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Characteristics of Polyaniline Electrosynthesized in Propylene Carbonate Medium in the Presence of Di- and Trichloroacetic Acids

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No presente trabalho a caracterização de polianilina eletrosintetizada em meio de carbonato de propileno na presença dos ácidos di- e trichloroacéticos foi realizada usando diferentes técnicas. A resposta eletroquímica por voltametria cíclica mostrou os processos redox devido à formação de polaron e bipolaron e à degradação do polímero. A caracterização usando as espectroscopias no infravermelho e ultravioleta-visível indica que os polímeros estão na forma de sal emeraldina com ânions perclorato incorporados. Os filmes produzidos com ambos os ácidos em carbonato de propileno apresentam morfologia compacta como observado por microscopia eletrônica de varredura. Através de testes de filmes de polianilina produzidos em condições selecionadas em um ambiente correspondente a uma bateria de lítio foi observado que estes apresentam uma eficiência coulômbica elevada promissora para aplicações em baterias.

In the present work the characterization of polyaniline electrosynthesized in propylene carbonate medium in the presence of di- and trichloroacetic acids was performed using different techniques. The electrochemical response by cyclic voltammetry showed redox processes due to the formation of polaron and bipolaron and polymer degradation. The characterization by infrared and UV-visible spectroscopies indicated that the polymers are in the emeraldine salt form with perchlorate anions incorporated. The films produced with both acids in propylene carbonate media presented a compact morphology as observed by scanning electron microscopy. By testing the polyaniline film produced in selected conditions in a lithium battery environment it was found that it presents a high coulombic efficiency, promising for battery applications.

Keywords: conducting polymers, polyaniline, dichloroacetic acid, trichloroacetic acid, propylene carbonate

Introduction

The characterization of polyaniline (PAni) films prepared electrochemically has shown that the properties of such materials depend on synthesis conditions such as, potential range¹, solvent nature^{2,3}, supporting electrolyte^{4,6}, substrate⁷, etc. Varela *et al.*² performed studies on the ionic exchange phenomena related with PAni in non-aqueous media (propylene carbonate (PC) and acetonitrile) and it was observed that both, cation and anion, contribute to the electroneutralization process, which occurs in the polymeric system. The changes in the protonation level of PAni were studied by Santiago *et al.*³ who observed that protonation increases after the electrochemical response in propylene carbonate medium containing thionyl chloride

and 0.1 mol L⁻¹ lithium perchlorate. The increase of the protonation level can be observed by an increase in the absorbance peak at 440 nm of the visible spectra, which is assigned to the presence of the cation radical in the polymer.

The importance of studies on PAni synthesized in a non-aqueous medium such as (PC) is due to its application in lithium batteries^{3,9-13}, in addition to the fact that its coulombic efficiency is higher than that observed for PAni obtained in aqueous media^{8,9}. In a previous work¹⁴, it was shown that PAni films can be electrochemically polymerized in PC medium in the presence of di- (DCA) and tri- (TCA) chloroacetic acids by using an appropriate concentration of a dehydrated supporting electrolyte. It is interesting to mention that both acids can be obtained with small amount of water and they not degrade in PC medium. Also, the behavior of these acids in this specific medium has been studied based on their dissociation, $HA = A^- + H^+$,

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homoconjugation, $\text{HA} + \text{A}^- = \text{HA}_2^-$, and dimerization, $2\text{HA} = (\text{HA})_2$ equilibria and it was observed that DCA has a tendency to dimerize¹⁵.

The aim of this paper is to characterize PANi films electrosynthesized in the presence of DCA and TCA in propylene carbonate medium¹⁴, by different techniques namely, ultraviolet-visible and infrared spectroscopy, scanning electron microscopy and electrochemical activity. Furthermore films produced in selected conditions were tested as cathodes in a lithium battery setup by applying multiple charge-discharge cycles.

