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REVERSIBLE ELECTROCHEMICAL REACTIONS IN CONDUCTING POLYMERS: A MOLECULAR APPROACH TO ARTIFICIAL MUSCLES

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Electrical currents trigger oxidation or reduction reactions in conducting polymers. Changes in volume associated with these redox processes can be transformed into macroscopic movements of more than 180° by the construction of a bilayer: polypyrrole-flexible and inactive polymer (artificial muscle). The effects of the applied potential, the nature of the solvent and the electrolyte concentration on the angular movement of the free end of the bilayer were analysed. The movement accelerates with increasing anodic (or cathodic, when the movement is reversed) overpotentials, with increasing electrolyte concentration or by using more polar solvents, leading to the conclusion that the movement is linked to electrochemically driven exchange of hydrated counterions between the solution and the conducting polymer. Geometrical considerations give a simple equation for both the microscopic and macroscopic changes of volume associated to the penetration of counterions during oxidation, which is able to explain the experimental behaviour.

INTRODUCTION

A chemomechanical device is a system able to transform chemical energy into mechanical work. In recent decades, a large number of simple chemomechanical systems have been investigated, including ion-exchange fibres,[1,2] fibrillate proteins,[3] crystalline polymers[3] and polymer membranes.[4,5] When the transformation of chemical into mechanical energy is driven by an electric pulse, an electrochemomechanical device is developed.

The presence of molecular movements in films of polyconjugated materials submitted to redox processes induced by electric currents has been reported and applied.[6–9] When a conducting polymer film (such as unsubstituted polypyrrole or polythiophene) is electrochemically oxidized, positive charges are generated along the chains and hydrated counterions from the solution are forced to penetrate into the polymer in order to compensate these positive charges. This promotes the opening of the polymeric structure and a concomitant increase in free volume. When the polymer is reduced, electrons are injected into the solid, positive charges are eliminated and counterions and solvent molecules are expelled into the solution. As a result, two main effects occur: the polymer recovers its neutral state and the volume of the film decreases.

Some applications such as artificial muscles have been developed exploiting reversible swelling and shrinking processes in conducting polymers. To construct an artificial muscle based on conducting polymers, three requirements have to be fulfilled:

1. synthesis of a conducting polymer having an optimum intermolecular mobility;[10]
2. control of these molecular movements;[11] and
3. transformation of the molecular movement, able only to produce a wrinkling of the polypyrrole film,[7] into a macroscopic movement.

Among the different possibilities studied in our laboratory, a bilayer structure, consisting of a conducting and flexible polypyrrole layer adhering to an elastic and non-conducting film (Figure 1) was chosen. The system is similar to bilayer thermometers consisting of two metallic sheets having different expansion coefficients. Here the change in volume taking place in the conducting film promotes an angular movement of the non-electroactive polymeric film. Thus the molecular movement in the conducting film, produced during oxidation and reduction (swelling and shrinking), is transformed into an angular macroscopic movement.[12]

In this paper, we report experimental results of the electrochemomechanical behaviour of polypyrrole based bilayers studied under different electrical and chemical conditions. The observed response led to the conclusion that the bending degree is essentially controlled by the

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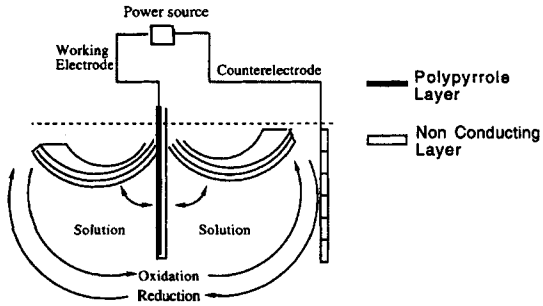

Figure 1. Scheme of the structure of the polypyrrole–non-conducting film bilayer and its movement by application of an electric potential between −200 mV (+90° position) and 400 mV (−90° position). The direction of the movement can be changed by inversion of the current.

electrical current and the concomitant movement of ions and solvent in the polymer lattice. With regard to this behaviour, a theoretical model able to explain the influence of the electric current on the movement was developed.

