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Effect of the Doping Ion on the Electrical Response of a Free-Standing Polypyrrole Strip Subjected to Different Preloads: Perspectives and Limitations Associated with the Use of These Devices as Actuators

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ABSTRACT: Understanding the effect of an external stretching force on the electromechanical response of a strip of free-standing conducting polymer is crucial for developing devices (actuators) based on these polymers. This work deals with the electromechanical characterization of a free-standing polypyrrole strip submitted to different stretching forces when they are immersed in aqueous solutions with different doping ions. By plotting the electrical energy associated with the oxi-reduction process of a strip of polypyrrole film vs an external stretching force applied to the polymer strip, two lineal zones were obtained: the first with a negative slope for increasing low forces and a minimum followed by a second positive slope for higher forces. In addition, the electrical energy involved in this electrochemical process was strongly dependent on the size of the doping ions. As a consequence of this behavior, a degeneration of the electrical energy vs the external stress was measured, which would seriously limit the use of these systems as electro-chemomechanical actuators.

1. Introduction

Since the 1970s, conducting polymers have generated a lot of expectation because of their possible technological applications[1−3] associated with their ability to change their physical properties according to their oxidation state. Thus, under a controlled external current, we are able to sweep a wide range of different physical properties such as color, volume, and charge storage capability[4−7] for different oxidation states.

Although some of these oxi-reduction processes can take place in the air, most of them take place in solution. In our specific case, the physical property that we are interested in is the volume change.[6,8,9,10] During oxidation (the process by which electrons are removed from the matrix of the conducting polymer), the repulsions between the generated charged sites along the polymer chains with the same sign promote penetration of the doping ions into the polymer matrix to balance the charge which emerges during the oxidation process, thus maintaining the electroneutrality of the system. As ions from bulk solution penetrate the polymer matrix, water molecules are also attracted toward the interior of the polymer. As a consequence of both processes (charge repulsions and water/ion penetration into the polymer), the polymer matrix swells.[11] On the other hand, during the reduction process (the opposite of the oxidation process described above) the net positive charges inside the polymer are removed by electron injection from the external electrical current, and hence doping ions and water molecules are expelled from the polymer matrix, which shrinks as a consequence. Hence, by alternating both processes described above in a cyclic way, the conducting polymer can be made to swell and shrink. On the other hand, in those families where cations play a prevalent role over the anions, swelling processes occur during reduction (with penetration of cations into the polymer matrix) and shrinking processes occur during oxidation (with expulsion of cations).

Furthermore, when a strip of conducting polymer is joined to a strip of flexible and nonconducting polymer, the stress emerging at the interface generates a macroscopic angular motion, which is the basis of electromechanical actuators known as *artificial muscles*. A great number of studies related to devices based on this type of actuator have been published over the past years while different arrangements of conducting/nonconducting polymers have been characterized from a mechanical and electrochemistry viewpoint.[12−15] Recently, Spinks et al.[16] studied the behavior of polypyrrole under an external preload. In this case they used an helix tube, where the polymer is supported by a Pt filament.

However, although some authors have considered to this issue, there is a general lack of information concerning the study of free-standing polymer films in the absence of any substrate. Okamoto et al.[17] studied the bending motion of some polypyrrole blends related to doping/undoping induced volume change as a function of the type of doping ions in solution, Otero et al.[18] studied the electrochemical behavior of a free-standing polypyrrole film in aqueous solution, and Chiarelli et al.[19] studied the mechanical behavior of a blend of free-standing polypyrrole strip. In this regard, a deeper knowledge concerning the electrochemical behavior of free-standing conducting polymer under an external stretching force is crucial as a previous step to the use of these systems as an electromechanical actuator.

Thus, the study of how a stretching force applied to both extremes of a free-standing strip of conducting polymer perturbs its electrical response and how both electrical and mechanical responses are modulated by the ion involved in the doping/undoping process seems to be of undoubted importance.

