

Influence of the electrolyte cation and anion sizes on the redox process of PPy/PVS films in acetonitrile solution

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Abstract Polypyrrole/poly(vinyl sulfonate) (PPy/PVS) films have been synthesized by a potentiodynamic method in aqueous solution. The voltammetric study of this polymer in acetonitrile (MeCN) reveals an anomalous behavior of its redox process in the three electrolytes used: LiClO₄, LiF₃CSO₃, and (Bu)₄NClO₄. The anion and cation sizes of the electrolyte clearly affect the reduction/oxidation process of a PPy/PVS film in MeCN medium. This result is explained by both anions and cations participating during the redox reaction of this polymer in MeCN medium: initially, the cations penetrate the polymer forming ion pairs with sulfonate groups, and the anions behave as the main mobile species during the potential sweeps. However, a large cation or anion will penetrate with difficulty inside the polymer, providing a lower amount of electroactive polymeric chains and a lower value of peak charges.

Keywords Potentiodynamic polymerization · Polypyrrole · Poly(vinyl sulfonate) · Electrochemical properties

Introduction

The electrochemical synthesis of conducting polymers, such as polypyrrole, polyaniline, and polythiophene, is generally accomplished at constant potential by cyclic potential sweeps or by galvanostatic polarization. However, these polymers are very sensitive to the growth conditions,

including the anion kind, the solvent, and the type of method used for the electropolymerization [1–4].

The attained polymer will exhibit different conductive, mechanical, or electrochemical properties [5–8] depending on the incorporated anion. Also, the ions interchanged with the solution during the redox switching are influenced by the doping anion of the polymer [5–7]. Various experimental techniques, such as cyclic voltammetry, electrochemical quartz crystal microbalance, energy dispersive X-rays (EDX), probe beam deflection, or electron paramagnetic resonance, have been used to determine the nature of ionic transport during its oxidation or reduction process [5–15].

The nature of the ionic transport is affected by several factors. Both anions, the one incorporated into the film during the polymerization process and the one used as electrolyte, play an important role in the ionic movement during the redox process due to three factors: anion size, their ionic nature (univalent or divalent), and their diffusion coefficient in solution and through the polymer. Similar considerations can be stated for electrolyte cations [14–21]. Moreover, the nature of the solvent also plays an important role in the doping–dedoping process of PPy films [11, 14, 16, 22–25]. Solvent molecules can be transported inside the polymer during the redox process and, hence, depending on solvent–ion and solvent–polymer interactions, the ionic transfer can be very different. Finally, anion or cation movements are strongly dependent on the structural disparities present in PPy films [14, 16, 26].

It has been reported that the use of polyelectrolyte in polymerization solution with pyrrole causes the growth rate to increase and improves environmental stability [27]. A wide number of electrolytes have been used in the direct electrodeposition of polypyrrole/polyelectrolyte molecular composite, such as poly(vinyl sulfonate), poly(styrene sulfonate), poly(vinyl sulfate), poly(vinyl phosphate), etc.

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In this kind of material, the polymeric dopant anions are expected to be entrapped and immobile. Thus, it is normally accepted that the electrolyte cations are the mobile species [28]. However, interchange of anions during the redox process has been reported previously for PPy/polyelectrolyte systems [14, 16, 18].

Polypyrrole/poly(vinyl sulfonate) (PPy/PVS) films synthesized maintaining the potential constant at +0.8 V have recently been studied by voltammetry, in situ Fourier transform infrared spectroscopy (FTIR), and EDX techniques [14, 16]. An anomalous behavior of this polymeric blend in 0.1 mol L⁻¹ LiClO₄/AN solution compared with PPy/ClO₄ films was observed with the cycling. A continuous increase in the voltammetric peaks was registered until they reached a steady state. ClO₄⁻ anions became the main mobile species in the PPy/PVS redox process in MeCN medium when a high number of cycles were carried out. This result was corroborated by theoretical treatments based on the Nernst and Butler–Volmer equations. The restructuring of the polymeric chains and the stabilization of the Li⁺ cations inside the polymer forming ion pairs with sulfonate groups of the PVS⁻ anions was the cause of this behavior.

In this work, PPy/PVS films have been synthesized by potentiodynamic method, and their redox behavior in MeCN medium has been studied using solutions of different electrolyte sizes: LiClO₄, LiF₃CSO₃, and (Bu)₄NClO₄. The aim of this article is to analyze how the kind of electrolyte affects the voltammetric behavior of PPy/PVS films in MeCN medium, described in references [14] and [16]. Thus, it will be possible to explore the possibility of using cations or anions of different sizes to modify electrodes to be used in batteries.

Experimental

Pyrrole monomer (Fluka; >97%) was distilled under vacuum before use. Sodium poly(vinyl sulfonate) (Aldrich), LiClO₄ (Fluka), NaClO₄ (Merck), LiF₃CSO₃ (Aldrich), (Bu)₄NClO₄ (Fluka), and MeCN (Merck; with a water content <0.01%) were used as received. Millipore water with resistivity >18 MΩ cm was used.

PPy/PVS films were generated on Pt foils by potentiodynamic polymerization, scanning the voltage linearly between +1.0 and -0.9 V at a constant scan rate in aqueous solutions of 0.1 mol L⁻¹ pyrrole and 0.05 mol L⁻¹ PVS (Fig. 1). Polymerization charges were obtained by integrating the anodic peak area in the 14th cycle, resulting in values of 550±30 mC cm⁻². Three different as-grown PPy/PVS films were studied in each electrolyte solution. After generating, the films were washed with water and MeCN and dried by N₂ flow. A three-electrode cell composed of a Pt modified working electrode, an Ag/AgCl reference

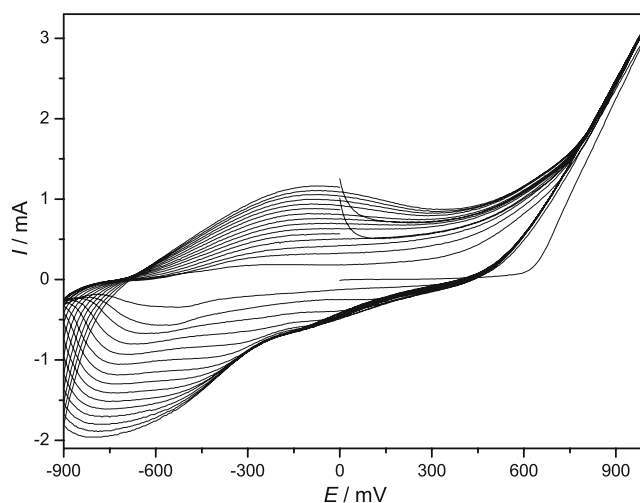


Fig. 1 Potentiodynamic synthesis of PPy/PVS films in aqueous 0.1 mol L⁻¹ Py and 0.05 mol L⁻¹ PVS solution. Scan rate is 0.05 V s⁻¹. Fifteen consecutive cycles were carried out

electrode, and a Pt wire as the auxiliary electrode was used. All solutions were purged with N₂ gas for a period of 15 min.

