Electro-chemo-mechanical response of a free-standing polypyrrole strip.

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Abstract. Further development of mechanical devices based on conducting polymers; require a precise understanding of their mechanical response, i.e. their control, under a controlled external current. In this work, we show some results for the relation between the electrical current consumed in the electrochemical process and the mechanical work developed by a free-standing polypyrrole strip, when it is subjected to a stretching force (stress). Under these conditions, from the results obtained in this work, we observe how it results almost impossible to predict a straight relationship between mechanical work and current consumed in the electrochemical process. In addition, we will quantify the variation of the mechanical properties of the free standing polypyrrole strip associated with the oxidation state of the polymer by measuring its Young's modulus.

1. Introduction.
For decades, several researching groups around the world are involved in the development of mechanical actuators [1-4], on the basis of the mechanical properties associated with the change in volume during the oxi-reduction processes of conducting polymers when these polymers are subjected to an external and controlled electrical current [5]. Due to the behavior developed by these type of polymers, some researchers called them artificial muscles [6-7], due to their resemblance with natural muscles (in behavior), where a change in volume, current and ions play a crucial role during the contraction/expansion process as in biological muscles. However, one of the critical aspects that nature solved cleanly and efficiently, is the way of working under an external force, for example, when we must lift a weight.

In this setting, our main concern in to know how a free standing polypyrrole strip (the heart of any artificial muscle) behaves when it is subjected to different external forces (stress) and which is their relation with the electrical current consumed during the process. Thus, this study is also crucial for further developments based on these electro-chemo-mechanical devices, in the sense that for going further in this scientific field, the following queries should be answered: Do we obtain an unique electrical response for each external stress or contrarily, for different external stresses we obtain the same electrical response?. Furthermore, is this electrical response independent of the type of doping ion involved in the chemical oxi-reduction process or not?. These questions must be undoubtly solved before going further in this field.
To carry out this study, a free standing polypyrrole strip was chosen, mainly due to its good and steady electrical properties in organic and aqueous solutions [8-9].

2. Experimental

Polypyrrole films were electrogenerated in one compartment electrochemical cell by square waves of potential in a potentiostat/galvanostat PAR 273A. We applied -0.372 V for 2 seconds followed by 0.872 V for 8 seconds from a solution of 0.2M pyrrole and perchlorate LiClO$_4$ 0.1M in acetonitrile with 2% of 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 reference electrode. This method allows both a good control of the morphology (obtaining a quite uniform and flat surface) and a low adherence to the metal [10].

The overall charge (anodic minus cathodic) consumed during the polymerization process was 27 Coulomb. The working electrode was coated with two polypyrrole films (one by each face) weighing 6.4 mg, having a surface area of 3.3 cm$^2$ and a thickness of 12.59 µm. Then, the coated electrode was rinsed with acetonitrile and dried later.

Each polypyrrole film electrogenerated on the surface of the working electrode was peeled off from the electrode with a sticky tape having a rectangular cavity. The free-standing strip of polypyrrole is obtained by removing the two lateral strips. The electric contact was guaranteed by fixing at the top of the film a metal wire using conducting carbon glue. The dimensions of the rectangular strip of free-standing polypyrrole film were, 17 mm height and 12.5 mm width.

Once the polypyrrole strips were prepared such as we described above, the mechanical properties of the polypyrrole film were studied by using a universal test frame machine MTS Qtest [11] with a special electrochemical cell, designed and developed in our own laboratory, allowing an "in situ" characterization of the mechanical response of the film immersed in aqueous solution, 1M in lithium chloride LiCl, 1M in lithium perchlorate LiClO$_4$ or 1M in lithium trifluoromethanesulfonate LiCF$_3$SO$_3$ respectively. Figure 1 depicts in a schematic manner the system used in this study. Thus, the load cell measures the force developed by the strip when both extremes of the strip were clasped. In all the cases studied, an initial preload of 0.05N was applied to the strips with the aim of removing undesired wrinkles in the strip.

![Figure 1. Schematic representation of the experimental equipment used in this study: Potentiostat, universal test machine, load cell and electrochemical cell.](image-url)
3. Results and Discussion.