EXPERIMENTAL

Synthesis of polypyrrole layers. Polypyrrole films were electrogenerated from 0·1 M pyrrole and 0·1 M $LiClO_4$ in acetonitrile containing 2% water. This solvent mixture provides films with a high charge storage ability.[13] Acetonitrile (LabScan, HPLC grade) was used as received. The monomer (pyrrole) and anhydrous $LiClO_4$ were supplied by Merck. The electrolyte was dried at 80 °C for several hours before use. The monomer was distilled under vacuum.

An AISI 304 stainless-steel sheet ($3{\cdot}5 \times 2$ cm^2 surface area) was used as the working electrode. Two 4 cm^2 platinum sheets were used as counter electrodes. Polymerizations were carried out by application of consecutive square waves of potential between −500 mV (2 s) and 800 mV (10 s). This method was optimized to obtain homogeneous polypyrrole films of good quality.[10] The charge consumed during polymerization was 2 C cm^{-2}, the average thickness of the polymer film being 15 μm, obtained by experimental determination of both density and weight of the polypyrrole film.

Construction of the bilayer. Once the polypyrrole film has been electrogenerated, the coated steel was removed from the solution, the polymer being partially oxidized. The polypyrrole films (one from each side of the electrode) were stuck to a commercially available double-sided plastic tape. Once good adherence between the polypyrrole film and the plastic tape had been obtained, the polypyrrole–adherent film bilayer was removed from the stainless steel.

Measurements. In order to carry out the study of the movement, a portion of the bilayer having an area of 2 cm^2 was placed in the background solution ($LiClO_4$ aqueous solution). Electrical contact between the polypyrrole layer and the electric current source was effected out using a platinum-coated clamp. The voltage was applied through a PAR 273 potentiostat/galvanostat. A platinum sheet (4 cm^2 surface area) was used as the counter electrode and a saturated calomel electrode (SCE) was employed as the reference electrode.

RESULTS AND DISCUSSION

Role of the solvent on the movement

A polypyrrole–non-conducting film bilayer was placed in 0·1 M $LiClO_4$ solution using water, acetonitrile or propylene carbonate as solvent, then submitted to consecutive potential steps between −200 mV and 400 mV vs SCE. The electrochemical reduction of polypyrrole at −200 mV promotes the contraction of the polypyrrole layer and the appearance of mechanical stresses at the interface between the two polymers. As a consequence, the free end of the bilayer moves towards the polypyrrole side (Figure 1). During oxidation the polypyrrole film expands, and the opposite macroscopic movement is produced. This reversible movement has been described previously.[8–10]

This behaviour was only observed in aqueous solutions. When acetonitrile or propylene carbonate was employed as solvent, no movement was observed using the same bilayer. These differences in the electrochemical behaviour are attributed to different degrees of interaction between solvent molecules and the polymer. Stronger interactions assume greater facility of the solvent molecules to penetrate and open the polymer network, whereas weak interactions assume a closed molecular structure. Water molecules have a higher dipole moment than the other solvents examined, so strong dipole–ion interactions occur between the oxidized polypyrrole chains and the water molecules. As a consequence, the polymer swells during oxidation. In the reduced film, polymer–polymer attractive interactions prevail and the polymer shrinks. In other solvents, ion–dipole interactions are weaker than in water. The differences in volume between the oxidized and reduced states are not so large and the subsequent macroscopic movement of the bilayer becomes less important.

Influence of the applied electrical potential on the movement

A bilayer constructed as described above was polarized at −200 mV (a potential where the conducting polymer

becomes neutral) for a long enough period to allow the free end of the bilayer to attain a position of +90° with respect to the vertical position. Then the potential was stepped to an anodic value in the range between 600 and 2000 mV. The times required to attain a position of −90° during oxidation were measured for the different anodic potentials. As can be seen from Figure 2, higher anodic overpotentials promote faster oxidation of the polypyrrole films.[14] Hence the expansion of the polymer network is faster, promoting a more rapid movement of the bilayer. On the other hand, the charge consumed to oxidize the polymer is constant for anodic overpotentials lower than 600 mV. The increase in the charge consumed by oxidation at potentials more anodic than 600 mV (see Figure 3) is related to the parallel oxidation of water and concomitant oxygen release.[15] A similar procedure was used to study the influence of the cathodic potential on the reverse movement by polarization from 800 mV to different cathodic potentials ranging between −400 and −2000 mV. The times

