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Ionic exchanges, structural movements and driven reactions in conducting polymers from bending artificial muscles

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Bending polypyrrole/tape muscles translate any reaction driven ionic and aqueous exchange into large (up to 270 degrees) bending movements. The polypyrrole film is reduced between 1.0 V and −2.5 V with continuous charge consumption driven anions and water expulsion under control of two consecutive structural processes: shrinking and conformational compaction.

1. Introduction

Developing new methodologies for the description of the biological and biomimetic reactions driving ionic and aqueous exchanges will constitute one of goals for chemists and biological scientists during the next century. A quantitative description of life, health and illnesses is there concerned. Among other recent carbon based materials like conducting polymers can be considered as the simplest reactive material model of the intracellular matrix: reactive macromolecules, ions and water [1,2].

The presence of reversible and irreversible electrodic reactions from the electroactive dense gel films can be analyzed and quantified from the coulovoltammetric responses (consumed charge vs. applied potential, QV) when submitted to cyclic potential sweeps [3]. Closed coulovoltammetric loops indicate the presence of only reversible oxidation and reduction processes in the film: the charge consumed during the film oxidation equals the charge consumed during the film reduction. When a conducting polymer coats a metal electrode, slow irreversible reactions present at relatively low cathodic potentials at the polymer/metal interface give an open part of the coulovoltammetric response [3]. Inside the closed loop oxidation and reduction branches present abrupt changes of the charge/potential slope indicating the presence of different possible electrochemical reactions in the film driving the exchange of different ions, or the change of the reaction rate under control of different structural processes as conformational relaxation and swelling during oxidation (p-doping) or shrinking, closing and conformational compaction during reduction (p-dedoping) [2,3]. The high content of anions and the absence of cations in films after reduction up to higher cathodic potentials than −2.5 V [4], points to the continuous expulsion of anions from the polypyrrole films during reduction from 1 V to −2.5 V in aqueous solutions. Nevertheless, the entrance of cations beyond the reduction maximum (−0.95 V) is postulated from the frequency variations of quartz crystal microbalance (QCM) electrodes coated with a conducting polymer (quartz/metal/polymer) from aqueous solutions [5,6]. The potential range assigned to this exchange of cations or to the polymeric reduction-compaction overlaps the presence of the irreversible hydrogen evolution at the metal/PPy interface detected from coulovoltammetric results [3].

Here we try to elucidate those controversial results by clarifying the driving reaction, whether it drives structural processes and which the ionic exchanges are by the use of the dimensional film variations induced by the reaction. Length variations of self-supported polypyrrole films and bending bilayer polypyrrole (PPy)/tape artificial muscles are used as macroscopic tools able to translate the exchange of small amounts of ions and solvent, driven by the electrochemical reaction, into film length variations or into large angular displacements (up to 300 degrees) [7–10], respectively. The same bilayer structure (here, conducting polymer film on

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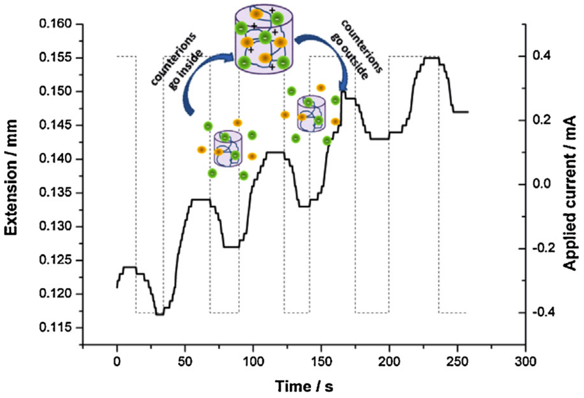

Fig. 1. Polypyrrole film length variations when, under a constant force of 0.1 N, it was oxidized and reduced by applying five consecutive square current waves (±0.4 mA, dotted line) in 0.1 M $LiClO_4$ aqueous solution. The dimension of polypyrrole film is 7.32 mm × 1.94 mm × 34 μm.

the left side and tape on the right side) gives opposite large angular displacements during oxidation, clockwise or anticlockwise, from polypyrrole materials exchanging anions or cations [7–9], respectively. Thus a good differentiation between prevalent anionic or cationic exchange is expected. In order to visualize the full process a new graphical plot of the reaction driven charges versus the described angle (coulo-dynamic responses) will be proposed.

2. Materials and methods

The used chemicals, the electrochemical cell, the used electrodes, the electrogeneration of the polypyrrole films, the peel off of self-supported PPy films, the construction of the PPy/tape bilayer muscles, the experimental electrochemical procedures and the working conditions have been described in previous papers [3,4]. The metal clamp-PPy electrical contact with the working electrode (WE) plug of the potentiostat–galvanostat is located outside the electrolyte in order to avoid uncertainties related to the possible presence of the irreversible hydrogen evolution by water electrolysis at the polymer/metal interface. A transversal lacquer strip around the bilayer below the clamp contact prevents the electrolyte ascension by capillarity. The bilayer muscle below the lacquer strip was immersed in the electrolyte.

