Structural Electrochemistry: Conductivities and Ionic Content from Rising Reduced Polypyrrole Films

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Free-standing polypyrrole films are submitted in NaCl aqueous solutions with different potentials corresponding to the swollen, closed, or reduced and rising conformational packed states, defined from the closed coulovoltammetric responses in the potential range between –1.5 and 0.65 V versus Ag/AgCl. Decreasing anion content from rising reduced and conformational packed films is detected by energy-dispersive X-ray spectroscopy (EDX) analysis. The cation, Na^+, is not present in the studied samples. At the closing potential, the film keeps over 30% of the counterions present in a fully oxidized film. The film reduction-compaction process at high cathodic potentials consumes over 15% of the full redox charge, expelling a similar percentage of counterions. By using free-standing PPy-DBS films, the Na^+ content increases for rising reduced states, but some increase of the chloride content is attained for deep oxidized and packed states. This polypyrrole blend experiences a major exchange of cations for charge balance. Some polypyrrole chains not balanced by DBS require perchlorate exchange at high anodic potentials. The continuous decrease of anion content promotes in polypyrrole films a parallel decrease of the electronic conductivities obtained in nitrogen atmosphere. Ionic content and conductivities in polypyrrole films support that the two structural reduction (shrinking and compaction) processes correspond to the same reaction: the injection of electrons and expulsion of counterions with two different kinetics imposed by two reaction-induced 3D structures (swollen or closed and rising packed) in the film.

1. Introduction

Coulovoltammetric data from films of conducting polymers on metals or from self-supported films present a clear graphical separation of the structural processes induced by oxidation (conformational relaxation and swelling) or reduction (shrinking, closing, and conformational compaction) during p-doping/p-dedoping processes in aqueous electrolytes.[1,2] Those structural changes were theoretically described and quantified by the electrochemically stimulated conformational relaxation model (ESCR).[3–13] When open, closed, or rising compacted conformational states are used as initial states for the determination of the kinetic magnitudes, the kinetic coefficients, activation energies, and reaction orders change as a function of the initial packed conformational state.[14]

By using self-supported polypyrrole (PPy) films with a prevalent exchange of anions with the aqueous solution, the film keeps a high electroactivity up to higher cathodic potentials than –2.5 V, inhibiting hydrogen evolution.[15] According to the ESCR model, the two reduction-induced structural processes (reduction-shrinking and reduction-compaction) should correspond to the same electrochemical reaction: electron injection into the positively charged polymer chains and counterion expulsion towards the solution. The ESCR model predicts a relatively high concentration of counterions and balancing polarons in the film at the closing potential. This concentration will decrease for deeply reduced and packed films by reduction at rising cathodic potentials. These hypotheses should be in good agreement with high spin[16–18] and charged state[19] content detected in reduced films by EPR or Raman spectroscopic studies. Counterions and polarons present in reduced and packed films are expected to provide them with a high relative electronic conductivity.

Alternatively, the conducting-insulator transition model and the percolation model[18,20–40] claim that the polymer becomes a fully reduced insulator film at the closing potential by total expulsion of the counterions from the film.

Here, we will try to clarify these controversies by following both ion (anion and cation) content (by EDX analysis) and conductivities after reducing different free-standing PPy films up to a different cathodic potential. Films of polypyrrole blends, like polypyrrole-dodecylbenzenesulfonate (PPy-DBS) are expected to follow a prevalent exchange of cations (swelling by reduction and shrinking by oxidation) during electrochemical reactions.[41–45] A parallel study of ionic concentrations and electronic conductivities with the oxidation state will be presented.

