

Nucleation, Relaxation and Diffusion During Oxidation-Reduction Processes in Conducting Polymers

T.F. Otero*, J. Rodríguez and H. Grande

Laboratorio de Electroquímica, Facultad de Química de San Sebastián, Universidad
del País Vasco, P.O. Box 1072, 20080 San Sebastián, Spain

Received: April 6, 1994; September 9, 1994

Quando um polímero condutor, como polipirrol, é oxidado eletroquimicamente, ocorre a entrada de contra-íons da solução no polímero sólido. Este processo promove substanciais mudanças configuracionais e variações de volume no polímero. Deste modo, a oxidação ocorre através de um processo de nucleação/relaxação do emaranhado polimérico, que se abre promovendo um aumento do volume. Quando a estrutura está aberta, a oxidação obedece às leis de difusão. Nas curvas de I-t, estes processos aparecem como respostas do tipo nucleação. A demora na resposta eletroquímica a um salto anódico de potencial é mais importante quando o filme é pre-polarizado em potenciais mais negativos.

When a conducting polymer, such as polypyrrole, is electrochemically oxidized, counterions from the solution enter the solid polymer. This process promotes substantial conformational changes and volume variations in the polymer. The oxidation occurs through a nucleation/relaxation process of the polymeric entanglement, which then opens, promoting an increase in volume. When the structure is opened the oxidation is governed by diffusion laws. These processes are presented as nucleation-like responses in the I-t curves. The delay in the electrochemical response to an anodic potential step is more important when the film is pre-polarized at more negative potentials.

Keywords: *polypyrrole, relaxation, nucleation, oxidation, diffusion, solid state*

Introduction

A considerable amount of work has been done related to the electrochemical doping of conducting polymers^{1,2}. This way of doping allows the achievement of an electrically tunable doping level, and thus appears to be of particular interest for possible applications based on the electrical control of appropriate properties, such as optical, mechanical and electronic^{3,4}.

The kinetics of the electrochemical doping of a conducting polymer film depends on the history of the electrochemical events undergone by the film^{5,6}. Thus, the electrochemical properties of a given conducting polymer film are not intrinsic characteristics. This fact is associated with the physical nature of the electrochemical doping processes.

When an electroactive polymer such as polypyrrole is used as an electrode and submitted to a positive potential for a long enough time, an equilibrium state is attained with the formation of positive charges along polymer chains⁷. To keep its electroneutrality, negative charges have to

penetrate the polymer. The opening of channels, changes of volume and important conformational changes take place. These conformational variations are relaxation processes in the polymer, controlled by the external electrical current. All the information related to the relaxation process can be described by the anodic current flowing through the external circuit, after the positive potential step. When the polymer is reduced, cathodic polarizations promote the injection of electrons into the polymer and the concomitant neutralization of positive charges. Reverse conformational changes occur, which promote the closing of channels, and counterions are expelled from the polymer.

The opening and closing of channels, with the inclusion and exclusion of counterions, promotes an expansion and contraction of the polymer volume. The hypothesis of a change in volume in the polymer film can be proven by translating the molecular movement to a macroscopic movement by constructing a conducting polymer/flexible non-conducting polymer bilayer. The overall process of oxidation and reduction in the film can be described as an overlap of relaxation, electrochemical reactions, nucleation

and diffusion processes taking place in a solid state. In this work we present a qualitative representation of the processes occurring in polypyrrole during the transition from neutral thick polypyrrole films to positive charged polypyrrole films.

Experimental

Polypyrrole films were electrogenerated and tested in a one-compartment electrochemical cell, connected to a M273 PAR potentiostat-galvanostat. The working electrode was a 1 cm² platinum sheet coated with an electrogenerated polypyrrole film. A 4 cm² surface area platinum sheet was employed as the counterelectrode. The reference electrode was a saturated calomel electrode (SCE) and was introduced directly into the cell. Acetonitrile (Lab Scan. HPLC grade) was used as received. The monomer (pyrrole) and LiClO₄ were supplied by Merck. The monomer was distilled under vacuum before use.

Generation of films

The polypyrrole films studied in this work were electrogenerated on platinum electrodes with a 1 cm² surface area. The solution used to generate the film was acetonitrile + 2% of water containing 0.2 M pyrrole and 0.1 M LiClO₄. Polymerizations were carried out by consecutive square waves of potentials between -500 (2 s) and 800 (10 s) mV. With this method homogeneous and very electroactive films are obtained⁸. Once the polymer film was generated, the working electrode was rinsed with acetonitrile and transferred to the background solution (0.1 M LiClO₄ in acetonitrile), in the absence of the monomer, where it was submitted to chronoamperometric analysis.

