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Ionic transport in conducting polymers/nickel tetrasulfonated phthalocyanine modified electrodes

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Abstract

This work describes the study of the ionic transport in polyaniline (PANI) and polypyrrole (PPY) modified electrodes polymerized in presence of nickel tetrasulfonated phthalocyanine (NiTsPc). Elemental analysis and infrared spectroscopy were used to characterize the resulting composite films. The impact of the phthalocyanine incorporation was evaluated by electrochemical quartz crystal microbalance under potentiodynamic conditions. Results have shown that the presence of the negative charge (SO_3^- groups) modifies the nature of the 'ionic exchange' membranes, during the cycling. In the case of PANI/NiTsPc modified electrodes, the electroneutralization is mainly achieved by the participation of protons both in HCl and in camphorsulfonic acid (HCSA) electrolyte solutions. For PPY/NiTsPc composites, the cation contribution is dominant in the case of LiCl and NaCl solutions and the anion transport becomes important when CsCl and $BaCl_2$ solutions are used.

Keywords: Polyaniline; Polypyrrole; Nickel phthalocyanine

1. Introduction

Nowadays, electrochemical phenomena involving electronically conducting polymers like polyaniline (PANI), polypyrrole (PPY), and polythiophene have been studied by using several techniques. In general, during the electrochemical polymerization of some monomers to form electronically conducting polymers, a stoichiometric amount of ionic species from the electrolytic phase is incorporated in the polymer layer to neutralize the charge in the polymer chain. A very important point to be investigated is the influence of these inserted ions on the cycling properties of the resultant polymers in order to evaluate its potential applications [1–3].

Metal phthalocyanines are attracting much attention in many areas like electrocatalysis [4], sensors [5–7], energy storage devices [8–11], and solar batteries [12–14]. Several papers concerning the incorporation of metal tetrasulfonated phthalocyanine (MeTsPc) into a conducting polymer matrix during the electropolymerization of PANI and PPY to produce conducting polymer/MeTsPc composites have been published [15–18]. In particular, these composites have shown successful applications in electrocatalytic reduction of oxygen [4,19,20], mainly due the possibility to disperse electrocatalysts at the molecular level in the conducting polymer matrix to stabilize the catalytic sites [21–23].

Concerning energy storage applications, in which the nature of the compensating ions during the cycling assumes capital importance, the incorporation of MePc into electronically conductive polymeric networks can change the identity of these ions and transform a typically anion exchanger film into a cation exchanger one. In fact, it is known that the incorporation of MePc into conducting polymers facilitates electrochemical process involving cation transport [24,25], but electrogravimetric experiments concerning this effect in a quantitative way, upon the charge compensation process, are still missing.

In the present contribution, we study the influence of the incorporation of nickel tetrasulfonated phthalocyanine (NiTsPc) (Fig. 1) upon the redox process in PANI and

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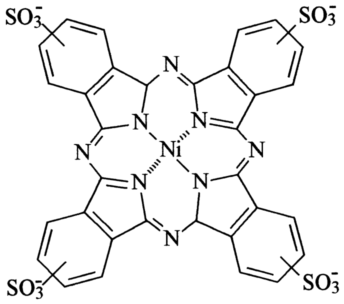

Fig. 1. Nickel (II) phthalocyaninetetrasulfonic acid.

PPY electrochemically obtained films. Both PANI/NiTsPc composites and PPY/NiTsPc were quantitatively and qualitatively characterized by using elemental analysis and vibrational spectroscopy (FTIR). The charge compensation process was investigated by using simultaneous electrochemical quartz crystal microbalance (EQCM) and cyclic voltammetry (CV) experiments. PANI/NiTsPc modified electrodes were studied in HCl and HCSA (camphorsulfonic acid) electrolytic solutions and PPY/NiTsPc ones in LiCl, NaCl, $BaCl_2$ and CsCl aqueous electrolytic solutions. The electroneutralization process was discussed and results are compared with PANI and PPY modified electrodes.

2. Experimental

2.1. Electrolytic solutions

Aniline ($C_6H_5NH_2$) and pyrrole (C_4H_5NH) were purchased from Aldrich and freshly distilled under vacuum prior to use. Hydrochloric acid (HCl), camphorsulfonic acid ($C_{10}H_{16}O_4S$, HCSA), lithium chloride (LiCl), sodium chloride (NaCl), cesium chloride (CsCl), barium chloride ($BaCl_2$) and nickel tetrasulfonated phthalocyanine tetrasodium salt (NiTsPc) (Aldrich) were used as received. All electrolytic solutions (HCl, HCSA, LiCl, NaCl, CsCl and $BaCl_2$) were prepared with purified water (Milli Q system) in a concentration of 0.5 mol l^{-1}.

2.2. Electrode preparation

Modified electrodes were obtained in two different ways, considering each monomer used. In the case of PANI, the electropolymerization was carried out under potentiodynamic conditions between -0.2 and 0.75 V vs. SCE at 0.05 V/s. Electrolytic solution consisting of aniline 0.005 and NiTsPc 0.01 mol l^{-1} was used. As aniline must be dissolved in an acid solution, an aqueous solution of NiTsPc was converted in the acid form by exchanging Na^+ by H^+ in a H^+-type ion-exchange resin (Dowex 50WX4-100, Sigma) to give a solution with a $pH \leq 1$. For PPY, a constant density current of 0.5 mA cm^{-2} was applied to obtain the polymer and an electrolytic solution of pyrrole 0.005 and NiTsPc 0.01 mol l^{-1} was used. For all modified electrodes, deposited mass was typically 45 ± 2 μg cm^{-2}, and thickness of about 300 nm in both composite films was estimated using a density of 1.5 g cm^{-3} for pure PANI and PPY [26, 27]. In these conditions, one can assume that such films behave rigidly and frequency change can be transformed into mass change without take into account changes in the viscoelastic properties [28,29]. In addition to the fact of the thin film limit, the rigid behavior assumption is corroborated by Yang et al. [30], who pointed out that the morphologic changes in the course of redox cycling of PPY/CuTsPc film are negligible and mass changes can be computed directly by the resonant frequency shift.