2. Results

Free-standing films that should be expected to follow a major exchange of anions (polypyrrole) or cations (polypyrrole-DBS) were subjected to consecutive potential sweeps. After

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DOI: 10.1002/adfm.201302514

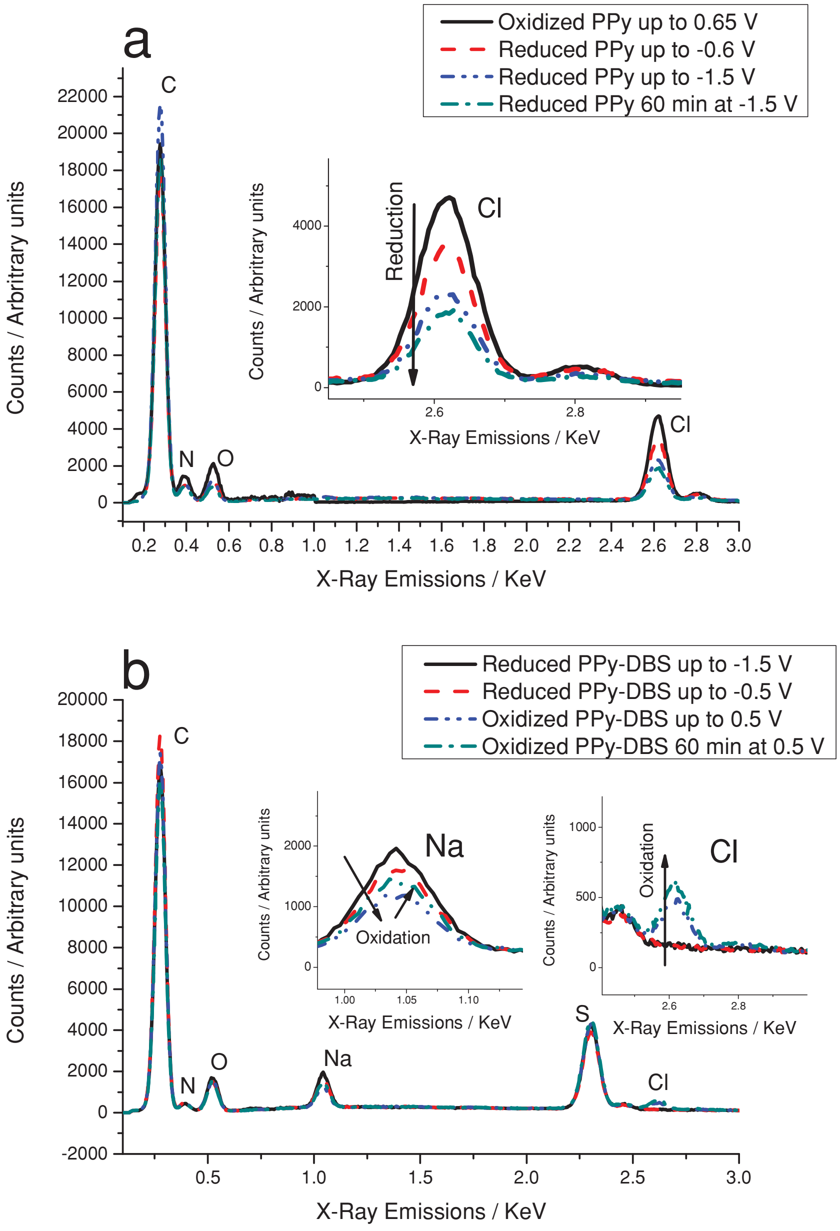

Figure 1. a) EDX spectra from four free-standing polypyrrole electrodes after two consecutive voltammetric cycles between –1.5 V and 0.65 V in 0.1 M NaCl aqueous solution at 1 mV s^{-1}: the second cycle was stopped at 0.65 V (full line: oxidized film), –0.70 V (dashed line; closing potential), or –1.50 V (dash-point-point line; reduced and packed), for each of three different films. A deeper reduction and packed state of a new film was attained by stopping the second cycle at –1.50 V (dash-point line), keeping this reduction potential for 30 min. b) EDX results from four polypyrrole-DBS films after stopping the second potential cycle at –1.5 V (full line; reduced film), at the closing potential (dashed line; –0.5 V), after partial compaction (dash-point line; 0.5 V), or after a deeper compaction (dash-point-point line; 0.5 V kept for 60 min). Inset: Cl and Na evolution detail.

attaining steady state voltammetric responses, the last sweep was stopped at a different potential for each of the studied films, corresponding to swollen (oxidized PPy or reduced PPy-DBS), closed, and deeper conformational packed states (reduction up to rising cathodic potential for PPy and oxidation up to rising anodic potentials for PPy-DBS). According with the coulovoltammetric results presented in previous papers[15] and its description by the ESCR model,[3–13] different concentration of anions or cations, and different conductivities, are expected from the attained materials.

