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Nucleation and Nonstoichiometry in Electrochromic Conducting Polymers

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1. Introduction

In the context of the Electrochemically stimulated conformational relaxation (ESCR) model,[1–4] when a conducting polymer such as polypyrrole is reduced, the polymer shrinks, and the diffusion of counterions towards the solution becomes more and more difficult. The reduction only can be completed by polarization at high cathodic potentials which provide enough energy to expel the remaining counterions by stimulation of conformational movements and creation of the required pores throughout the increasingly compacted structure. The kinetic process is now under conformational relaxation control. Those pores close behind the moving ion due to the strong polymer–polymer interactions between reduced chains, and the structure becomes more and more compact and closed as the reduction goes on. The degree of compactness depends on both the cathodic electric potential applied to the polymer and the polarization times. Longer times or more negative potential of prepolarization will promote more compact polymeric films, which will produce a perturbation on the subsequent oxidation responses of the prepolarized films.[5–8]

For every conducting polymer there exists a cathodic potential, known as the closing potential (E_s), which limits those regions where the reduction occurs under diffusion control or relaxation control. When the polymer is polarized at anodic potentials greater than E_s, the subsequent oxidation occurs under diffusion control of the counterions. When the reduction is produced by polarization at more cathodic potentials, the polymer is compacted and the subsequent oxidation will occur under conformational relaxation control of the polymeric chains. The anodic potential step promotes the extraction of electrons from the chains. Polarons and bypolarons are formed[9–11] inducing coulombic repulsions between neighboring chains. The subsequent conformational movements generate the necessary free volume for those counterions required[12–14] to keep the electroneutrality, and the polymer swells. As the compaction of a material is not uniform, the oxidation is initiated on singular points (nuclei) of the surface where the entangle-

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ment of the polymeric chains is not so dense. The oxidation progresses very fast toward the metal interface due to the higher potential gradient across a thinner reduced film of polymer, and a cylinder of oxidized, swollen and conducting material is formed from every nucleus (Figure 1). A mechanical stress will appear
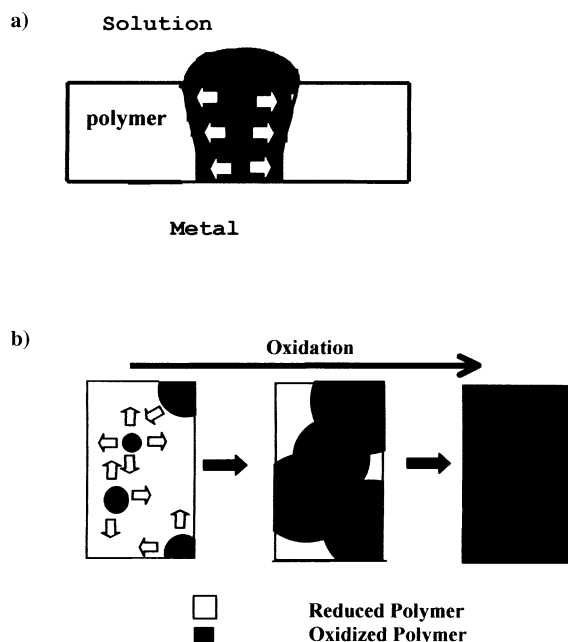

Figure 1. *Proposed formation and expansion of the nuclei on an electrochromic film of a conducting polymer after a potential step from a cathodic potential of compaction to an oxidation potential. a) Lateral view: formation of an oxidized polymer cylinder b) Top view: expansion of the cylinders during the oxidation times.*

across each cylinder border due to this change of volume, which favors the oxidation of the reduced regions by expansion of the oxidized cylinders. Thus, columns of conducting material are formed, which expand on the reduced film until their coalescence. This coalescence process can be quantified by the Avrami expression.[15] Once the structure of the film is opened and all the nuclei have coalesced, the oxidation is completed under diffusion control. The proposed process is shown in Figure 1.

