Int. J. Electrochem. Sci., 8 **(2013)** 12499 - 12508

International Journal of ELECTROCHEMICAL SCIENCE
www.electrochemsci.org

A Strategy to Electropolimerization of Poly(2,5-Dicyano-*p*-Phenylenevinylene) on Different Substrates.

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Received: 5 August 2013 / *Accepted:* 19 September 2013 / *Published:* 20 October 2013

This work describes the characterization of DCNPPV films obtained electrochemically over different substrates like Pt, Au, ITO and Al. This characterization was performed by infrared (IR), UV-Visible (UV-Vis) and fluorescence (Fl) spectroscopy and by cyclic voltammetry measurements (CV). The obtained results has demonstrated that the formed films present a hight purity grade in all studied substrates, just like was observed in the IR spectra that shown only the characteristics bands of this polymer. The UV-Vis, Fl and CV characterization revealed that this material presents a hight electron affinity value of 3.45 eV. This fact possibilitated that the organic electronic devices formed with this polymer and Al used like cathod electrode, could present a lower electron injection barrier. It was also observed that the solvent used to the electropolymerization process can modulate the nucleation and growth mechanism for the polymeric layer formation.

Keywords: conjugated polymer, DCNPPV, electropolymerization, nucleation and growth mechanism.

1. INTRODUCTION

The conjugated *poly(p-phenylenevinylene)* (PPV) and its derivatives were one of the first class of conjugated polymers used in organic electronics and currently they are important materials with potential use for organic light emitting diodes and optical displays [1-4]. However, the widespread use of these polymers in practical devices is still hampered by problems like electron and hole injection efficiency, charge carrier mobility and environmental stability. The hole and electron charge injection can be improved by adjusting the HOMO and LUMO levels of the polymer in such a manner that these levels could be closer to the work function of the electrodes where the polymer is deposited. The control of the energy levels of the polymer can be accomplished by introducing substituents at the polymer backbone. Cyanide groups attached to the PPV backbone stabilizes the polymer electron affinity, thus decreasing the energy difference between the LUMO and the work function of the aluminum electrode [4-7].

Although theoretical investigation pointed out to the *poly(2,5-dicyano-p-phenylenevinylene)* (DCNPPV) as a good candidate for hole injection and acceptor material, the non-electrochemical synthesis of this polymer did not yield a good quality material and film formation was not possible, due to short chain length of the polymer [8-13]. The synthesis of good quality DCNPPV films were reported by our group [14], opening the possibilities to explore this material as active layer in organic electronic. This synthesis was carried out electrochemically by reduction of the *α,α,α’,α’-tetrabromo-2,5-dicyano-p-xylene* precursor on an ITO electrode in non-aqueous solvent. With this procedure a film of good quality, purity and environmental stability was obtained.

The electrochemical synthesis, usually, depends on several synthetic parameters, like purity of the electrolyte, the reduction potential and, in some cases, on the nature of the substrate, since some materials can be good decomposition catalysts for the polymer precursors, leading to bad quality polymers. Examples of PPV-like polymer formed with a large amount of impurities were already discussed in a previous communication [15]. Depending on the reduction potential used the formed film could contain cationic species that are inserted into the film to compensate the negative charge created by the reduction of the polymeric chain.

Although for device construction, usually the film is deposited onto a transparent electrode and then a low work function material is evaporated on the organic layer, for some purposes it can be interesting to obtain the organic layer directly on the low work function electrode, like in multilayer devices, when the organic layer is electrodeposited. In that case it is important to be sure that the good quality of the deposited polymer.

In the present study we report the most advantageous conditions to the synthesis, by electropolymerization, of high purity *poly(2-5-dicyano-p-phenylenevynilene)* on different metallic substrates. A special attention is paid to the deposition onto an aluminum substrate, since it is known that on aluminum there is always a native very stable oxide when aluminum is manipulated in atmospheric pressure that hindered the electrodeposition of the polymer film, moreover, this native oxide will produce a further barrier to charge injection. In the present study we report a strategy to eliminate *in situ* this native oxide in order to provide a fresh metallic surface for the polymer deposition. It is also evaluated the influence of the solvent used to produce the electrolytic solution on the nucleation and growth mechanism of the electropolymerization of DCNPPV.

