Study of polaron and bipolaron states in polypyrrole by in situ Raman spectroelectrochemistry

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Abstract

The transitions from the reduced-polaron–bipolaron states of polypyrrole (ppy) were analyzed by in situ Raman spectroelectrochemistry. The distinct vibrational modes presented by the polymer in different oxidation levels were assigned to specific signatures of polaron and bipolaron states. As the polymer was oxidized from the neutral state, an intermediary phase featuring vibrational bands from both the benzoid (reduced) and the quinoid (oxidized) forms were observed. This intermediary phase was correlated to the polaron state. The results were compared with previous ESR data that confirm the presence of polaron and bipolaron states in the potential region where the vibrational modes of these phases were identified.

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1. Introduction

The effect of doping and undoping on the conductivity, optical and electronic properties of polypyrrole has been studied by several methods [1–5]. The polaron–bipolaron model is widely used to explain electrochromic and electrochemical behavior of conducting polymers. In fact, polaron and bipolaron states are associated to the intermediary energy levels that arise within the electronic band gap region of the polymer due to oxidation [6]. The ionized states are also stabilized by geometrical chain distortion [7]. The polymeric chain has to accommodate the charges created by the oxidation process. The accommodation of these extra charges (cation and dication) involves conformational and structural changes. The favorable structural and conformational forms of the chains in the oxidized and in the reduced states have been predicted by ab initio calculations [8–10]. According to Bredas et al. [7], the formation of the bipolaron species is energetically favorable as compared to the formation of two polarons. Bredas et al. [6] combined UV–vis measurements of polypyrrole (ppy) at different oxidation levels with theoretical calculations to correlate the evolution of the UV–vis absorption bands with the formation of polaron and bipolaron species. ESR measurements have been used to confirm the existence of polarons as species with spin and bipolarons as spinless species [2,11–13].

The discussion above implies that there are at least two pathways to utilize in situ spectroscopy to probe the oxidation states of conducting polymers. One is to follow the changes in the electronic properties of the film upon oxidation. This is readily done by UV–vis, since sub-band gap transitions became allowed due to polaron–bipolaron formation. These new electronic levels provide intermediate channels to the promotion of electrons from the valence band (VB) to the conduction band (CB), decreasing the energy required for the electronic transition and leading to a red shift in the UV–vis spectrum. The other pathway to study polymer oxidation spectroscopically is to follow the structural changes that accompany the doping (oxidation) process. Vibrational techniques, including Raman scattering, provide molecular-level information that is highly sensitive to conformation changes. Furukawa et al. [14] reported a study where the Raman spectra of polypyrrole in several oxidation levels were obtained. The vibrational modes were assigned and a band at 1082 cm\textsuperscript{−1}, observed for the most oxidized state at 2.8 V, was correlated to the bipolaron state. Since then, in situ Raman
spectroscopy has been widely used to study conducting polymers [15–20]. Although the technique has provided valuable information about the various oxidation state of the polymer, no study has used Raman to assign the initial polaronic states, and then the transition from the polaron to the bipolaron states of ppy. Recently, Bernard and Hugot-Le Goff [21] reported an in situ Raman study on the characterization of polaron and bipolaron states of polyaniline.

Our motivation for this work is that even for ppy, probably the most studied conducting polymer, there are no in situ Raman reports showing a straight correlation between the evolution of the vibrational modes and the formation of polaron and bipolaron species. Therefore, the key result of this work is the characterization of the structural behavior of ppy chains and their correlation with the formation of polaron and bipolaron species. As Genoud et al. [22] had previously pointed out in their ESR study of ppy, polaron and bipolaron species are shown to coexist at intermediary oxidation levels.

2. Experimental

2.1. Materials

Sodium perchlorate (NaClO₄) (ACP) and evaporated gold films deposited on glass (gold slides) (EMF) were used as received. The thickness of the gold layer is 100 and 5 nm layer of chromium is deposited on the glass to help the gold adhesion. Pyrrole (Aldrich) was purified by distillation. Nanopure water (Barnstead) was used in all solutions.