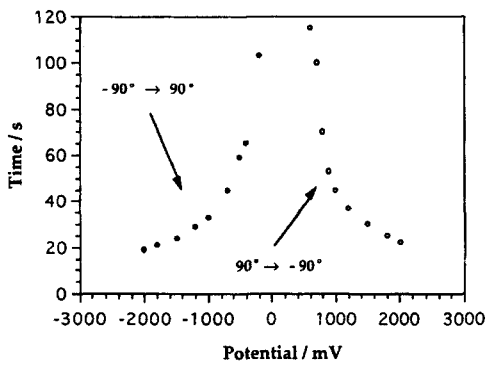

Figure 2. Evolution of the time required to complete a cycle of movement (−90° → +90° and +90° → −90°) for a bilayer as a function of the applied potential

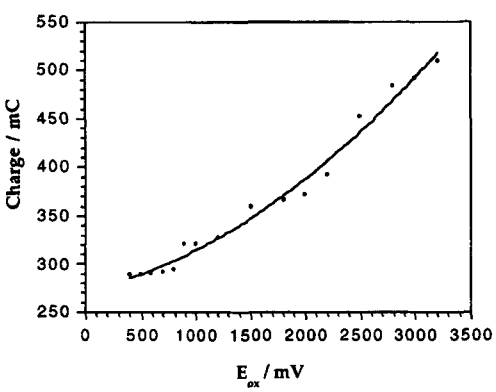

Figure 3. Evolution of the charge consumed during bending at different anodic potentials

needed to complete the movement from 90° to −90° are also shown in Figure 2. More cathodic potentials give faster movements.

Thus the rate of movement of the artificial muscle is related to the applied electric potential, and hence to the kinetics of the redox reaction taking place in the conducting film. In other words, movement rates during oxidation or reduction are governed by gradients of anodic or cathodic potentials, respectively.

Influence of electrolyte concentration

A bilayer was submitted to potential steps from −200 to 400 mV in aqueous solutions with different $LiClO_4$ concentrations. The times required to complete an angular movement from +90° to −90° decrease when the electrolyte concentration increases (Figure 4), as expected. Moreover, movements related to anodic processes are always slower than those related to cathodic movements. This is related to the extra energy required to open the molecular entanglement and allow the penetration of counterions during oxidation. During reduction, in contrast, counterions diffuse along the opened structure towards the solution without any resistance, giving a faster shrinking effect. In other words, oxidation, but not reduction, is controlled by conformational relaxation of the polymeric chains.[16]

THEORETICAL APPROACH

On the basis of the above description, an attempt will be made to develop a theoretical model able to explain some of those experimental results. A bilayer will be considered, consisting of an electroactive and homogeneous polypyrrole film adhering to a non-electroactive and flexible tape. Anodic or cathodic currents will pass through the polyconjugated film to allow electrochemical oxidation or reduction processes. The redox level

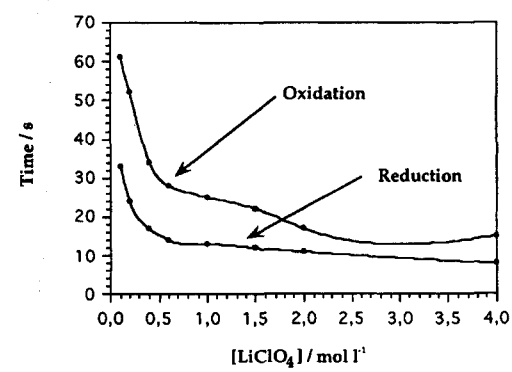

Figure 4. Evolution of the time per cycle (−90° → +90° and +90° → −90°) for a bilayer as a function of the electrolyte concentration ($LiClO_4$). The final potentials were −200 mV (reduction) and 400 mV (oxidation)

attained is a steady state related to the consumed charge and the applied potential. It is assumed that only one type of dopant ion is present, that the temperature is constant and that the environment of the conducting polymer (metal clamps, counter electrode, solvent, etc.) is inert.