2. EXPERIMENTAL

The starting material for the electropolymerization process, *α,α,α’,α’-tetrabromo-2,5-dicyano-p-xylene* (DCNPX), was prepared from commercial *p*-xylene following synthetic methods described earlier in the literature [14]. The metallic gold, platinum and aluminum electrodes were prepared as a thin film either sputtered (Pt and Au) or evaporated (Al) onto a glass plate. Commercial ITO substrate was used as a transparent electrode.

The DCNPPV films were obtained on Pt, Au and ITO by polarizing the metallic substrate at –0.15 V and –0.25 V (vs. Ag/AgBr) in a solution of 0.1 mol.L^{-1} of tetraethylammonium bromide (TEAB) using acetonitrile (ACN) or Dimethylformamide (DMF) as solvent with 0.05 mol.L^{-1} of DCNPX. For the DCNPPV deposition on Al the film was obtained after a pre-treatment to remove the native oxide layer, (see details in the result and discussion section). The electrochemical experiments were performed using a PGSTAT100N Metrohm-Autolab Potentiostat/Galvanostat. A graphite sheet with 4.0 cm^2 of geometric area was used as counter electrode and Ag/AgBr (0.1 mol L^{-1} $Br^-_{(diss.)}$) as reference electrode.

IR spectra were recorded on a Bomem M-102 spectrophotometer with a Spectra Tech # 500 specular reflectance accessory. UV-Vis spectra were obtained, by transmission; on a HITACHI U-321 spectrophotometer only for films grew over Au and ITO. The emission spectra were obtained on a HITACHI F-4500 fluorimeter. The microscopy images (SEM) were obtained on a Shimadzu SSX- 550 Superscan microscope.

The CV measurements were performed at the same electrochemical approach used in the film preparation; however a CH_2Cl_2/TBAP solution/electrolyte system was used. After the performed of the electropolymerization and the CV measurements, N_2 was bubble at the solvent/electrolyte system to remove dissolved O_2.

3. RESULTS AND DISCUSSIONS

To establish the preparative potential values to be used for the electrosynthesis of the DCNPPV films a measurement of cyclic voltammetry (CV) was performed and the obtained voltammograms are showed in the Figure 1.