2.1. Counterion Concentration in Deep Reduced and Packed PPy Films

Different self-supported PPy film electrodes were subjected to two consecutive voltammetric cycles in 0.1 M NaCl aqueous solutions at 1 mV s^{-1} between –1.50 and 0.65 V. During the second cycle, the cathodic potential sweep (reduction) was stopped at a different potential for every film: 0.65 V (oxidized material), –0.70 V (closing potential), or –1.50 V (reduced and packed material). A more reduced state was obtained using a different film by reduction after cycling at –1.50 V for 30 min. Every film was then immersed in ultrapure water, to eliminate the adhered liquid electrolyte, and dried.

Each of the dry films was analysed by energy-dispersive X-ray spectroscopy (EDX). Results are shown in **Figure 1**. Clear signals from carbon and oxygen are observed at 0.227 and 0.525 KeV, respectively. Chloride presents two main emission lines at 2.622 and 2.621, showing a secondary emission at 2.816 KeV (Figure 1 inset), indicating that high concentrations of perchlorate exist in the four studied samples. The intensity of the signals shows that the counterion (Cl$^-$) content decreases in the film for deeper reduced and conformational packed states. At the closing potential, the film keeps around 30% of the counterions (related to those present in the film after oxidation at 0.65 V). After reduction/compaction at –1.50 V for 30 min the counterion content is greater than 15%, related to that of the oxidized film. The Na$^+$ should be expected to give a signal at 1.05 KeV, being absent in each of the studied samples.

Those results support a progressive decrease of the anion concentration, according with the ESCR model, during reduction-compaction. Such a high concentration of balancing counterions points to a similar concentration of balance positive charge carriers on the polymeric chains that must support relatively high electronic conductivities. The absence of Na$^+$ ions in the deep reduced and packed film indicates that there is no entrance of cations during reduction, as proposed from quartz crystal microbalance results.[20,46–54]

As a partial conclusion, the coulovoltammetric responses from polypyrrole films electrogenerated in the presence of small anions present two reduction reaction rate evolution slopes in the potential range from 0.65 V to –3 V.[15] Both of them, according with the EDX results, correspond to the same reaction, backwards:

$$(Pol^{*})_s + n(A^{-})_{sol} + m(s) \underset{red}{\overset{ox}{\rightleftarrows}} \left[(Pol)^{n+}(A^{-})_n(S)_m\right]_{gel} + ne^{-} \qquad (1)$$

The initial reduction occurs by expulsion of the anions through an open gel structure under kinetic control of the counterion's diffusion through the gel, during the reduction-shrinking process, before the closing potential is attained.[55]

2.2. Cation Content in Rising Oxidized Polypyrrole/DBS Films

A similar analysis was performed using PPy/DBS films, which are supposed to exchange cations during oxidation/reduction reactions: swelling by reduction and shrinking and packing by oxidation. This is a more complex material than the PPy doped with small ions above presented: here, ions (DBS^{-}) take part of the material whatever its oxidized state.

The attained EDX results are depicted in Figure 1b. Increasing concentration of Na^{+} is obtained for deeper reduced states, corroborating the entrance of cations during film reduction. Nevertheless, after the closing potential, now taking place at anodic potentials, increasing amounts of chloride are detected in deep oxidized (and supposedly packed) films. This fact should indicate that a small fraction of the PPy chains are not compensated by the DBS^{-} macroanion, forcing the entrance of anions (and polymer swelling) when they are submitted to deep oxidation processes.

In conclusion, the EDX results corroborate that the oxidation reaction before and after the closing potential is the same reaction (under different structural reaction rate controls), promoting the expulsion of cations in both potential ranges,

$$\left[(PPy^{0})(DBS^{-})_n(C^{+})_n(S)_m\right]_s \underset{red}{\overset{ox}{\rightleftarrows}} \times \left[(PPy^{n+})(DBS^{-})_n\right]_s + n(C^{+})_{sd} + n(e^{-})_{metal} + mS \qquad (2)$$

as stated by the ESCR model.