Results and Discussion

Figure 1 shows a typical chronoamperometric response of a 15 μm polypyrrole film, submitted to a potential step between -2200 and 100 mV, in a 0.1 M LiClO₄ acetonitrile solution. The chronoamperogram shows a sharp initial current maximum related to the charge of the electrical double layer at the polymer/solution interface. After a minimum the current increases again. This minimum is related to the relaxation process of the molecular entanglement, the opening of channels and the penetration of counterions. When the oxidation step starts from a closed film (polarized at a high negative potential), counterions have more difficulty penetrating the film, and the oxidation process occurs much more slowly. Molecular movements (relaxations) begin at specific points of the surface, nucleating the formation of a conducting phase, where the entanglement of the polymeric chains is not so compact. Oxidation progresses toward the metal/polymer interface, and it expands on the surface (Fig. 2). The second maximum on the chronoamperogram is related to the coalescence between different expanding regions to complete the

oxidation. After this maximum, the structure is opened and the oxidation takes place following diffusion laws.

The relaxation-oxidation-nucleation and expansion processes are dependent on the starting cathodic potential of polarization. This fact is observed in Fig. 3, which represents the time needed to attain the maximum of nucleation/relaxation in a polypyrrole film, submitted to a potential step from different cathodic potentials to a constant potential of 100 mV. As observed, the more cathodic the initial potential, the greater the delay in the beginning of the oxidation related to the opening of the polymer structure. The electrical charge consumed during oxidation is always the same regardless of the cathodic potential, because it is only controlled by the anodic limit of potential. The results shown in Fig. 3 are reproducible, indicating the more negative potential at which a polymeric film was polarized.

The explanation for the influence of the cathodic polarization arises from the relaxation effect that occurs in the polymer, accompanying the oxidation process. Polarization at more negative potentials gives a more effective release of counterions, a more effective contraction of the polymeric entanglement, and therefore a more effective closing of the polymeric structure. This effect hinders the

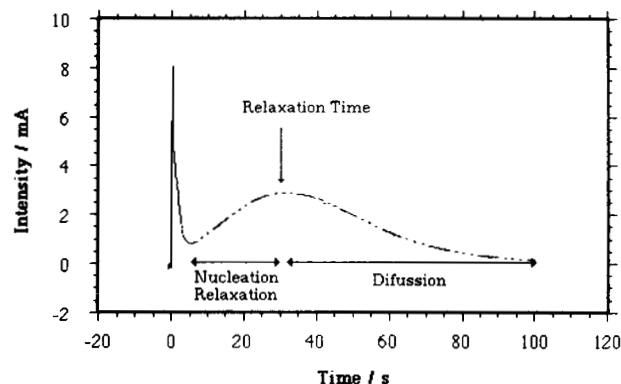


Figure 1. Chronoamperometric response of a polypyrrole film (15 μm thickness), submitted to a potential step from -2200 mV to 100 mV, in a 0.1 M LiClO₄ acetonitrile solution.

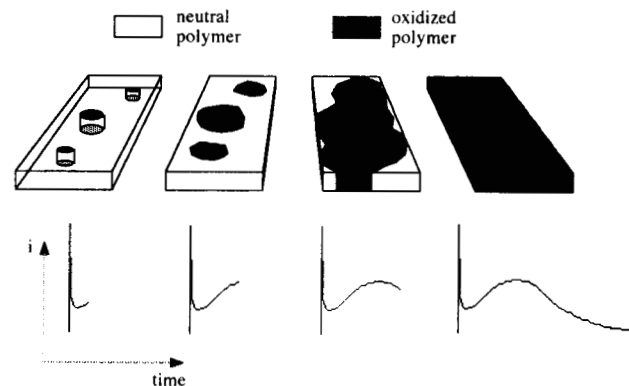


Figure 2. Evolution of the surface aspect of the polypyrrole film during the oxidation reaction initiated from high negative potentials. The chronoamperometric response is shown at the bottom.

