



Optimization of electrochemical capacitor stability of poly(o-methoxyaniline)-poly(3-thiophene acetic acid) self-assembled films



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ABSTRACT

In the development of supercapacitors and rechargeable batteries based on conducting polymers, the stability of the material is an important concern. The objective of this work is to investigate the electrochemical aging of layer-by-layer (LBL) films of two polymers, namely poly(o-methoxyaniline) and poly(3-thiophene acetic acid), which present a self-doping effect, and compare them with poly(o-methoxyaniline) casting film electrochemical properties. Cyclic voltammetry and impedance spectroscopy are used to analyze the behavior of the films. The results show that POMA/PTAA LBL films have a higher electrochemical stability than POMA casting films. This last one presents a continuous degradation as the number of ageing cycles are increased resulting in an 80% decrease from the initial specific capacitance value after 3000 cycles. For LBL films, on the other hand, film stability has a different behavior, and after 3000 cycles, only 1% of decrease in the specific capacitance is observed. Impedance data shows a continuous increase in both polymer resistance and ionic charge transfer resistance in the case of the POMA casting film whereas no changes is observed for the LBL one indicating the film degradation is possible related to the counter ion intercalation/deintercalation which occurs mainly in POMA samples.

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1. Introduction

In recent years, capacitors and rechargeable batteries have attracted attention mainly due to the urgent need for efficient and low residue emission energy storage devices. Supercapacitors have been investigated due to their pulse power capability, long life cycle, and high kinetic of charge/discharge making them an alternative in the development of friendly energy storage devices [1,2]. Different materials have been proposed to build these devices such as metal oxides [3,4] or conducting polymers, CPs [5,6]. When CP are used as active material in electrochemical capacitors, besides the redox reaction of the polymer chains themselves there is the injection and ejection of counter ions to compensate the generated charges, which is generally accepted as the slow step of the process [7–9]. In a recent publication [10], we have investigated the effect of layer-by-layer to build a two polymer system, where one layer (poly-3-thiophene acetic acid, PTAA) just act as counter ion source for the second one (poly-o-

methoxyaniline, POMA). In this synthesis procedure, few monolayers thick films are produced at each bilayer deposition cycle. In that case, an unexpected increase in the specific capacitance occurs as the number of bilayers is increased. We have proposed that it is a consequence of the self-doping process which occurs in this system [11]. It is also expected that ion intercalation reactions also affect the electrochemical cycling stability. In these materials, as described above, the oxidation (reduction) processes lead to the intercalation (deintercalation) of counter ions to compensate the generated charge in the material. It is well discussed in the literature that the electrochemical reaction has as side effect a mechanical stress in the film resulting from a volume change [6,12,13]. Besides, the same process could lead to the electrochemical degradation of the films. Finally, the mass transport is much slower than the electronic transport and, then, the inhibition of the former can improve the redox process rate as well as decrease the degradation of the films. For this reason, several authors studied preparation methods to optimize mass transport in CPs. Among them, self-doping have been largely explored in the literature [11,14–20]. In this case, a side chain group of layer-by-layer material structure provides the ionic charge compensation required to keep the system electrically neutral. Considering the

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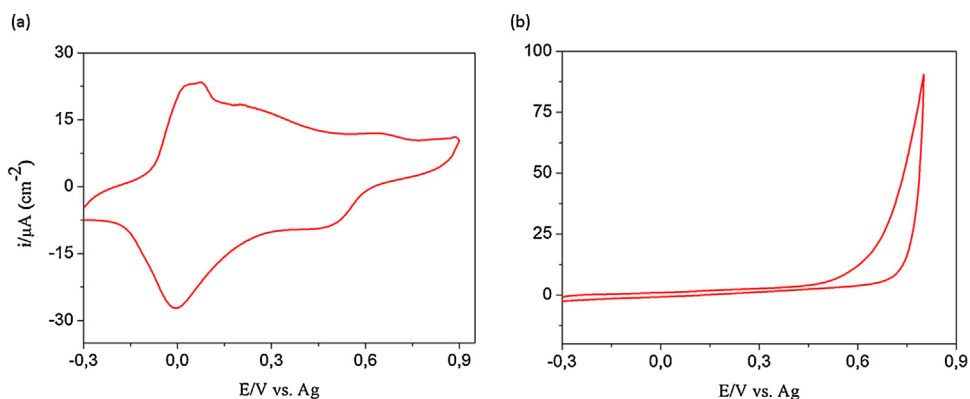


Fig. 1. Typical cyclic voltammograms for (a) POMA and (b) PTAA film on ITO substrate deposited by casting technique. Measurements were made in 0.1 M LiClO₄ in acetonitrile at 20 mV s⁻¹ at room temperature.

points discussed above, this work aims at the investigation of the ageing process of electrochemical capacitors using LBL POMA/PTAA films and its effect on the electrochemical stability.