Among other electroactive conducting polymers (polyacetylenes, polythiophenes, polyaniline, and others), polypyrrole has been widely studied mainly due to its excellent conductivity, steady electrical properties in both aqueous and organic solutions, and its good weather stability.[20−23]

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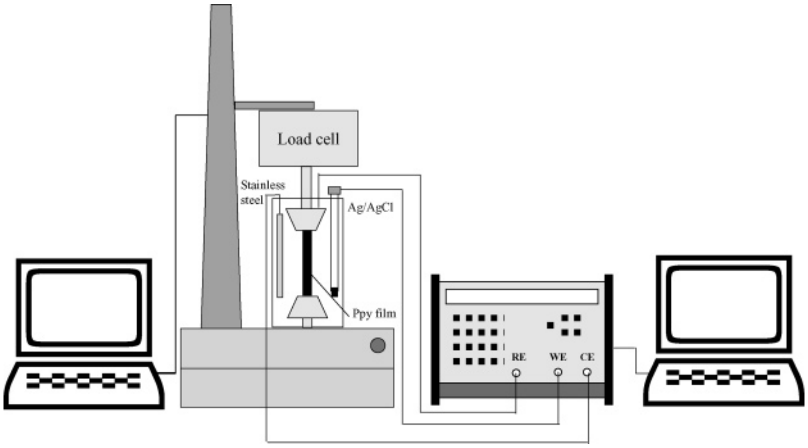

Figure 1. Experimental equipment. The basic elements are the following: potentiostat, universal test machine with a load cell and cylindrical electrochemical cell.

In this study, we provide an insight into how the electrical response of a free-standing polypyrrole film is affected by an external stress applied to the strip and how its electrical response also depends on the nature of the doping ion involved in the electrochemical reactions.

2. Experimental Section

Polypyrrole films were electrogenerated in a compartment electrochemical cell by square waves of potential in a PAR 273A potentiostat/galvanostat. We applied −0.372 V for 2 s followed by 0.872 V for 8 s in a solution of 0.2 M pyrrole and 0.1 M lithium perchlorate ($LiClO_4$) in acetonitrile with 2% water. The working electrode was an AISI 304 stainless steel sheet with a surface area of 3.5 cm^2. Another two steel sheets were used as counter electrodes. An Ag^+/AgCl electrode was used as a reference electrode. This method allows a good control of the morphology (obtaining a uniform and flat surface), and it ensures a low adherence to the metal.[24]

The overall charge (anodic minus cathodic) consumed during the polymerization process was 27 C. The working electrode was coated with two polypyrrole films (one per face) weighing 6.4 mg, with a surface area of 3.3 cm^2 and a thickness of 12.56 μm. Then, the coated electrode was rinsed with acetonitrile and dried.

Each polypyrrole film electrogenerated on the surface of the working electrode was peeled off from the electrode using a two-side adhesive tape with a rectangular cavity. The free-standing strip of polypyrrole was obtained after cutting and removing the two lateral frame sides of the adhesive tape. The electrical contact between the strip and the electrode was guaranteed by fixing a metal wire at the top of the film using a conducting carbon glue. The dimensions of the rectangular strip of the free-standing polypyrrole film were 17 mm (height), 12.5 mm (width), and 0.0125 mm (thick).

Once the polypyrrole strips were prepared, the mechanical properties of the polypyrrole film were studied by using a universal test frame machine, MTS Qtest,[25] with a special electrochemical cell designed and developed in our own laboratory, which allowed an in-situ characterization of the mechanical response of the films, when they were immersed in a 1 M aqueous solution of lithium chloride (LiCl), lithium perchlorate ($LiClO_4$), or lithium trifluoromethanesulfonate ($LiCF_3SO_3$). Figure 1 depicts schematically the experimental assembly used in this study. In this way, the load cell measured the force developed by a strip when both extremes of the strip were fixed at a certain distance between both clamps. In all the cases studied, an initial preload (or force) of 0.05 N was applied to the strips with the aim of eliminating undesired wrinkles in the strip. Finally, we mention that the loads in newtons (or force) applied to the strips were converted to stress (MPa) by dividing by the cross-sectional area of the strips (1.56×10^{-7} m^2) in order to provide the geometry-free data.