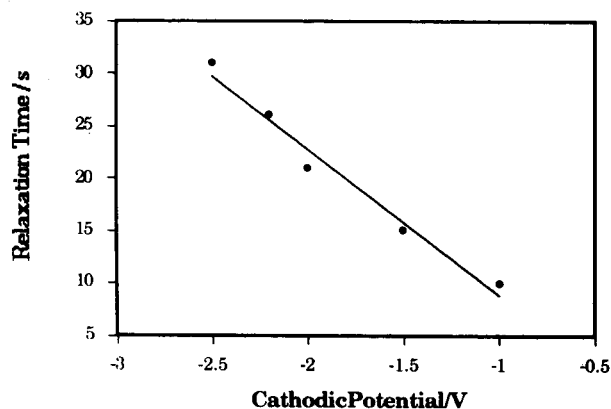


Figure 3. Relaxation times as a function of the cathodic potential of pretreatment, for polypyrrole films (15 μm thickness), submitted to a potential step from different cathodic potentials to 100 mV, in a 0.1 M LiClO_4 dry acetonitrile solution. The times were measured at the maximum of the chronoamperometric responses.

entrance of the counterions during subsequent oxidations. Thus, the effect of the cathodic polarization is observed as a delay on the oxidation process of the polypyrrole film. Similar behavior has been observed in voltammetric studies. In these cases, the overpotential of the maximum on the I-V responses shifts to being more anodic when the cathodic limit is made more negative⁹.

In conclusion, the comprehension of these structural relaxation/nucleation processes appears to be of particular interest for the emergent applications of conducting polymers based on the electrical control of their electrochemical properties, such as in electrochromic devices (for the control of the response times)¹⁰ or polymeric batteries (for controlling the time of discharge)¹¹. In addition, the control of the molecular movements has been used in the construction of artificial muscles, using a conducting polymer/non conducting flexible polymer bilayer¹²⁻¹⁴. In this case, small dilatations or contractions in the conducting polymer due to its oxidation/reduction, can be translated into an asymmetric stress between the faces of the flexible layer, promoting mechanical movements of 180° (Fig. 4). This movement could be applied in the future to artificial muscles, ion sensors or switching systems¹².

Acknowledgments

This work was supported by Diputación Foral de Guipúzcoa and the Universidad del País Vasco.

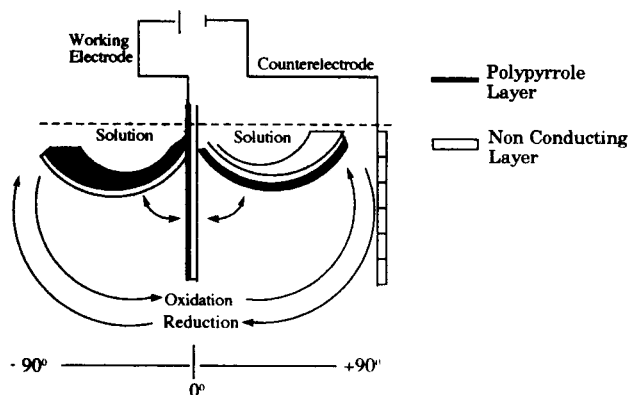


Figure 4. Scheme of the structure of the polypyrrole/non conducting film bilayer and its movement by application of an electrical potential, between -200 (-90° position) and 400 mV (+90° position). Electrolyte: 0.1 M LiClO_4 aqueous solution.

References

1. J.W. Sease and L. Zechmeister, *J. Am. Chem. Soc.* **69**, 270 (1987).
2. G.B. Street, S.E. Lindsey and A.J. Nazzari, *Mol. Cryst. Liq. Cryst.* **118**, 137 (1985).
3. S. Roth, *Synth. Met.* **21**, 51 (1987).
4. M. Gazar, *Handbook of Conducting Polymers* (T.A. Skotheim, ed., N.Y., 1986), vol. 1, p. 673.
5. C. Odin and M. Nechtschein, *Synth. Met.* **55**, 1287 (1993).
6. G. Tourillon and F. Garnier, *J. Electroanal. Chem.* **161**, 51 (1984).
7. M. Yuki, M. Kasuji, L. Nyholm and L.M. Peter, *Synth. Met.* **55**, 1515 (1993).
8. T.F. Otero, E. Angulo, C. Santamaría and J. Rodríguez, *Synth. Met.* **54**, 217 (1993).
9. T.F. Otero and E. Angulo, *Solid State Ionics* **63**, 803 (1993).
10. T. Kobayashi, H. Yoneyama and H. Tamura, *J. Electroanal. Chem.* **161**, 419 (1984).
11. P.G. Pickup and R.A. Osteryoung, *J. Electroanal. Chem.* **195**, 271 (1985).
12. T.F. Otero and J. Rodríguez, *Intrinsically Conducting Polymers: An emerging Technology*. (M. Aldissi, ed., Kluwer Academic Publ., Vermont, 1993), p. 179.
13. T.F. Otero, J. Rodríguez, E. Angulo and C. Santamaría, *Synth. Metals* **57**, 3713 (1993).
14. T.F. Otero, E. Angulo, J. Rodríguez and C. Santamaría, *J. Electroanal. Chem.* **341**, 369 (1992).