



About the species formed during the electrochemical half oxidation of polyaniline: Polaron-bipolaron equilibrium

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ABSTRACT

The UV–Vis spectra of polyaniline (Pani) films were measured in the range 200 nm–900 nm, at constant potential as well as sweeping the potential. Both free standing films and Pani films deposited on ITO substrates were employed. These measurements were carried out at different electrolyte pHs, covering the range $-0.6 < \text{pH} < 3.0$. The experimental results were analyzed considering two potential regions: that corresponding to the occurrence of the faradaic reaction; and that corresponding to the purely capacitive response. The oxidation of the leucoemeraldine form to the emeraldine form leads to the formation of two species that could be associated to bipolarons and a polaron lattice. The experimental data show that these two species are in chemical (not electrochemical) equilibrium with each other. It is shown that bipolarons convert into a polaron lattice and that this conversion is favoured by the external applied potential, in order to satisfy the charge requirements at the polymer fibril/internal solution interface. In this way, the nature of the capacitance of Pani can be explained.

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1. Introduction

The electrochemical behaviour of polyaniline has attracted the attention of many workers because of its complexity and the insulator - conductor transition of this material.

Much effort has been done in understanding the oxidation mechanism of Pani films and the nature of the species involved in it; particularly, in those species related to the conductive properties of the resulting half oxidized state of Pani, and the nature of the capacitive currents present in its voltammetric response. To this end, a variety of *in situ* and *ex situ* techniques have been employed such as voltammetry, spectroelectrochemistry, EIS, EPR, conductivity, etc. [1].

Also, the electronic structure of Pani has been much investigated. This task has been carried out by quantum chemistry calculations (see, for instance [2–11]) and the results have been tested by UV–Vis spectroscopy (see, for instance [12–18]). The latter has been mostly carried out *ex situ*, in controlled atmosphere and without potential control. The quantum chemistry calculations have been performed by different computational methods in

vacuum and mostly on isolated chains of limited length.

As an outcome of these experiments and calculations, it deserves to point out that two tables have been published in the literature that summarize the frequency assignments to the different forms of Pani at different protonation and oxidation states [17–19]. Also, it is important to remark that the peak frequencies as well as the theoretically predicted spectra agrees reasonably well with those obtained experimentally in vacuum in the absence of applied potential. On the other hand, the absorption spectra obtained *ex situ* in gas atmosphere are very similar to the *in situ* ones (Fig. 1).

Some time ago it was proposed that the oxidation of leucoemeraldine (LE) leads to the formation of polarons (P), at low doping levels, which can be further oxidized to bipolarons (BP) at higher doping levels (see for instance Ref. [20]), as it happens with other conductive polymers such as polypyrrole and polyacetylene. This conclusion was challenged by several workers that proposed that bipolarons are generated in a first step of the oxidation and that their instability leads to the formation of polarons by an internal conversion. Finally, they separate into a polaron lattice (PL) [4,5] that would be the species responsible for the charge transport in the polymer. All these structures are represented in Fig. 2.

Ever since, there has been many theoretical works employing more powerful methods of calculus [6–9] and including, for

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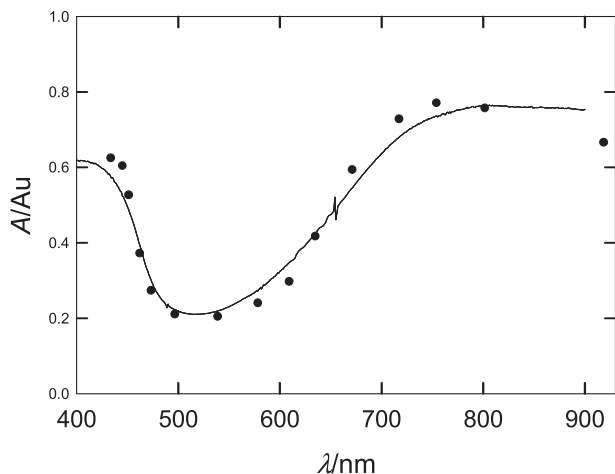


Fig. 1. Comparison of the spectra of Pani free standing films: (●) *ex situ* (data taken from Ref. [5]), and (—) *in situ*. *Ex situ* films were emeraldine base treated with HCl. *In situ* films were deposited on ITO and measured at 0.45 V in 3.7 M H₂SO₄.