Experimental

PAni was electrochemically synthesized on platinum electrodes by using linear sweep cyclic voltammetry in a Pyrex cylindrical reactor with a single compartment. The working (area of *ca.* 1 cm²) and auxiliary electrodes were platinum foils. The reference electrode was an Ag / AgNO₃ 0.01 mol L⁻¹ in PC connected to the working solution by a glass bridge filled with the working solution without the monomer. The propylene carbonate (Aldrich 99.9% anhydrous), the different acids (Carlo Erba 99%) and the lithium perchlorate (Merck Suprapur) were used without further purification. More details can be found elsewhere¹⁴. The electrochemical response experiments were performed in a propylene carbonate solution containing 0.5 mol L⁻¹ LiClO₄ and the same acid used in the synthesis: 2 mol L⁻¹ DCA or 1.5 mol L⁻¹ TCA. A potentiostat 273A (EG&PARC) controlled by the software M270 was employed in the electrochemical experiments. In order to remove the residual monomer, the polymer was washed for two min upon stirring in a PC solution containing lithium perchlorate and the same acid used in the synthesis. The samples were then dried under dynamic vacuum for 24 h.

The spectroscopic studies in the infrared region were performed from pellets of the dried polymer and potassium bromide, in the range of 500 to 4000 cm⁻¹. A BOMEM model MB-102 was used for these measurements.

For the UV-visible experiments the polymer was first undoped by immersion in a solution of 0.1 mol L⁻¹ NH₄OH in PC, followed by the extraction of the residual monomer by keeping the sample immersed in pure PC, gently stirred. After this procedure the polymer was dried under dynamic vacuum during 24 h and dissolved in N-methyl-2-pyrrolidone. These experiments were performed in a spectrophotometer HITACHI model U3210 using a solution of the original acid (DCA or TCA) in PC and 0.5 mol L⁻¹ LiClO₄, as reference.

For the Scanning Electronic Microscopy (SEM) analysis, the polymers were electrochemically synthesized using a

thin gold layer deposited on a glass plate (10 x 30 x 1 mm) as electrode. SEM experiments were done with a Zeiss equipment model DSM 960 operating at 20 kV with 10,000 times magnification.

The charging-discharging tests were carried out in a PC solution containing 1 mol L⁻¹ LiClO₄ at a current density of 20 μA cm⁻². The potential values were measured against a Li/Li⁺ electrode. The electrochemical responses were performed between 2.5 and 3.8 V, at a scan rate of 5 mV s⁻¹.

Results and Discussion

Typical cyclic voltammograms obtained during the electrosynthesis of PANi in PC medium are shown in Figure 1. Since the acids used are organic and relatively weak (dissociation constants, K_{HA} , of 7.55×10^{-8} and 7.75×10^{-8} for DCA and TCA¹⁵, respectively) compared with mineral acids commonly used it is necessary to add an adequate supporting electrolyte to the solution in order to obtain an electroactive polymer. The growth of good quality (homogeneous and cohesive) PANi films in PC medium is possible when basic requirements are satisfied, as demonstrated in a detailed work previously published¹⁴. Of particular interest is the observation made by Pandey and Bapat¹⁵ that DCA presents a tendency to dimerize, so the proton concentration decreases due to the dimerization process¹⁴. Therefore the acid concentration had to be larger for DCA (2.0 mol L⁻¹, Figure 1a) than for TCA (1.5 mol L⁻¹, Figure 1b) in order to have a satisfactory polymer growth. For TCA the polymer growth is much more prominent as observed mainly by the increase in the current of the first oxidation peak (peak I) (Figure 1b). Interestingly the film grown in TCA also presents a smaller ratio between the oxidation peaks associated with degradation as compared to polymer growth, $i_{\text{p,II}}/i_{\text{p,I}}$. In both cases, the peak related to polymer degradation (peak II) can be minimized by the reduction of the positive potential limit after the third initial potential cycle. The adherence of the film to the metallic substrate, as well as other physical characteristics, was not significantly affected by the use of this procedure.