2. Experimental

2.1. Materials and Methods

POMA has been synthesized by chemical direct oxidation of the monomer as described by MacDiarmid [21]. The polycation solution of POMA was prepared by dissolving the polymer in a mixture of H₂O and acetonitrile (ACN), in a proportion of 59:1 (v/v), using ACN to enhance the solubility of the polymer in water. PTAA was chemically synthesized and purified as described elsewhere [22]. The polyanion solution was prepared by dissolving PTAA in

0.1 M NH₄OH solution, with the final pH being adjusted to 8 by addition of 0.1 M HCl solution. Both solutions were centrifuged, and the insoluble residues were discarded. Glass substrates covered with indium tin oxide (ITO) (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 ultrapure water (Milli-Q system) to prepare a hydrophilic surface. The layer-by-layer films were assembled by first immersing the substrate in the POMA polycation solution for 3 min, using a homemade robot developed specifically for this task [23]. After deposition of the first monolayer, the substrate was immersed in the PTAA polyanion solution for 3 min. Between each step, the films were washed with water with pH adjusted to the same value as the deposition solution, i.e., after deposition of the poly cation the washing process is carried out using water with pH=3 and

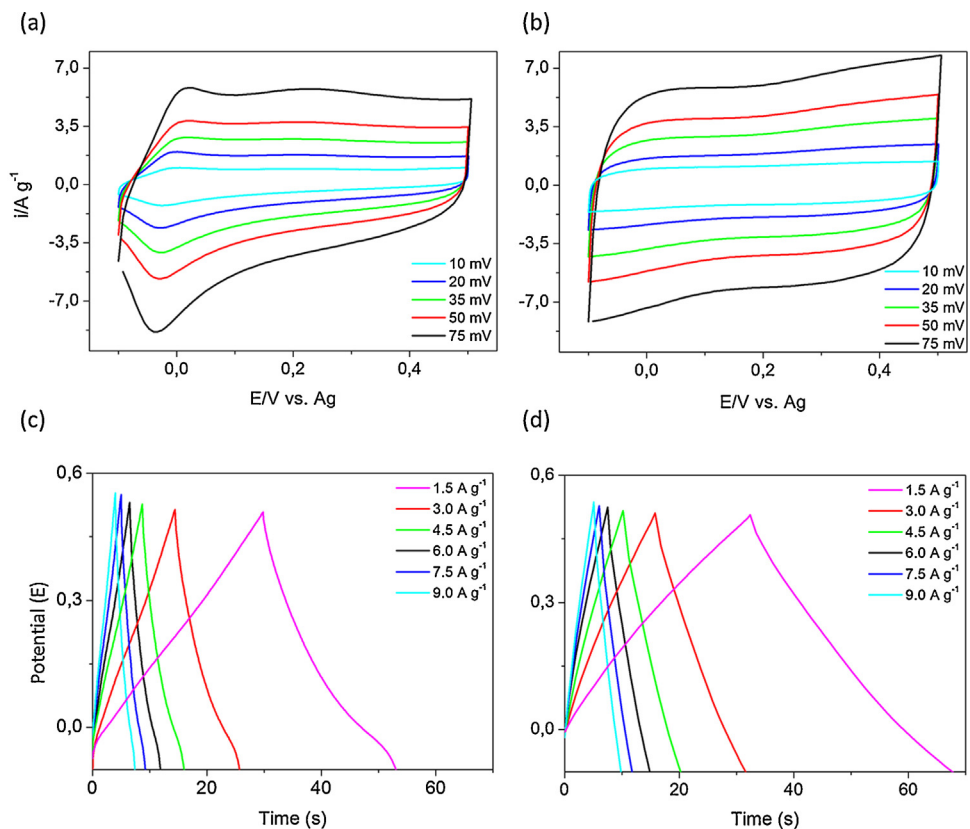


Fig. 2. Cyclic voltammogram and charge/discharge response at different scan rates and current density, respectively, for (a, c) POMA casting film and (b, d) POMA/PTAA LBL film deposited on ITO substrate.

after the deposition of the polyanion the water has the pH adjusted to 8. After each washing step the film is dried using N_2 flux. These steps were repeated until the desired number of layers was reached. In order to compare the results with conventional conducting polymer films, POMA electrodes were used which were prepared by *casting* POMA solution of the ITO substrate. To obtain comparable films, both electrodes, POMA/PTAA LBL and POMA *casting* films, with similar cyclic voltammetry anodic charges were analyzed.

2.2. Characterization

Films containing 60 bilayers of POMA/PTAA and 80 μL of POMA were built by LBL and *casting* techniques, respectively, and they were electrochemically characterized. The films prepared by both methods, LBL and casting, were followed by visible spectroscopy using UV–VIS–NIR spectrophotometer (Cary model 5G) and by mass measurements. Its morphology was measured by Atomic Force Microscopy (AFM), using a 2100 SPM microscope (molecular imaging) model Pico LETM. The films morphology was studied by Field Emission Gun – Scanning Electron Microscopy (FEG-SEM) images which were obtained using a ZEISS microscope (model 105 DSM940A) with 10 keV of accelerating voltage.

In order to have comparable data, we choose the preparation values in a way that both films, LBL and *casting*, have the same values of voltammetric charges in a cyclic voltammetry. Electrochemical experiments were carried out in a three-electrode glass cell using an EG&G PARC 273 potentiostat. The electrochemical performance was measured using galvanostatic, voltammetry cyclic and electrochemical impedance spectroscopy techniques. All experiments were carried out at room temperature. For galvanostatic charge/discharge cycling, the current load was 1.5 A g^{-1} .