2.2. Methods

The electropolymerization of ppy was carried out galvanostatically at 0.1 mA cm⁻² for 200 s in aqueous 0.05 M of pyrrole, containing 0.1 M of NaClO₄ (dopant). A three-compartment electrochemical cell was used for the synthesis and electrochemical analyses. The gold slide was used as working electrode, a Pt wire was the counter electrode and an Ag/AgCl/Cl⁻(sat)⁻ was the reference electrode. The UV–vis–reflectance experiments were carried out using a USB2000 miniature fiber optic spectrometer (Ocean Optics) attached to the ocular of the Olympus BHSM microscope. The Raman spectra were obtained using a He–Ne laser (Melles Griot) as excitation source, with a 632.8 nm excitation wavelength. The laser was focused on the ppy film using a long working distance 50× Olympus microscope objective (NA = 0.55). The Raman microscope system operates in back-scattering mode, and the same objective is used for both excitation and collection. The collected scattered light was filtered, using a Kaiser super notch filter, to remove the contributions from the excitation. The remaining radiation was directed through a Kaiser Holospec ™ 1.4 spectrograph coupled with an Andor CCD detector (model DV-401-BV). A three-compartmented spectroelectrochemical cell with a 1 mm glass window was mounted on the microscope stage. The incident laser was focused through the window into the ppy film for the in situ Raman measurements, and the halogen light source of the microscope was used for the UV–vis spectroelectrochemical measurements. The system was allowed to reach the equilibrium, by observing the stabilization of the current at a given potential, before each spectrum (either Raman or UV–vis) was recorded. The electropolymerization and all the electrochemical measurements were carried out with an Autolab PGSTAT 30 potentiostat/galvanostat.

3. Results and discussion

Fig. 1 shows the cyclic voltammogram (CV) of the synthesized ppy film on gold slide. The ppy film was analyzed from −0.8 to 0.8 V at a scan rate of 20 mV s⁻¹, and the CV was obtained in 0.1 M NaClO₄ aqueous solution. The potential interval was selected to obtain the polymer in its reduced and oxidized states. The CV shown in Fig. 1 displays an anodic peak at 0.1 V, and a cathodic peak at −0.28 V. CV experiments are useful to determine the potential range in which the polymer undergoes the redox process. However, bipolaron formation does not require extra charge transfer, since it evolves from the combination of two polaron states. Hence, the CV does not provide exact information about the potential range correspondent to the polaron–bipolaron transition. A broad range of oxidation potentials is observed in Fig. 1, due to the inhomogeneity of the polymer and a non-uniform chain size distribution.

Fig. 2 shows the in situ UV–vis spectra of ppy/NaClO₄ obtained in reflectance mode in the potential range between 0.8 and −0.8 V. The ppy film was synthesized on a smooth gold surface. The reflectance in Fig. 2 is expressed in Eq. (1):

\[
\frac{\Delta R}{R_{\text{bare}}} = \frac{R_{\text{ppy}} - R_{\text{bare}}}{R_{\text{bare}}} \tag{1}
\]

where \(R_{\text{bare}}\) is the reflectivity of the bare gold surface at a given potential and \(R_{\text{ppy}}\) is the reflectivity of the gold surface covered by ppy at the same potential. The bare gold reflectivity is large in the energy range covered. \(\Delta R/R_{\text{bare}}\), presented in Fig. 2, is then a measurement of how much the gold reflectivity decreases by the presence of the film at a given potential.

![Fig. 1. Cyclic voltammogram of ppy/NaClO₄ film synthesized on a gold surface. CV obtained in 0.1 M NaClO₄ aqueous solution, at scan rate of 20 mV/s.](image-url)
Light absorption by the film decreases the reflectivity of the ppy-covered slide ($R_{ppy}$), producing $\Delta R/R_{bare}$ values closer to $-1$. As seen in Fig. 2, the maximum of reflectance is displayed around $1.45 \text{ eV} \ (\sim 855 \text{ nm})$ for the most oxidized state, at 0.8 V. This band shifts steadily toward the blue as cathodic potentials are applied, reaching $1.56 \text{ eV} \ (\sim 790 \text{ nm})$ at $-0.8$ V (Fig. 2).

Fig. 2 shows a broad reflectance minimum (absorption) between 1.7 and 2.3 eV ($\sim 730$ and 540 nm, respectively) at 0.8 V related to the transition from the valence band to the antibonding polaron state [6]. Intermediary energy levels are created between the VB and the CB during the oxidation process; hence, a higher absorbance is expected for the polymer in oxidized state in this range of wavelength. At $-0.8$ V the minimum reflectance is displayed around $2.25 \text{ eV}$. This region of minimum reflectivity is narrower than the one observed at 0.8 V (see Fig. 2). This is expected, since a larger dispersion of states should be present at high oxidation level leading to broader bands. The inhomogeneity of the polymer also contributes to the energy dispersion of the polaronic states, as it can be seen from the broad redox peaks observed in the CV (Fig. 1). Moreover, the reflectivity for $-0.8$ V is larger than for $+0.8$ V in the whole range investigated. The decrease in reflectivity at the oxidized state (Fig. 2) is in agreement with the electrochromic behavior of ppy [23–26]. The wavelength range studied here does not cover other absorption bands at high oxidation levels, e.g., at 1.0 and 3.6 eV [6].