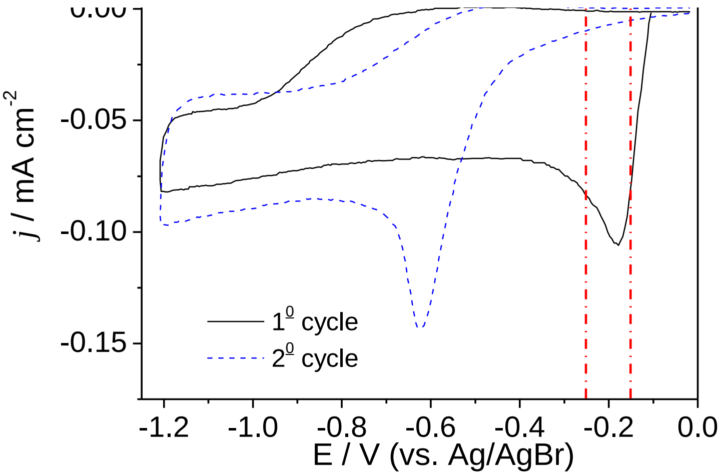


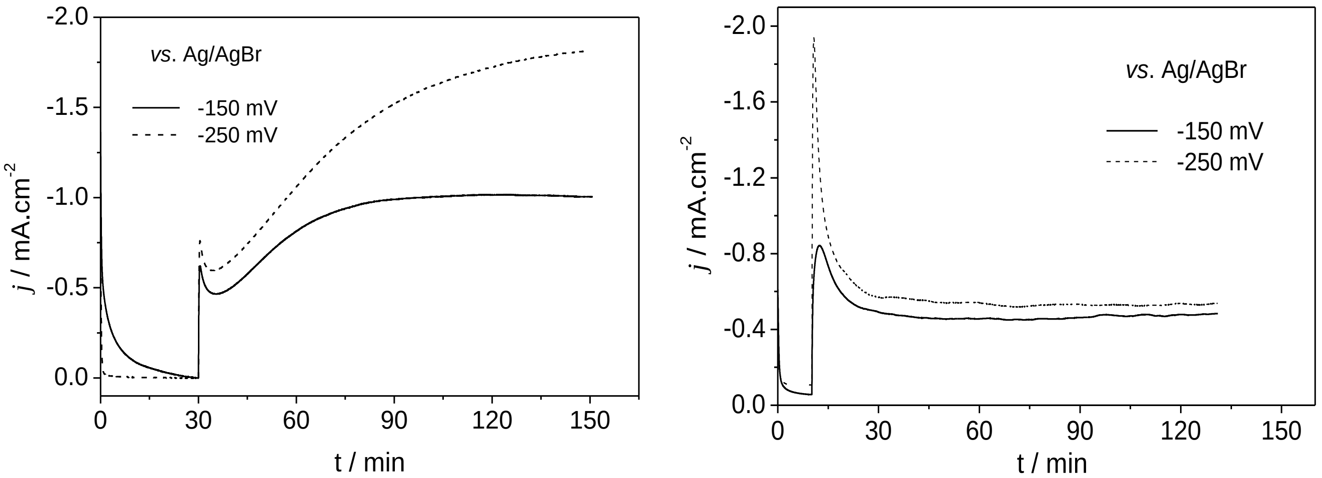
Figure 1. The first and the second cyclic voltammograms of gold substrate obtained during the electrodeposition of the DCNPPV in a solution of 0.1 mol L^{-1} of TEAB in DMF containing 0.005 mol L^{-1} of DCNPX, scan rate = 50 mV s^{-1}. The segmented red lines represent the values of potential chosen for the potentiostatic deposition of the polymer.

It could be observed in Figure 1 a cathodic peak current (Ep_c) at *ca.* -0.18 V in the first cycle assigned to the reduction of the DCN-PPV precursor and formation of the conjugation in the polymer backbone [15]. As discussed by Garcia *et al.* [14] this cathodic process occurs in potential values less negative than for the electropolymerization of PPV [15], this displacement could be assigned to the strong electron-withdrawing character of the cyano groups that changes the energy levels of the molecule, facilitating the electrochemical reduction of this polymer precursor. In the second cycle, the reduction peak was strongly shifted to more negative potentials due to the semiconductive nature of the film deposited on the first cycle [14].

The segmented red lines shown in Figure 1 represent the potential values chosen for the potentiostatic deposition of the DCNPPV on the different substrates discussed in this work. We have chosen two potential values to evaluate the influence of the rate of the electrochemical reduction on the morphology of the film, then it has been chosen a value previous to the Ep_c for the first cycle and another one closely after this peak to avoid the influence of the ion and solvent intercalation that could occur intensely in potentials much more negatives than Ep_c.

The voltammetric profile is very similar for all the substrates used in this work except for the Al, also the change on the solvent (DMF to ACN) did not produced remarkable changes on the voltammetric behavior of the DCNPPV electropolymerization (figures not shown).

Figure 2 shows the curves of current density as a function of time (chronoamperometric curves) for the potentiostatic growth of the DCNPPV films applying -0.15 V and -0.25 V on Au electrode as substrate using ACN (Figure 2a) and DMF (Figure 2b) as solvent. As could be seen in this figure, the profiles of the current density x time curves are very different when compared the two electrolytic solution used.



a) ***b)***

Figure 2. The chronoamperometric curves for the electropolymerization of the DCNPPV on gold substrate in a solution of ***a)*** 0.1 mol L^{-1} of TEAB in ACN containing 0.005 mol L^{-1} of DCNPX and ***b)*** 0.1 mol L^{-1} of TEAB in DMF containing 0.005 mol L^{-1} of DCNPX.