Cyclic voltammetry studies were performed in a similar three-electrode cell using a PAR 273A potentiostat/galvanostat.

An EDX analysis was carried out with a Scanning Electron Microscope S-3500N. Thick PPy/PVS films were synthesized to separate them easily from Pt sheets, using conductive carbon adhesive films. EDX measurements performed with a polymeric film joined to an electrode produced a large peak of Pt masking the other peaks. PPy/PVS films were cycled in the electrochemical cell until steady voltammograms were reached. Then, they were removed from solution, washed with MeCN, and dried. The oxidized or reduced films were obtained by stopping the last cycle at the wished potential.

In situ FTIR studies were performed in a three-electrode spectroelectrochemical all-glass cell. A Bruker IFS 66v spectrometer with an angle specular reflectance accessory (incidence angle of 65°) was used. The procedure to obtain the in situ FTIR spectra has been previously described [16].

Results and discussion

Potentiodynamic synthesis and cyclic voltammetry in LiClO₄/MeCN of PPy/PVS films

Potentiodynamic polymerization of PPy/PVS films was carried out in an aqueous solution shifting the potential between -0.9 and +1.0 V (Fig. 1). All the voltammograms obtained during polymerization showed a strong increase in the current at approximately +0.4 V in the anodic scan,

indicating the onset of monomer oxidation/polymerization processes. Electrochemical reduction and oxidation of the generated polymer occurred at lower potentials, confirming that the conjugated polymers are more easily oxidized and reduced than their monomers.

Figure 1 shows 15 consecutive cycles of a PPy/PVS polymerization carried out in 0.1 mol L^{-1} Py and 0.05 mol L^{-1} PVS aqueous solution. An increase in the oxidation and reduction peaks of the generated polymer is observed with the cycling. PPy/PVS films generated were immersed in a 0.1-mol L^{-1} $\text{LiClO}_4/\text{MeCN}$ solution, and several consecutive voltammetric cycles between $+0.8$ and -0.8 V at scan rate of 0.05 V s^{-1} were registered until they reached a steady state (Fig. 2). As can be seen, an increase in the voltammetric peaks is obtained with the cycling, reaching a stable behavior after 45 consecutive cycles. The charge value obtained from the 44th anodic peak was 29.2 mC cm^{-2} .

After the steady state was accomplished in this potential range, more negative cathodic limits than -0.8 V were reached (Fig. 3). In this case, noticeable changes in the voltammograms were observed: anodic peak potential was shifted to more positive values and greater anodic peak charges were obtained. Charges of 49.5 mC cm^{-2} were measured when the voltammograms were registered reaching -2.1 V as the most negative potential.

The behavior obtained for a PPy/PVS film synthesized by the potentiodynamic method is coincident with that observed for a PPy/PVS film generated at $+0.8$ V constant potential, recently reported by our group using different techniques: cyclic voltammetry, EDX, and in situ FTIR [14, 16]. A behavior similar to the above was interpreted as due to an irreversible restructuring of the polymeric chains with consecutive scans (see Scheme I in ref. [16]). Since the size of the PVS^- anion is large, the Li^+ cations are forced to

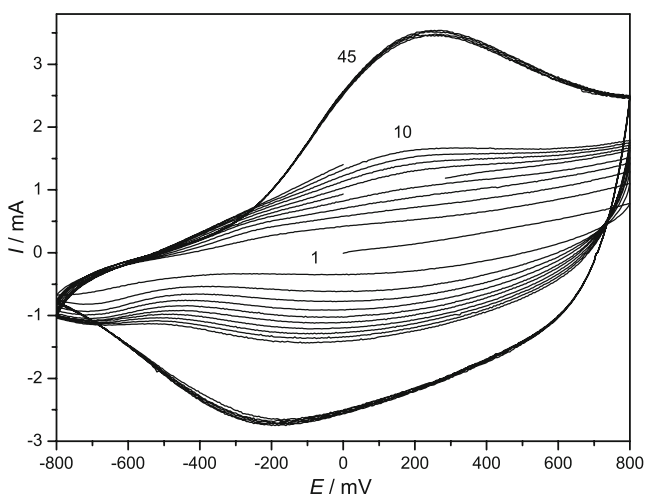


Fig. 2 Cyclic voltammograms of PPy/PVS polymer in 0.1 mol L^{-1} $\text{LiClO}_4/\text{MeCN}$ solution. Scan rate is 0.1 V s^{-1} . The ten initial and the five final cycles are shown. The numbers indicate the scan numbers