The electrochemical responses of PANi films in PC solutions containing DCA and TCA are shown in Figure 2. One can observe in both cyclic voltammograms the occurrence of characteristic oxidation peaks related to electroactive PANi^{1,7} at *ca.* -0.25 / -0.45 V (peaks A/A'), *ca.* 0.2 / -0.05 V (peaks B/B') and *ca.* 0.5 / 0.3 V (peaks C/C'). Electrochromism was observed for all samples with the color varying from light yellow, for less positive potentials, to dark blue for more positive potentials. Comparing Figures 1 and 2 one can observe that the CV's in the presence (Figure 1) and absence (Figure 2) of the

monomer are quite different. For the case where the polymerization was performed by reducing the potential range after the third cycle, the CV's of the electro-synthesis process showed a behavior closer to that in Figure 2.

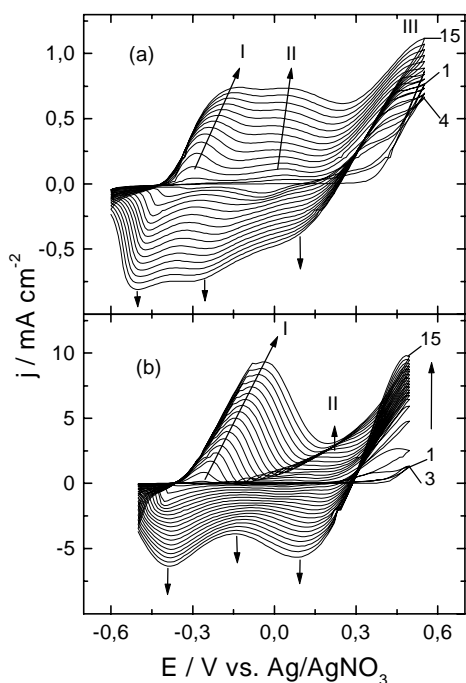


Figure 1. Cyclic voltammograms (15 cycles) of PANi growth on platinum in propylene carbonate solution containing $0.5 \text{ mol L}^{-1} \text{ LiClO}_4$, 0.25 mol L^{-1} aniline and (a) 2 mol L^{-1} DCA with scan rate of 10 mV s^{-1} ; (b) 1.5 mol L^{-1} TCA with scan rate of 20 mV s^{-1} . Cycle numbers are indicated in the figures.

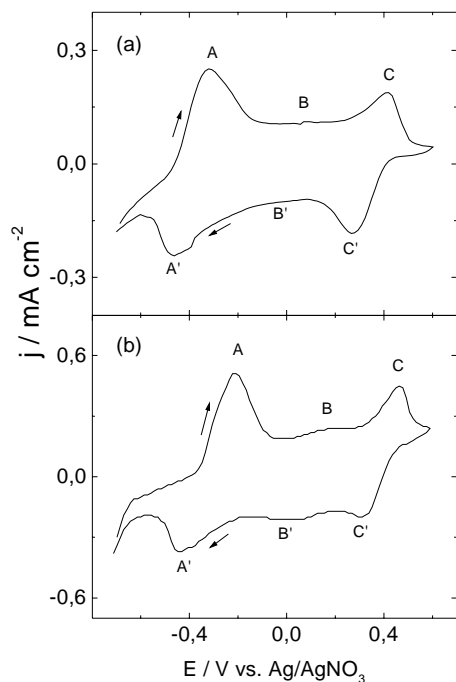


Figure 2. Electrochemical response, performed in the synthesis solution without the monomer, for PANi electro-synthesized on platinum in propylene carbonate solution: (a) 2 mol L^{-1} DCA; (b) 1.5 mol L^{-1} TCA. Scan rate 10 mV s^{-1} .