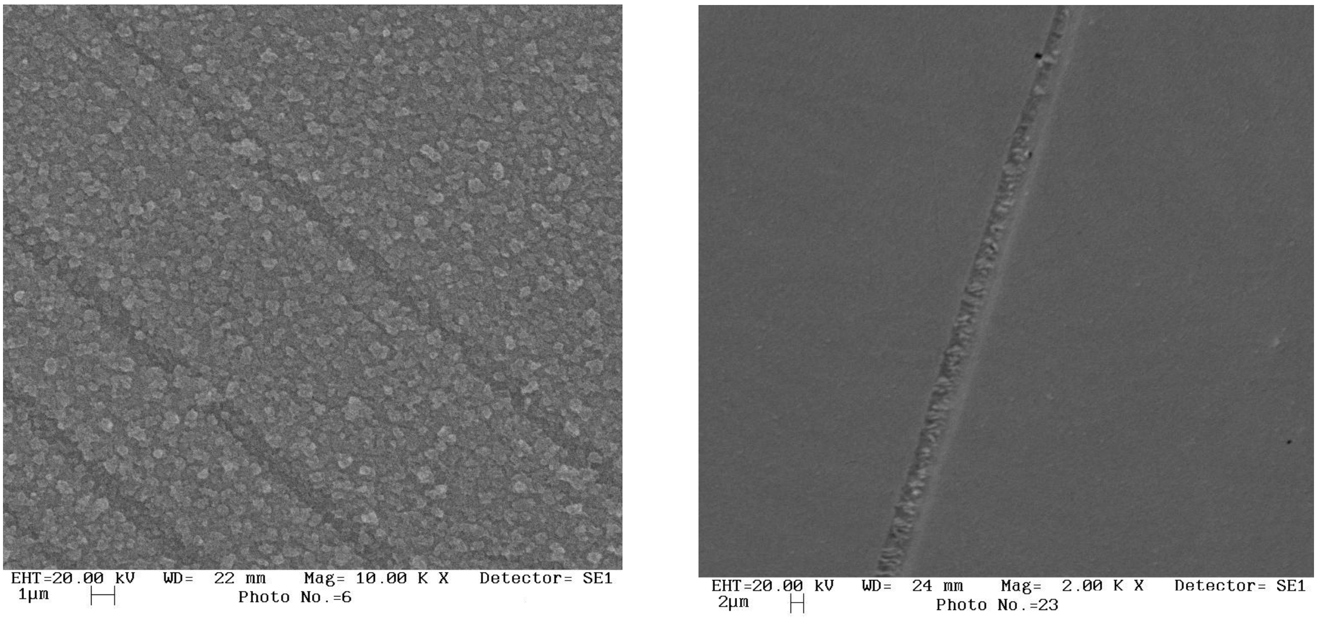
When the films are obtained in the electrolytic solution with ACN as solvent (Figure 2a) there are a sudden increase of the cathodic current followed by a peak and a second increase in reduction current tending toward a constant value. An increasing in the deposition potential causes an augment in the value of the peak current observed in short times of deposition and also in the cathodic current value reached in longer deposition times. For the films obtained in the electrolytic solution with DMF as solvent (Figure 2b) there is also a sudden increase of the cathodic current followed by a peak, but after the peak the current density decrease exponentially to reach a value very similar for both applied potentials. In this case the augment in the deposition potential causes only an augment in the value of the peak current observed in short times of deposition. It is important to remark that there are no important differences in the chronoamperometric curves profile for the ITO, gold and platinum electrodes in which one of the solvent studied.

The observation described above could be explained considering the different ways that a polymeric film could be formed. It could be found, on literature, numerous articles discussing different models for layer formation during the electrodeposition of conducting polymers [16-18]. It is established on literature that the electrodeposition of conducting polymers occurs by a process of nucleation and growth, similar to one that occurs for the metallic layers formation [18]. There are two kinds of nucleation; instantaneous and progressive, and three types of growth: one- (1D), two- (2D), and three- (3D) dimensional processes and the nucleation and growth (NG) processes involve several stages: the first one is the oxidation of the monomer, followed by the formation of oligomers and by the polymerization step [18]. In instantaneous nucleation, the number of nuclei is constant and the film is formed without the creation of additional nuclei. In progressive nucleation, nuclei are generated constantly. The 1D growth occurs only in one direction (perpendicular to de substrate surface). The 2D growth occurs by the nuclei grow preferably on parallel direction to the electrode. The 3D growth, the rates for these processes perpendicular and parallel to the electrode are comparable [16].

The profile of the current density versus time curves for different potential applied could be used to evaluate the mechanism of nucleation and growth that occurs during the electropolymerization of a specific polymer on different experimental conditions. In our case, the profiles showed in Figure 2a and Figure 2b, when compared with the results published by del Valle *et al.* [17] and Romero *et al.* [18] indicating that, once ACN is used as solvent, during the first time occurs an instantaneous nucleation as could be observed by the presence of the early peak of current, however for longer electropolymerization time the DCNPPV film formation changes to a progressive nucleation with a three dimension growth. Moreover for the film prepared using -0.25 V in ACN it could be observed a slight continue increase in current density at longer times. This behavior is an indicative that the mechanism of electropolymerization changes to a progressive nucleation with three dimension growth under diffusion control [17] due to the decrease of the DCNPPX concentration at the electrode surface.