Cyclic voltammetry characteristics of films were recorded after each 100 cycles of charge/discharge cycles at 20 mV s^{-1} from -0.1 to 0.5 V versus Ag. The specific capacitance was estimated from charge/discharging and cyclic voltammetry measurements proposed by Ramya [24]. The measurements of electrochemical impedance spectroscopy (EIS) were carried out at 0.3 V , frequency range from 10 kHz to 10 mHz with an applied ac potential of 0.01 V . The measurements were performed in acetonitrile solution with 0.1 M LiClO_4 . As reference and auxiliary electrodes, an Ag pseudo reference electrode and a Pt sheet (area 1 cm^2) were used, respectively.

3. Results and Discussion

The buildup of POMA/PTAA LBL and POMA *casting* films deposited on ITO substrate was followed using UV–vis measurements which have been previously published in a different paper [10]. The results are also presented in Fig. S1 of the supplementary information.

In Fig. 1 is presented the voltametric behavior of both polymers. Fig. 1a shows the results for POMA film deposited on ITO substrate. It is possible to observe the CV fingerprint for POMA with redox couple located between -0.1 and 0.1 V , and a second one between 0.4 and 0.7 V . According to MacDiarmid [21], the current peak near 0.1 V is associated with the oxidation of leucoemeraldine to emeraldine oxidation state and the peak close to 0.6 V could be explained by the insertion of anions which leads to the conversion of the emeraldine state to the fully oxidized state form, called pernigraniline. In the case of CV of the PTAA films, Fig. 1b, it is not possible to observe any electrochemical process in the potential range from -0.2 to 0.6 V , although its electrochemical activity in a wider potential range has been described in the literature [22].

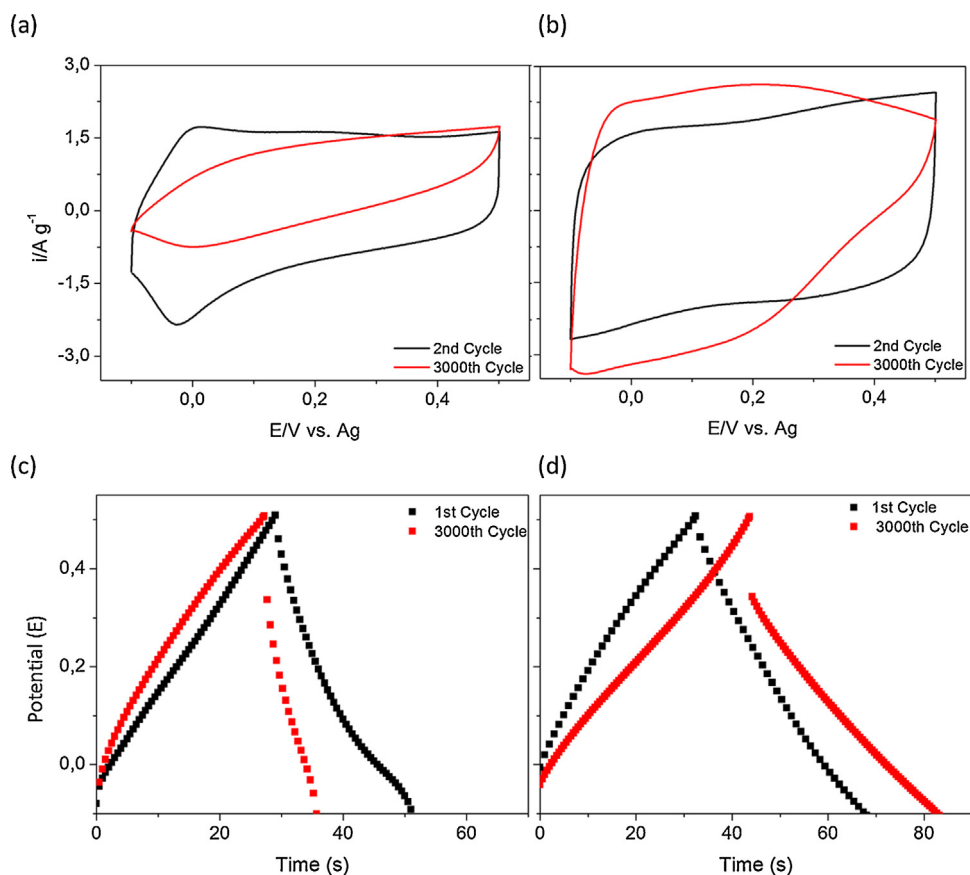


Fig. 3. Cyclic voltammogram and charge/discharge response for (a, c) POMA casting film and (b, d) POMA/PTAA LBL film deposited on ITO.

