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Electrochromic properties of poly(o-methoxyaniline)-poly(3-thiophene acetic acid) layer by layer films



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ABSTRACT

In this work, a new material was developed to be used as the active electrode in an electrochromic device based on layer-by-layer poly(o-methoxyaniline) and poly(3-thiopheneacetic acid) films. Its properties were compared to a poly(o-methoxyaniline) film prepared by *casting* with similar electrochemical properties. The film preparation technique, layer-by-layer, guarantees molecular interaction between layers. In this case, the interaction leads to a self-doping effect, inhibiting the ion transport from the solution to the polymer which is the rate limiting step during the device operation. The results show both a decrease in the time constant for color change as well as a strong increase in the coloration efficiency, from 144.7 to 542 cm² C⁻¹ for POMA *casting* and LBL films, respectively.

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1. Introduction

A broad class of optically active materials has been continuously investigated by different research groups aiming at their use to decrease energy consumption in buildings. In this sense, chromogenic windows have been proposed as an important device to decrease the energy spent, since they optimize energy usage by controlling the daylight input [1]. These materials have the property of changing color as a response to external stimuli such as temperature, pressure, light irradiation or electrical field. This last effect is called electrochromism. The first electrochromic device (ECD) was described in 1969 [2] using WO₃ thin films which reversibly changed color upon electrical polarization. Since then, several electrochromic materials have been studied such as transition metal oxides, Prussian blue, cyanine derivatives, viologens and conducting polymers [3]. WO₃ is one of the most promising inorganic electrochromic materials. However, single color change and slow switching speed limit its application. Nowadays, organic electrochromic materials, i.e., conducting polymers (CPs), are promising samples for usage in these devices due to multicolor, fast switching speed, low cost, flexibility and processability advantages [4]. The electrochromic properties of conducting polymers have been receiving much attention in the last years [5–19]. Polyaniline and derivatives are between the most common CPs studied. However, the values for the coloration efficiency of PANI are not higher than 200 cm² C⁻¹ [13,15,20,21] and this is one of

the most important parameters, together with cycling stability, for the optimization of electrochromic devices.

An electrochromic device is an electrochemical system in which the color variation occurs by reversibly polarizing the electrodes anodically and cathodically. For this reason, these materials must support a large number of cycles and present a high switching speed. In addition, a high coloration efficiency (CE) is important, meaning that small charge densities are required to lead to the color switching, i.e., a high CE provides faster color changes and a longer power supply [22]. Instabilities in ECD can be caused by different sources, such as mechanical degradation and accumulation of ions in the electrodes after several cycles. Mechanical instabilities arise from the stress during the cycling, which is very common in conducting polymers. In CPs, the switching cycles are promoted by redox processes in which the oxidation (reduction) processes lead to the intercalation (deintercalation) of counter ions to compensate the generated charge in the material resulting also in a volume change. Then, due to the redox reaction, both degradation factors, ion accumulation and mechanical degradation, can occur.

Considering these facts, it is proposed that the self-doping effect is one way to optimize these properties. The self-doping is commonly reached by the introduction of SO₃⁻ lateral groups in the polymeric chain. In a different approach to achieve self-doping, we have proposed, in previous papers, the use of layer-by-layer materials in which one layer is electrochemically active and the other has the counter ions necessary to compensate charges during the redox reactions [23]. In addition, the self-doping effect of layer-by-layer electrodes leads to important improvements in their properties such as an increase in the specific capacitances [24] and extended life cycle [25].

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Considering the exposed above, in this work, we have investigated a poly(*o*-methoxyaniline)/poly(3-thiophene acetic acid) - POMA/PTAA film prepared by the layer-by-layer technique on an indium tin oxide/glass (ITO) substrate in order to investigate its electrochromic properties. It is important to stress out that one layer (poly-3-thiophene acetic acid, PTAA) just acts as a counter ion source for the second one (poly-*o*-methoxyaniline, POMA). In this synthesis procedure, films with a few monolayers of thickness are produced at each bilayer deposition cycle, promoting the self-doping effect, which has already been reported in previous works [23,24,26].