A universal test frame machine *Q* test from MTS Systems Corporation with a special electrochemical cell designed and developed in our laboratory for "in situ" measurements was used to get linear electrochemically induced dimensional changes of self-supported polypyrrole, PPy, films [11].

3. Results and discussion

Swelling/shrinking processes and correlated dimensional changes induced by inclusion/expulsion of ions and solvent driven by electrochemical reactions in films of conducting polymer have been widely studied due to its applications for the development of artificial muscles [2,7–12]. Fig. 1 shows the length variations of a PPy film (7.32 mm × 1.94 mm × 34 μm) under a constant force of 0.1 N when submitted to 5 consecutive square current waves of ±0.4 mA (during oxidation/reduction) in 0.1 M $LiClO_4$ aqueous solution starting from a reduced state of the film.

The material swells by oxidation promoting the increase of the film length and shrinks by reduction with the subsequent decrease of the film length. Those results support the entrance of anions and water during the films oxidation by flow of anodic currents to compensate the chain positive charges and the anions' expulsion by reduction:

$$\left[\left(PPy^{n+}\right)\left(A^{-}\right)_{n}(S)_{k}\right]_{gel}+me^{-}_{metal} \rightleftarrows \left(PPy^{(n-m)+}\right)\left(A^{-}\right)_{(n-m)}+m\left(A^{-}\right)_{aq}+kS \qquad (1)$$

where PPy represents the polypyrrole chains; A^- represents the exchanged counterions for charge balance; aq, the aqueous solution and *S* are the solvent (water) molecules required for osmotic balance. Fig. 1, and similar results from the literature [7–11], have a very low precision in order to elucidate small volume variations in different potential ranges and the possible entrance of cations at the end of the reduction process as postulated from the QCM results, or the possible presence of irreversible hydrogen evolution at the polymer/metal interfaces in the same potential region [3].

Bending artificial muscles PPy/tape (a full polymeric system, without any metal in-between both films) translate very small PPy volume variations into large macroscopic bending angles of up to 300 degrees [7–12]. The bilayer muscle was submitted in 0.1 M $LiClO_4$ aqueous solution to consecutive potential cycles between 1 and −2.50 V, vs. Ag/AgCl (3 M KCl), at a sweep rate, ν, of 5 mV s^{-1}, using a stainless steel plate (4 cm^2) as the counterelectrode. Fig. 2a depicts the third consecutive and stationary voltammetric response from the bilayer. Six characteristic reference points (1 to 6) were indicated on the voltammetric response. The voltammogram was integrated to get the evolution of the charge consumed by reactions: the coulovoltammetric (charge-potential, QV) response (Fig. 2b). A negative increment of the charges indicates reduction reaction and positive increments mean oxidation reactions. Points 1 to 6 correlate those from the voltammogram. The reduction reaction gives two different Q/V slopes: a high slope from the maximum to the point 3 and a much slower slope from 3 to 6. Slope quantifies the reaction rate:

$$\frac{\Delta Q\,(C)}{\Delta E\,(V)}\,\frac{v\left(V\ s^{-1}\right)}{F\left(C\,mol^{-1}\right)}\,\frac{1}{m\,(g)}=\frac{v\times\Delta Q}{F\times\Delta E\times m}\left(mol\,s^{-1}\,g^{-1}\right)=r\left(mol\ s^{-1}\,g^{-1}\right) \qquad (2)$$

where Δ indicates variation, *F* is the Faraday constant (96 500 C mol^{-1}) and ν (mV s^{-1}) is the experimental potential sweep rate. The electrochemically stimulated conformational relaxation (ESCR) model proposes that both processes correspond to the same reaction (1) (backwards) under control of two different structural processes: reduction-shrinking from the maximum up to the closing of the gel structure (point 3) involving most of the reduction charge, followed by the reduction compaction of the conformational structure that involves (Fig. 2a) around 10% of the reduction charge [3]. Results from the QCM should indicate the expulsion of anions from the maximum to point 3 followed by the entrance of cations from 3 to 4:

$$\left(PPy^{n+}\right)\left(A^{-}\right)_{n}(S)_{k}+mC^{+}+me^{-} \rightleftarrows \left(PPy^{(n-m)+}\right)\left(A^{-}\right)_{n}\left(C^{+}\right)_{m}(S)_{k} \qquad (3)$$

Reduction reaction (1) should give PPy decreasing volume by expulsion of anions, meanwhile reduction reaction (3) should promote a volume increase required to lodge the cations. Thus, reactions (1) and (3) should produce opposed bending movements of the muscle between points 3 and 6. The bending movement of the muscle was recorded during the voltammetric response, Fig. 2a, with a video camera correlating frames and potential. From the video frames the described angles were determined from the horizontal line of the electrolyte surface and the line going from the muscle/electrolyte contact to the muscle bottom, as indicated in Fig. 3. Then the angle from each frame and the muscle potential at that frame was plotted in Fig. 2b, dotted red