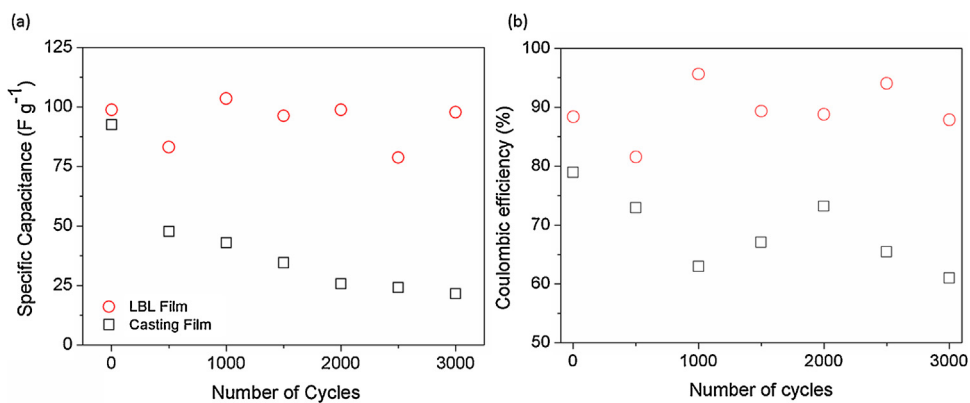


Fig. 4. (a) Specific capacitance aging and (b) Coulombic efficiency for POMa casting film and POMa/PTAA LBL film during 3000 cycles of charge/discharge measurements.

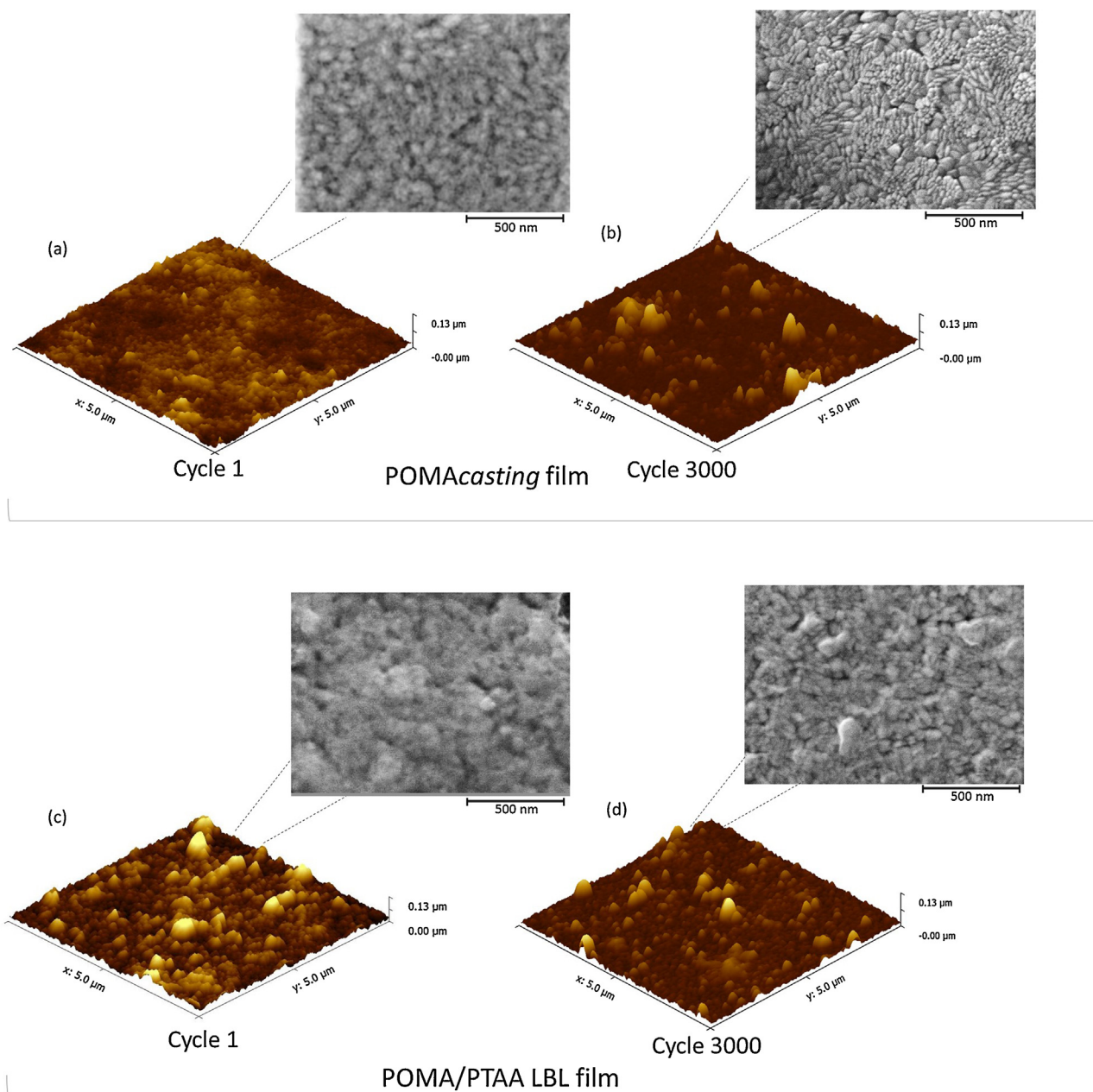


Fig. 5. SEM micrographs and AFM images of the 1st and 3000th cycles for (a, b) POMa casting film and (c, d) POMa/PTAA LBL film on ITO substrate.