2. Experimental

2.1. Materials and Methods

POMA (Research Chemicals) and PTAA (Aldrich) have been synthesized by direct chemical oxidation of the monomer as described by MacDiarmid [27] and Sugimoto [28], respectively. The layer-by-layer films were prepared from solutions of POMA (polycation) and PTAA (polyanion). The polycation solution was prepared by dissolving 20 mg of POMA in a mixture of H₂O and acetonitrile (J.T. Baker), ACN, in a proportion of 59:1 (v/v). ACN was used to enhance the solubility of the polymer in water. The polyanion solution was prepared by dissolving 13.5 mg of PTAA in 25 μ L of a 0.1 M NH₄OH (Chemis) solution, with the final pH adjusted to 8 by the addition of a 0.1 M HCl (Synth) solution [29]. Both solutions were centrifuged using an EPPENDORF centrifuge model 5804, and the insoluble residues were discarded. To prepare all solutions reverse osmosis ultrapure water (Milli-Q system) was used.

The layer-by-layer films were assembled first by immersing the substrate in the POMA polycation solution for 3 min, then in the PTAA solution using a homemade robot developed specifically for this task [30]. Between each step, the material was washed in water with pH adjusted to the same value used in the deposition solution and then dried in N₂ flux. These steps were repeated until the desired number of layers was reached. Glass substrates covered with indium tin oxide, ITO, (MTI Corp. area = 1 cm²) were used as substrates for the working electrodes. These substrates were previously etched with a H₂O₂/NH₄OH/H₂O [1:1:5 (v/v)] solution and washed in ultrapure water in order to prepare a hydrophilic surface.

To compare the results with conventional conducting polymer films, POMA film electrodes were prepared by *casting* the POMA solution onto an ITO substrate. To compare the electrochemical properties of the films, both electrodes, POMA/PTAA LBL and POMA *casting* films, had similar voltammetric charges. Considering this purpose, films containing 100 bilayers of POMA/PTAA and 250 μ L of POMA were built by LBL and *casting* techniques, respectively. Their UV–vis transmittance spectra were measured using an Ocean Optics model HR2000+ spectrometer. The film morphologies were studied using Field Emission Gun - Scanning Electron Microscopy (FEG-SEM) (ZEISS model 105 DSM940A) with 10 keV of accelerating voltage.

Electrochemical experiments were carried out in a three-electrode glass cell using an Autolab potentiostat model PG Stat 30, and all experiments were carried out at room temperature. The measurements were performed in 0.1 M LiClO₄ (Alfa Aesar) acetonitrile solution. As reference and auxiliary electrodes, an Ag pseudo reference electrode and a Pt sheet (area 1 cm²) were used, respectively.

The electrochromic properties of the films were investigated by measuring the UV–vis optical density during an electrochemical experiment. For this task, the spectrophotometer was coupled to

the potentiostat and a potential step between -0.2 V and 0.5 V for 30 s in each value was applied to the working electrode. To test the stability of the electrodes for 3000 cycles, a potential step between -0.2 V and 0.5 V during 3 s in each potential was used. In both set of experiments, the optical density was measured at 700 nm, a condition in which the color change is significant.

3. Results and discussion

To compare the electrochromic properties of both films we have proposed to study electrodes with similar voltammetric charges. This aspect is important because of the existence of ion intercalation (deintercalation) during the oxidation (reduction) of the POMA active layer. Then, if the charges were different, the time constant for this process could be different, i.e., different times are necessary to complete the color changing process. As consequence, the experimental conditions used for the POMA *casting* film would not be adequate to be compared with the LBL film. Considering these facts, we have prepared films for which the voltammetric charges were 2.0 mC and 2.4 mC for *casting* and LBL films, respectively, assuring that the films are electrochromically comparable (Fig. 1(a) and (b)).

Fig. 1(a) and (b) present CV curves for both electrodes. The voltammetric profiles have the same general shape, which are fingerprints of POMA films, i.e. the LBL film (Fig. 1d) presents important electrochemical fingerprints of POMA (Fig. 1b). In Fig. 1a, CV of the POMA *casting* electrode, it is possible to observe one redox process; an anodic current peak at $E = -0.04$ V and the reduction current peak at $E = -0.07$ V can be identified, which are also observed in the same potential range in Fig. 1b. Under the experimental conditions investigated, the PTAA layer is not electrochemically active [23,24,26]. Then, the large current peak in the 0.4 V range could be related to POMA as was observed, for example, for the quinone/hydroquinone redox pair, which has been observed for polyaniline electrodes as well as for its derivatives [31] under some conditions. A second possible explanation is an interaction of both polymers due to the heterostructure characteristics of the film. It is important to stress out that both samples have similar globular morphologies that are typically observed in conducting polymers [32], as can be observed in Fig. 1(c) and (d).