The infrared spectrum of PANi growth on platinum in the presence of TCA is shown in Figure 3. No significant changes were observed for PANi growth in the presence of DCA. In general the spectrum presented characteristics of the emeraldine salt oxidation state deduced by the ratio between the magnitudes of the peaks at *ca.* 1590 cm^{-1} (quinoid form) and *ca.* 1494 cm^{-1} (benzenoid form)¹⁶⁻²⁰. The assignment of the PANi bands found in this work is in agreement with the literature¹⁶⁻²⁰ with special attention to the bands at $1080\text{-}1147 \text{ cm}^{-1}$ which are assigned to the ClO_4^- anion¹⁷. Such a band was also observed by Neoh *et al.*¹⁸ in emeraldine films treated with HClO_4 , but not for films treated in different organic acids. Such observation is strong evidence that the perchlorate anion, from the salt used as supporting electrolyte in the electro-synthesis, was incorporated into the polymer. Previous works^{18,21} demonstrated that their extraction from the polymer film becomes more difficult as the size of the anion increases, consistent with our results.

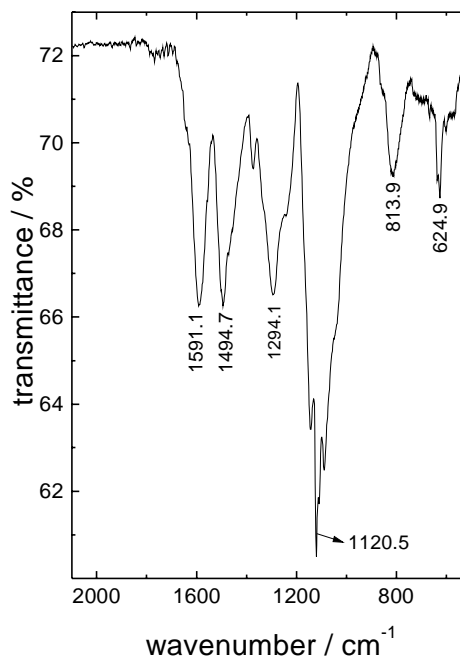


Figure 3. Infrared spectrum (KBr pellet) of PANi, in emeraldine salt oxidation state, electro-synthesized on platinum in propylene carbonate medium containing 1.5 mol L^{-1} TCA. Resolution of 4 cm^{-1} .

Two other interesting features about the ClO_4^- incorporation in the PANi films were observed during this analysis. Firstly, when thicker films are prepared, the band between $1080\text{-}1147 \text{ cm}^{-1}$ increases, since it becomes more difficult for the ClO_4^- anion to move out from the film. The second feature is that when the ratio between the peaks at 1590 cm^{-1} and 1494 cm^{-1} increases (PANi becomes more oxidized), the band corresponding to the ClO_4^- incorporation also increases, probably due to the attraction of the anions to the oxidized sites.

In Figure 4 the UV-vis spectra of PANi films electrosynthesized in the presence of DCA and TCA are presented for the doped and undoped forms. In the undoped form both spectra (for DCA and TCA) are the same and therefore, only the polymer grown in TCA is presented in Figure 4. These undoped PANi spectra present bands which are characteristic of PANi in the leucoemeraldine base oxidation state. Two bands are observed at 329-335 nm and at 645 nm attributed to the π - π^* transitions in the aromatic rings of benzene and to the charge transfer between quinoid and benzenoid rings²²⁻²⁴, respectively. The polymer doped by the addition of DCA or TCA to the solution of NMP presents a color change from dark blue to green and the characteristic bands at 320-350, 420-430 and 760-780 nm^{25,26} associated to the conducting form, *i.e.* protonated emeraldine. The shift of the bands in the region from *ca.* 645 to *ca.* 763 and 778 nm, respectively for DCA and TCA, upon doping the PANi solution are attributed to the formation of the polaronic band in emeraldine salt^{21,22}.

The scanning electron microscopy analysis shows that PANi electrosynthesized in PC medium in the presence of DCA and TCA presents a compact structure [Figure 5 (a) and (b)], similar to that obtained by Yonezawa *et al.* in PC medium¹⁰. This morphology is different from the globular one observed for PANi synthesized in aqueous medium [Figure 5(c)] in the presence of TCA and LiClO₄. It is suggested that these morphological differences could be due to an effect of the solvent, *i.e.*, a consequence of the hydrogen bonding occurring in aqueous medium that interferes in the interaction between the chains. This kind of interaction is absent in the case of PC which is a typical example of a non-associated solvent.