The oxidation of a microscopic element of volume is shown in Figure 5. The polymer presents a compact structure in the neutral state, being opened during oxidation owing to the penetration of counterions. The overall change in volume occurring during the oxidation of the polymer, expressed in terms of changes in the length of a given polymeric segment (Δl), can be separated into two components:

1. During oxidation, electrons are lost from the polymeric chains and solvated counterions penetrate into the polymer to compensate for the generated positive charges. The relative change in the length of a polymeric segment (Δl_1) will be proportional to the number of solvated counterions penetrating into the polymer. This number is equal to the number of electrons flowing through the external circuit. Hence

$$\frac{\Delta l_1}{l} = h_1 \frac{Q_{\text{segment}}}{l^3} \tag{1}$$

where h_1 is a constant related to the volume of the hydrated anions (which depends on ion–solvent interactions) and Q_{segment} is the anodic charge required to oxidize an unitary segment of the polymer.

2. The second component is related to charged polymer–charged polymer, charged polymer–anion, anion–anion and polymer–solvent interactions. According to the theory of swelling of cross-linked gels,[17] the relative increase in the length of the segment can be expressed by

$$\frac{\Delta l_2}{l} = h_2 \frac{Q_{\text{segment}}}{l^3} \tag{2}$$

where h_2 includes all the physical and chemical properties related to the system, such as interaction parameters, dielectric constant of the solvent, screen effects and electrolyte concentration.

By addition of equations (1) and (2), the following expression for Δl is obtained:

$$\Delta l = (h_1 + h_2) \frac{Q_{\text{segment}}}{l^2} = h \frac{Q_{\text{segment}}}{l^2} \tag{3}$$

where $h = h_1 + h_2$ is defined as the electrochemical swelling coefficient. Under steady-state conditions, the relative increase in the length of the polymeric segment is a linear function of the overall charge consumed during the oxidation process (Q), as can be deduced when equation (3) is transformed to

$$\Delta l = h \frac{Q_{\text{seg}}}{l^2} = h \frac{Q}{l^2} \times \frac{V_{\text{seg}}}{V_{\text{pol}}} = h \frac{Ql}{Ae} \tag{4}$$

where V_{seg} is the volume of the considered segment, V_{pol} is the overall volume of the polyconjugated material studied, A is the area of the polymer–polymer interface and e is the thickness of the conducting layer. According to equation (4), the relative increase, or decrease, in length is proportional to the electrical charge consumed during the oxidation, or reduction, processes. Nevertheless, when the conducting polymer film adheres to a flexible and non-electroactive tape, a stress gradient appears across the polymer during the oxidation process (Figure 6): the electron loss induced by the anodic potential attempts a swelling process at the polymer–polymer interface, but fibres adhere to the non-conducting polymer and the swelling is hindered by a mechanical opposite force. Owing to the cross-linking of the polyconjugated material, the stress gradient reaches a distance δ from the polymer–polymer interface. For distances longer than δ, the polyconjugated film expands following equation (4). For this reason, δ will be called the distance of influence of the non-electroactive tape.

Assuming a linear strain gradient from the interface to δ, the elongation of an element of volume present at a

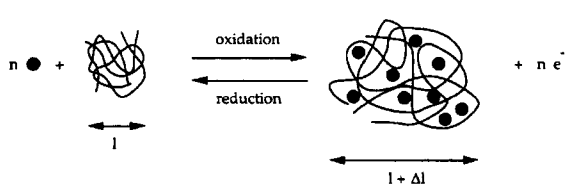

Figure 5. A compact element of volume with a length l increases its length to $l + \Delta l$ during oxidation: electrons are lost from the polymer, channels are opened and hydrated counterions penetrate from the solution, to maintain electroneutrality