Comparing the data obtained from in situ UV–vis spectroscopy (Fig. 2) and the CV (Fig. 1), it is observed that the maximum of reflectance shifts more steadily at the oxidation potential range, between 0.1 and 0.4 V.

Fig. 3 displays the in situ Raman spectra of the ppy film obtained between 0.8 and $-0.8$ V, using an excitation laser at 632.8 nm and accumulation time of 60 s. (a) Region between 875 and 1100 cm$^{-1}$; and (b) region between 1100 and 1650 cm$^{-1}$.

<table>
<thead>
<tr>
<th>Potential (V)</th>
<th>Species</th>
<th>$\nu_{\text{C-C}}$</th>
<th>$\delta_{\text{ring}}$</th>
<th>$\delta_{\text{C-H}}$</th>
<th>$\nu_{\text{C-H}}$</th>
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<tr>
<td>0.8</td>
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<td>1620</td>
<td>–</td>
<td>925</td>
<td>1316</td>
</tr>
<tr>
<td>0.6</td>
<td>Dication</td>
<td>1617</td>
<td>–</td>
<td>927</td>
<td>1316</td>
</tr>
<tr>
<td>0.4</td>
<td>Dication</td>
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<td>–</td>
<td>929</td>
<td>1316</td>
</tr>
<tr>
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<td>976</td>
<td>930</td>
<td>1319</td>
</tr>
<tr>
<td>0.2</td>
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<td>1607–1585</td>
<td>979</td>
<td>933</td>
<td>1320</td>
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<tr>
<td>$-0.4$</td>
<td>Neutral</td>
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<td>986</td>
<td>–</td>
<td>1310</td>
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<tr>
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<td>990</td>
<td>–</td>
<td>1310</td>
</tr>
<tr>
<td>$-0.8$</td>
<td>Neutral</td>
<td>1557</td>
<td>990</td>
<td>–</td>
<td>1310</td>
</tr>
</tbody>
</table>

Only selected potentials are indicated. The vibrational energies are in cm$^{-1}$. 
632.8 nm. Fig. 3a covers the 875–1100 cm$^{-1}$ region and Fig. 3b the 1100–1650 cm$^{-1}$ region. The assignment of the vibrational bands of ppy in 0.1 M NaClO$_4$ aqueous solution at different oxidation levels is displayed in Table 1. The Raman spectra (Fig. 3a and b) of the film conditioned at $-0.8$ V, displays the vibrational bands characteristic of the reduced state at 1557 cm$^{-1}$, related to a mixed $\nu$C=C and inter-ring $\nu$C=C vibration, 1310, 1253, 1044 and at 990 cm$^{-1}$, assigned to a ring deformation mode ($\delta_{\text{ring}}$). At 0.8 V the bands characteristic of oxidized state are displayed at 1620 cm$^{-1}$ related to a mixed $\nu$C=C and inter-ring $\nu$C=C vibration of short conjugation length, 1310, 1253, 1081 cm$^{-1}$, assigned to the dication state by Furukawa et al. [14] and the 925 cm$^{-1}$-band related to C–H out-of-the-plane deformation.

The Raman data presented in Fig. 3 clearly show the transition between the most oxidized state (bipolaron) to the most reduced state. Fig. 3 also shows that some small bands and shoulders at 1550 and 980 cm$^{-1}$, assignable to the reduced form, are still present at the most oxidized state. According to Yakushi et al. [27], the observation of bands characteristic of the reduced state when the polymer is oxidized is due to the presence of a range of conjugation lengths in the polypyrrole films. The presence of defects in the chains also leads to incomplete redox process. The intermediary phase between these extremes will now be examined with more details. The goal is to identify the spectral signature of the polaron state.