3. Results and Discussion

3.1. Electrical Energy. All the experiments were carried out under a controlled external electrical current. The oxidation degree of the polymer could be closely controlled because the electric charge consumed in the electrochemical process is directly related to this parameter (once we had discarded other paralell reactions in the process). Thus, considering that the experiments were carried out at a constant current, the electrical energy consumed during the oxidation process can be calculated as follows:

$$E = \int iV \, \mathrm{d}t \tag{1}$$

where V is the electrical potential registered by the potentiostat (against an Ag^+/AgCl reference electrode) for each instant of time, i is the intensity of the applied current (which is considered constant), and dt is the integration time. Thus, eq 1 can be rewritten as follows:

$$E = i\int V \, \mathrm{d}t \tag{2}$$

where the intensity can be taken out from the integral since it is constant during the interval of time studied. From numerical integration of the potential measured in each experiment vs time, we can quantify how much electrical energy is consumed in the electrochemical process. Figure 2 depicts the experimental chronopotentiogram during the oxidation process of a free-standing polypyrrole film, by flow of a constant current of 9 mA, where the trifluoromethanesulfonate was used as the doping ion in solution for three different values of external stress.

Thus, from numerical integration of the different curves obtained from the chronopotentiograms for different stretching forces (or preloads), we can provide information on how the external preload affects the electrical energy consumed by the system. Thus, Figure 2 depicts the electrical energy consumed during 5 s of oxidation for different doping ions involved in the electrochemical process and different preloads.

A full description of how these experiments were performed is as follows: A strip of conducting polymer was synthesized and peeled off, as we described in section 2. After polymerization, the free-standing strip of polypyrrole film was immersed in a 1 M aqueous solutions containing lithium chloride, lithium perchlorate, and lithium trifluoromethanesulfonate, respectively. To stabilize the electrochemical properties of the polymer strip, the system was first submitted to several voltammetric cycles with the aim of reaching a steady state in its electrochemical

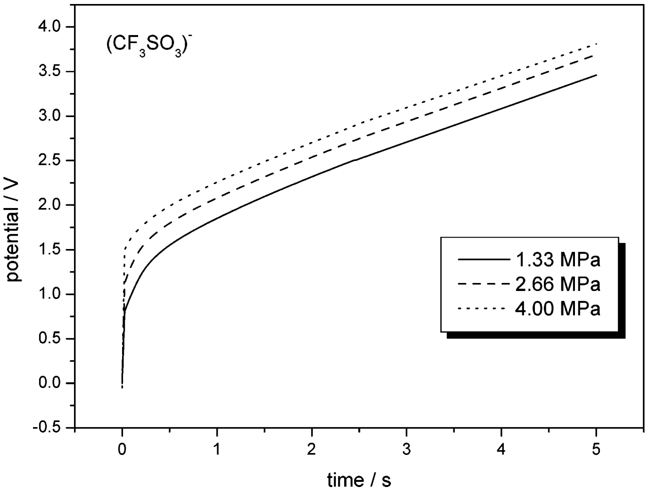

Figure 2. Chronopotentiogram of a strip of free-standing polypyrrole under different stretching forces, using a 1 M aqueous solution lithium trifluoromethanesulfonate as electrolyte. The three cases were performed at a constant current of 9 mA and different preloads.

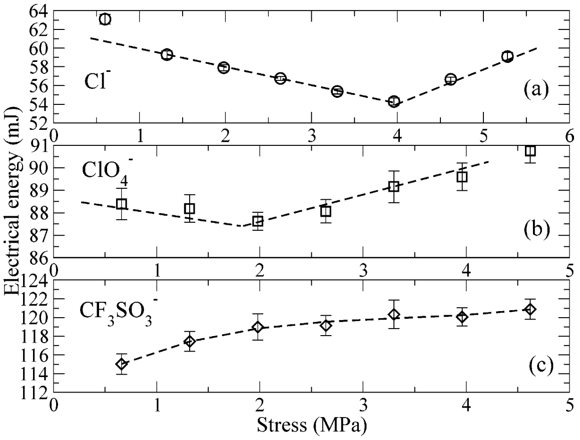

Figure 3. Electrical energy for a strip of polypyrrole film in the presence of several doping ions subjected to a range of external stress (stretching forces or preloads) and a constant electrical current of +9 mA: (a) chloride ions (Cl$^-$), (b) perchlorate ions (ClO$_4^-$), and (c) trifluoromethanesulfonate (CF$_3$SO$_3^-$).

properties. It should be mentioned that the first voltammetric cycles were discarded before the experiments were performed due to restructuration of polymer conformation and the exchange of doping ions between the polymer and the aqueous solution. (The reader must bear in mind that the polypyrrole film was electrogenerated using perchlorate as doping ion and the strips were immersed in solutions with different electrolytes.)