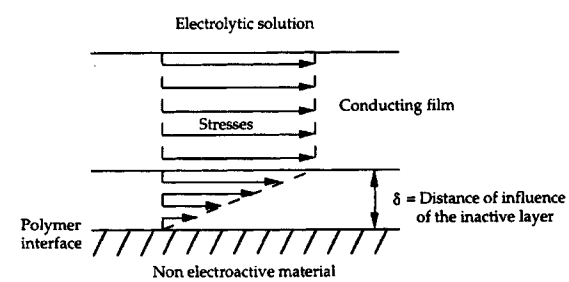

Figure 6. Stress gradient appearing at the polymer–polymer interface as a consequence of the volume increment in the conducting film during oxidation

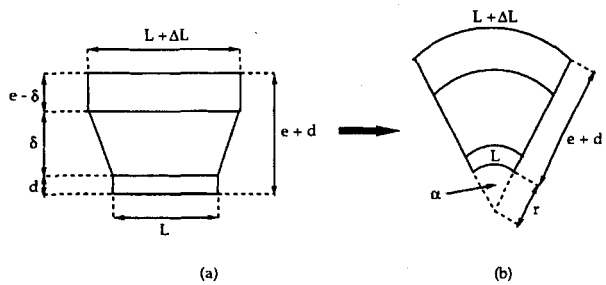

Figure 7. Changes in (a) length and (b) concomitant bending in a bilayer muscle; d represents the thickness of the non-electroactive film, δ the distance of influence of the inactive tape, e the overall thickness of the polypyrrole layer and α the bending angle.

distance x from the interface will be

$$h\frac{Ql}{Ae}\times\frac{x}{\delta} \tag{5}$$

The concomitant length variation in our bilayer (ΔL) will be

$$\Delta L=\begin{pmatrix}\text{length increment}\\ \text{per segment}\end{pmatrix}\times\begin{pmatrix}\text{number of segments}\\ \text{along } L\end{pmatrix} \tag{6}$$

where L is the overall length of the bilayer. Hence we obtain

$$\Delta L=\begin{cases} h\dfrac{QL}{Ae} & \text{if } x>\delta \\ h\dfrac{QL}{Ae}\times\dfrac{x}{\delta} & \text{if } x<\delta \end{cases} \tag{7}$$

Taking into account the change in length as a function of the charge and the distance to the interface, changes in the angle experienced by the free end of the bilayer as a function of the consumed charge can be obtained (Figure 7). The arc of circumference (L), the bending radius (r) and the thickness of the inactive layer (d) are related through the bending angle (α) as follows:

$$\left.\begin{aligned} L&=\alpha r\\ L+\Delta L&=\alpha(r+e+d)\end{aligned}\right\}\rightarrow\ \alpha=\frac{\Delta L}{e+d} \tag{8}$$

Including ΔL in equation (8):

$$\alpha=\begin{cases} h\dfrac{QL}{Ae(e+d)} & \text{if } e>\delta \\ h\dfrac{QL}{A\delta(e+d)} & \text{if } e<\delta \end{cases} \tag{9}$$

These expressions can be written as a function of the doping level (positive charges per volume unit), $\Psi=Q/V_{\text{pol}}$. Hence the expressions for α become

$$\alpha=\begin{cases} h\dfrac{L}{e+d}\Psi & \text{if } e>\delta \\ h\dfrac{Le}{\delta(e+d)}\Psi & \text{if } e<\delta \end{cases} \tag{10}$$

Hence for a constant doping level (Ψ), α is a function of the thickness of the polyconjugated film (Figure 8). Moreover, from an electrochemical point of view, δ can be considered as the optimum thickness of the conducting film to form a bilayer. A greater thickness gives an electroactive material which consumes charge but does not participate in the mechanical stress. A smaller thickness gives a lower ΔL and a concomitant lower α.