3.1 Mechanical characterization: The Young's Modulus.
One important aspect in the study of this type of devices is the determination of the Young's modulus of wet free standing polypyrrole strips. In our case, we focused our interest in the study of the behavior of the Young's modulus with the oxidation state of the polymer. The Young's modulus was calculated as follows:

\[
\text{Young's Modulus} = \frac{F}{S} \frac{\Delta L}{L_0}
\]  

(1)

where \( F \) corresponds to the force in newtons, \( S \) the transversal area of the strip in \( \text{m}^2 \), \( \Delta L \) the extension along the applied stretching force, and \( L_0 \) the relaxed original length of the strip.

Thus, figure 2 shows the variation of the Young's modulus with the potential for a stretching force of 0.5 N. From this figure we observe how the mechanical properties of the system, becomes strongly dependent of the oxidation state of the polymer. The explanation at molecular level of this behavior is that in a reduced state, polymer chains adopt a random coil conformation and then, much higher elasticity is expected (low Young's modulus), but at high oxidate states where the polymer is swollen, the polymer chains are more stretched and their elasticity diminishes (higher Young's modulus).

![Figure 2](image)

**Figure 2.** Young's modulus variation with the oxidation state of the polymer for a constant stretching force of 0.5N.

3.2 Mechanical displacement
One of the main aspects to be studied related these devices are related with the relation existing between electricity consumed in the process (charge) and the mechanical displacement developed by the system. Thus, figure 3 depicts the periodical variation in length of the free standing polypyrrole strip with time, when the system is subjected to a constant external stretching force. In our case, the external force was 0.1N and electrical current of ± 5mA during 5 seconds.
From figure 3 we observe a linear dependence between displacement and intensity of the current applied to the system. For a much clearer evidence of this behavior, figure 4 depicts how the displacement developed by the system is directly related with the charge consumed in the process obtained from numerical integration of the values of the figure 4.

**Figure 3**: Length variation of the polymer strip for ±5 mA and constant preload of 0.1 N.

**Figure 4**: Polypyrrole strip extension vs. electrical charge consumed in the process for different electrical currents during 5 s.
3.3 Electrical energy.

All the experiments were carried out under a controlled electrical current and in this way, the electric charged consumed in the electrochemical process is directly related to the oxidation degree in the polymer. Thus, considering that the experiment was carried out at constant current, the electrical energy consumed during the oxidation process can be calculated easily as follows:

\[
E = \int i \cdot V \cdot dt
\]  

(2)

where \( V \) is the electrical potential registered by the potentiostat (against an \( \text{Ag}^+ / \text{AgCl} \) 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, the equation 2 can be rewritten such as follows:

\[
E = i \int V \cdot dt
\]

(3)

where the intensity can be taken out from the integral, due to be constant during the interval of time studied. Thus, from numerical integration of the potential measured in each experiment versus time, we are able to quantify how much electrical energy was consumed in the electrochemical process. Figure 5 depicts the chronopotentiogram during the oxidation process of a free-standing polypyrrole film using Lithium Perchlorate \( \text{LiClO}_4 \) as electrolyte, being the perchlorate the doping ion involved in the oxi-reduction process.

![Chronopotentiogram](image)

**Figure 5:** Chronopotentiogram for the oxi-reduction process of a free standing polypyrrole strip under a stretching force of 0.1N.

Thus, from numerical integration of the different curves obtained from the chronopotentiograms for different stretching forces, we are able to gather some information related to how the external preload modifies the electrical energy consumed by the system. Thus, Figure 6 depicts the electrical energy
consumed during 5 seconds during the oxidation and reduction process, using perchlorate as doping ions involved in the electrochemical process and different preloads.

In this regard, we wish to make a full description about how these experiments have been performed: A strip of conducting polymer was synthesized and peeled off such as we described in the section 2. After polymerization, the free-standing strip was immersed in an aqueous solutions containing 1M lithium perchloride (LiClO₄). With the goal of stabilizing the electrochemical properties of the polymer strip, in a first instance, the system was submitted to several voltametric cycles with the goal of reaching a steady state in its electrochemical properties. In this regards, we must mention that the first voltametric cycles were discarded before performing the experiments due to restructuration in the polymer conformation and exchange of doping ions between the polymer and the aqueous solution (the reader must keep in mind that the polypyrrole film was electrogenerated using perchlorate as doping ion and the strips were immersed in solutions with different electrolytes).

Figure 6 depicts the results of the electrical energy against the external stretching force used in this study. From this figure we observe how the electrical current consumed in the oxi-reduction process is dependent of the stretching force applied to the sample. Thus, we observe how for low stretching forces, a negative slope is obtained till achieving a certain critical value in which the sign of the slope change to a positive value. We must emphasize how this value is almost the same for the oxidation and reduction process, and furthermore, this value is independent of the electrical intensity at which the experiment was carried out.