A chronoamperometric response showing relaxation/nucleation or diffusion-controlling domains is depicted in Figure 2. The chronoamperogram shows a sharp initial current maximum related to the charge of the electrical double layer at the polymer – solution interface and to the beginning of the relaxation process. After a minimum the current increases again; this increase fits the theoretical formation and growth of a progressive nucleus,[16–19] and the model suggests that this occurs under conformational relaxation kinetic control. The nuclei then expand on the reduced and compacted film, and the second maximum is related to the coalescence between different expanding regions. The relaxation time is the time at which the maximum occurs.[1, 4] After this maximum all the polymeric structure is opened and the oxidation is completed under diffusion control.
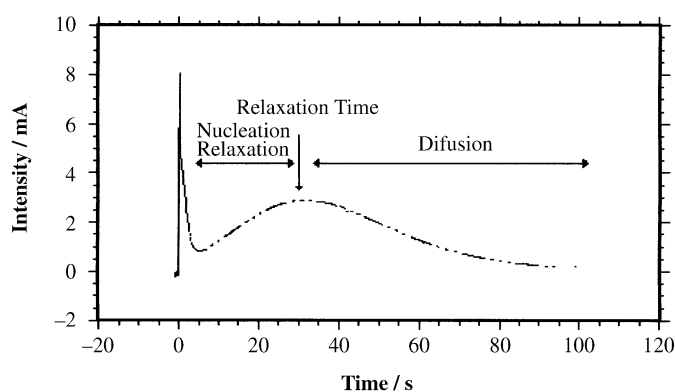

Figure 2. *Chronoamperometric response using a 22-μm thick polypyrrole film submitted to a potential step from − 600 mV (maintained for one minute) to 900 mV in 0.2 M LiClO$_4$ acetonitrile solution at room temperature. The different kinetic controlling processes are shown.*

The aim of this work is to prove, by using thin and electrochromic films and macroscopic pictures, that nucleation and correlated facts such as conformational movements and relaxation are general features of the oxidation of compacted conducting polymers. In this way we will electrogenerate and control electrochromic films of poly(1-methylpyrrole), polyaniline, poly(methylaniline), polythiophene and poly(3-methylthiophene). If the nucleation process is observed we will try to check if the oxidized electrochromic material forms a stable and stoichiometric material.

2. Results and Discussion

As predicted by the ESCR model, all the studied conducting polymers show that the formation of nuclei when the polymer is oxidized by a potential step (Figure 3) after compaction by cathodic polarization at a potential 300 mV more cathodic than the closing potential of each studied polymer.[1, 20]

So, choosing suitable experimental conditions for both electrochemical synthesis and control of the films' nucleation processes can be observed by the electrochromic nature of the films, as was proved here. The nucleation process of an amorphous material, the oxidized polymer, into another amorphous material, the reduced and compacted polymer, is described by the ESCR model. The nucleation is a consequence of the compaction and structural changes, swelling and shrinking, and is promoted by the electrochemical stimulation of the conformations along the polymeric chains. The number of nuclei per square centimetre (n), the magnitude required by the theoretical equations for the simulation of the experimental responses, can be experimentally obtained by amplification of the obtained pictures, or by treatment of the recorded images.