Figure 3 depicts the electrical energy against the values of external stress used in this study. The results were averaged over four different measurements using four different strips, and the error bar was included in this figure. From the results obtained, the following comments may be made: (1) For chloride ions (Figure 3a), the consumed electrical energy diminished lineally with the increase of the external stress. When a critical stress of 4.0 MPa was reached, the sign of the slope changed to a positive value, and the electrical energy increased following a straight line. (2) For perchlorate ions (Figure 3b), the energy followed a similar trend to that described above for the chloride ions, although the critical stress was located at 2.0 MPa instead of 4.0 MPa. (3) In presence of trifluoromethanesulfonate (Figure 3c), the electrical energy rose steadily with the stress from the beginning, reaching a plateau for a stress around of 4.0 MPa. From these results, it can be seen how the external stress perturbs the electrical energy consumed during the oxidation process and how this behavior closely depends on the doping ion involved in the oxidation process.

To help understand the possible mechanism by which the preloads and the doping ions perturb the electrochemical response of the polypyrrole strip, Figure 4 depicts our explanation of the process based on the ESCR model described by Otero et al.[26] and the mechanical reaction of a polymer strip under external stress.[27] Thus, when an external stress is applied to the free-standing polypyrrole, this stress produces the unfolding of the polymer chains, generating a certain free volume inside the polymer matrix. As a consequence, the doping ions can very easily penetrate into the polymer matrix toward the charged sites of the polymer to balance the excess of positive charge which emerged during the oxidation process. In this sense, a reduction of the electrical energy consumed during the oxidation process is to be expected, and this agrees with the experimental results observed for chloride and perchlorate ions. In addition and due to the fact that this behavior depends on the ratio between the free volume generated by the external stress and the size of the doping ions involved in the process, and assuming in a first instance that the stress provides the same free volume regardless of the doping ion involved in the process, the limiting step of this process will also depend on the size of the doping ion involved in the electrochemical process. This trend in the polymer behavior coincides with preliminary results provided by Madden[28] where the impedance droped with the external load.

On the other hand, when the unfolding process of the polymer chains associated with an increasing in the external stress finishes (as mentioned above), almost no additional free volume is generated inside the polymer that can assist the counterion penetration into the polymer matrix, and then the electrical energy steadily increases. We called the value of the external stress at which the slope changes from a negative to positive value a *critical stress*.

Using the same arguments for the trifluoromethanesulfonate as were proposed for chloride and perchlorate ions, the larger size of this ion means that the free volume generated inside the polymer (associated with the unfolding of its polymer chains) by the external stress does not facilitate its penetration (compared to Cl $^-$ or ClO$_4^-$). As a consequence, the electrical energy increases steadily from the outset for the whole range of stress studied.

However, in all the cases studied, above the critical stress (if it exists), the electrical energy increases as the external stress does. This behavior is associated with the diminution in the polymer flexibility when it is immersed in a solution with a sufficiently high stress. Figure 5 depicts Young's modulus of a free-standing polypyrrole film vs different preloads in the range of preloads studied, where the modulus was calculated following a procedure analogous to that described by Chiarelli et al.[19] In this sense, the values of the Young's module depicted in Figure 5 were calculated as follows: For different external preloads (forces) the extension of a strip was measured, such as we depicted in Figure 6. Thus, from the force measured in the MTS Qtest machine for a certain displacement of the clasps, by eq 3, Young's modulus depicted in Figure 5 was obtained as follows:

$$\text{Young's modulus} = \frac{F/S}{\Delta L/L_0} \tag{3}$$

where F corresponds to the force measured (in newtons), S the transversal area of the strip in m^2, ΔL the extension of the strip