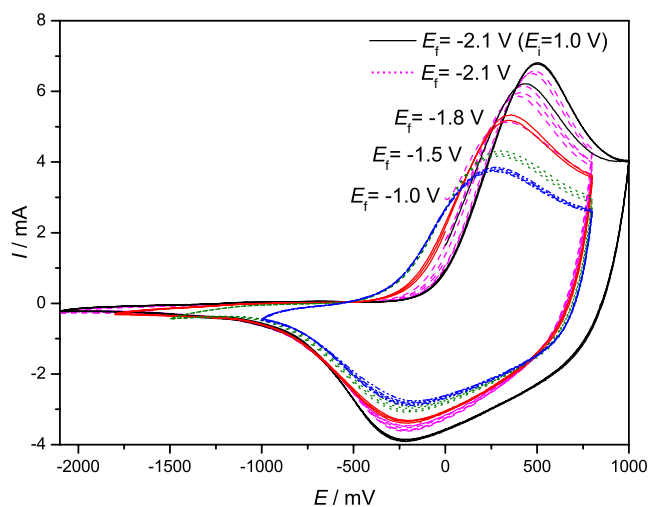


Fig. 3 Voltammetric behavior of PPy/PVS film in 0.1 mol L^{-1} $\text{LiClO}_4/\text{MeCN}$ solution changing the reduction potential limit, E_f , to more negative values. All scans were registered for the same film after a steady state had been reached switching between $+0.8$ and -0.8 V. The numbers indicate the E_f values. Scan rate is 0.1 V s^{-1}

enter the polymer during the reduction process to balance the negative charges remaining now free on the PVS chains. In each cycle, a fraction of Li^+ cations penetrates the polymer where they are stabilized, probably forming ion pairs with the sulfonated groups of the PVS. At each cycle, the Li^+ cations enter the more internal polymeric layers, increasing the amount of electroactive polymeric chains. Because Li^+ cations are stabilized inside the polymer, the ClO_4^- anions will become the main mobile ionic species during the redox process of the PPy/PVS.

The in situ FTIR spectra registered for PPy/PVS films in a 0.1-mol L^{-1} $\text{LiClO}_4/\text{MeCN}$ solution confirm the voltammetric results described previously. Figure 4 shows the $1,620\text{--}1,480 \text{ cm}^{-1}$ band obtained, stopping the potential at $+0.7$ V in several consecutive cycles. The voltammetric cycles were performed between -1.0 and $+0.8$ V at a scan rate of 0.1 V s^{-1} . As can be seen, a continuous increase in the intensity of FTIR bands is observed, suggesting a rise in the amount of infrared-active polymeric chains, as it was described in detail in reference [16].

Furthermore, the inset in Fig. 4 displays the shifting of this band with the cycling. Zerbi et al. [29, 30] reported a shift of this band for strictly α,α' -connected oligopyrroles and polypyrrole with the number of pyrrole units in the molecular chain. These authors considered that the conformation of the chain changes with chain length and the observed dispersion must originate from an increase in π -electron delocalization when the number of chemical units increases. Hence, the band shift shown in Fig. 4 would indicate an increase in the π -electron delocalization, which is a consequence of the increase in the amount of electroactive and infrared-active polymeric chains. This is indi-

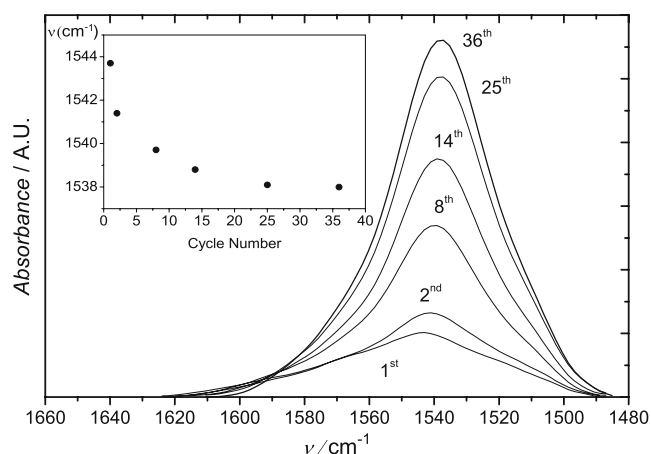


Fig. 4 In situ FTIR spectra obtained for a PPy/PVS film in 0.1 mol L^{-1} $\text{LiClO}_4/\text{MeCN}$ solution registered at $+0.7 \text{ V}$ for different cycles. The voltammetric cycles were performed between $+0.8$ and -1.0 V with a scan rate of 0.1 V s^{-1} . The number of cycles is indicated in the figure. *Inset* shift of the $\sim 1,640 \text{ cm}^{-1}$ band with the number of cycles

cated by the rise observed in the voltammograms and FTIR spectra, respectively (see also the discussion in references [14] and [16]). In other words, the chains conjugation length will rise with the number of potential scans because the cations penetrate into the more internal layers of the polymer, thus increasing the amount of polymeric chains that intervene in the redox process.

Redox process of a PPy/PVS film in MeCN using electrolytes with different cation and anion sizes

As it has been commented above, during the redox process of a PPy/PVS film in MeCN, both the cations and the anions of the electrolyte participate. Initially, cations are incorporated into the polymeric matrix where they are stabilized with sulfonate groups of the PVS. This makes it necessary for the anions to interchange between polymer and solution during the oxidation/reduction process.

Therefore, we have used electrolytes with different sizes of cations and anions so as to examine their effects on the voltammetric behavior of PPy/PVS in MeCN medium. In this section, PPy/PVS films synthesized by the potentiodynamic method have been studied in LiCF_3SO_3 and Bu_4NClO_4 MeCN solutions by cyclic voltammetry, in the same way as they were studied in $\text{LiClO}_4/\text{MeCN}$. Table 1

Table 1 Estimated ionic radii reported in the literature

Ion	Ionic radii (nm)	Ionic radii (nm) [31]
Li^+	0.078 [32]	0.076
Bu_4N^+	0.415 [33]	0.415
ClO_4^-	0.283 [34]	0.237
CF_3SO_3^-	0.602 [34]	0.270

shows the estimated ionic radii of the cations and anions used in this work [31–34]. As can be seen, the size of the Bu_4N^+ cation is higher than Li^+ . Thus, since the same anion is used in both electrolytes, we can discover how the kind of cation affects the redox behavior of this polymer, comparing the voltammograms registered for a PPy/PVS film in a $\text{Bu}_4\text{NClO}_4/\text{MeCN}$ solution with the results obtained in $\text{LiClO}_4/\text{MeCN}$.

On the other hand, CF_3SO_3^- anions have to be incorporated into the polymeric matrix with more difficulty than ClO_4^- anions due to their large size (Table 1) and the structural form of the CF_3SO_3^- anion, which is cylindrical (nonspherical) and carries a highly delocalized charge [20, 21]. Hence, using a $\text{LiCF}_3\text{SO}_3/\text{MeCN}$ solution instead of a $\text{LiClO}_4/\text{MeCN}$ one, we will examine the influence of the anions on the PPy/PVS redox process.