Having shown that compaction and nucleation are general processes of the electrochemistry of the studied conducting polymers, we now explore the nonstoichiometric nature of those materials.[21] If a nucleus is growing and the composition of the oxidized material is constant and well-defined when the polarization is switched off at the middle of the growth, both the shape and color of the nuclei will remain constant.
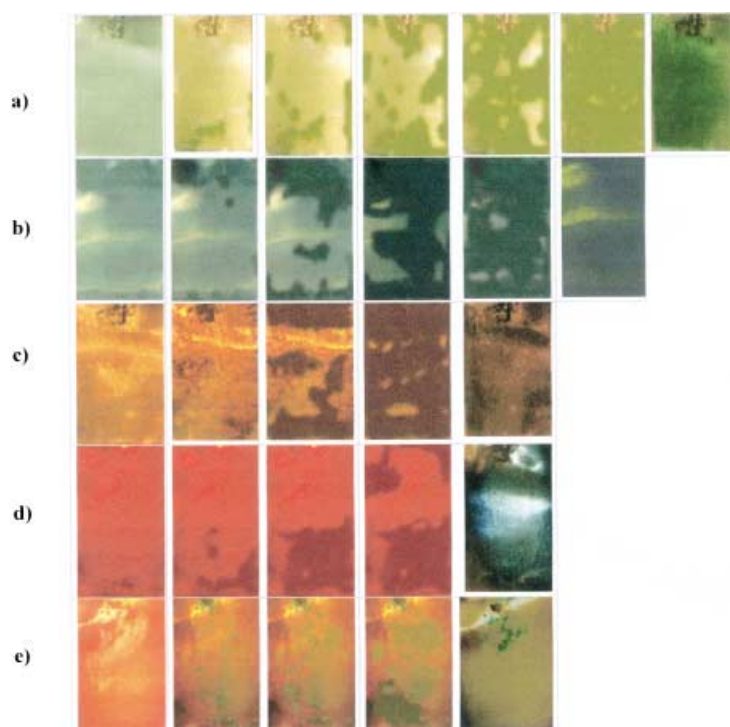
Figure 3. *Formation and growth of nucleus during the oxidation of conducting polymer films, previously compacted by polarization at high cathodic potential, under constant temperature (25 °C) in 0.1 M LiClO₄ acetonitrile solution (electrode 1 × 0.5 cm). a) Polyaniline, reduced and compacted at −850 mV, kept for 60 s (initial picture), during the oxidation time photos were taken at 0, 5, 8, 10, 12, 14, and 16 s after a potential step to 300 mV. b) Poly(methylaniline) compacted at −1200 mV for 60 s, during the oxidation time; photos were taken at 0, 5, 9, 12, 14, and 16 seconds after a potential step to 400 mV. c) Poly(1-methylpyrrole) compacted at −1800 mV for 60 s, along the oxidation time; photos were taken at 0, 5, 9, 12, and 15 seconds after a potential step to 300 mV. d) Poly(3-methylthiophene) compacted at −900 mV for 60 s, during the oxidation time photos were taken at 0, 5, 9, 12, and 15 s after a potential step to 900 mV. e) polythiophene compacted at −600 mV for 60 s, during the oxidation time photos were taken at 0, 5, 9, 12, and 15 s after a potential step to 800 mV.*

after 3, 5, or 8 s, from the beginning of the anodic polarization. Thus the growth of the nuclei was interrupted in different states of growth, and we continued taking pictures after switching the polarization off. New pictures were taken after 11, 14, and 18 s; these are shown in Figure 4.

The first point to be recognized is the perfect reproducibility of the nuclei and their geographic distribution at equal times from the different series. Our hypothesis is that the molecular structure of the material and the material morphology is responsible for those points at the polymer – solution interface, where the compacted polymeric chains have greater mobility and a stronger field. When the oxidation potential is applied, conformational movements and penetration of counterions were always initiated at the same points; those with higher chain mobility. Our results suggest that oxidation/swelling and reduction/compaction are reciprocal processes which, if applied sequentially, leave the material in the same initial state. This explains the origin of the reproducibility of the nucleation.