When DMF is used as solvent, the current density versus time profile for the DCNPPV electropolymerization (Figure 2b) indicating that the mechanism for the polymeric layer formation follows an instantaneous nucleation with a two dimension growth. These different behavior cold be understood if the solubility of the oligomers formed during the electropolimerization is taking into account. Utley and Gruber [19] discussed that the better solvent to be used in the process of electrochemical polymerization of PPV-like polymers is DMF due to a catalytic effect on the cleavage of the C-Br bond and also due to the high solubility of the oligomers formed in this solvent. Then, if it is considered that the DMF is a better solvent to the oligomers than ACN, it could be thought that during the formation of the DCNPPV film, in this solvent, the oligomers concentration species will remain soluble for a higher period of time reaching higher concentration near of the electrode surface, in this way when a critical concentration is reached then the oligomers will precipitated on the electrode surface in a limited numbers of nuclei forming a massive film that could block the further passage of current at the polymer-solution interface, inhibiting the process of electropolymerization. When ACN is used as solvent the oligomeric concentration could not reach higher values and the precipitation of the oligomers may occurs in a progressive way forming continues number of nuclei. As the film formed in this way is not massive (formed by the junction of various small nuclei) it could not block the surface and the electropolymerization could continue for longer times.

This different NG mechanism must produce films with very different morphology. Figure 3 shows the SEM images obtained for the films produced in ACN (Figure 3a) and DMF (Figure 3b) with the appliance of -0.25 V on gold substrate. As could be seen in this figure the morphology for the film obtained in ACN has a granular feature as expected for a progressive nucleation mechanism. While for the films formed when DMF is used as solvent it could be observed a smooth and massive film as also expected for an instantaneous nucleation with a two dimension growth.



a) ***b)***

Figure 3. The SEM images for the films obtained by the electropolymerization of the DCNPPV on gold substrate, applied potential = -0.25 V in a solution of ***a)*** 0.1 mol L^{-1} of TEAB in ACN containing 0.005 mol L^{-1} of DCNPX and ***b)*** 0.1 mol L^{-1} of TEAB in DMF containing 0.005 mol L^{-1} of DCNPX (the experimental conditions used for obtaining images are describe in the bottom of images).

As discussed for chronoamperometric curves profile it was observed no important differences in the films morphology when the films were also grown on ITO and platinum electrodes in which one of the solvent studied. The fact that DCNPPV could be obtained over ITO [14] is important because its opens the possibility of construction of devices for use in organic electronics. However the use of his polymer in multilayer devices, where the DCNPPV will work as low barrier for electron injection polymer and good electron mobility layer require that this polymer may perhaps be obtained on a low work function metal as Al.