Redox process of a PPy/PVS film in $\text{LiCF}_3\text{SO}_3/\text{MeCN}$

Once the PPy/PVS film was synthesized by the potentiodynamic method, the modified electrode was immersed in a $\text{LiCF}_3\text{SO}_3/\text{MeCN}$ solution where a voltammetric study of this film was carried out. Consecutive cycles were registered for a PPy/PVS film in this solution, scanning the potential between -0.8 and $+0.8 \text{ V}$ (Fig. 5). As it occurred in $\text{LiClO}_4/\text{MeCN}$, a continuous increase in the voltammetric peaks with the cycling is obtained, until a stable behavior is reached, after 30 consecutive cycles. From the anodic peak on the 34th cycle, a charge value of 18.4 mC cm^{-2} resulted. This value is lower than 29.2 mC cm^{-2} obtained in the same conditions using $\text{LiClO}_4/\text{MeCN}$ as electrolyte.

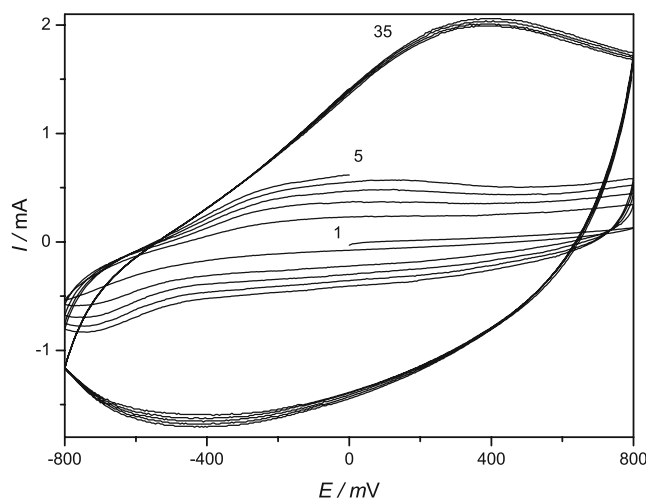


Fig. 5 Cyclic voltammograms of PPy/PVS polymer in 0.1 mol L^{-1} $\text{LiCF}_3\text{SO}_3/\text{MeCN}$ solution. Scan rate is 0.1 V s^{-1} . The five initial and the five final cycles are showed. The numbers indicate the scan numbers

Proceeding in the same way as in the $\text{LiClO}_4/\text{MeCN}$ solution, the potential cathodic limit was shifted to more negative values (Fig. 6). Once again, the anodic peak shifted to a higher potential and the peak charge increased when a more negative potential was reached. A charge of 30.0 mC cm^{-2} was measured when -2.1 V was reached as the most negative potential. This value is rather lower than 49.5 mC cm^{-2} obtained in $\text{LiClO}_4/\text{MeCN}$.

From the voltammograms registered for PPy/PVS films in $\text{LiClO}_4/\text{MeCN}$ and $\text{LiCF}_3\text{SO}_3/\text{MeCN}$, we may assume a similar voltammetric behavior of this polymer in both solutions. However, an additional EDX study of PPy/PVS films cycled in $0.1 \text{ mol L}^{-1} \text{ LiCF}_3\text{SO}_3/\text{MeCN}$ solution was carried out to confirm this hypothesis. Figure 7 includes the EDX spectra of different PPy/PVS films. The pristine film as prepared before being subjected to any voltammetric cycling is compared with those of oxidized and reduced films in $0.1 \text{ mol L}^{-1} \text{ LiCF}_3\text{SO}_3/\text{MeCN}$. In the pristine film, an S peak, caused by the sulfur of the sulfonate groups, is observed, which indicates the presence of PVS inside the polymeric material. In the solution of synthesis, we have used a PVS-Na salt, thus some Na^+ cations can remain entrapped inside the generated polymer, and this is why a Na peak is present also in all three spectra ($\sim 1 \text{ keV}$). A similar Na peak was observed for PPy/DBS films when they were synthesized by the potentiodynamic method from DBS-Na and pyrrole solutions [35].

In the reduced and oxidized films spectra, the S peak may be attributed to CF_3SO_3^- anions, which would be able to substitute PVS^- anions inside the polymeric blend. This hypothesis is rejected because this anion also has to produce an F peak due to the three fluorides included in

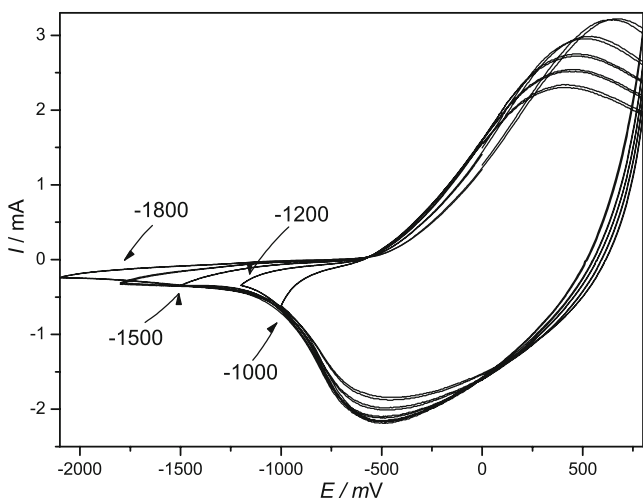


Fig. 6 Voltammetric behavior of PPy/PVS film in $0.1 \text{ mol L}^{-1} \text{ LiCF}_3\text{SO}_3/\text{MeCN}$ solution changing the reduction potential limit, E_f , to more cathodic values. All scans were registered for the same film after a steady state had been reached switching between $+0.8$ and -0.8 V . The numbers indicate the E_f values. Scan rate is 0.1 V s^{-1}