On the other hand, whatever the intermediate oxidation time and the dimensions attained by the generated nuclei, after interruption of the polarization,
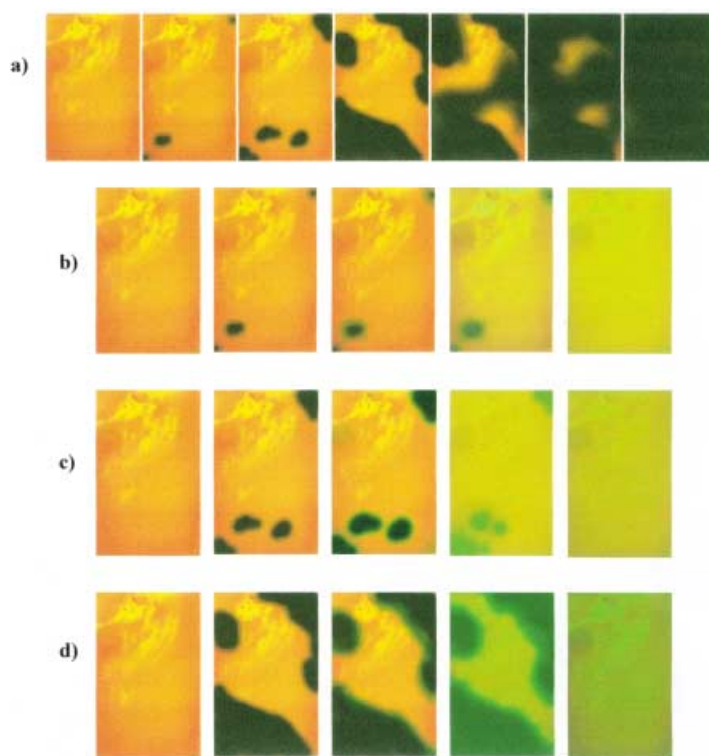

Figure 4. *Polypyrrole films compacted by cathodic polarization at −1200 mV, maintained for 60 s, and oxidized by a potential step to 100 mV at constant temperature (25 °C) in 0.1 M LiClO₄ acetonitrile solution, showing the formation and growth of nuclei (blue dark) on the compacted and reduced film (yellow). a) The film was oxidized at 100 mV for 0, 3, 5, 8, 12, 15 s, and until the end of the nucleation/coalescence and oxidation processes. The procedure was repeated switching off the oxidation/nucleation after: b) 3, c) 5, and d) 8 s. After that new photos were taken to follow the evolution of the system at intervals of 3 s.*

If the amorphous material behaves as a nonstoichiometric material, the stress existing between oxidized and reduced regions, due to the increase of volume during oxidation, will promote the oxidation and swelling of the reduced region, at the expense of the partial reduction and shrinking of the oxidized nuclei. The process will take place whatever the attained dimensions of the nuclei when the current is switched off, however, the concomitant final uniform oxidation states and colors are more important the larger the nuclei are before the interruption of the polarization.

In this way a film of polypyrrole ($E_{s=}$ − 900 mV) was compacted by cathodic polarization at − 1200 mV, then the potential was stepped to the oxidation potential of 100 mV. The formation and growth of nuclei at 25 °C in 0.1 M LiClO₄ acetonitrile solution can be followed in Figure 4a after 0, 3, 5, 8, and 10 s of polarization. After this time the relaxation – nucleation and coalescence processes were completed.

The process was repeated three times by compaction of the film and subsequent oxidation but interrupting the polarization

the reduced material is oxidized at the expense of the oxidized nuclei and attains a uniform final state of oxidation after 6 – 7 s. The final state is oxidized more (the oxidized regions are a dark blue), the longer the oxidation time and the greater the number of nuclei generated before the interruption of polarization. All these facts point to the behavior of the oxidized conducting polymer as a nonstoichiometric material: any of the polymer – counterion compositions in the range between those of the reduced and compacted state and that of the oxidized state can be attained. Any intermediate growth of nuclei is not stable energetically: the equilibrium potentials of the oxidized and reduced domains are different, establishing a potential gradient that promotes the oxidation of the reduced domains at the expense of the oxidized ones, which will be partially reduced. Electrons extracted from the reduced domains flow to the oxidized regions to compensate polarons, and the concomitant counterions migrate from the oxidized domain to the reduced region (see Figure 5). If the conductivity of the reduced and compacted domains is very low, all the transfer of charge (electrons and counterions in opposite senses) will occur throughout the interface between both states: after interruption of the oxidation, an expansion of every nucleus will take place at the same time as the intensity of their color decreases. If the conductivity of the reduced domains is adequate the electrons will flow towards the oxidized nuclei from the entire reduced domain, the counterion compensation taking place through the

solution: the increasing blue color is uniform in the reduced domains.

In addition to the potential gradient between both domains, there exists a mechanical stress gradient, due to the swelling process occurring during oxidation. The chains of polymer crossing the border between both domains contributes to the mechanical stress gradient, thus favoring the expansion of the nuclei after interruption of the oxidation.

