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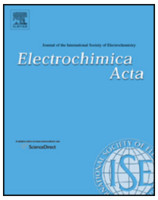

# Effects of anions size on the redox behavior of poly(o-toluidine) in acid solutions. An in situ vis-NIR cyclic spectroelectrogravimetry study

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## ABSTRACT

The combination of different in situ techniques allows a more complete analysis combining several physical and chemical processes of polymer-modified electrodes to be obtained. The hybrid technique -cyclic electrogravimetry coupled with visible-near infrared spectroscopy- was used to study in depth the electrochemistry of poly(o-toluidine) (POT) thin films. In this work, a POT modified electrode was polarized between the pernigraniline and leucoemeraldine forms in 0.5 M $HNO_3$ and 0.5 M $HClO_4$ solutions. The electrochromic properties of POT-$ClO_4^-$ and POT-$NO_3^-$ were localized in the experimental potential range associated to the transfer of charged species during the redox reactions. The analysis of all the experimental results has allowed the main contribution of proton, anion and water transfers to be separated in three redox transitions together with the electrochromic properties of POT. Semi-quantitatively, the better electrochemical and electrochromic properties of both films take place predominantly at potentials where the higher accumulation of the radical cations (polarons and bipolarons) in the polymer structure involves great lattice reorganization. The analysis of this work is a complete objective manner to discriminate the better conditions where a film can be used for a specific technical application.

## 1. Introduction

Over the past several decades, spectroelectrochemistry has revealed as a powerful tool for the elucidation of electron transfer processes [1,2]. One direction in this field of study is to modify the kind of interaction between matter and radiated energy. Interesting information about different physical properties can be obtained by analyzing altogether the information provided by the coupling of different in situ techniques. The high reflectance gold electrodes of electrochemical quartz crystal microbalances (EQCM) allow the spectroscopic radiation to be recorded together with the mass changes of a modified electrode during a cyclic voltammogram. In this manner, the cyclic spectroelectrogravimetry could be a good candidate to obtain a complete analysis during the continuous polarization of polymer-modified electrodes. It avoids any question of polymer history effects when sequential experiments and subsequent correlation of the data neglect temporal structural changes, such as relaxation within polymers [3,4]. Afterward, a subsequent intensive mathematical analysis is necessary to extract the interesting information from the large amount of experimental data. The coupling of different in situ techniques has been shown to be a powerful approach for studying electrochemically active materials as it allows different physical and chemical properties to be correlated [5–7].

Intrinsically conducting polymers (ICPs) have been the subject of many research efforts because of their environmental stability, good processability and their low relative cost [8–14]. The electrical conduction through the film needs to pass some potential barriers: 1) the electron transfer at the electrode|film interface, b) the electron transport through the film which will be neglected in this layer by supposing that deposited polymers are thin enough and finally c) the exchange of charged species (cations and anions) at the film|solution interface necessary for the electrical charge balance. During these processes, free solvent transfer between the solution and the polymer often occurs.

The understanding of the electrochemical behavior of these permselective polymers is essential and provides an important motivation for the present study since the potentiometric response, electrical conductivity, insertion kinetics of ions and/or free water molecules depends significantly on the size of incorporated ions [15,16]. Spectroscopy will allow an unequivocally identification of the electroactive species causing these transfers during the

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complex electrochemical redox reactions of conducting polymers [5]. Elucidation of these mechanisms will help to improve their properties of interest in several technologies like electrochromic devices [17,18], photogalvanic cells [19], artificial muscles [20,21], light-emitting electrochemical cells [22,23], biosensors [24–28], biofuel cells-based devices [29,30].

Among ICPs, poly(o-toluidine) (POT) is one of the most studied polymers [31–39]. Previously in a diprotic acid [5], three different redox reaction steps were isolated between the non-conductive forms of POT: the oxidized form (pernigraniline salt, PN) and the reduced form (leucoemeraldine salt, LE). The intermediated conductive forms of POT (polarons, P, and bipolarons, BP) were considered as single entities with specific and independently measurable electrochemical properties. The reaction scheme proposed was:

$$\mathrm{LE} + n_1\mathrm{HSO_4^-} \underset{k_1}{\overset{k'_1}{\rightleftarrows}} \mathrm{P} + n_1\mathrm{e^-} + x_1\mathrm{H_2O} \tag{1}$$

$$\mathrm{P} + n_2\mathrm{HSO_4^-} \underset{k_2}{\overset{k'_2}{\rightleftarrows}} \mathrm{BP} + n_2\mathrm{e^-} + x_2\mathrm{H_2O} \tag{2}$$