Fig. 2 shows the transmittance spectra in the visible region for both films in the reduced, $E = -0.2$ V, and oxidized, $E = 0.5$ V, states. The spectra are qualitatively similar, although, due to the absorption related to the PTAA polymer in the visible range, there is an important decrease in the maximum transmittance value. In the oxidized state, there is a maximum of 80% at 500 nm and 38% at 530 nm for the POMA and POMA/PTAA LBL film, respectively. From a different point of view, the observed electrochromic changes upon oxidation are similar, meaning a decrease in the transmittance in the red portion of the spectra. Such decrease is more important in the LBL film. In addition, considering that the voltammetric charges for both electrodes are close to each other, the electrochromic effect is stronger for the LBL film than for the POMA *casting* electrode. An extensive investigation of the electrochromic behavior of these samples is presented in Fig. 3, where the potential step perturbation, the current and transmittance responses for both samples are presented.

Fig. 3 presents the variation of transmittance vs. time due to the application of a potential step perturbation as well as the current density response for each studied sample. In this experiment, the polarization time used was 30 s in order to follow a complete change in color. As expected, for both samples, the current transients have a maximum value at 4.70 and 4.76 mA cm⁻² for POMA *casting* and POMA/PTAA LBL films, respectively,

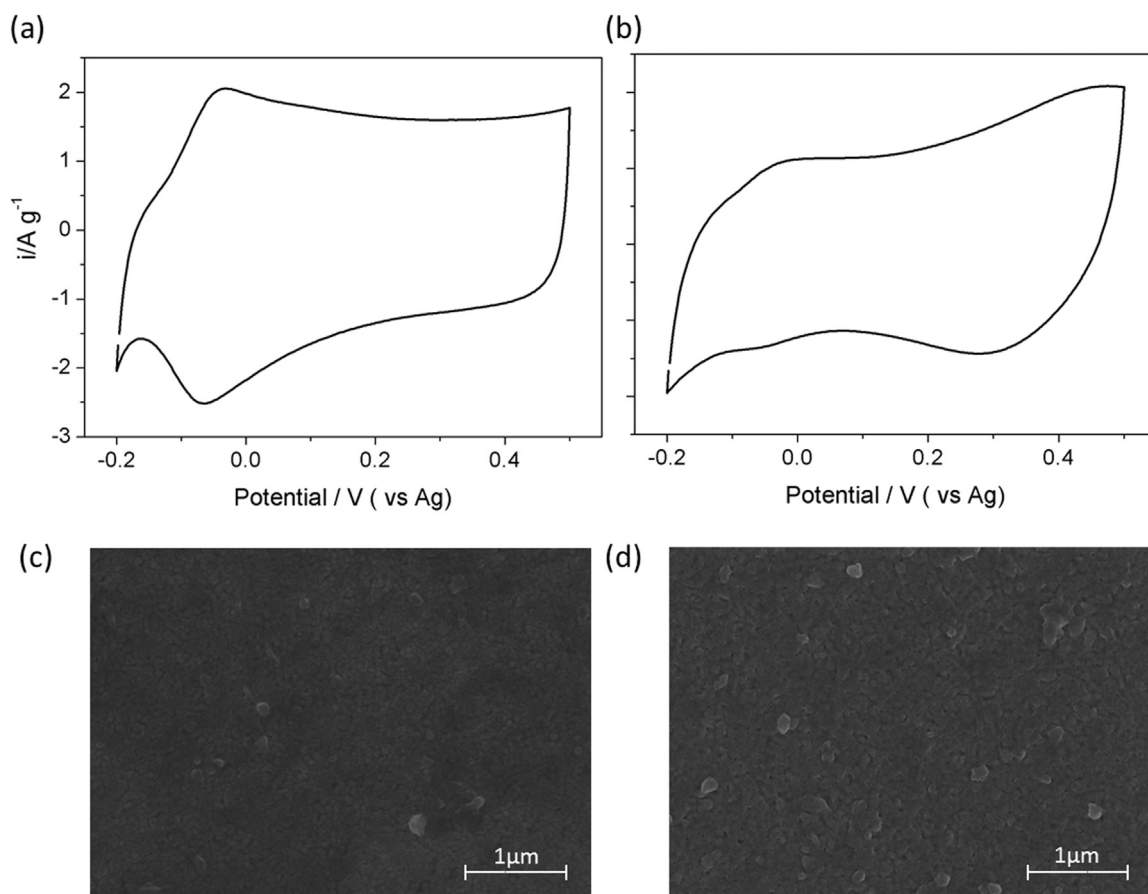


Fig. 1. Cyclic voltammograms for (a) POMA casting film and (b) POMA/PTAA LBL film and SEM micrographs (c) POMA casting and (d) POMA/PTAA LBL films on ITO substrates. Measurements were made in 0.1 M LiClO₄ in acetonitrile at 20 mV s⁻¹ at room temperature.