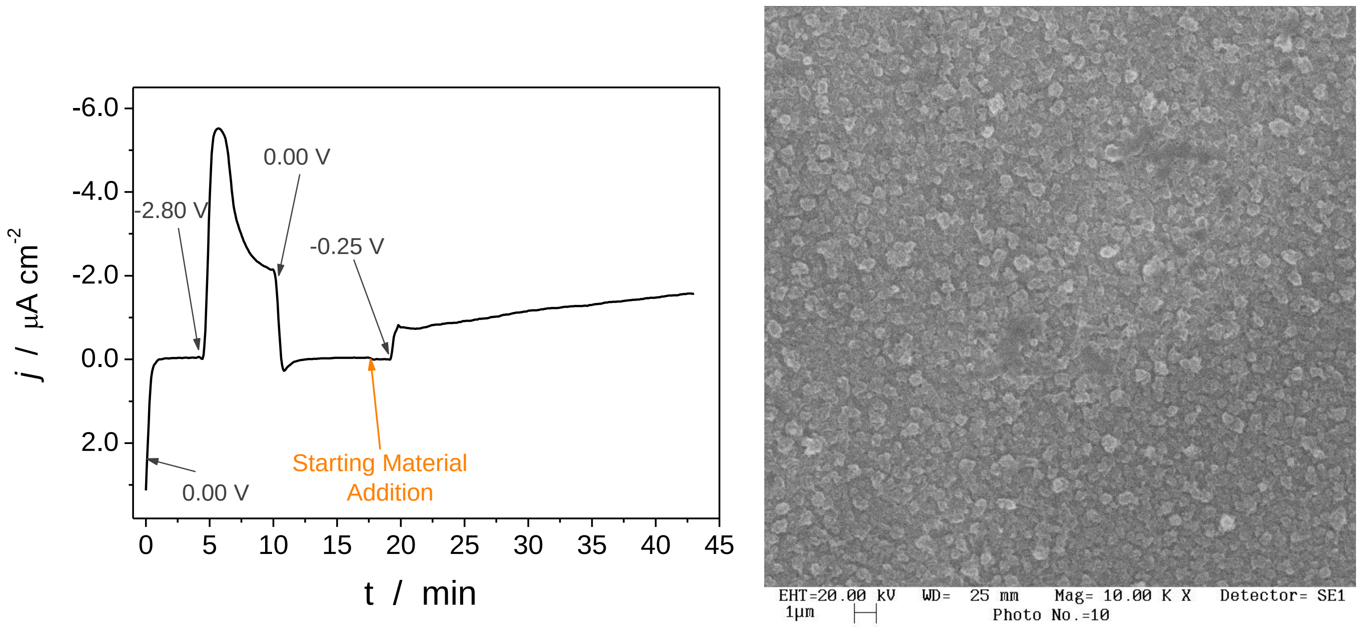
The electrochemical deposition of DCNPPV on the aluminum substrate was not possible by just polarizing at -0.15 V or -0.25 V as in the case of platinum, gold and ITO. It is well established in the literature whenever a fresh aluminum surface is exposed to the oxygen or humidity; a very stable native oxide is formed very quickly. The native oxide is highly resistive and prevents the charge transport in order to reduce the precursor. Therefore, the strategy to deposit DCNPPV onto the aluminum substrate is to remove the native oxide to allow the precursor to be reduced and deposited on the aluminum surface. In organic solutions the native oxide can be reduced without growing a new oxide layer on the surface, as long as water is not present and the solution is free from oxygen, or the electrode is hold at a potential where the metal is not oxidized.

The tactic consequently is to reduce the oxide under electrochemical control in solution and hold the potential after the oxide elimination. We found that the aluminum oxide can be reduced at –2.8 V in a 0.1 mol.L^{-1} of tetrabutylammonium perchlorate TBAP in ACN and after 90 s of polarization; the current due to the reduction of the oxide was very low and constant. At this point the electrode was fully active for the polymer deposition. Since the reduction potential of the aluminum oxide is far more negative than the reduction potential of the precursor, all the procedure to clean the aluminum surface from the oxide is made in the absence of the precursor. The potential is then fixed at 0 V, where the aluminum is protected and the precursor is not reduced. After that the precursor could then be introduced to the solution. After stirring the solution to homogenize, the electrode potential was shifted to –0.25 V to reduce the precursor. All this procedure is demonstrated in Figure 4a, where each step is indicated by arrows. The reduction current curve is very similar to the deposition of the DCNPPV on the other electrodes.

The Figure 4b shows the SEM image of the DCNPPV film obtained in the Al surface. It is interesting to note that the change in the support electrolyte (TEAB to TBAP) do not change the NG mechanism for the DCNPPV polymerization, indicating that the solvent is the more important factor in determining the NG mechanism.

The characterization of the obtained film was performed then by spectroscopic and cyclic voltammetry (CV) measurements. The IR characterization of the films obtained at Pt, Au, ITO and Al substrates are showed at Figure 5. The spectra of the DCNPPV film over the different substrate are quite similar They show a weak band at 3045 cm^{-1}, which can be assigned to the C-H stretching vibration of the *trans*-vinylene unit. The corresponding out-of-plane angular deformation for the *trans*-vinylene unit is signified by the feature at 960 cm^{-1}, the closest feature to the 965 cm^{-1}, typical of *trans*-alkene out-of-plane C-H deformation. Other features at 1490 and 1262 cm^{-1} are associated with ring stretching vibrations and a strong feature at 2230 cm^{-1} with the C≡N stretching.

The most important information bring on by this IR characterization is the fact that the DCNPPV films could be formed at the two most used substrates in organic electronic devices construction with a high purity grade, fact that is very important thinking forward the polymer application.



a)

b)

Figure 4. ***a)*** The chronoamperometric curve obtained during the process of elimination the superficial Al native oxide followed by the electropolymerization of the DCNPPV in a solution of 0.1 mol L^{-1} of TBAP in ACN containing 0.005 mol L^{-1} of DCNPX; ***b)*** SEM image of the DCNPPV film obtained on the Al surface with the conditions described above.