$$\mathrm{BP} \underset{k'_3}{\overset{k_3}{\rightleftarrows}} \mathrm{PN} + n_3\mathrm{e^-} + n_3\mathrm{H_3O^+} \tag{3}$$

where $n_i$ represents the number of electrons or available sites inside the polymer for the insertion/expulsion of ionic species and $x_i$ is the number of water molecules exchanged during the electrochemical reaction. The redox reactions involving the anions ($HSO_4^-$) and water molecules are faster than the redox reaction involving hydrated protons, in other words, $k'_1>k_3$ and $k'_2>k_3$ in the oxidation direction and $k_1>k'_3$ and $k_2>k'_3$ in the reduction direction [40].

In this work, POT films were generated in 0.5 M $H_2SO_4$ aqueous solutions on a gold electrode. These modified electrodes were studied by in situ spectroelectrogravimetry in two different aqueous solutions of 0.5 M monoprotic acids: $HClO_4$ and $HNO_3$. The influence of these anions on the electrochemical response of the film and on the transfers of the other species during the electrochemical transitions was compared.

## 2. Theoretical Approach

The simplest model used to interpret voltammetric curves of electroactive films is assume that the reduced and the oxidized forms of the film are adsorbed and the Nernst equation is satisfied [41]. Simultaneously, the redox process involves insertion/expulsion of charged species for electrical stability. As an example for anions, it comes:

$$\left\langle \mathrm{P} \right\rangle + \mathrm{A^-} \underset{k_{\mathrm{A^-}}}{\overset{k'_{\mathrm{A^-}}}{\rightleftarrows}} \left\langle \mathrm{P^+}, \mathrm{A^-} \right\rangle + \mathrm{e^-} \tag{4}$$

where $A^-$ is the anion, $\langle P \rangle$ is the site in the host polymer and $\langle P^+,A^- \rangle$ is occupied site in the polymer matrix doped with anions. A similar approach can be made for the exchange of cations and solvent [42,43].

At the polymer|solution interface, the flux of anions is $J_{A^-} = -d_f \left( {}^{dC_{A^-}}\!/_{dt} \right)$ where $d_f$ is the polymer film thickness and $C_{A^-}$ the concentration of anions. For very thin films, the insertion/expulsion of species at the polymer|solution interface is considered the rate-limiting step and the change of $C_{A^-}$ is:

$$\frac{dC_{\mathrm{A^-}}}{dt} = -k_{\mathrm{A^{-1}}}(C_{\mathrm{A^-}} - C_{\mathrm{A^-}}^{\mathrm{min}}) + k'_{\mathrm{A-}}(C_{\mathrm{A^-}}^{\mathrm{max}} - C_{\mathrm{A^-}})C_{\mathrm{A^-}}^{sol} \tag{5}$$

where $C_{\mathrm{A^-}}^{\mathrm{max}}$ and $C_{\mathrm{A^-}}^{\mathrm{min}}$ are the maximum and minimum concentrations of the electrochromic sites where anions can be inserted and $C_{\mathrm{A^-}}^{sol}$ is the outer concentration of anions. This equation can be simplified as:

$$\frac{dC_{\mathrm{A^-}}}{dt} = -k_{\mathrm{A^-}}(C_{\mathrm{A^-}}) + k'_{\mathrm{A-}}(C_{\mathrm{A^-}}^{\mathrm{max}} - C_{\mathrm{A^-}})C_{\mathrm{A^-}}^{sol} \tag{6}$$

when $C_{\mathrm{A^-}}^{\mathrm{min}} = 0$.

For a potential sweep where Eq. (4) occurs, the current ${}^{dq}\!/_{dt}$ considering $q$ in C $cm^{-2}$ is equal to:

$$\frac{dq}{dt} = -\nu d_f F \frac{dC_{\mathrm{A^-}}}{dE} \tag{7}$$

where $E$=$E_0$-$\nu t$, $\nu$ is the scan rate, $F$ is the Faraday constant and

$$\frac{dC_{\mathrm{A^-}}}{sE} = k'_{\mathrm{A^-}} k_{\mathrm{A^-}} C_{\mathrm{A^-}}^{sol} \frac{(b'_{\mathrm{A^-}} - b_{\mathrm{A^-}})C_{A^-}^{\mathrm{max}}}{(k'_{\mathrm{A^-}} C_{\mathrm{A^-}}^{sol} + k_{\mathrm{A-}})^2} \tag{8}$$