The charge-discharge tests were performed with PANi films (thin films containing approximately 0.139 mg of PANi) electrosynthesized in PC medium containing TCA¹⁴. In Figure 6 a typical electrochemical response of these PANi films in 1 mol L⁻¹ LiClO₄ is presented. The doping and

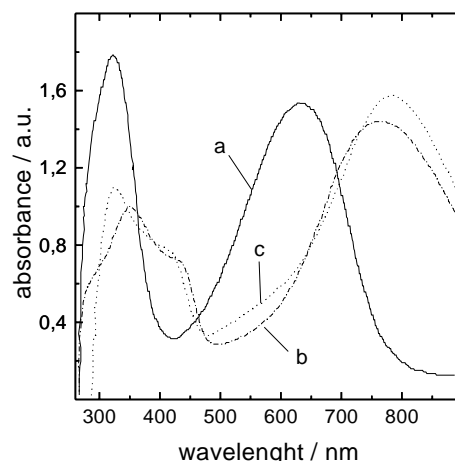


Figure 4. Electronic UV-visible spectra of a N-2-methylpyrrolidone solution containing PANi electrosynthesized on platinum in propylene carbonate medium containing 1.5 mol L⁻¹ TCA (curve a undoped and curve c doped form) and 2 mol L⁻¹ DCA (curve b doped form).

undoping processes can be observed occurring between 2.6 and 3.6 V (peaks A/A'), in agreement with the results obtained by Yonezawa *et al.* in PC medium¹⁰.

A charging-discharging curve for the Li / 1 mol L⁻¹ LiClO₄ - PC / PANi system at 20 mA cm⁻² is illustrated in Figure 7. The films were charged up to 3.8 V and the calculated coulombic efficiency was 98.9 %, similar to that observed by Osaka *et al.*⁹ who studied PANi galvanostatically synthesized in the presence of trifluoroacetic acid (TFA). The discharging capacity obtained in the present work (107 mA h g⁻¹) can be considered high and comparable to the values observed in the literature^{11,27}. Echigo *et al.*¹¹ studied chemically synthesized PANi and they observed a discharging capacity of 118.6 mA h g⁻¹. Hwang *et al.*²⁷ studied the charge/discharge characteristics of sulfonated chemically synthesized PANi determining a discharging capacity around 80 mA h g⁻¹ and a coulombic efficiency equal to 90 %. These observations indicate that PANi films electrochemically synthesized in PC solution containing TCA