The UV-Vis spectra were obtained only for the films formed over Au and ITO because these substrates are transparent to visible light. The fluorescence characterization was performed with the films obtained over all the used substrates (figure not shown). These spectra are identical for all the films analyzed and the. The absorption spectrum present a maximum of absorbance at 425 nm and an onset point at 555 nm. This onset point is used to determinate the Eg value [14, 20], that results in a value of 2.22 eV for this parameter. The emission spectra is broad and poorly defined structured compared to the *p*-PPV one [21] and has its maximum of emission at 575 nm. Both absorption and emission spectra are red-shift compared to the PPV ones, fact that is attributed to the CN presence attached to the polymeric backbone [6,23,24].

The CV characterization was also performed with the films obtained over all the used substrate (figure not showed). The objective of this characterization was to determinate the value of ionization potential (IP) and electronic affinity (EA) of the polymer that. These parameter were related to voltammetric measurements by Brèdas *et al.* [25] that determinate empiric relationships to determinate IP and EA through the onset potential of the oxidation and reduction of the polymer respectively [14,20,21]. The voltammetric profile obtained is similar for all the films and the mean values found are 5.55 eV for IP and 3.43 eV for EA. The most important information that results from these experiments was that the polymer synthesized presents a higher EA value than other PPV derivatives open a possibility to use it to reduce the electron injection barrier and improve the electron mobility, facts that could cause an enhancement of the efficiency of electronic devices constructed with this polymer.

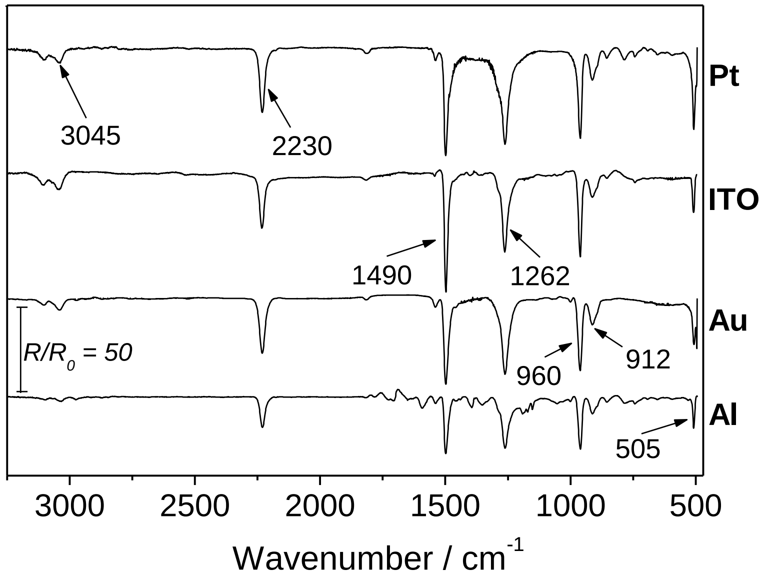


Figure 5. The IR spectra of the DCNPPV films obtained at Pt, Au, ITO and Al substrates in a solution of 0.1 mol L^{-1} of TBAP in ACN containing 0.005 mol L^{-1} of DCNPX, applied potential = -0.25 V.

4. CONCLUSIONS

The results presented in this work indicating that the electrochemical approach has demonstrated to be an efficient method to produce DCNPPV films over different substrates, principally over the two ones frequently used for organic electronic devices construction.

It was also verified that the use of different solvents in the experimental setup to produce the electropolymerization of DCNPPV change the nucleation and growth mechanism that are responsible for the polymeric layer formation. This change in mechanism produce a dramatically modification in the film morphology.

This methodology is able to produce films with a high purity grade as was demonstrated by the IR characterization. Moreover, the larger electron affinity of the DCNPPV produced pointed in order to the possibilities of the use of this material in organic electronic devices having metals with higher environmental stability such as Al without a lost in efficiency due to the increase in the electron injection barrier.

ACKNOWLEDGEMENTS
F.S.S. and K.C.C.W.S.K are grateful for the fellowship granted from CAPES. Authors also thank the financial support provide for this research by the Brazilian Agency: CNPq and Fundação Araucária (Paraná State).

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