Here, the kinetic constants are supposed to be activated by the potential (the classical Tafel law), such as:

$$k'_{\mathrm{A^-}} C_{\mathrm{A^-}}^{sol} = k'_{\mathrm{A^-}0} C_{\mathrm{A^-}}^{sol} \exp(b'_{\mathrm{A^-}} E) = k'_{\mathrm{A^-}00} \exp(b'_{\mathrm{A^-}}(E - E_p)) \tag{9}$$

$$k_{\mathrm{A^-}} = k_{\mathrm{A^-}0}(b_{\mathrm{A^-}} E) = k_{\mathrm{A^-}00} \exp(b_{\mathrm{A^-}}(E - E_p)) \tag{10}$$

where

$$b_{\mathrm{A^-}} - b'_{\mathrm{A^-}} = \frac{nF}{RT} \tag{11}$$

and $R$ is the gas constant, $T$ is the absolute temperature, $E_p$ is the peak potential where the maximum current is reached. ${}^{nF}\!/_{RT}$ is about 40$V^{-1}$ at 298 K for a single electron transfer ($n$ = 1) [44,45].

Finally, we can obtain

$$\frac{dq}{dt} = \nu d_f \frac{F^2}{RT} \frac{C_{\mathrm{A^-}}^{\mathrm{max}} \exp((b_{\mathrm{A^-}} - b'_{\mathrm{A^-}})(E - E_p))}{[1 + \exp((b_{\mathrm{A^-}} - b'_{\mathrm{A^-}})(E - E_p))]^2} \tag{12}$$

which may be mathematically rewritten by considering ${}^{(e^{-x} + e^{+x})}\!/_{2} = \cosh(x)$ as:

$$\frac{dq}{dt} = \nu d_f \frac{F((b_{\mathrm{A^-}} - b'_{\mathrm{A^-}})C_{\mathrm{A^-}}^{\mathrm{max}}}{\cosh^2[\frac{(b_{\mathrm{A^-}} - b'_{\mathrm{A^-}})}{2}(E - E_p)]} \tag{13}$$

where $\nu d_f F((b_{\mathrm{A^-}} - b'_{\mathrm{A^-}})C_{\mathrm{A^-}}^{\mathrm{max}} = \left(\frac{dq}{dt}\right)_{peak}$

This equation can be easily convert in changes of mass considering the molar mass of anion, $M_{\mathrm{A^-}}$ and the direction of anion transfer $\delta_{\mathrm{A^-}}$ during the electrochemical reaction as.

$$\frac{dm}{dt} = \nu d_f \frac{\delta_{\mathrm{A^{-1}}} M_{\mathrm{A^-}}(b_{\mathrm{A^-}} - b'_{\mathrm{A^-}})C_{\mathrm{A^-}}^{\mathrm{max}}}{\cosh^2[\frac{(b_{\mathrm{A^-}} - b'_{\mathrm{A^-}})}{2}(E - E_p)]} \tag{14}$$

where $\nu d_f \delta_{\mathrm{A^-}} M_{\mathrm{A^-}}(b_{\mathrm{A^-}} - b'_{\mathrm{A^-}})C_{\mathrm{A^-}}^{\mathrm{max}} = \left(\frac{dm}{dt}\right)_{peak}$

In this case $\delta_{\mathrm{A^-}} = +1$ since the anions are inserted during the oxidation. On the contrary, δ is negative for species inserted during the reduction (i.e. cations).

Likewise, the absorbance changes at each wavelength λ, ${}^{dA^\lambda}\!/_{dt}$ of an electrochromic film can be related to the charge when the Lambert-Beer's law is satisfied:

$$\frac{dA^\lambda}{dt} = \frac{1}{F} \varepsilon_{\mathrm{A^-}}^{\lambda} \cdot l \frac{dq}{dt} \tag{15}$$

where $\varepsilon_{A-}^{\lambda}$ is the absorbance coefficient of the electrochromic sites and $l$ the length of the light pass. So,

$$\frac{dA^\lambda}{dt} = \nu d_f \frac{\varepsilon_{\mathrm{A^-}}^{\lambda}(b_{\mathrm{A^-}} - b'_{\mathrm{A^-}})C_{\mathrm{A^-}}^{\mathrm{max}}}{\cosh^2[\frac{(b_{\mathrm{A^-}} - b'_{\mathrm{A^-}})}{2}(E - E_p)]} \tag{16}$$