



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



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ARTICLE INFO

Article history:

Received 22 December 2015

Received in revised form 25 February 2016

Accepted 26 February 2016

Available online 3 March 2016

Keywords:

Conducting polymers

supercapacitors

layer-by-layer films

self-doping

electrochemical stability

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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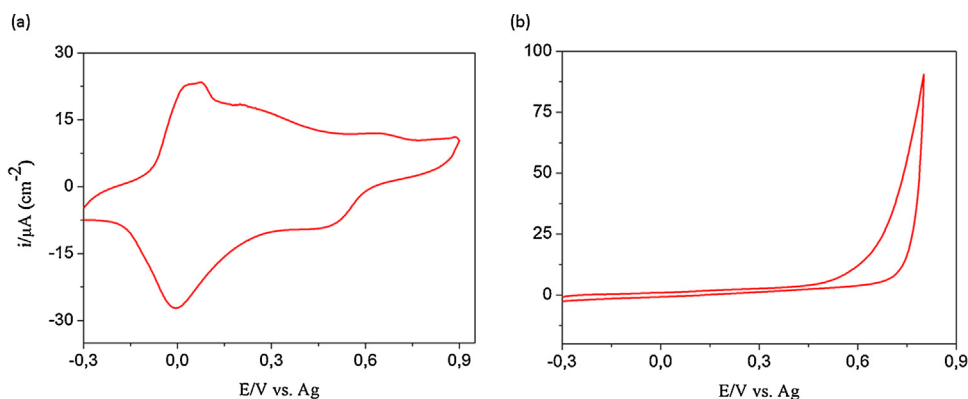


Fig. 1. Typical cyclic voltammograms for (a) POMA and (b) PTAA film on ITO substrate deposited by casting technique. Measurements were made in 0.1 M LiClO₄ in acetonitrile at 20 mV s⁻¹ at room temperature.

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

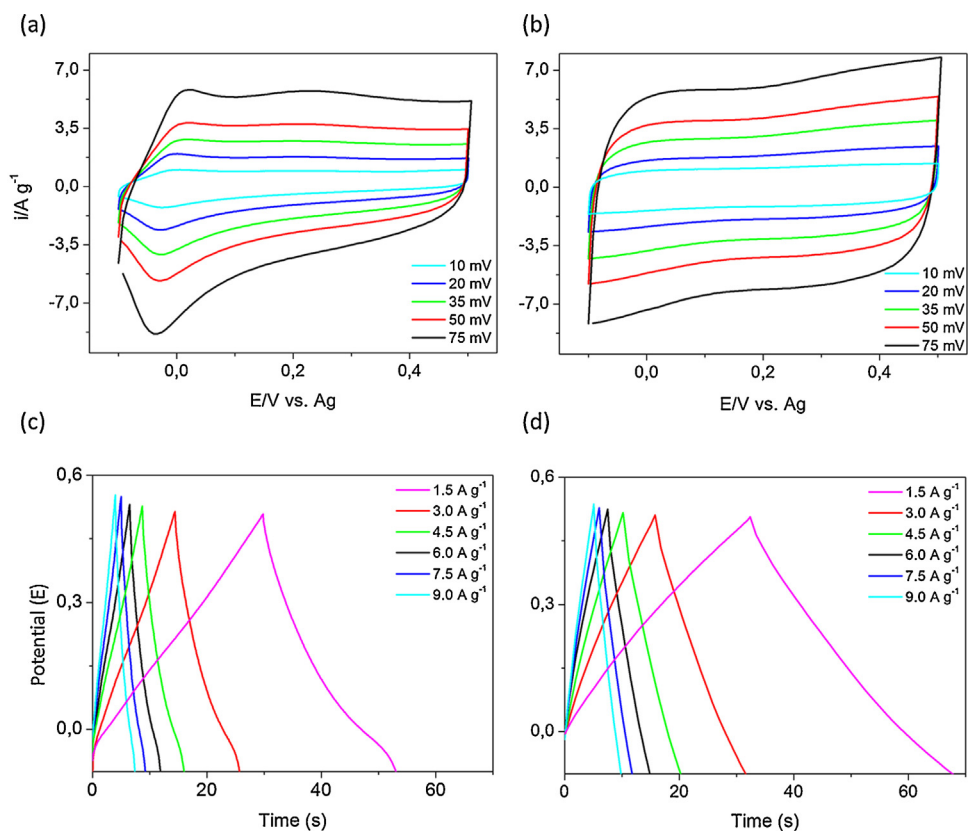


Fig. 2. Cyclic voltammogram and charge/discharge response at different scan rates and current density, respectively, for (a, c) POMA casting film and (b, d) POMA/PTAA LBL film deposited on ITO substrate.

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