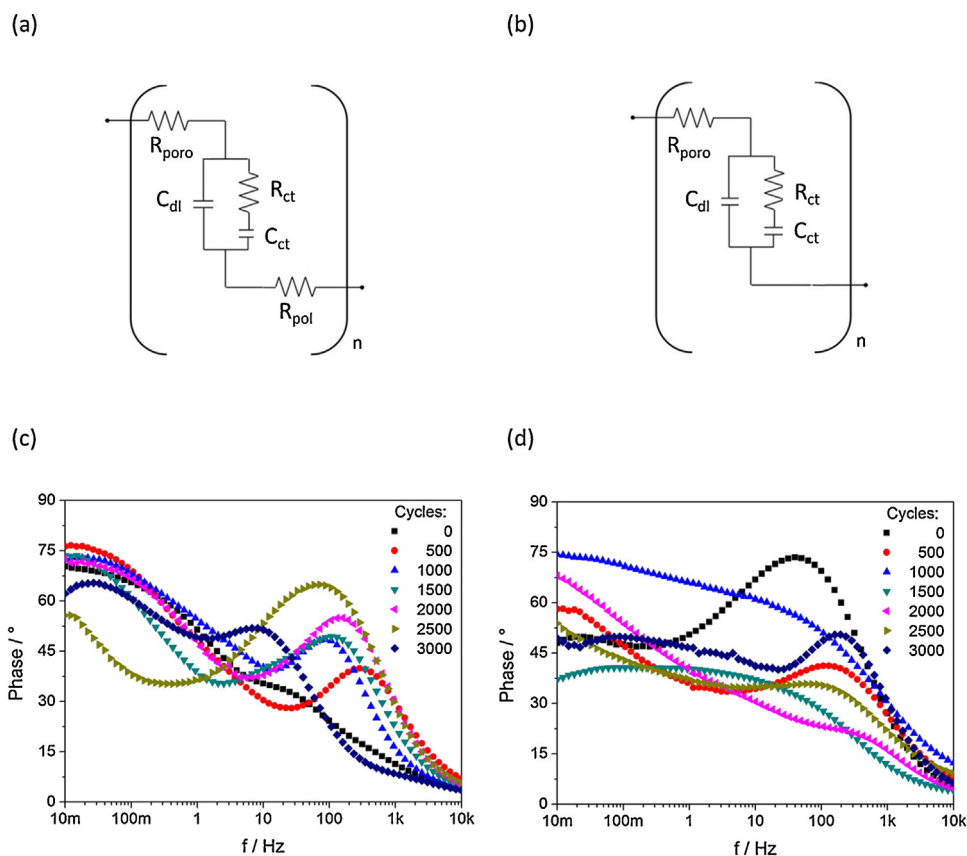


Fig. 6. Schematic presentation of the models proposed for (a) POMA casting and (b) POMA/PTAA films. Bode diagrams for (c) POMA casting and (d) POMA/PTAA LBL films. The data were collected in ACN solution with 0.1 M LiClO₄ as supporting electrolyte at room temperature.

Then, in the LBL POMA/PTAA films, the only role of the PTAA layer is to provide the counter ion balance to the positive charge generated in the POMA chains [11].

Fig. 2 presents the CV and charge/discharge measurements at different scan rates and current densities for POMA casting and POMA/PTAA LBL film, respectively. As expected, considering that PTAA layer is not electrochemically active, it resembles the POMA CV fingerprint. The loss of definition compared to those data published in the literature could be explained by the high number of bilayers deposited. To corroborate this point, the electrochemical behavior of a POMA film with comparable charge is also presented in which such loss of definition is also observed (Fig. 2a).

The charge/discharge measurements (Fig. 2c and d) were carried out at the potential cut-off limits of -0.1 and 0.5 V. The specific capacitance was calculated from the slope of the linear region of the discharge curves as proposed by Ramya [24]. In the case of LBL film, the active mass was considered to be half of the sample total mass. This consideration can be made because only POMA is electroactive in this potential window, and both polymers, POMA and PTAA, have close densities. Furthermore, the absorbance of the polymer solutions during the buildup of the LBL film is linear as the number of bilayers increases (Fig. S1). Analyzing those data in Fig. 3, we choose to investigate the electrochemical ageing of the films using galvanostatic charge/discharge experiments at a current density of 1.5 A g^{-1} and a potential range between -0.1 V and 0.5 V (vs. Ag). In this case, the necessary experimental time is 60 hours and 3000 cycles which is reasonable for this kind of test.

Fig. 3, shows the changes in the CV and charge/discharge curves after 3000 cycles. For the POMA casting film, there is an important decrease of voltammetric current values, after the galvanostatic

electrochemical ageing, and the result resembles those found for resistive materials. It is important to emphasize that the current values, after the ageing process for the LBL films, there was just minor changes in its values, apart from the fact that these changes characterize an improvement in the responses to electrochemical tests.

