0 cm²) and graphite as the counter electrode. The potentials in the synthesis experiments were measured using Ag/AgCl/KCl_{sat} as the reference electrode. Polymeric films were electrodeposited by the potential pulse technique: the potential was square-wave modulated from a base potential without observable faradaic reaction (-0.15 V) to a potential at which anodic oxidation of the starting materials occurs (+1.3 V). The potential modulation frequency was 0.5 Hz. This technique allows a continuous and homogeneous film buildup²⁸. Following these conditions the PANI synthesis procedure was applied during 8 minutes and the SPAN one during 20 minutes to obtain 400 ± 26 nm thick films. After synthesis, the films were reduced through the application of -0.5 V during 60s.

The polymers film thickness and Average Roughness were determined using a surface profiler and the deposition time was selected in order to produce films of the same thickness for both polymers, allowing a comparison of the electrochromic properties. After electropolymerization the deposited films were rinsed with purified water and dried in an oven in air at 60 °C. In the sequence, measurements aiming at the quantification of the electrochromic performance were carried out in 0.5 mol dm⁻³ lithium perchlorate dissolved in propylene carbonate (LiClO₄/PC). A silver wire immersed in the electrolytic solution was used as the pseudo-reference electrode and platinum wire as counter-electrode. Spectroelectrochemical studies were done in a glass cell of 1 cm path length. The absorbance spectra ranging between 350 to 800 nm were measured at different equilibrated potentials; the *ex situ* spectra wavelength range was 350 - 1800 nm. The dynamic transmittance responses were measured *in situ* by a double potential method.

Both electrochemical synthesis and spectroelectrochemical studies were performed in both conditions, in the presence and in the absence of oxygen. Since these conditions lead to comparable results, the work was performed in the presence of oxygen.

The surface morphology was analyzed with a Jeol-JSM-6306LZ scanning electron microscope.

The conductivity of the polymeric films was estimated using sandwich-like structured devices, in the two terminals mode. The bottom contact was ITO followed by polymer electrodeposition through of the above-cited method. In the sequence, the upper metallic contact (aluminum) was thermally deposited at 10⁻⁶ torr onto the polymer film to complete the device. The resistance can be estimated using this two-terminal measurement technique because such polymer films form ohmic contacts with these electrodes²⁹.

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