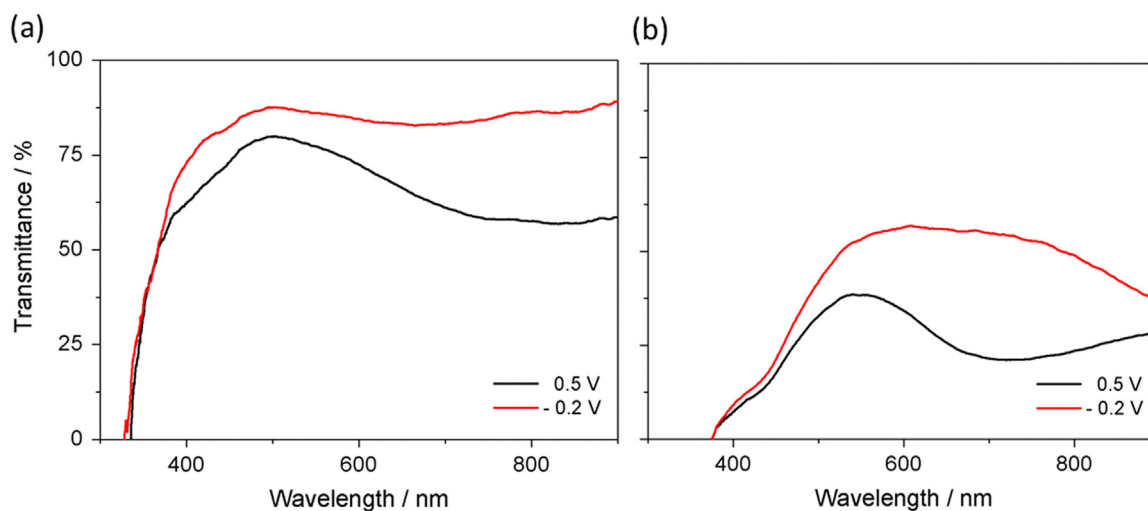


Fig. 2. Visible transmittance spectra of (a) POMA casting and (b) POMA/PTAA LBL films under different applied potentials.

indicating that they are electrochemically equivalent materials. From a different point of view, in the case of POMA/PTAA LBL, the electrochromic change has reached approximately 35%, while it was 24% for the POMA casting film. This is even more impressive considering the maximum transmittance value for the LBL film. The same kind of behavior was observed for the aging of the polymers during 3000 cycles, i.e. the LBL sample presents a stronger and more stable electrochromic behavior compared to the POMA casting film. In this case, presented in Fig. 4, we have used a shorter polarization time of 3 s in each polarization step

because both films have a long range electrochemical and electrochromic stability.

From the data presented in Fig. 4, it is possible to calculate the coloration efficiency defined as [22]:

$$CE(\lambda) = \frac{\Delta OD}{Q} \quad (1)$$

in which $CE(\lambda)$ is the coloration efficiency for a given wavelength, λ , ΔOD is the variation in the optical density and Q is the charge density; these data are presented in Fig. 5 for fresh and 3000