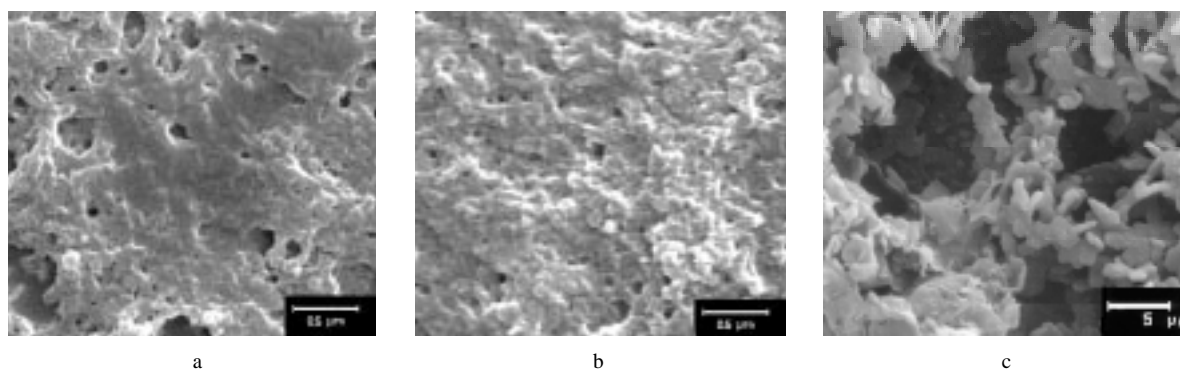


Figure 5. Scanning electron micrographs of PANi, in the emeraldine salt oxidation state, electrosynthesized on platinum from a solution containing: 0.25 mol L⁻¹ aniline, 0.5 mol L⁻¹ LiClO₄ and (a) 2 mol L⁻¹ DCA in PC medium; (b) 1.5 mol L⁻¹ TCA in PC medium; (c) 1.5 mol L⁻¹ TCA in aqueous medium.

give similar results to those obtained in the presence of TFA⁷. It is important to observe that organic acids such as DCA and TCA, which are weaker, less volatile and less corrosive than TFA, can be used to produce good quality PANi films, with very interesting charging-discharging properties²⁸.

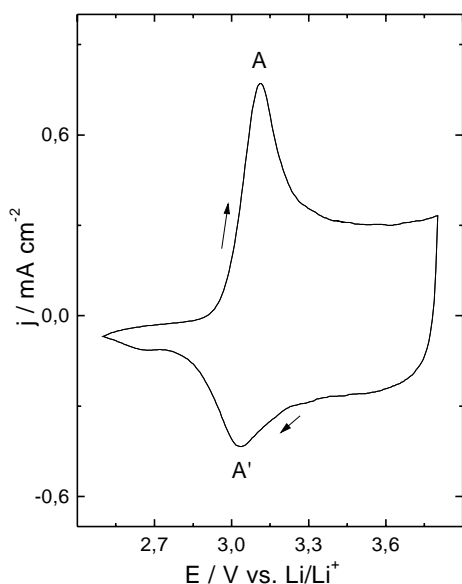


Figure 6. Electrochemical response of the PANi film in a propylene carbonate solution containing 1 mol L⁻¹ LiClO₄. Scan rate 5 mV s⁻¹.

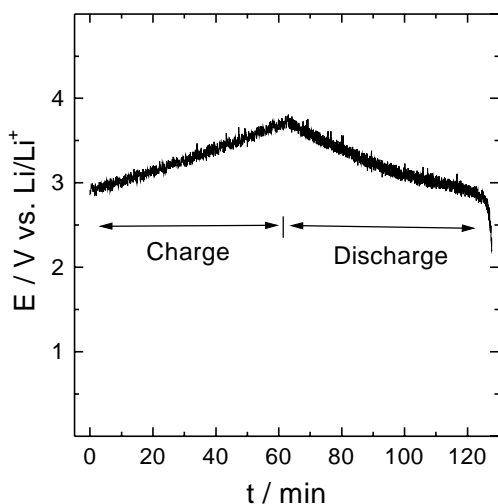


Figure 7. Charge and discharge curves for PANi prepared in 1.5 mol L⁻¹ TCA and 0.5 mol L⁻¹ LiClO₄ PC solution containing 0.25 mol L⁻¹ aniline. Current density: 20 μA cm⁻². Cutoff potential: 3.8 V.

Conclusions

The electrochemical response of PANi films synthesized in PC solution containing DCA and TCA showed the characteristic redox process of PANi in aqueous medium. The spectroscopic studies indicated the formation of PANi in the emeraldine salt state, with incorporation of the

perchlorate ion from the electrolyte used for the electrosyntheses, in both acids. The doped polymer obtained in the presence of DCA and TCA presents a compact structure when prepared in PC medium. A morphological difference was observed between the polymer electrosynthesized in aqueous and propylene carbonate media indicating the strong influence of hydrogen bonding interaction in the polymer growth. Finally, the applicability of the PANi films synthesized in the presence of TCA to lithium rechargeable batteries was demonstrated by the high coulombic efficiency and discharging capacity of the films used as cathodes in a lithium battery setup.

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