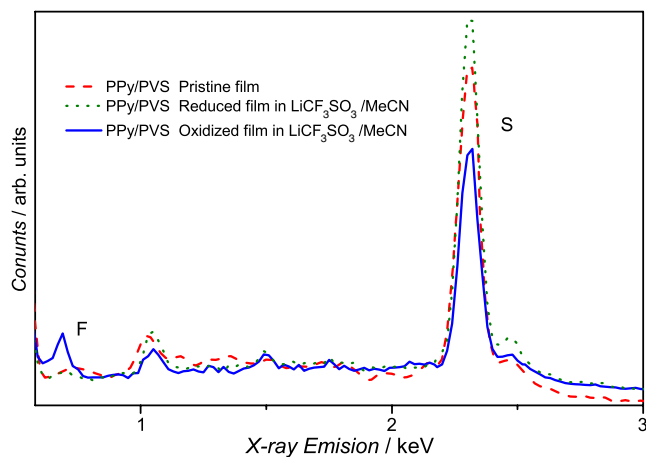


Fig. 7 EDX spectra of free-standing PPy/PVS films: as-grown film, reduced film in $0.1 \text{ mol L}^{-1} \text{ LiCF}_3\text{SO}_3/\text{MeCN}$ solution, and oxidized film in $0.1 \text{ mol L}^{-1} \text{ LiCF}_3\text{SO}_3/\text{MeCN}$ solution

its composition. However, the S peak appears but the F peak is not present in the spectrum of the reduced PPy/PVS film.

In the oxidized film spectrum, the F peak is observed, demonstrating that CF_3SO_3^- anions have entered the oxidized film. However, no F peak is detected in the reduced PPy/PVS film spectrum, indicating that these anions have been expelled from the polymer by electrochemical reduction.

These results and the voltammograms included in Figs. 5 and 6 point to a similar redox behavior of PPy/PVS films in $0.1 \text{ mol L}^{-1} \text{ LiCF}_3\text{SO}_3/\text{MeCN}$ and $0.1 \text{ mol L}^{-1} \text{ LiClO}_4/\text{MeCN}$. In spite of this, some differences between the behaviors in both electrolytes have to be remarked.

Comparing the voltammetric steady states in Figs. 2 and 5, we observe an ΔE_p much wider in $\text{LiCF}_3\text{SO}_3/\text{MeCN}$ with respect to that obtained in $\text{LiClO}_4/\text{MeCN}$. This result has been attributed to a slowing down of electrolyte motion in the polyanionic blend during charging–discharging [36]. Therefore, once the cations are stabilized inside the polymeric matrix, CF_3SO_3^- anions are incorporated into

Table 2 Charge values obtained for PPy/PVS films cycled in different electrolytes

Electrolyte	Q_A^a (mC cm^{-2})	Q_B^b (mC cm^{-2})	Q_C^c (mC cm^{-2})
LiClO_4	29.2	49.5	–
LiCF_3SO_3	18.4	30.0	50.0
Bu_4NClO_4	22.5	22.8	33.5

^a Charges measured reaching -0.8 V as the most negative potential limit

^b Charges measured reaching -2.1 V as the most negative potential limit

^c Charges measured in LiClO_4 after cycling the same film in LiCF_3SO_3 or Bu_4NClO_4

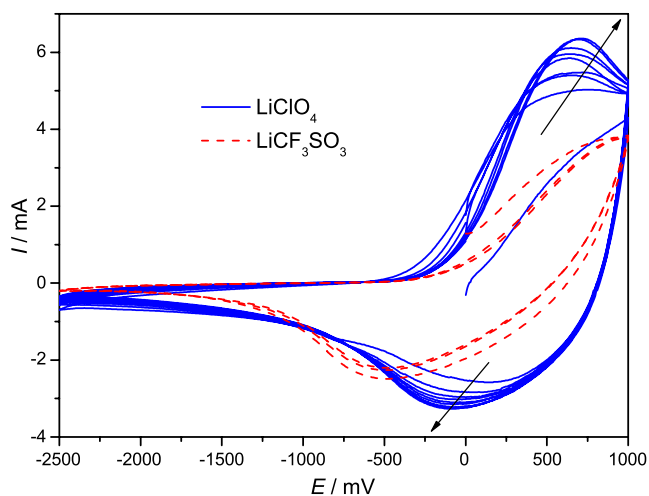


Fig. 8 Voltammograms registered in $0.1 \text{ mol L}^{-1} \text{ LiClO}_4/\text{MeCN}$ solution (solid line) compared with those recorded previously in $0.1 \text{ mol L}^{-1} \text{ LiCF}_3\text{SO}_3/\text{MeCN}$ using the same modified electrode. Scan rate is 0.1 V s^{-1}

the polymer and expelled from it with more difficulty than ClO_4^- anions due to the larger volume, cylindrical shape, and delocalized charge of the CF_3SO_3^- anions [20, 21].

Moreover, the charge values measured from the voltammetric peaks obtained in $0.1 \text{ mol L}^{-1} \text{ LiCF}_3\text{SO}_3/\text{MeCN}$ are much lower than those obtained in $0.1 \text{ mol L}^{-1} \text{ LiClO}_4/\text{MeCN}$ (Table 2). This result is in accordance with the difficulty of the anion motion: CF_3SO_3^- anions are more voluminous than ClO_4^- anions, thus those will not be allowed to penetrate the most internal layers of the polymer matrix. Note that Li^+ cation is common in both of the electrolytes, and then it is assumed that these ions do not influence the redox behavior.

Assuming a redox behavior of PPy/PVS films in $\text{LiCF}_3\text{SO}_3/\text{MeCN}$ similar to that in $\text{LiClO}_4/\text{MeCN}$, we can consider that, in each cycle, a fraction of Li^+ cations is incorporated into the polymeric matrix during the cathodic scan, which will be stabilized inside the polymer forming ion pairs with sulfonate groups. Thus, these cations will not be expelled during the anodic branch of the voltammogram, demanding the entrance of CF_3SO_3^- anions from the solution. At each cycle, an additional amount of cations will enter the polymer, making it necessary for a higher quantity of anions to incorporate into the polymer in the cathodic branch. Thus, at each cycle, the amount of anions participating in the redox process of the polymer will increase.