The final result shown by the pictures is intermediate: every nucleus tries to expand, but at the same time a uniform oxidation of the reduced regions is also present.

We can conclude that all the studied conducting polymers can be reduced and compacted by polarization at high cathodic potentials. After compaction, electrochromic films are oxidized under relaxation – nucleation control and the formation and growth of oxidized nuclei of dark colors can be followed on the reduced and clear domain.

Compaction, relaxation and nucleation are very reproducible processes: the nuclei start to grow always on the same places under cyclic electrochemical processes.

The oxidized material is nonstoichiometric: any intermediate state of oxidation or polymer – counterion composition can be attained. This is the origin of the instability of the oxidized nuclei. After interruption of the electrochemical oxidation, the oxidized nuclei suffer a partial reduction, promoting the partial oxidation of the reduced domains.
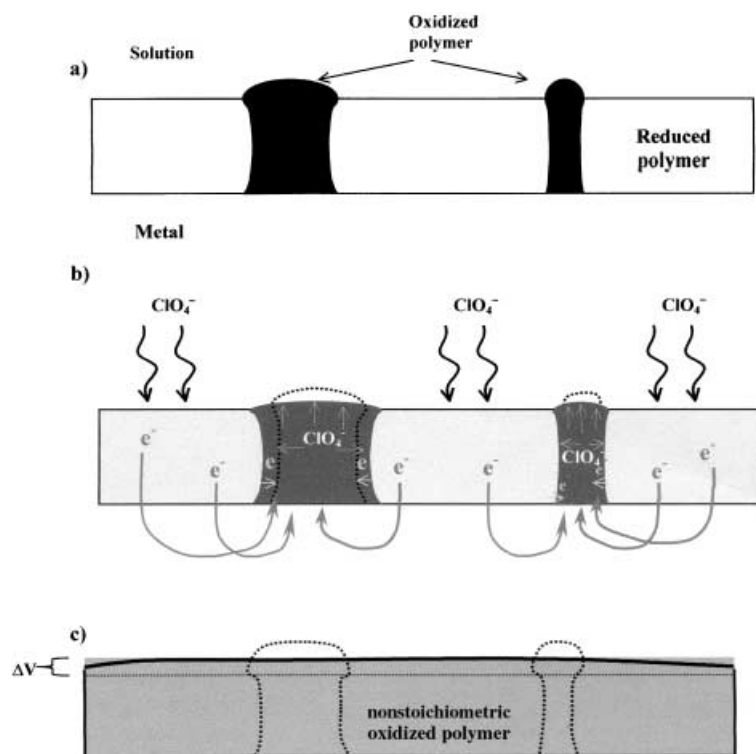

Figure 5. a) Lateral representation of the formation of an oxidized polymer cylinder after a potential step from a cathodic potential of compaction to an oxidation potential. b) Lateral representation of the nuclei expansion when the chronopotentiostatic oxidation is stopped. This figure shows electron flow towards the oxidized nuclei from the entire reduced domain and the counterion compensation through the solution. c) Final state of the partially oxidized polymer.

Experimental Section

Polymer films were electropolymerized and checked in a one-compartment electrochemical cell, connected to a PAR M270 potentiostat-galvanostat and controlled from a PC. Working electrode and counter electrode were platinum sheets with a 1 and 4 cm^2 surface area, respectively. The working platinum electrode was polished to a mirror finish using a Struers Dap-7 polishing machine and Struers alumina paste with grain sizes less than 9 μm. A saturated calomel electrode (SCE) from Crison Instruments was used as reference electrode. Monomers (pyrrol, Aldrich 98%; 1-methylpyrrole, Fluka 98%; aniline, Merck for analyse, methylaniline, Aldrich 98%; thiophene, Janssen 99%; 3-methyl thiophene, Janssen 99%) were distilled under vacuum before use and stored under N_2 at $-10\,°$C. Acetonitrile (Lab Scan, HPLC grade), anhydrous lithium perchlorate (Aldrich, 95% content), and sulfuric acid (Merck, 95 – 97% content) were used as received. All the solutions were deaerated by bubbling N_2 through them for 10 min before the current flow. A Casio LCD digital camera was used to take photographs.