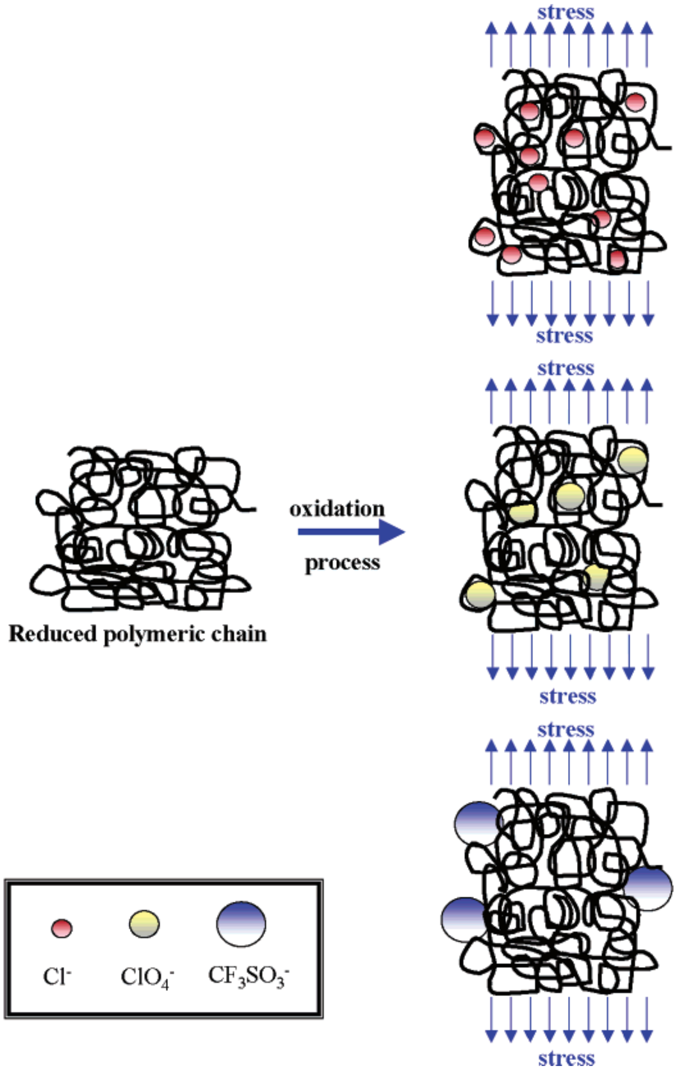

Figure 4. Scheme of the role played by the preload and doping ions in the electrochemical behavior of a strip of free-standing polypyrrole.

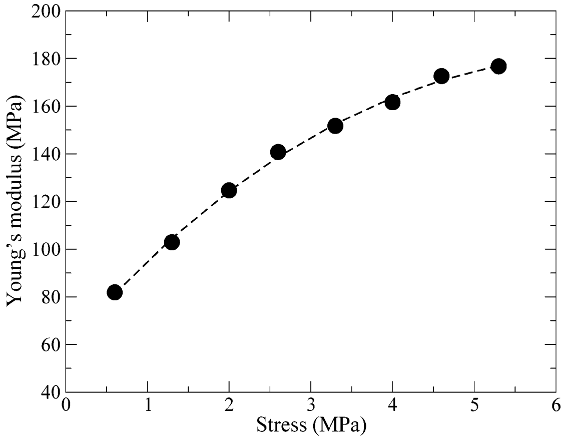

Figure 5. Young modulus of a wet free-standing polypyrrole strip under different preloads.

along the direction of the force applied (in meters), and L_0 the relaxed length of the strip before stretching (in meters).

Hence, taking into consideration how the Young modulus increases with the stress (i.e., its diminution in flexibility), from a molecular viewpoint, this behavior is related with the change in the polymer structure, adopting the chains an unfolded conformation[29] with the stress. As a consequence, it becomes much more difficult for the ions to penetrate the polymer in all the cases, and hence, the electrical energy associated with the oxidation process increases.

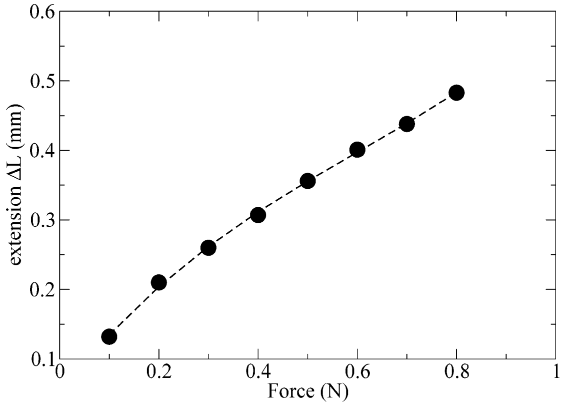

Figure 6. Extension of a free-standing polypyrrole strip vs several external loads (forces).