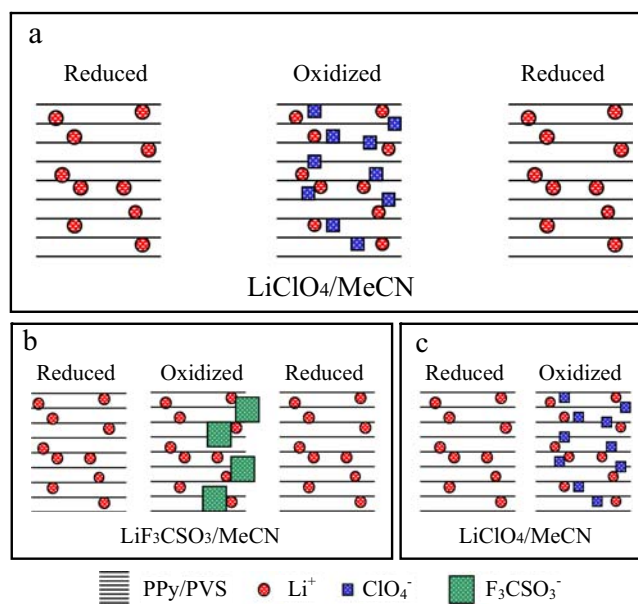
Up until this point, the behavior is similar to that described previously for PPy/PVS in $\text{LiClO}_4/\text{MeCN}$. However, due to the large volume of CF_3SO_3^- anions compared with ClO_4^- , a smaller amount of anions will penetrate the polymer during the reduction process, which is in accordance with the lower charge values measured

from voltammetric peaks in Figs. 5 and 6 with respect to those obtained from Figs. 2 and 3 (see Table 2).

With the aim of clarifying this result, we have carried out an additional experiment: a modified electrode of PPy/PVS cycled in $0.1 \text{ mol L}^{-1} \text{ LiCF}_3\text{SO}_3/\text{MeCN}$ solution was taken out and subsequently immersed in $0.1 \text{ mol L}^{-1} \text{ LiClO}_4$ solution. Figure 8 shows the cyclic voltammograms registered in this solution compared with those recorded previously in $0.1 \text{ mol L}^{-1} \text{ LiCF}_3\text{SO}_3/\text{MeCN}$. As can be seen, the voltammetric peak charges increase notably in $\text{LiClO}_4/\text{MeCN}$. The charge measured for the last cycle registered was of 50.0 mC cm^{-2} . Note that this value is very close to that obtained for a PPy/PVS film cycled only in LiClO_4 (Table 2).

This result demonstrates a mainly anionic exchange during the redox process of PPy/PVS in MeCN medium, as it was already postulated. When the electrode cycled in $\text{LiCF}_3\text{SO}_3/\text{MeCN}$ solution is reduced in LiClO_4 solution, the anions present in the polymeric blend are expelled to the solution, and in the subsequent anodic scan, other anions are incorporated into the polymer from the solution. Hence, the CF_3SO_3^- anions included inside the polymer are substituted by ClO_4^- anions, which have a smaller size and can access the more internal portion of the polymer, providing an increase in the peak charges.

To clarify the differences exposed for the redox behavior of PPy/PVS in $\text{LiCF}_3\text{SO}_3/\text{MeCN}$ and $\text{LiClO}_4/\text{MeCN}$ solutions, Scheme 1 has been proposed. The ionic exchange in $\text{LiClO}_4/\text{MeCN}$ during the redox process of a PPy/PVS film when the steady state is reached is displayed in



Scheme 1 Ionic exchange during the redox process of PPy/PVS film in $\text{LiClO}_4/\text{MeCN}$ solution (a), in $\text{LiCF}_3\text{SO}_3/\text{MeCN}$ solution (b), and in $\text{LiClO}_4/\text{MeCN}$ after cycling in $\text{LiCF}_3\text{SO}_3/\text{MeCN}$ (c)

Scheme 1a. In the reduced film, the Li^+ cations are present in the polymer because they are stabilized, forming ion pairs with the PVS^- anions. During the oxidation, the ClO_4^- anions penetrate the film to compensate the PPy^+ positive charge, and subsequently, these anions are expelled when the polymer is reduced again.

In Scheme 1b, the ionic composition of the polymer during its redox process in $\text{LiCF}_3\text{SO}_3/\text{MeCN}$ is shown. In the reduced film, the Li^+ cations are fixed by ion pair formation, while the CF_3SO_3^- anions are incorporated into the polymer during the oxidation and expelled during the reduction. However, the number of CF_3SO_3^- anions incorporated into the film is lower than ClO_4^- anions in Scheme 1a, though the number of Li^+ can be similar in both cases. When the film previously cycled in $\text{LiCF}_3\text{SO}_3/\text{MeCN}$ is reduced in $\text{LiClO}_4/\text{MeCN}$, all CF_3SO_3^- anions are expelled from the polymer with only Li^+ cations remaining inside the film (Scheme 1c). Thus, in the subsequent oxidation, ClO_4^- anions penetrate the blend due to its higher concentration in the solution with respect to CF_3SO_3^- anions. In this case, a number of ClO_4^- anions similar to that in Scheme 1a will be included in the polymer, providing very close charge values (Table 2).

Redox process of a PPy/PVS film in $\text{Bu}_4\text{NClO}_4/\text{MeCN}$

The influence of the cation size on the redox behavior of PPy/PVS in MeCN medium will be studied in this section. To this aim, we will compare the voltammetric behavior of this polymer in $0.1 \text{ mol L}^{-1} \text{ Bu}_4\text{NClO}_4/\text{MeCN}$ with respect to that in $0.1 \text{ mol L}^{-1} \text{ LiClO}_4/\text{MeCN}$. Thus, a greater size cation than Li^+ is used (see Table 1), while the same anion is maintained in the electrolyte solution.

Once again, a PPy/PVS film is synthesized by the potentiodynamic method, obtaining a similar voltammogram to that in Fig. 1. This film was immersed in a $0.1\text{-mol L}^{-1} \text{ Bu}_4\text{NClO}_4/\text{MeCN}$ solution and it was cycled reaching -0.8 V as the most negative potential limit. As in the previous electrolytes, an increase in anodic and cathodic peaks was obtained to reach the steady state (red dashed lines in Fig. 9). The charge value obtained from the integration of anodic peak was of 22.5 mC cm^{-2} .