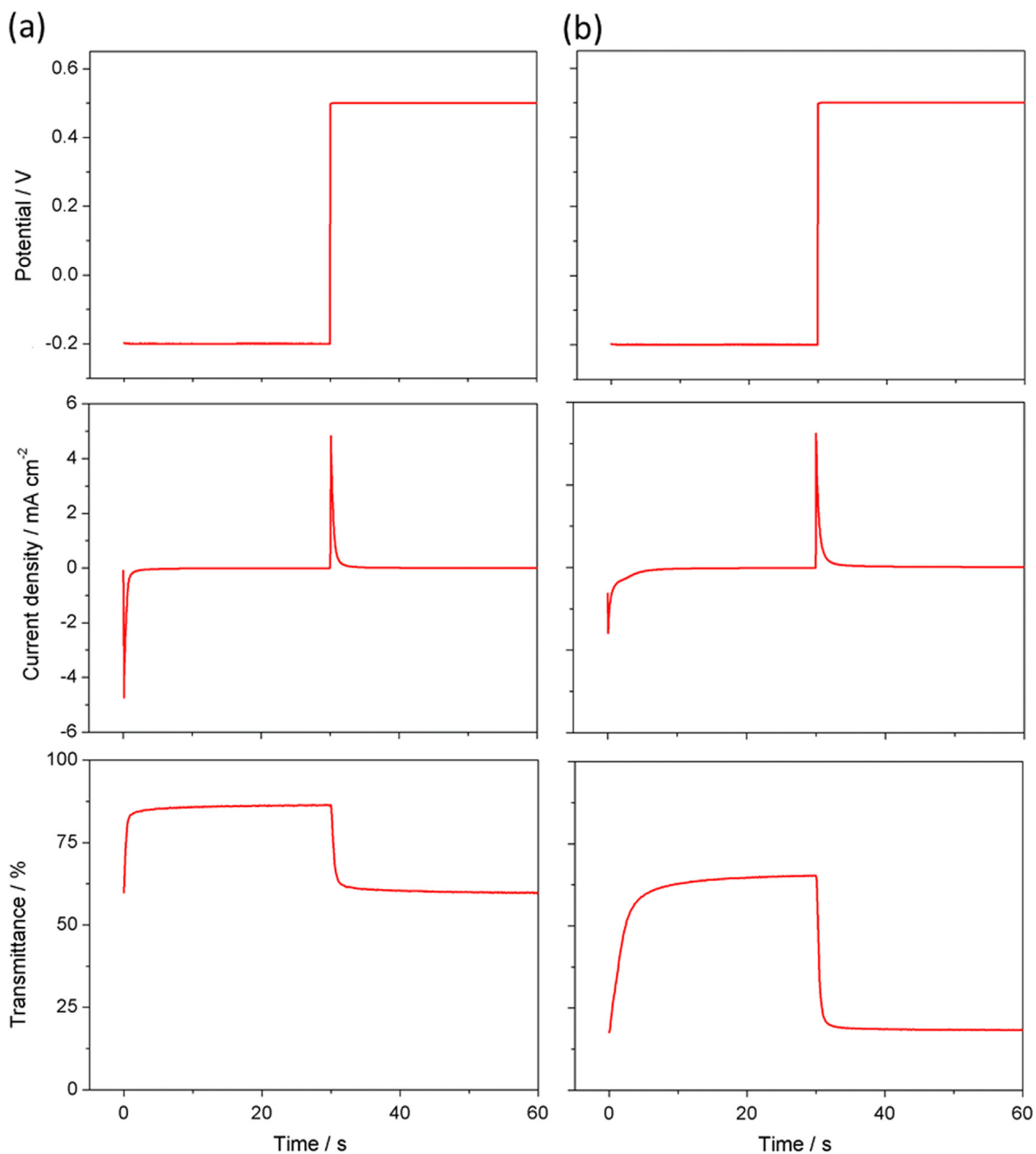


Fig. 3. Electrochromic response of (a) POMA casting and (b) POMA/PTAA LBL films from -0.2 V to 0.5 V during 30 s.

cycles aged samples. The charge densities were calculated by integration of the positive region of the current density versus time curve from Fig. 3. The calculated coloration efficiencies for each film, obtained from Eq. (1) and the data presented in Fig. 5, are presented in Table 1 for fresh materials and for samples aged after 3000 cycles.

Two different results arise from Table 1. Indeed, the coloration efficiency for the POMA/PTAA LBL film is about 3.5 times higher than those observed for the POMA casting film. In addition, both films are stable after 3000 cycles. The values obtained for the LBL electrode is higher than those described in the literature [13,15,20,21].

From the results presented above, it is clear that the LBL POMA/PTAA films have a superior performance regarding their application in electrochromic devices. One possible explanation for such

behavior is the morphological structure of the material that is associated with ion transport inside (outside) the electrode during polarization. During the redox reaction, for the POMA samples, there is a counterion intercalation process that happens to keep the electroneutrality of the system. This intercalation can be represented by the following equation:



where OMA represents a monomeric unity of poly(*o*-methoxyaniline).