![Figure 6](image_url)

**Figure 6:** Electrical energy consumed in by a free standing polypyrrole strip under an external stretching force of 0.1N. Left oxidation and right reduction process.

With the goal of elucidating if this type of behavior is also dependent of the type of ions involved in the doping/undoping process, we reproduced the above study using different electrolytes, such as lithium trifluoromethanesulfonate (LiCF₃SO₃) and lithium chloride (LiCl).
Figure 7: Electrical energy consumed during the oxidation process for a free standing polypyrrole subjected to different stretching forces in different electrolytical solutions. (a) Lithium chloride (LiCl), (b) Lithium perchloride (LiClO₄) and (c) Lithium trifluoromethanesulfonate (LiCF₃SO₃).

The explanation at molecular level of this behavior is as follows: when an external stretching force is applied to the free-standing polypyrrole, the stress generated on the film produces the unfolding of the polymer chains, and hence, some empty volume inside the polymer matrix is generated. As consequence, the doping ions can penetrate much easily into the charged sites of the polymer to balance the excess of charge emerging during its oxidation process. In this sense, a reduction of the electrical energy consumed during the oxidation process is expected, which agrees with the experimental results observed for chloride and perchlorate ions. In addition and due to the fact that this behavior depends of the ratio between the free volume generated by the stretching force and of the size of the doping ions involved in the process, then, assuming in a first instance that the stretching force provides the same free volume independently of the doping ion involved in the process, the limiting step of this process also depend of the size of the doping ion involved in the electrochemical process. On the other hand, whether the stretching force increases until reaching a certain value big enough, such that from that point, almost no additional free volume is generated inside the polymer that can assist the ion penetration into the polymer, from that point, the electrical energy monotonically raises. In this regard, the stretching force at which the slope changes from a negative to positive value, we called it as critical preload. Using for the trifluoromethanesulfonate the same arguments that we used above for chloride and perchlorate ions, due to its big size compared to chloride or perchlorate ions, the free volume generated inside the polymer (associated to the unfolding of its polymer chains) by the
stretching force applied on the polymer, it doesn't assist its penetration into the polymer and as a consequence, the electrical energy increases monotonically from the begin for the full range of stretching forces studied.

However, in all the cases studied and beyond the critical preload (in the case that exists), the electrical energy rises up when the stretching force increases. This behavior is associated to the diminution of the polymer flexibility when it is immersed in solution under a stretching force big enough. In this regard, Table 1 depicts the Young's modulus of a free-standing polypyrrole film versus different stretching forces in the range studied, following an analogous procedure to the described by Chiarelli et al [1]. Hence, considering how the Young's modulus increases with the preload (i.e. a diminution in its flexibility) from a molecular viewpoint, this behavior is related with the stretching of the polymer chains from a coil to a stretching conformation, and as a consequence, the ion penetration inside the polymer becomes much more difficult, and hence, the electrical energy associated with the oxidation process increases.

Table 1. Young’s Modulus of free-standing polypyrrole films for different stretching force in a LiClO₄ aqueous solution.

| Force (N) | 0.2     | 0.3     | 0.4     | 0.5     | 0.6     | 0.7     | 0.8     |
|----------|---------|---------|---------|---------|---------|---------|---------|
| Young’s Modulus (MPa) | 102.86  | 124.62  | 140.72  | 151.69  | 161.6   | 172.61  | 176.7   |

4. Conclusions
This work was focused on the study of the electro-mechanical behavior of a free-standing polypyrrole strip under an external preload.

From the results obtained in this work, we can point out how the mechanical properties of electro active conducting polymers are strongly dependent of their oxidation state, such as it was evidenced from the Young's modulus measured for different oxidation states of the polymer. In addition, the electrical energy consumed in developed a mechanical work is also strongly dependent of the stretching force applied to the strip. In this sense, a critical stress was confirmed, in which the sign of the slope changes from negative to positive value, independently of the current used in the process. Furthermore, this critical stress is also dependent of the doping ion involved in the oxi-reduction process.

Considering these results, we can assert that the developing of devices based on free standing polypyrrole strips presents a great challenge to solve the limitations coming from non steady mechanical properties of the polymer with the external stress and their correlation with their electrical properties.

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