Trying to get deeper oxidized and packed states to promote the entrance of anions points to the presence of reaction (1), forwards, related to a fraction of oxidized PPy chains not compensated by DBS^{-} in the film.

2.3. Electronic Conductivities

The steady state coulovoltammetric results are good qualitative indicators of the high electroactivity, electronic, and ionic conductivities of deep reduced PPy films.[1,15] In order to determine why films after reduction up to –2.5 V can be re-oxidized, different self-supported electrodes were cut from the same electrogenerated and reduced polypyrrole film and prepared as for the EDX experiments. The second cathodic potential sweep was stopped at a different potential every time: 0.65 V, –0.70 V, –1.50 V, and –1.50 V, now kept for 30 min in order to get a more reduced state. Each film was rinsed with de-aerated water and kept in nitrogen atmosphere. The conductivities of each of the prepared films were measured in a nitrogen atmosphere (containing only 1.2 parts per million of oxygen) in a glove box after remaining for several hours in this inert atmosphere. The average evolution of the current (among 5 measurements in a different part of the material every time) as a function of the potential gradient applied to the two points is presented, for the different samples, in **Figure 2**. The non-linear responses are characteristic of semiconductor materials. The conductivity was determined from the slope of the linear part around 0 V.[56] The average conductivities of the oxidized, closed, and rising reduced and packed films were: 0.2700 S cm^{-1}, 0.0205 S cm^{-1}, 0.0033 S cm^{-1} and 0.0025 S cm^{-1}, respectively, with a precision of $\pm 1 \times 10^{-4}$ S cm^{-1}. The conductivity decreases for rising reduced and packed films, in good agreement with the experimental (EDX) decrease of the counterion content and the concomitant decrease of the concentration of the balancing polarons on chains.

In a similar way to the counterion content, the conductivities of the PPy-DBS films (always higher than those from PPy films) evolve in a complex way: rising values were obtained from more oxidized films (0.36 to 12.35 S cm^{-1} from films for which a second voltammetric sweep was stopped in the potential range

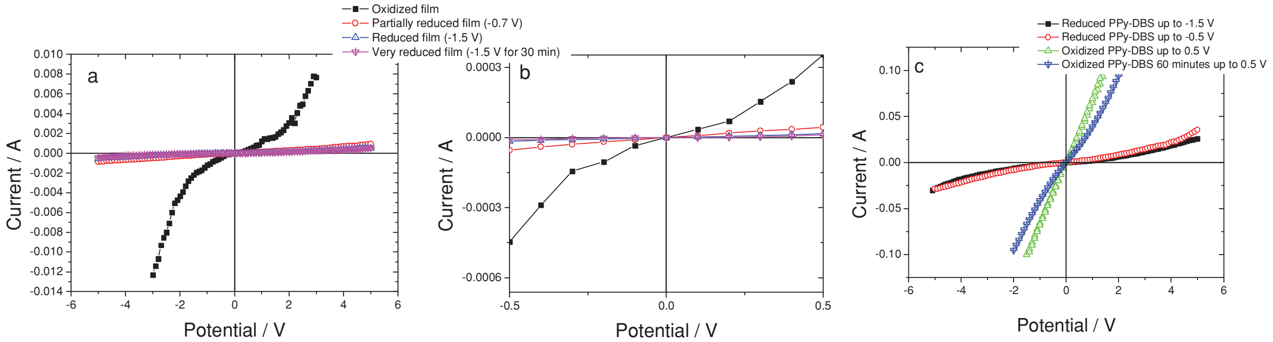

Figure 2. *I–V* curves obtained from four PPy films in nitrogen atmosphere after two consecutive potential cycles in 0.1 M NaCl aqueous solution at 2 mV s^{-1} stopping the second cycles at 0.65 V (oxidized film, of –0.7 V (reduced up to the closing potential)), –1.5 V (reduced and partially packed) and deep reduced and packed at –1.5 V over 60 min, obtained in a glove box under nitrogen atmosphere. a) Full studied range, b) detail of the –0.5 to 0.5 V. c) Same results from PPy-DBS films, reduced up to –1.5 V, reduced up to -0.5 V, oxidized up to 0.5 V, and oxidized and compacted up to 0.5 V for 60 min.