From a different point of view, the POMA/PTAA LBL films have a different reaction pathway, as described in different papers [23–25], which is represented in Fig. 6.

In this case, each layer with thickness of a few monolayers interacts at a molecular level with another layer. Then, a self-

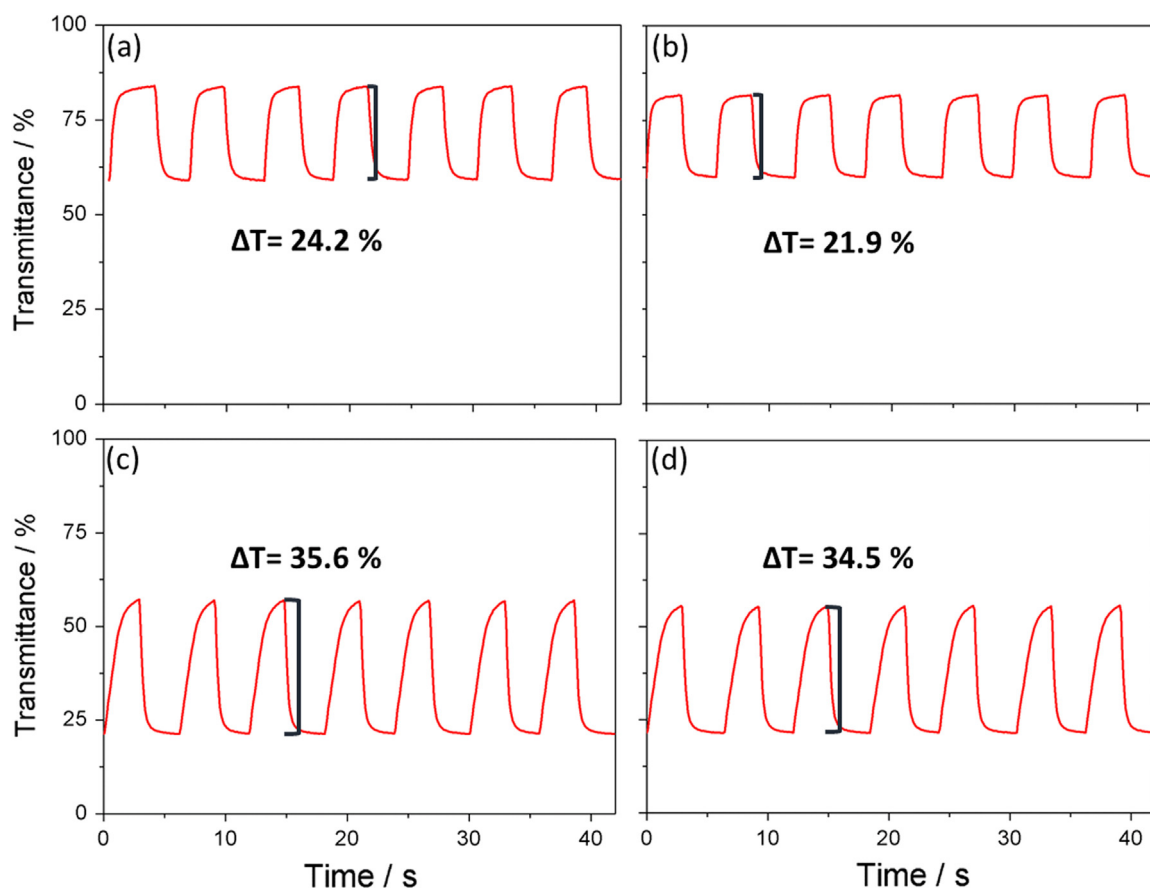


Fig. 4. Electrochromic response during 3000 cycles for (a) POMa cast (first 7 cycles), (b) POMa cast (last 7 cycles), (c) POMa/PTAA LBL (first 7 cycles), (d) POMa/PTAA LBL (last 7 cycles).