The continuous peak increases with the cycling point up to a similar behavior to those obtained in the previous solution. However, when the negative potential limit was shifted to more negative values, the anodic and cathodic peaks did not increase their area. Therefore, similar peaks to those obtained reaching -0.8 V resulted when more negative potential limits were reached: -1.0 , -1.5 , -1.8 , -2.1 , and -2.5 V (blue solid lines in Fig. 9). The charge measured from the anodic peak was of 22.8 mC cm^{-2} when -2.5 V was reached. This value is very close to 22.5 mC cm^{-2} obtained for the same film when -0.8 V was used as

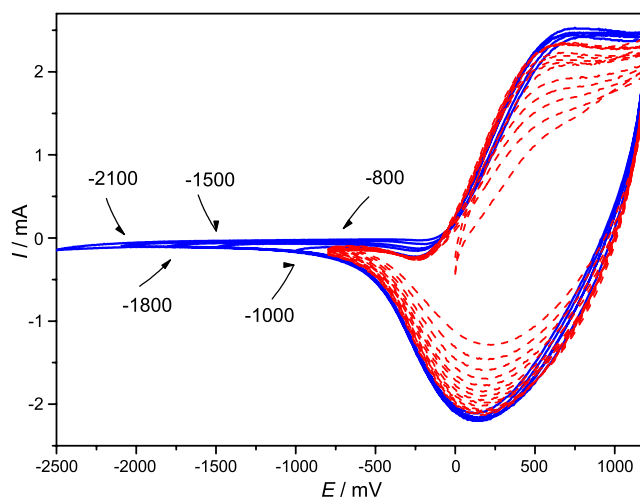


Fig. 9 Cyclic voltammograms of PPy/PVS film in $0.1 \text{ mol L}^{-1} \text{ Bu}_4\text{NClO}_4/\text{MeCN}$ solution. Dashed lines display the initial increase of the peaks when -0.8 V is reached as the most negative potential. Solid lines show the voltammetric behavior of the same film in $0.1 \text{ mol L}^{-1} \text{ Bu}_4\text{NClO}_4/\text{MeCN}$ changing the reduction potential limit, E_f . The numbers indicate the E_f values reached. Scan rate is 0.1 V s^{-1}

the most negative potential limit. This result is notably different to those obtained in $\text{LiClO}_4/\text{MeCN}$ and $\text{LiCF}_3\text{SO}_3/\text{MeCN}$ (Table 2). This behavior agrees with previous results reported by Bidan et al. [8], which showed that, in MeCN medium, small Li^+ cation diffuse more easily than Bu_4N^+ in the PPy/DBS $^-$ matrix.

An additional experiment was carried out with a PPy/PVS film cycled in $0.1 \text{ mol L}^{-1} \text{ Bu}_4\text{NClO}_4/\text{MeCN}$. This film was introduced in a $0.1\text{-mol L}^{-1} \text{ LiClO}_4/\text{MeCN}$ solution and it was cycled in this medium. The voltammograms obtained are displayed in Fig. 10. As can be seen, in this solution, the anodic and cathodic peaks increase quickly with the cycling, reaching a charge value of 33.5 mC cm^{-2} for the stabilized anodic peak. This value is higher than 22.8 mC cm^{-2} obtained in $0.1 \text{ mol L}^{-1} \text{ Bu}_4\text{NClO}_4/\text{MeCN}$, but is lower than 49.5 mC cm^{-2} obtained when a $\text{LiClO}_4/\text{MeCN}$ solution was used from the initial cycles. Note that the anion used in both electrolytes was ClO_4^- , indicating that the anomalous result obtained in $0.1 \text{ mol L}^{-1} \text{ Bu}_4\text{NClO}_4/\text{MeCN}$ is caused by the Bu_4N^+ cations.

The voltammetric results obtained for a PPy/PVS film cycled in $0.1 \text{ mol L}^{-1} \text{ Bu}_4\text{NClO}_4/\text{MeCN}$ can be explained in similar terms to those obtained for films studied in the other electrolyte solutions. We consider that the initial increase in the voltammograms indicates that the cations have to be incorporated slowly into the polymeric matrix during the reduction scans and they will remain inside the polymer stabilized by the sulfonate groups of the PVS. Hence, the anions will be the main mobile ionic species during the oxidation/reduction processes. This behavior has been demonstrated for $\text{LiClO}_4/\text{MeCN}$, $\text{NaClO}_4/\text{MeCN}$, and

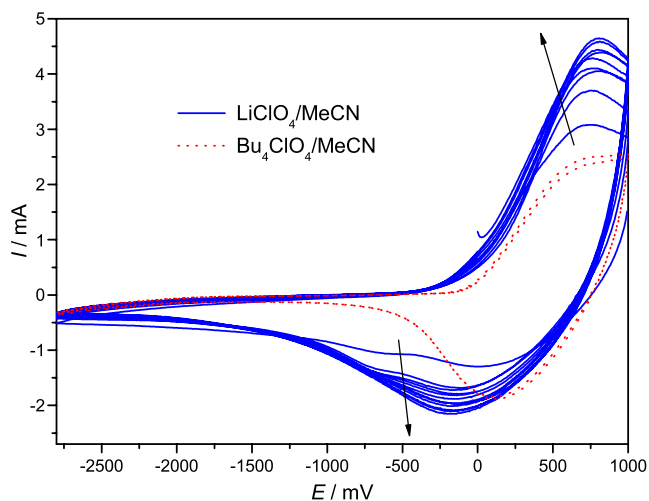
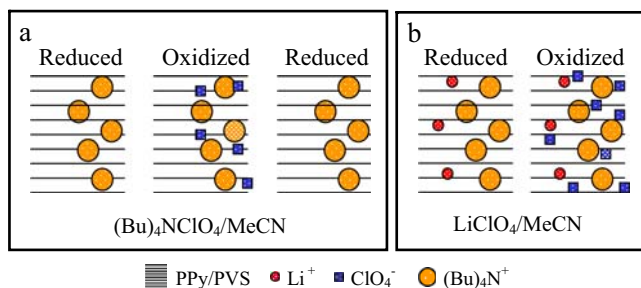


Fig. 10 Voltammograms registered in $0.1 \text{ mol L}^{-1} \text{ LiClO}_4/\text{MeCN}$ solution (solid line) compared with those recorded previously in $0.1 \text{ mol L}^{-1} \text{ Bu}_4\text{NClO}_4/\text{MeCN}$ using the same modified electrode. Scan rate is 0.1 V s^{-1}

$\text{LiCF}_3\text{SO}_3/\text{MeCN}$ (this work and ref. [14]). In contrast, in this case, the Bu_4N^+ cations are very voluminous and they are not able to access the more internal layers of the polymeric matrix. Thus, although a very negative potential is reached, some polymeric chains will remain electroinactive, and a lower quantity of anions will be exchanged during the redox process. However, when the film is immersed in $\text{LiClO}_4/\text{MeCN}$, the small Li^+ cations penetrate the polymeric matrix easily, increasing the interchanged charge during the redox process.