from –1.5 V, reduced film, to 0.5 V, oxidized film). Nevertheless, after oxidation at 0.5 V for 60 min, the electronic conductivity of the dry film decreases to 5.10 S cm^{-1}, indicating that a partial degradation of the polymer film by overoxidation was present during the long-term polarization.[57,58]

The conductivities of the deep reduced PPy-DBS film (here long-term reductions are not required to get a stationary state due to the open and swollen structure of the reduced films) are several orders of magnitude higher than the expected conductivities for an insulator material.

2.4. Practical Consequences and Future Experiments

Even after reduction at –1.5 V versus Ag/AgCl for 30 min, the electronic conductivity of a PPy film is high enough (2×10^{-3} S cm^{-1}) to support the flow of tens of mA/cm^2 at low cathodic overpotentials. Consequently, free-standing PPy films can support any reduction reaction (molecules or ions) from aqueous solutions without any initial interference of the hydrogen release up to –3 V. Evidently, similar reduction processes can also be studied from different organic solvents. This high conductivity opens many analytical and technological possibilities. In a following paper we will explore the possibility to get metal electrodepositions from aqueous solutions using deep reduced films.

The relatively high electronic conductivity of the deep reduced PPy and PPy-DBS films may allow the subsequent oxidation starting at the polymer/solution interface, as proposed by the ESCR model, and not at the polymer/metal interface, as claimed by the percolation or the insulator/conductor transition models. The fact that the deep reduced film doesn't need a metal/polymer contact inside the solution to be re-oxidized was proven using free-standing films with the metal contact located outside the solution. Nevertheless, the general support of the scientific community to those models is based on experimental results from the electrochromic front border models.[59–65] In a following paper we will try to re-design those electrochromic experiements presenting the attained results.

Results from EDX contradict most of the literature related to EQCM experiments from PPy films, claiming by the entrance of cations during reduction after the closing potential. We will repeat those results following the coulovoltammetric responses and indicate the possible origin of the discrepancies.

3. Conclusions

Around 30% of the balancing counterions participating in film redox processes remain in the film at the closing potential after the voltammetric reduction maximum, as corroborated by EDX analysis (Figure 1). After reduction at –1.5 V for 30 min, the counterion content remains higher that 10%. Around 15% of the balancing counterions participating in the film redox processes are expelled from the film during the reduction-compaction process, as obtained from coulovoltammetric (QV) results[15] and now corroborated by EDX analysis.

Cations (Na$^+$) were not present in deep reduced and packed polypyrrole films, but their concentration increased in films of the blend PPy/DBS after reduction at rising cathodic potentials.

Reduction-shrinking and reduction-compaction processes correspond in PPy films to the same electrochemical reduction reaction (1) (electron injection into the chains and expulsion of charge-balancing anions towards the solution), driving two different structural processes.

In parallel to the concentration of counterions, or co-ions, in the thick freestanding film, the concentration of the balancing charge carriers declines giving a progressive decrease of the film's electronic conductivity from 0.2 up to 0.002 S cm^{-1} in PPy films or from 12.35 to 0.36 S cm^{-1} in PPy-DBS films.

The high electronic conductivities of the two reduced materials (PPy and PPy-DBS) contradict any consideration of those materials as insulators. Any of the reduced films can be used as either an organic electronic conductor competing with most of the inorganic semiconductors, or as an organic electrode in both aqueous or organic solutions, able to support the electrochemical reduction of molecules and ions from aqueous solutions without hydrogen release interference.

4. Experimental Section

Pyrrole (Fluka 97%) was purified by distillation under vacuum using a diaphragm vacuum pump MZ 2C SCHOTT. Lithium Perchlorate ($LiClO_4$, Aldrich); Sodium Chloride (NaCl, Panreac) and Sodium Dodecylbenzenesulfonate (DBS, Aldrich) were used as received. Ultrapure water was obtained from Millipore Milli-Q equipment.

