



# A new generation of electrochemical supercapacitors based on layer-by-layer polymer films



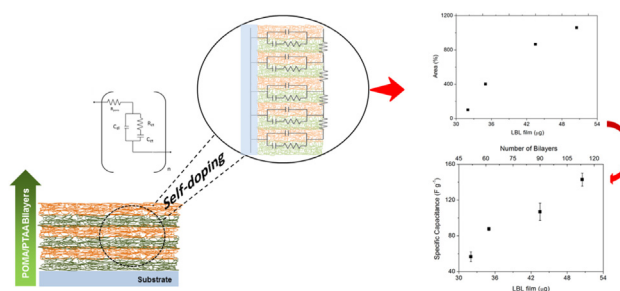
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## HIGHLIGHTS

- A new layer-by-layer conducting polymer is used as electrode.
- An important in the specific capacitance is observed.
- The results are explained by a self-doping effect in the layer-by-layer film.

## GRAPHICAL ABSTRACT



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## ABSTRACT

Here we report supercapacitors fabricated with the layer-by-layer (LBL) technique using two polymers, namely poly(*o*-methoxyaniline) (POMA) and poly(3-thiophene acetic acid) (PTAA). The electrochemical performances of POMA/PTAA supercapacitors were characterized by cyclic voltammetry and electrochemical impedance spectroscopy. The results were compared with POMA *casting* film. The specific capacitance of LBL films increases almost linearly with a number of bilayers which were not observed for POMA *casting* films. The results of this investigation demonstrate that the self-doping effect between POMA and PTAA can change the properties on films and can be successfully used as a supercapacitor technology.

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## 1. Introduction

Research on new sources of energy conversion and storage is an issue that currently is an important need for the development of society. The synthesis of new materials for the production of modern devices enabling solutions for the world's energy problem has been the subject of intense research. This interest is not only

related to the shortage of energy, but also new energy sources with low or even an absence of environmental impact. Considering the concerns mentioned, supercapacitors are promising devices [1–10]. Based on an energy storage mechanism, supercapacitors can be classified into two groups, electrochemical double layer capacitors (EDLC) and pseudocapacitors. To build a supercapacitor electrode, there are many factors which must be considered: surface area, electronic and ionic conductivity, and mechanical/chemical stability [11,12]. In particular, pseudocapacitors store charges by fast and reversible redox reactions. These devices are becoming an attractive research area because of their higher power density once they provide higher capacitance per gram than EDLCs devices [13,14]. As

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proposed in a recent review [15], conducting polymers are interesting materials to use in supercapacitors, as they are characterized by high specific capacitance, low environmental impact, and high cycle stability [16]. In this application, it is important to stress that the polymers are cycled between reduced and oxidized phases during the discharge/charge procedures. Therefore, the kinetics of the redox process, which in this case involves also an ion intercalation (deintercalation) step to counterbalance the charge generated during the oxidation (reduction), must be studied and optimized once this is generally described as the slow step in the redox process [17]. One option to optimize this last process is the use of materials that present a self-doping effect [2,18–20] and, then, the neutralization of the charges generated is performed by self-doping itself. In most papers, self-doping is reached by the introduction of  $\text{SO}_3$  lateral groups in the polymeric chain [18,21]. In this case, consequently, the intercalation is at least partially inhibited. In a different approach to decrease the importance of the intercalation is the use of layer-by-layer (LBL) film to provide the self-doping effect in conducting polymers [22–26], and in this case, the self-doping effect occurs between two successive layers. In this sense, the present work investigates the specific capacitance of the LBL films of poly(o-methoxyaniline)/poly(3-thiopheneacetic acid) [POMA/PTAA], as electrochemical supercapacitors and compare it with those built using POMA *casting* films. It is important to stress that, in the present work, the only role of the PTAA layer is to provide the counter ion balance to the positive charge generated in the POMA chains. This occurs due to the carboxylic groups in the thiopheneacetic acid monomer, which can easily be deprotonated and could have a strong interaction with the amine/imine group in aniline monomers by both H-bond and/or electrostatic interaction.

## 2. Experimental

### 2.1. Materials and methods

All the reactants were supplied by Sigma–Aldrich, the anisidine monomer was used after distillation process and the 3-thiophene acetic acid monomer was used without previous purification. Analytical grade lithium perchlorate and acetonitrile were used for the electrochemical characterizations.