If the doping level is assumed to be proportional to the electric potential at which the conducting polymer is submitted (this approximation sufficiently represents real data), a linear dependence between the bending angle and the electric potential is obtained, as observed experimentally.[12] On the other hand, the variation of the bending angle (α) with time as a function of current flow will be given by differentiation of equation (9): $d\alpha/dt=kI$, where I is the current intensity flowing through the electroactive layer and k is a constant which

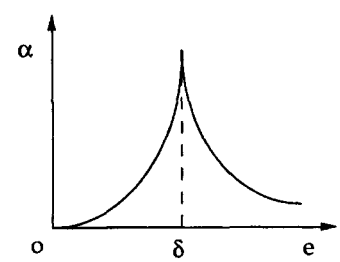

Figure 8. Theoretical variation of the bending angle of a muscle, for a constant consumed charge, as a function of the polypyrrole thickness, according to equation (10). The optimum thickness (δ) is indicated

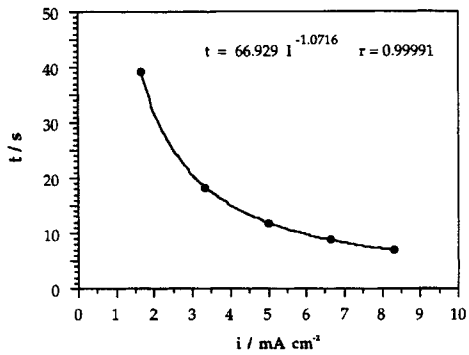

Figure 9. Time required to cross over 180° the free end of a bilayer during oxidation at different current densities. A 1 M $LiClO_4$ aqueous solution was used as the electrolyte and a platinum sheet as the counter electrode

includes all structural and geometrical parameters of the film. From this result, the developed model can easily be compared with experimental results at constant current.[18] By integration under constant current, the time (t) required to describe a constant angle will be given by

$$t = \frac{\alpha}{k} \times \frac{1}{I} \tag{11}$$

As can be seen, the bending time decreases when I increases, as was observed experimentally (Figure 9): a slope of -1 was obtained from a double logarithmic representation of these results, according to theoretical predictions.

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REFERENCES

1. A. Katchalsky and M. Zwick, *J. Polym. Sci.* **16**, 221 (1955).
2. W. Kuhn, I. Toth and H. Kuhn, *J. Makromol. Chem.* **60**, 77 (1963).
3. I. Z. Steinberg, A. Oplatka and A. Katchalsky, *Nature (London)* **210**, 568 (1966).
4. Y. Osada and Y. Saito, *Makromol. Chem.* **176**, 2761 (1975).
5. Y. Osada, *J. Polym. Sci., Polym. Chem. Ed.* **15**, 255 (1977).
6. R. H. Baughman and L. W. Shaklette, in *Science and Applications of Conducting Polymers*, edited by W. R. Salanek, D. T. Clark and E. J. Samuelsen, p. 47. IOP Publications, Bristol (1990).
7. P. Burgmayer and R. W. Murray, *J. Am. Chem. Soc.* **104**, 6139 (1982).
8. T. F. Otero, E. Angulo, J. Rodríguez and C. Santamaría, *J. Electroanal. Chem* **341**, 369 (1992).
9. T. F. Otero, J. Rodríguez, E. Angulo and C. Santamaría, *Synth. Met.* **55**, 3713 (1993).
10. T. F. Otero, E. Angulo, C. Santamaría and J Rodríguez, *Synth. Met.* **54**, 217 (1993).
11. T. F. Otero, H. Grande and J. Rodríguez, *J. Electroanal. Chem.* **394**, 211 (1995).
12. T. F. Otero and J. Rodríguez, in *Intrinsically Conducting Polymers: an Emerging Technology*, edited by M. Aldissi, pp. 179–190. Kluwer, Dordrecht (1993).
13. T. F. Otero and J. Rodríguez, *Synth. Met.* **55**, 1418 (1993).
14. T. F. Otero, C. Santamaría, E. Angulo and J. Rodríguez, *Synth. Met.* **43**, 2947 (1991).
15. T. F. Otero and C. Santamaría, *J. Electroanal. Chem.* **312**, 285 (1991).
16. T. F. Otero, J. Rodríguez and H. Grande, *Synth. Met.* **76**, 285 (1996).
17. P. J. Flory, *Principles of Polymer Chemistry*. Cornell University Press, Ithaca, NY (1953).
18. T. F. Otero and J. M. Sansiñena, *J. Bioelectrochem. Bioenerg.* **38**, 411 (1995).