In Fig. 3c and 3d are presented the galvanostatic charge/discharge curves before and after the ageing process. As can be observed for POMA casting film (Fig. 3c), there is an important change in the slope of the discharge part of the curve after 3000 cycles, indicating a fall-off in the capacitance value. In a different way, for POMA/PTAA LBL sample, the ageing process results in almost no change in the discharge part curve and there is an important increase in the slope of the charge part. As consequence, this means that the capacitance values do not change and the coulombic efficiency is increased. These results are presented in a different form Fig. 4.

In Fig. 4a, POMA casting material has a specific capacitance of 98 F g^{-1} at the beginning of charge/discharge measurement, and, after 3000 cycles, this value falls down to 22 F g^{-1} . On the other hand, for LBL POMA/PTAA film, the initial specific capacitance value was 99 F g^{-1} , and after 3000 cycles of charge/discharge measurements, the value observed was 98 F g^{-1} . These results indicate that POMA/PTAA LBL films have a higher electrochemical stability than POMA casting films which is an important property to build electrochemical devices. For cast films, an 80% decrease was observed from its initial value in the specific capacitance after 3000 cycles. For LBL film, the initial capacitance value is close to the cast film, on the other hand, a value less than 1% of degradation was observed after 3000 cycles. Moreover, the cyclic voltammogram

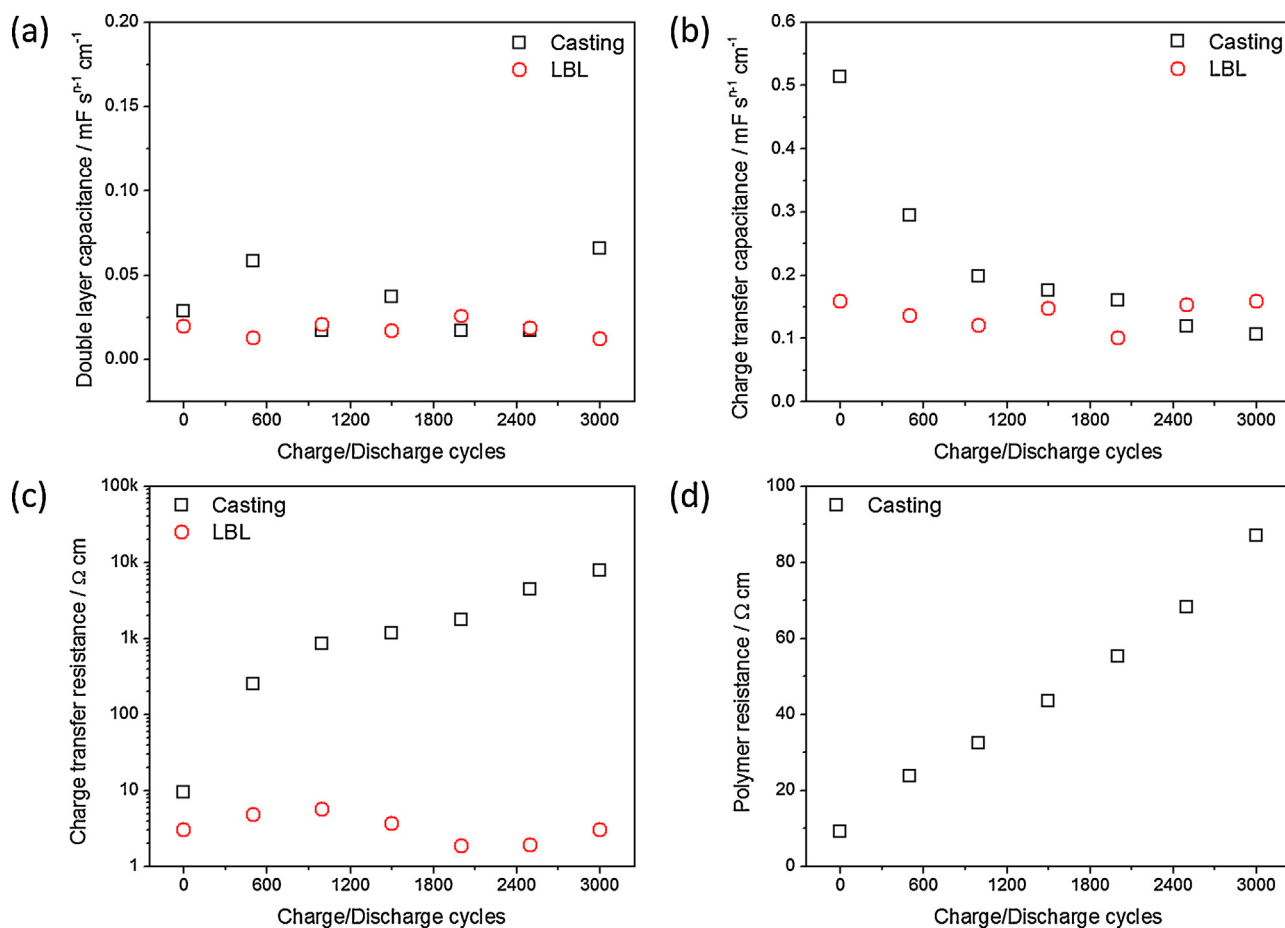


Fig. 7. Parameters from impedance spectra fitting for each film (a) Double layer capacitance, (b) charge transfer capacitance (c) charge transfer resistance and (d) polymer resistance as function of charge/discharge cycles.