All the electrochemical studies were performed using an Autolab electrochemical workstation (PGSTAT-100potentiostat/galvanostat) controlled from a personal computer by GPES electrochemical software. The reference electrode for all the electrochemical experiments was a Crison Ag/AgCl (3 M KCl) electrode. All the potentials reported in this work are referred to this electrode. A stainless steel electrode (6 cm^2) was used as counterelectrode. Before every electrochemical experiment the solution was de-aerated by nitrogen bubbling for 10 min. For maintaining the inert atmosphere, the nitrogen was kept flowing over the solution during characterization. All the experiments were performed at 25 °C (room temperature).

For the electrogeneration of the PPy films, three stainless steel electrodes having a surface area of 6 cm^2 were used, one of them as working electrode and the other two as counterelectrodes. Polypyrrole films were synthesized from pyrrole (0.2 M), $LiClO_4$ (0.1 M) acetonitrile solution (50 mL) having 1% of water content. The films were electrodeposited by consecutive square potential waves from –0.322 V, kept for 2 s, to 0.872 V, kept for 8 s, during the time required to consume a total polymerization charge (anodic minus cathodic) of 30 C getting average thicknesses of 23 μm. After reduction at –0.322 V for 1 min, the coated electrode was rinsed with water and dried in air. The two films (one by side) were peeled off from the metal, divided into four samples, and used as free-standing electrodes after mass determination using a Sartorious SC2 balance with a precision of 10^{-7} g.

The solid-state conductivity measurements were performed using an Agilent digital multimeter attached to a computer allowing to record the *I–V* curves, controlled by home-made software, having a precision 1 picoampere. After preparation of the samples by cyclic voltammetry (getting different redox states) in a three electrodes electrochemical cell (**Figure 3**), the samples were kept in nitrogen atmosphere in order to avoid the oxidation of the samples in air. Conductivity measurements were performed in a glove box (MBraum) containing less than 1.2 parts per million of oxygen. The two points methodology was used, following the evolution of the current as a function of the applied potential gradient, ranging between –5 and +5 V. Energy-dispersive X-ray spectroscopy (EDX) analysis was carried out with a Bruker AXS Microanalysis in a scanning electron microscope (SEM-Hitachi S-3500N). SEM images of the electrodeposited Pb were obtained with the same microscope at 15 kV.

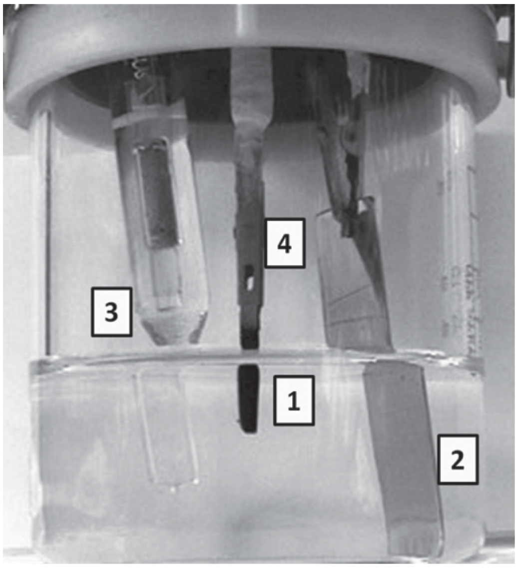

Figure 3. Three electrodes electrochemical cell: 1, Free-standing polypyrrole electrode (working electrode), 2, Stainless steel counter electrode, 3 Ag/AgCl reference electrode, 4, metal clamp.

Acknowledgements

We acknowledge financial support from the Spanish Government (MCINN) Projects MAT2011–24973, MAT2008–06702 and from the Seneca Foundation. J.G. Martinez acknowledges the Spanish Education Ministry for an FPU grant (AP2010–3460). The authors acknowledge Prof. E Coronado from the Instituto de Ciencias Moleculares (Valencia) for allowing us to use the globe box and the conductivity meter.

Received: July 26, 2013
Revised: September 13, 2013
Published online: October 31, 2013

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