3.2. Electromechanical Response. The electromechanical response of a free-standing polypyrrole film can be considered as a function of the doping ion involved in the process. Figure 7 depicts the force developed by the system when a square current of +9 mA and −9 mA is applied to the strip for 5 s each and for different preloads (or stresses), keeping the distance between both clasps constant.

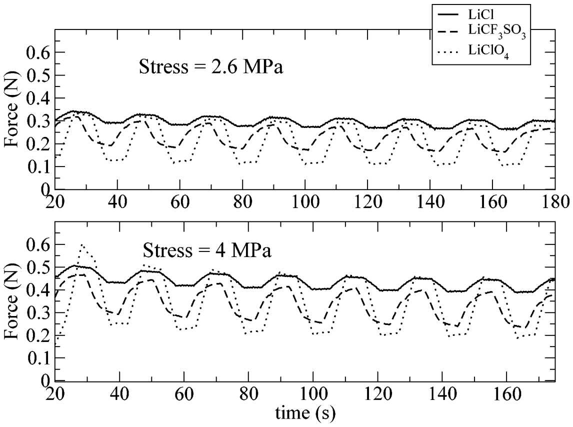

Figure 7. Mechanical force developed by the strip of conducting polymer submitted to different stresses and a current of +9 and −9 mA for 5 s.

Since the forces measured in the experiment are associated with changes in the volume of the polymer matrix, polymer shrinkage associated with reduction process generates a positive force which is released by the polymer swelling during oxidation process. From the results depicted in Figure 7, we conclude that the mechanical force developed by the polymer is strongly dependent on the ion involved in the process in the following order: $ClO_4^- > CF_3SO_3^- > Cl^-$. This order remains the same independently of the stress applied to the strip. That means that the swelling/shrinking volume per unit of charge decreases in the same order. Considering the relative ionic volumes, $CF_3SO_3^- > ClO_4^- > Cl^-$, and recovering the above-mentioned (and experimentally proved fact) that water molecules accompany the ions into the polymer matrix, we could assume that the number of water molecules going with each anion inside the polymer is greater for ClO_4^- than for $CF_3SO_3^-$. This assumption should require a subsequent experimental checking, which is beyond the aims of this paper.

This behavior can also be justified on the basis of the ion size involved in the doping/undoping process. Thus, for chloride ions, the force developed by the polymer is smaller than in the case of perchlorate due to their smaller size. In other words, a lower change in the polymer volume during the doping/undoping process is to be expected using chloride ions than when using perchlorate ions. The case of trifluoromethanesulfonate falls between chloride and perchlorate. In this case, its behavior is related to the fact that even though the size of the trifluoromethanesulfonate ion is much greater than that of perchlorate ion, its penetration into the polymer matrix is much more difficult than it is for perchlorate, and so the net effect on the swelling of the polymer matrix is smaller. However, the effect is greater than when chloride ions are used. As a consequence, the force developed by the strip using trifluoromethanesulfonate as doping ion lies between that obtained by chloride and perchlorate.

4. Conclusions

This work has focused on a study of the electromechanical behavior of a free-standing polypyrrole strip under an external stress.

First, we observed how the electrical response of a strip of free-standing polypyrrole submitted to an external stress is strongly dependent on the stress applied. Thus, up to a certain stress, the deformation that occurs in the conformation of the polymer chains assist the doping process, and as a consequence, the electrical energy associated with the electrochemical process diminishes. However, when we increase the stress to a certain critical value (which depends of the doping ion involved in the process), the electrical energy increases during the oxidation process.

In this way, from the experiments carried out in our laboratory, we conclude that the use of strips of free-standing polypyrrole as an electromechanical actuator present two critical aspects:

1. The stress (or preload) applied to a strip of free-standing polypyrrole film critically affects the electrochemical response of the system. In this way, even two different stress values can generate the same electrical response, and consequently, the electrical energy consumed in the process cannot be directly related with the force developed by the strip (in other words, there is a degeneration in the electrical energy as a function of the stress applied).
2. The force developed by strips of free-standing polypyrrole is dependent on the type of doping ions and stress involved in the process.

The above-described behavior observed for a free-standing polypyrrole strip under different external stress values and exposed to different doping ions points to important limitations for the use of these systems as electro-chemomechanical actuators since it makes no sense to try to relate their electrical response with the stress applied to the strip.

However, further studies are under way in our laboratory exploring the sensor properties of free-standing polypyrrole under external preloads.

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