(Fig. 3a and b) obtained for both films after 3000 cycles reveals that POMA *casting* film presents no more redox process while POMA/PTAA LBL film shows a small change in its CV fingerprint.

Then, we decide to carry out experiments to investigate the reason of such changes in both systems. Fig. 5 present the morphology measured both by AFM and FEG-SEM techniques before and after the ageing process. For the fresh made samples, it is possible to observe that both films show a typical globular topography. From a different point of view, it is not observed any change in the roughness factor comparing both films. POMA *casting* presents roughness of 4.15 ± 0.79 and POMA/PTAA LBL films present roughness of 5.29 ± 0.50 nm. After 3000 cycles, there is not any alteration in the roughness of the POMA *casting* film (4.43 ± 1.12) nm or POMA/PTAA film (5.36 ± 1.12) nm.

The impedance spectra were fitted using a transmission line model, which allows describing ion intercalation considering it as a porous system. In this case, the potential drop inside the films associated with both ion intercalation process and/or ohmic (or capacitive) drop in the polymer chains are the necessary condition to describe them as porous materials. These systems differ from a rough one once in this last case there is only an increase in the surface area instead of a real potential drop in the pores. The models used to fit data are presented in Fig. 6 and the Nyquist plots of all films as well as the Bode Module plots are shown in the Supplementary Information (Fig. S2). We chose to show the Bode (Fig. 6) phase plots because, in the present case, they allow the visualization of several qualitative information at naked eye which help to interpret the data. The models used here has been used

before to describe the behavior of conductive polymers [25–28] and LBL films [29]. The main characteristic of the model is the use a two branch, related with the solution in the pores and the polymers chains themselves, connected by an interface branch. In the present case, the difference between the two models is in the polymer branch, which is a short circuit for the case of LBL samples. In the literature, such kind of behavior has been associated with a full conducting polymer and also to a self-doping effect in the case of LBL materials [29].

In Fig. 6c (*casting* film) it is observed a shift in the time constant to lower frequencies from 326 Hz to 8.57 Hz, meaning an increase in its value from 3.08 ms for 116 ms. As the time constant is not well defined for the zero cycle, to calculate it we have used the values obtained by multiplying the pseudocapacitance and resistance concerning this process after 500 cycles. After this ageing step there is not any important change in the time constant comparing to the 0th cycle, but it is clearly defined. Analysing these data using the model, Fig. 6a, this time constant is associated with those processes which occur at the interface pore/polymer chains. Then, probably this change is associated with a decrease in the charge transfer rate, in other words an increase in the charge transfer resistance. This last proposition is supported by the data presented in Fig. 7c, where for POMA *casting* film there is an increase of 3 orders of magnitudes in this parameter.

On the other hand, for LBL sample (Fig. 6d) there is a constant time shift, but in an opposite direction. For fresh made film it is 44.4 Hz which, after 3000 charge/discharge cycles, changes to 218 Hz, i.e., from 225 ms to 45.9 ms, a subtle change compared to