Fig. 4 is derived from Fig. 3, and displays only the Raman spectra of selected spectral regions at 0.1, 0.2, 0.3 and 0.4 V. The polaron state is expected to be present within this potential range, since this corresponds to the early oxidation of the polymer according to Fig. 1. Fig. 4a shows the 900–1000 cm$^{-1}$ region and Fig. 4b covers the 1525–1640 cm$^{-1}$ region. The spectral evolution shown in Fig. 4a and b implies that two different structures are present in this potential range, which can be assigned as an intermediate state between the most oxidized and the most reduced forms of ppy. In Fig. 4a, the vibrational band at 990 cm$^{-1}$ originates clearly from the benzoid form [14] and it is strong at 0.1 V. At the early stages of ppy oxidation, an electron is removed from the chain leading to a lattice deformation, followed by the diffusion of an anion from the nearby electrolyte into the polymer to stabilize the cation. This new structure is the polaron state. The lattice deformation results in the loss of planarity of the chain. This geometrical distortion, although localized [7], leads to changes in bond strengths and torsion angles that affects the ring deformation mode at ca. 990 cm$^{-1}$. In fact, the ring deformation frequency abruptly shifts to ca. 980 cm$^{-1}$ when 0.1 V is applied (Fig. 4a). This shift is followed by a 60% decrease in the Raman intensity of this band. Simultaneously, a new band is observed in the 930 cm$^{-1}$ region. The important point is that these two vibrational bands coexist within the potential range between 0.1 and $0.4$ V (Fig. 4a). In this case, the ca. 980 cm$^{-1}$-band indicates that certain sites of the ppy chain are still in the benzoid form (reduced state), where the vibrational mode at 930 cm$^{-1}$, assigned to a C–H out of the plane deformation of the quinoid form, is related to the oxidized sites. This intermediary phase, where different vibrational modes assigned to the reduced and the oxidized forms coexist, is assigned in this work to the vibrational signature of the polaron state. The ca. 980 cm$^{-1}$-band disappears at potentials more positive than 0.4 V, and the quinoid vibration reaches 929 cm$^{-1}$. At this oxidation level, most of the rings are in the quinoid form. Hence, the vibrational frequency of the ca. 929 cm$^{-1}$-band does not change significantly as the potential is made more positive than 0.4 V. Therefore, the presence of only 925 cm$^{-1}$-band in this spectral region is assigned to the bipolaron state.
A similar analysis can be carried out by examining Fig. 4b. At 0.1 V, the 1560 cm$^{-1}$-band is due to the benzoid form, and the small shoulders at 1610 cm$^{-1}$ are the initial indications of structural deformations due to the oxidation. Both bands are assigned to the $\nu\text{C}=$C, as shown in Table 1. Similarly, than observed in Fig. 4a, the intensity of the benzoic band decreases abruptly as 0.2 V is applied, and a significant shift in the vibrational energy (to 1585 cm$^{-1}$) is observed. The intensity of the $\nu\text{C}=$C of the quinoid form increases as more positive potentials are applied and this band (at ca. 1610 cm$^{-1}$) eventually dominates at 0.4 V. This analysis agrees with previous ESR study of the polaron and bipolaron states of ppy [22]. In the reduced state, at $-0.6$ V, the ESR signal vanishes, the maximum of spin $-\frac{1}{2}$ (polaron state) was obtained at 0 V, and the bipolaron state was found from 0.4 V.

Fig. 5 shows a plot of the intensities of the vibrational bands due to the benzoid and the quinoid forms measured from Fig. 4a. Fig. 5 clearly demonstrates the potential region where the polaron state is dominant. The decrease in the intensity of the benzoid band (ca. 990 cm$^{-1}$) at $-0.2$ V coincides with the onset of the oxidation current observed from the CV in Fig. 1. The vibrational bands due to the quinoid form (ca. 925 cm$^{-1}$) are still not visible at $-0.2$ V, which can be simply correlated with the lack of sensitivity of the Raman method to the small amount of cations formed at that potential. The intensity of the quinoid band is measurable at 0 V, and it increases as the potential becomes more positive, reaching a stable value after 0.4 V. The region between 0 and 0.3 V, shadowed in Fig. 5, correspond to the potential range where the polaron is the dominant species.

4. Conclusions

This work demonstrates that in situ Raman spectroelectrochemistry is a useful method to determine the neutral–polaron–bipolaron transitions in conducting polymers. The coexistence of vibrational bands attributable to both benzoic and quinoid forms confirm the presence of two different structures in the polymeric chain at the same oxidation level. These spectral features were assigned to the polaron state, where some sites on the chain are oxidized, while other sites are still in the reduced state. The potential range where the polaron state is observed by Raman scattering is in close agreement to the potential values obtained by ESR [22]. The electronic changes that followed the oxidation process were also measured by in situ UV–vis reflectance. The transitions between the reduced and oxidized obtained from UV–vis were consistent with the Raman data.

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References