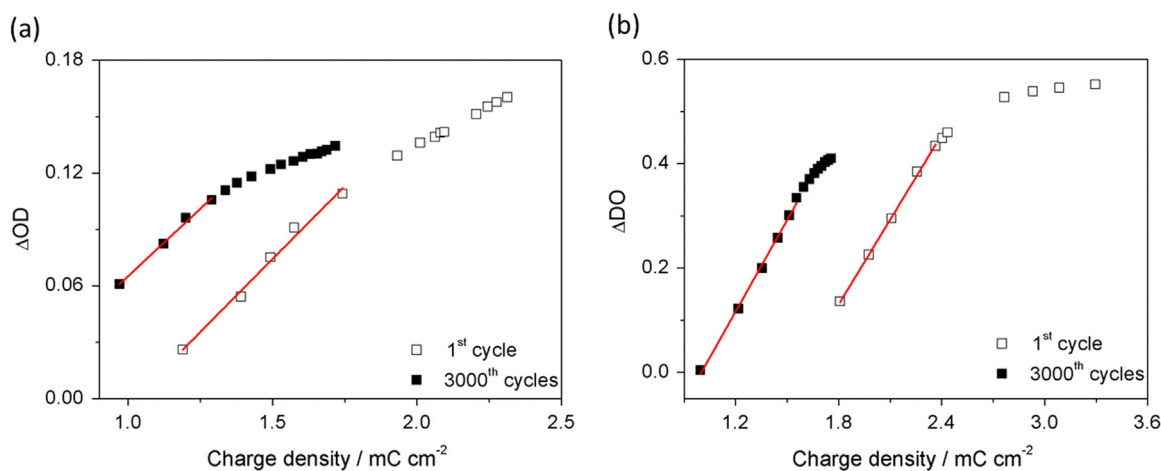


Fig. 5. Variation of the optical density vs. charge density and coloration efficiency for (a) POMa and (b) POMa/PTAA LBL films for 1st and 3000th cycles.

Table 1
Coloration efficiency for POMa casting and POMa/PTAA LBL films. Initial values and after 3000 polarization cycles.

	POMa casting ($\text{cm}^2 \text{C}^{-1}$)	POMa/PTAA LBL ($\text{cm}^2 \text{C}^{-1}$)
Initial values	155.4	542.5
After 3000 cycles	143.7	584.5

doping effect can be proposed, as demonstrated in previous papers [23,24], to explain the observed differences. As described elsewhere [23], during self-doping, the carboxylate group of PTAA

contributes to the doping of the amine group of POMa, inhibiting the need for ions intercalation, which is carried out by Li^+ in acetonitrile media, to neutralize the charge generated in the polymer. It is well described in the literature that the slow step in the conducting polymer redox reaction is the ion intercalation (deintercalation). Then, one possible explanation for the increase in the coloration efficiency is the stabilization of the colored state of the polymer due its interaction with PTAA charge layer. If this is true, it is expected that the time constant during a potential step must be faster for the LBL film. From Fig. 4, using the transmittance data, we have calculated these parameters for both films obtaining

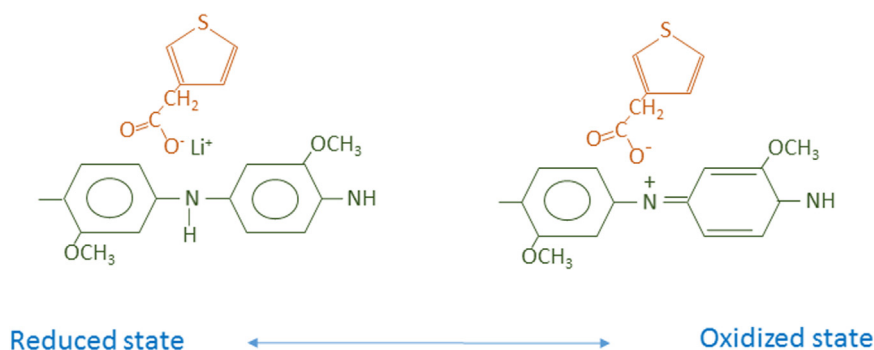


Fig. 6. Schematic representation of the self-doping effect in POMA/PTAA LBL films.

0.72 s and 0.36 s for POMA casting and POMA/PTAA LBL films, respectively, supporting the explanation given above.

4. Conclusions

In this work, we have found an important increase in the coloration efficiency, CE, of a layer-by-layer POMA/PTAA film compared to a POMA casting film with similar electrochemical properties. The POMA/PTAA LBL film presented a CE of $542 \text{ cm}^2 \text{ C}^{-1}$, which is 3.7 times the value obtained for the POMA casting material (CE=143.7). In addition, the optimized material is stable after 3000 cycles of coloring change under potentiostatic control. We have attributed these results to the self-doping effect which was previously described for this material. Finally, the decrease in the time constant for the coloration process observed for the LBL material supports this explanation.

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