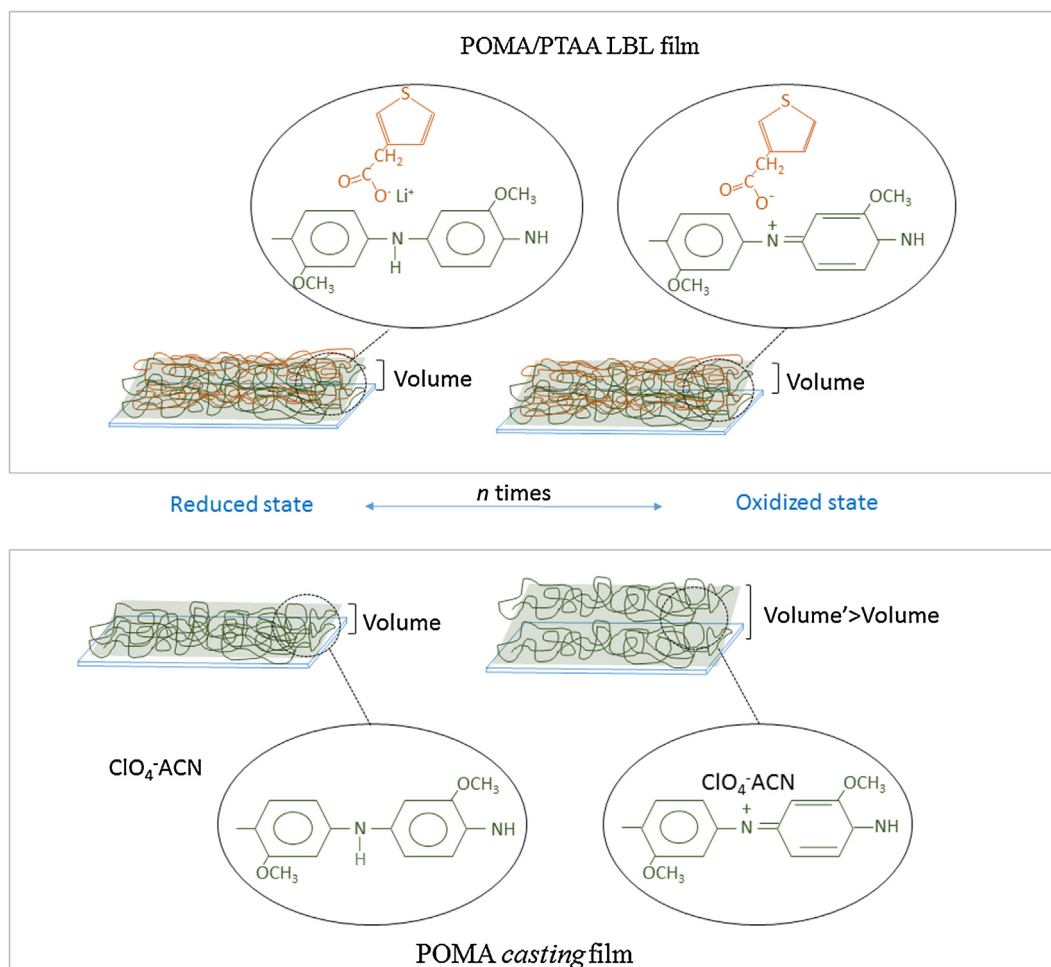


Fig. 8. Schematic representation of self-doping effect on POMA/PTAA film.

those observed for POMA *casting* sample. Indeed, Fig. 7c, shows a smooth variation in the charge transfer resistance, to lower values, corroborating the results presented in Fig. 6d.

Besides those data described above, in Fig. 7 are presented the parameters which have important changes upon electrochemical ageing. Among them, the most important variation occurs in the description of the interface pore/polymer chains. First of all, in agreement with those morphological data from both SEM as AFM images, it was not observed any significant change in the capacitance of the electrical double layer (Fig. 7a), meaning that the electroactive area of polymers is constant after the ageing. For LBL films, the charge transfer resistance (Fig. 7c) and the charge transfer capacitance (Fig. 7b) which are related to charge compensation during the electrochemical process do not change which corroborate the stability of the material presented in Figs. 3 and 4. For *casting* POMA sample, otherwise, there are important increase in the charge transfer resistance and a decrease in the charge transfer capacitance which indicate a severe degradation process to the ionic transfer from the solution to the pore of the polymer chains. In this case, the decrease of charge transfer capacitance values could be related to a decrease in the amount of the ions to compensate the positive charges generated in the polymer chains. In the same direction, the increase of 1000 times in the charge transfer resistance for the casting film indicates also an important decrease in its electrochemical activity. Finally, *casting* POMA samples presents also a 10 times increase in the polymer resistance (Fig. 7d), indicating also a polymer chain degradation besides the pore/polymer chain interface.

Then, to explain the results described in the previous Figures, we consider that in conducting polymers, the oxidation (reduction) processes leads to the intercalation (deintercalation) of counter ions to compensate the generated charge in the material [12]. This explanation describes the typical behavior observed for POMA *casting* film (Figs. 3 and 4). From a different point of view, in POMA/PTAA LBL films, the PTAA layer provides, at least partially, the counter ion balance to the positive charge generated in the POMA chains as demonstrated previously for this material using quartz crystal microbalance data [11].

In that paper, Trivinho-Strixino proposed that the deprotonated COO^- group which is pendant group PTAA monomer unit could interact with the protonated imine groups in the POMA chain, i.e., when POMA is in its oxidized state. Otherwise, when the positive charge in the POMA chain is removed, the PTAA COO^- groups then interact with Li^+ or H^+ ions in the polymeric matrix. As consequence, at least partially, there is no need of ion transport from the solution to compensate the positive generated charges. A schematic representation of this mechanism is presented in Fig. 8. It is well discussed in the literature that the electrochemical reaction has a side effect a mechanical stress in the film resulting in their electrochemical degradation. The data presented in Fig. 7 supports this proposition. Therefore, it is expected an increase of the LBL material electrochemical stability, once the self-doping effect inhibit the intercalation and, as consequence, decreases the mechanical stress generally involved in the redox process in pure conducting polymer films.

4. Conclusions

The behavior of POMA/PTAA LBL electrochemical capacitors have been compared with POMA films prepared by *casting* method. In order to compare the results, we choose *casting* and LBL films with the same values of voltammetric charges. Initially, both materials present close values of capacitance, near 100 Fg^{-1} . During the electrochemical ageing process, the POMA *cast* film loses its electrochemical activity, whereas the POMA/PTAA LBL films maintained its values up to 3000 cycles. After 3000 cycles, the POMA/PTAA LBL sample showed a decrease of only 1% of its initial values. A possible explanation for these results is the self-doping mechanism which occurs during the electrochemical processes observed in POMA/PTAA LBL films. This high cycling stability of POMA/PTAA films shows great promising application in supercapacitors.

Acknowledgments

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.electacta.2016.02.187>.

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