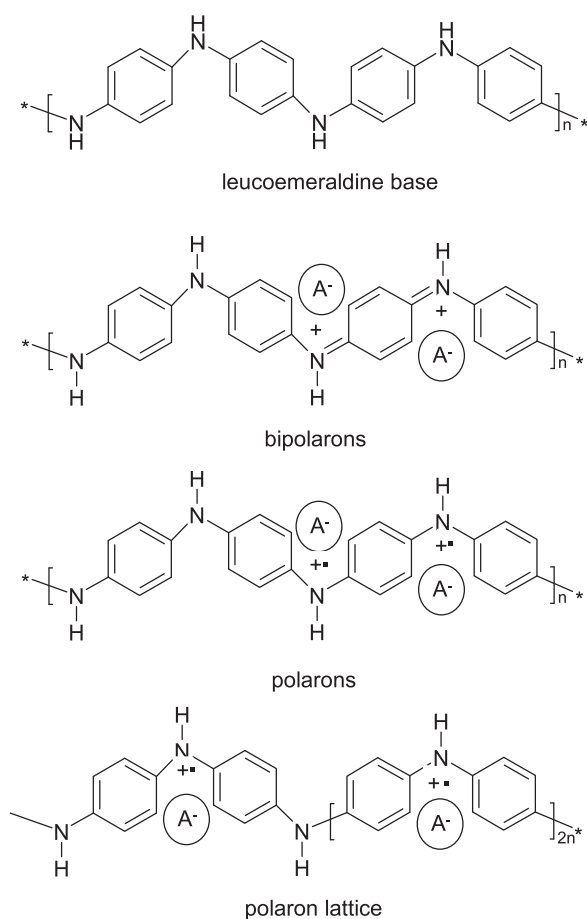


Fig. 2. Structures of leucoemeraldine base and emeraldine salt in its different forms: bipolarons, polarons and polaron lattice.

instance, protons and the corresponding counter ions [6]. A very useful account of more recent research is given in Ref. 9. However, as mentioned by Bernard and Hugot-Le Goff, besides the amine, imine and polaron sites, it is necessary to consider partially charged nitrogen atoms that do not belong exactly to these categories [21].

From the experimental viewpoint, the oxidation products

absorb at about $\lambda \approx 400\text{--}440$ nm and $\lambda \approx 750\text{--}800$ nm, generating broad bands that are surely composed of two or more other contributions. There is general consensus about the species absorbing at 750–800 nm being the PL, whereas those absorbing at 440 nm are BPs [18].

Although most of the works show a good agreement between the calculated and the experimental data for the different species, there is still no consensus about how many chemically different species forms as products of the oxidation of leucoemeraldine, and which ones are the carriers, that is, the species actually responsible for the charge transport and the capacity of the polymer. Moreover, other workers associate the conductivity of Pani with electrons and trapped ions [22–24].

In this work, we combine spectroscopic and electrochemical measurements to show that the charge of the double layer and the conductivity of the polymer are related to the formation of chemical structures that can be followed by UV–Vis spectroscopy. Also, it is proposed that two forms of emeraldine (E) are generated from the beginning of the oxidation reaction and that they are in chemical equilibrium. These species can be associated with BP and PL, and the latter would be the responsible for the conduction in the polymer.

In the present study, we measured Pani UV–Vis spectra in the range 200 nm–900 nm; both at fixed potential and sweeping it at selected fixed wavelengths. Free standing Pani films and Pani films deposited on ITO substrates were employed. The measurements were carried out at different pHs in the range $-0.6 < \text{pH} < 3.0$.

2. Experimental

Pani films were electro synthesized onto ITO (Indium Tin Oxide) plates ($R_s = 5\text{--}15 \Omega \text{ cm}$, Delta Technologies). These plates were prepared as described in a previous work [25]. The active area of the polymer film onto the ITO plate was around 1.0 cm². The electro synthesis was carried out by cycling the potential at 0.1 V s⁻¹ between -0.2 V vs. SCE and a positive potential limit set at the beginning of the monomer oxidation (around 0.7 V–0.8 V). To improve the adherence and homogeneity of the film, after a few cycles, the positive potential limit was decreased. After the synthesis, the films were washed with pure water and cycled in 3.7 M H₂SO₄ solution during some minutes and then introduced in the spectrophotometric cell. This was a square quartz cell (Spectrocell, 1 cm side) in which the electrode was inserted perpendicular to the light path. Inside the cell it was placed a Pt plate that served as the counter electrode, and a fine capillary connected to an external reference electrode. This was a saturated calomel electrode (SCE). All potentials in the text are referred to this electrode.

Free standing films were obtained by electro synthesis of the polymer on ITO as described above. Then, they were detached from the ITO plates by applying a potential of about -1 V vs. SCE. Afterwards, they were placed onto a Pt gauze of 1 cm² area that worked as support and electrical contact. The ensemble was placed in the quartz cell as described above for the ITO plates.

Solutions were made of Milli-Q purified water, NaOH and H₂SO₄ (Carlo Erba, RPE-ACS). The latter were employed as received. A potentiostat PARC Model 273 equipped with a data logger Dataq DI-710-UH was employed for all the electrochemical experiments. The potential was varied in the range $-0.2 \text{ V} < E < 0.45 \text{ V}$. Spectra were taken with an Agilent model 8453E diode array spectrophotometer. For the films deposited on ITO the spectral range was comprised between 300 nm and 900 nm, and for the free standing films between 200 nm and 900 nm.

Electrolytic solutions of different pH and constant ionic strength of 3.7 M of H₂SO₄ + NaHSO₄, were employed. The pH of these solutions was previously measured with a glass electrode (Ross, Orion

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