Scheme 2 is incorporated to explain the above behavior. In Scheme 2a, the Bu_4N^+ cations only enter the more external polymeric layers during the reduction process due to their large size. Thus, in the steady state, a low number of anions is necessary to balance the positive charge of the polymer during the oxidation. On a subsequent reduction, the ClO_4^- anions are expelled to the solution and the Bu_4N^+ remains inside the film.

Scheme 2b shows the experiment where the above film is immersed in a $\text{LiClO}_4/\text{MeCN}$ solution. In this case, the



Scheme 2 Ionic exchange during the redox process of PPy/PVS film in $\text{Bu}_4\text{NClO}_4/\text{MeCN}$ solution (a) and in $\text{LiClO}_4/\text{MeCN}$ after cycling in $\text{Bu}_4\text{NClO}_4/\text{MeCN}$ solution (b)

cations present in the solution, Li^+ , have a smaller size with respect to Bu_4N^+ (Table 1). This fact makes it possible for other small cations to penetrate the film during the initial voltammetric cycles in the new solution and to reach more internal layers of the polymeric blend. Hence, two kinds of cations are likely to coincide inside the polymeric matrix: Bu_4N^+ , which are not expelled because they formed ion pairs with the sulfonate groups when the film was cycled in the first electrolyte, and Li^+ , which will now be stabilized forming new ion pairs with other sulfonate groups. This fact causes a higher quantity of polymeric chains to be electroactivated and so, during the oxidation, the number of positive charges created inside the polymer will rise, also increasing the amount of ClO_4^- anions that are incorporated into the film.

As it has been commented above, the charge value of 33.5 mC cm^{-2} measured for a film cycled consecutively in $0.1 \text{ mol L}^{-1} \text{ Bu}_4\text{NClO}_4/\text{MeCN}$ and $0.1 \text{ mol L}^{-1} \text{ LiClO}_4/\text{MeCN}$ is much lower than 49.5 mC cm^{-2} obtained when a $0.1\text{-mol L}^{-1} \text{ LiClO}_4/\text{MeCN}$ solution was used from the initial cycles. However, a film cycled in $0.1 \text{ mol L}^{-1} \text{ LiClO}_4/\text{MeCN}$ after it was voltammetrically studied in $\text{LiCF}_3\text{SO}_3/\text{MeCN}$ produced a charge value of 50.0 mC cm^{-2} , very close to the value obtained for a film cycled only in $0.1 \text{ mol L}^{-1} \text{ LiClO}_4/\text{MeCN}$ (Table 2).

These different results can be explained remembering that whatever the electrolyte used, the cations are stabilized inside the polymer and they are not exchanged during the redox processes, demanding an anionic interchange. Thus, when $\text{LiCF}_3\text{SO}_3/\text{MeCN}$ is utilized as electrolyte, the Li^+ cations are fixed and the CF_3SO_3^- are the exchanged species, while in $\text{Bu}_4\text{NClO}_4/\text{MeCN}$, the large Bu_4N^+ cations are stabilized inside the polymer and the perchlorate anions are the moving species.

From this, when the first film is immersed in LiClO_4 solution, the CF_3SO_3^- anions are expelled from the polymer, reaching a similar behavior to that obtained for a film cycled only in LiClO_4 (see Scheme 1a, c). On the other hand, in the second film, the Bu_4N^+ cations are not expelled from the polymer, and due to their large volume, they impede the penetration of cations and anions from the solution. Thus, a behavior similar to that in LiClO_4 cannot be obtained, producing a lower charge value (compare Schemes 1a and 2b).

Conclusions

PPy/PVS films have been synthesized by potentiodynamic method in aqueous solution. The cycling of this polymer in $0.1 \text{ mol L}^{-1} \text{ LiClO}_4/\text{MeCN}$ led to a gradual increase of the voltammetric peaks. This behavior was similar to that observed for PPy/PVS films generated by the constant

potential method, suggesting that the method of synthesis is not critical.

The use of electrolytes with large size anions, $\text{LiCF}_3\text{SO}_3/\text{MeCN}$, and cations, $\text{Bu}_4\text{NClO}_4/\text{MeCN}$, demonstrates that both cations and anions participate during the redox processes of PPy/PVS in MeCN medium. Despite their large sizes, the cations are initially included in the polymer where they are stabilized, forming ion pairs with the sulfonate groups of the PVS anions. This fact makes a mainly anionic exchange necessary during the oxidation/reduction of the PPy/PVS polymer, though large size anions were used.

Like ClO_4^- , the large CF_3SO_3^- anions are interchanged in the reduction/oxidation process of the PPy/PVS polymer in 0.1 mol L^{-1} $\text{LiCF}_3\text{SO}_3/\text{MeCN}$ solution. However, their larger volume hinders their moving inside the polymer and, as a result, a fraction of the polymer remains electroinactive, providing a lower charge value. This part of the polymer will become electroactive upon changing the electrolyte to a LiClO_4 solution.

The voltammetric study of PPy/PVS film $\text{Bu}_4\text{NClO}_4/\text{MeCN}$ reveals that Bu_4N^+ cations are incorporated into the film in the same way as Li^+ cations. However, their large sizes prevent them from penetrating the more internal chains of the polymer, which remain electroinactive. Due to the fact that these cations are stabilized inside the polymer, these parts of the polymer will not be activated in LiClO_4 either.

Finally, we have demonstrated that PPy/PVS films can be used to stabilize different cations inside a polymeric matrix, which can be applied to prepare new polymeric electrode to be used in different fields, such as batteries or electrochromic systems.

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