The layer-by-layer films were assembled using a homemade robot developed specifically for this task [27]. The polycation solution of POMA was prepared by dissolving the polymer in a mixture of  $\text{H}_2\text{O}$  and acetonitrile (ACN) in a proportion of 59:1 (v/v), the use of ACN are to enhance the solubility of the polymer in water. The polyanion solution, PTAA, was prepared by dissolving PTAA in 0.1 M  $\text{NH}_4\text{OH}$  solution, with the final pH being adjusted to 8 by the addition of 0.1 M HCl solution [28]. Both solutions were centrifuged using EPPENDORF centrifuge 5804, and the insoluble residues were discarded. POMA and PTAA has been synthesized by chemical direct oxidation of the monomer as described by MacDiarmind [18] and Sugimoto [29], respectively. Glass substrates covered with indium tin oxide (ITO) (Geometrical area =  $1 \text{ cm}^2$ ) was used as substrate for the working electrodes. These substrates were previously etched with a  $\text{H}_2\text{O}_2/\text{NH}_4\text{OH}/\text{H}_2\text{O}$  [1:1:5 (v/v)] solution and ultra-pure water (Milli-Q system) to prepare a hydrophilic surface. Thus, the first monolayer was assembled by immersing the substrate in the POMA polycation solution for 180 s. Then, the substrate was immersed in the PTAA polyanion solution for 180 s. Between each of those steps, the films were washed in water with pH adjusted to the same value as the deposition solution and then dried in  $\text{N}_2$  flux for 100 s. These steps were repeated until the desired number of layers was reached. Fig.1 presents a schematic representation of experimental buildup of self-assembled films.

In order to compare the results with conventional conducting

polymer films, it used POMA electrodes prepared by *casting* from the POMA solution on the ITO substrate. Films containing different masses by both techniques, LBL and *casting*, were built and they have been characterized by different methods.

### 2.2. Characterizations

The growth of 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 LE™. Electrochemical experiments were carried out in a three-electrode glass cell using an EG&G PARC 273 potentiostat. The measurements were performed in an acetonitrile solution with 0.1 M  $\text{LiClO}_4$ . As a reference to auxiliary electrodes, an Ag pseudo-reference electrode and Pt sheet (area  $1 \text{ cm}^2$ ) were used, respectively. The electrochemical performance was carried out using voltammetry cyclic and electrochemical impedance spectroscopy techniques. All experiments were carried out at room temperature. Cyclic voltammetry (CV) was carried out at a scan rate of  $20 \text{ mV s}^{-1}$  from  $-0.3$ – $0.5 \text{ V}$  versus Ag. 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 specific capacitances were calculated by the CVs using the method proposed by Ramya [16] and Zhao [30].

## 3. Results and discussions

The growth of the POMA *casting* and LBL POMA/PTAA films was monitored by UV–VIS absorption after the deposition process. Fig. 2a presents the UV–VIS absorption spectra of the POMA *casting* films on the ITO substrate. There is an increase in the absorption between absorbance and the POMA mass deposited on the substrate. The behavior is quantitatively reproducible. The POMA spectra exhibit a typical absorption peak around 450 nm, (Insert of Fig. 2a), in agreement with the literature [26,31].

The mass measurement of POMA *casting* films is shown in Fig. 2b. The nearly linear increase of mass with POMA indicates that the buildup of film is reproducible. The active mass considered was the total mass shown in Fig. 2b.

Scanning Atomic Force Microscopy (AFM) images were recorded over a scan area from  $0.3 \times 0.3 \mu\text{m}$  with a scan rate of  $1 \text{ line s}^{-1}$ , Fig. 2c, were used for determination of morphology of films. The AFM images show a complete cover of the polymeric material over the substrate, and that film has the typical globular topography also in agreement with literature [32–34].

To compare these data, Fig. 3a shows UV–VIS absorption spectra of POMA/PTAA LBL films on the ITO substrate. The increase of absorbance as an increase in the number of bilayer absorbance indicates that the deposition is reproducible from one layer to another. The POMA/PTAA exhibit a typical absorption peak at around 450 nm (Insert of Fig. 3a), as observed for POMA *casting* films. The mass measurement of LBL films was shown in Fig. 3b. The nearly linear increase of mass with the number of bilayers indicates that the amount of polymers adsorbed in each bilayer are the same. The active mass considered was a half value of the total mass showed in Fig. 3b. This consideration can be made because only POMA is electroactive in the potential window used. Furthermore, the polymeric adsorption and total mass on LBL films increases linearly the number of bilayer increases, as described above. Comparing those results presented in Figs. 2 and 3, it is important to stress out that the higher mass of the LBL films could be attributed to the presence of the PTAA layers in the material.

Finally, AFM, Fig. 3c, show that film has the typical globular

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