Polymer films were generated electrochemically on the mirror polished platinum electrodes by flow of 50 mC cm^{-2} throughout the solution. After checking potentiostatic and galvanostatic methods, three different electrochemical methods, those which resulted in the flattest, most uniform and most electrochromic films, were used to generate the films.

1) At constant potential: Polypyrrole, and poly(1-methylpyrrole) were generated at a constant potential

of 700 mV in 0.2 M $LiClO_4$ + 0.1 M monomer (pyrrole or 1-methyl-pyrrole) acetonitrile solution.

2) By consecutive square waves of potential (3 seconds at −300 mV followed by 8 seconds at 700 mV and back to −300 mV until established polymerization charge (oxidation minus reduction charge) was completed. Polythiophene and poly(3-methylthiophene) were generated in 0.2 M $LiClO_4$ + 0.1 M monomer (thiophene or 3-methylthiophene) acetonitrile solution by those consecutive potential steps.

3) By potential cycling (polyaniline and poly(methylaniline) films were grown by potential cycling at 50 mVs^{-1} between −100 and 900 mV in 0.2 M aniline + 0.1 M H_2SO_4 aqueous solutions, until the overall polymerization charge was completed.

The thickness of the obtained films was around 0.22 μm, according to SEM observations of the dry films. After electrogeneration each polymer-coated electrode was rinsed with acetonitrile and transferred into the solution in which both electrochemical and electrochromic control would take place: 0.2 M lithium perchlorate acetonitrile solutions. There the electrodes were reduced at the compaction potential (E_c) for 1 min. Each of the studied polymers has a different value for its closing potential[22] (E_s) and the selected compaction potentials, −600 mV for polythiophene, −900 mV for poly(3-methylthiophene), −1800 mV for poly(1-methylpyrrole), −850 for polyaniline and −1200 mV for poly(methylaniline), were 300 mV more cathodic that each closing potential (E_s), as the compaction overpotential, $\eta = E_c - E_s$, is constant, whatever the studied polymer.

Once the polymer films were compacted the potential was stepped to an anodic potential able to oxidize the polymer (800 mV for polythiophene, 900 mV for poly(3-methylthiophene), 300 mV for poly(1-methylpyrrole), 300 mV for polyaniline and 400 mV for poly-(methylaniline)). The polymers were oxidized under an inert atmosphere by bubbling N_2 during oxidation.

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Freely Suspended Actin Cortex Models on Arrays of Microfabricated Pillars

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Numerous chemomechanical processes of cells, such as pseudopod formation during cell locomotion[1] and the capping process preceding the engulfment of pathogens by macrophages during immunological responses,[2, 3] are mediated by the actin-based cytoskeleton. In quiescent cells, the cytoskeleton consists of a partially crosslinked network of actin filaments forming a shell, several hundreds of nanometers thick, called the actin cortex. On the other hand, the activation of cells (for example, the endothelial cells lining the inner walls of blood vessels, by inflammation-mimicking agents such as thrombin) often leads to the formation of actin bundles coexisting within the random actin network.[2, 4] Several families of actin-manipulating proteins control the structure and viscoelastic properties of the actin cytoskeleton. These proteins include: 1) sequestering molecules which control the fraction of polymerized actin; 2) severing proteins which control the filament length; and 3) linker proteins mediating crosslinking between actin filaments and their coupling to membranes.

Several studies of the structural reorganization of the actin-based cytoskeleton during pseudopod formation,[5] the centripetal contraction of endothelial cells by inflammation signalers, such as thrombin,[6] and the formation of focal contacts to stabilize cell adhesion[7, 8] have yielded some insight into the regulation of the actin cytoskeleton by biochemical signaling. Micromechanical studies of cell membranes have provided some information on the correlation between the viscoelastic behavior of cells and the structure of the actin cortex,[9] and on its role for the generation of forces.[10]

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