The electropolymerization process in the case of PANI/NiTsPc modified electrode is illustrated in Fig. 2 in terms of j/E and $\Delta m/E$ profiles during the last growth cycle. The voltammetric response is quite similar to the typical one observed in PANI film in different conditions (see for example Refs. [31–33]), the mass change reflects the concomitant film growth and electroneutralization process.

2.3. Chemical characterization

Elemental analysis was carried out with a CE instrument EA-1110 and samples of the polymer were obtained by scraping the electrodeposited polymer film from the gold electrode. The electropolymerization (always up to a deposited mass about 45 ± 2 μg cm^{-2}) was repeated several times in order to obtain the necessary amount of polymer. Polymer/NiTsPc relative compositions were inferred by the sulfur/nitrogen (S/N) ratios. FTIR spectroscopic measurements at a resolution of 4 cm^{-1} were carried out with a Bomen MB-102 spectrometer. A polymer sample was mixed with KBr and the spectrum was obtained in the transmittance mode.

2.4. Electrochemical and EQCM measurements

After film formation, modified electrodes were placed in

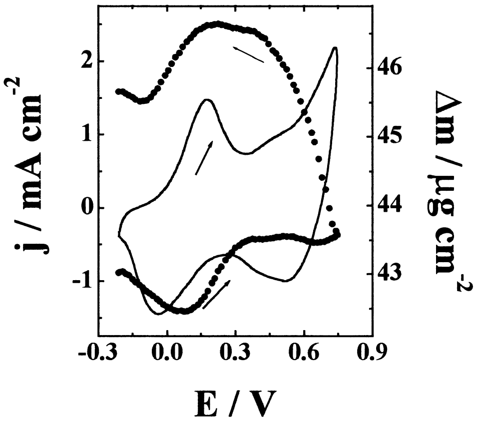

Fig. 2. j/E (line) and $\Delta m/E$ (full circle) characteristics showing the last cycle during the electropolymerization of PANI/NiTsPc films. An aqueous electrolytic solution consisting of aniline 0.005 and NiTsPc 0.01 mol l^{-1} was used. $v = 0.05$ V/s.

a conventional three-compartment cell and the redox behavior was studied in different monomer/NiTsPc free electrolytic solutions. PANI/NiTsPc films were cycled in HCl and HCSA electrolytic solutions. In the case of PPY/NiTsPc modified electrodes, LiCl, NaCl, CsCl and $BaCl_2$ electrolytic solutions were used. Cyclic voltammetry experiments were carried out at 0.05 V s^{-1} at 25 °C, before each experiment, 20 min of N_2 purge was carried in order to remove dissolved oxygen. A platinum wire was used as counter electrode and all potentials are referred to saturated calomel reference electrode (SCE). Working electrodes were 6 MHz overtone polished AT-cut quartz crystals of 26 mm diameter (Valpey-Fisher). Both sides of the quartz crystals were coated with thin (ca. 200 nm thickness) gold films over a ca. 5 nm Cr adhesion layer, but only one of the faces was exposed to the electrolyte solution (active area of 0.2 cm^2). The resonance frequency shift was measured with a HP-5370B Universal Time Counter. These shifts can be used to calculate mass changes using the Sauerbrey equation [34]. The integral sensitivity constant (5.2×10^7 Hz cm^2 g^{-1}) was obtained by calibration using silver deposition [35]. Electrochemical measurements were performed with a FAC 2001 potentiostat/galvanostat. The experimental details for EQCM measurements have been previously presented [32,36].

3. Results and discussions

3.1. Chemical characterization

Before scraping the electrodeposited polymer film from the gold electrode in order to proceed with elemental analysis measurements, modified electrodes were extensively cycled (PANI/NiTsPc films in HCl and PPY/NiTsPc films in LiCl electrolytic solutions) in order to be sure that the NiTsPc is immobilized in the polymer matrix, that is to say that the NiTsPc content remains the same during the cycling and there is no loss of NiTsPc. The NiTsPc is incorporated in the polymer matrix as counter-ion during the oxidative polymerization. As can be seen in Table 1, the S/N ratio of about 0.17 corresponding to aniline:NiTsPc relation of 16:1. For the NiTsPc incorporation in PPY films the elemental analysis results are shown in Table 2 and a PY:NiTsPc relation of 12:1 was found.

Fig. 3 shows the FTIR spectra of a sample of NiTsPc (curve a), PANI (curve b), PANI/NiTsPc (curve c), PPY (curve d) and PPY/NiTsPc (curve e). As can be seen, the strong bands corresponding to the various ring modes (in the range 1000–1700 cm^{-1} [37]) for NiTsPc in curve a specifically, the bands at ca. 1638, 1180, and 1030 cm^{-1} correspond to the C=N bending, asymmetric O=S=O and symmetric O=S=O stretching, respectively. Curve b shows the FTIR spectrum for PANI and the bands observed are in agreement with literature data [38]. The bands at 1580 and

Table 1
Elemental analysis results for PANI/NiTsPc composite

Element	N	C	H	S
Mass percent	10.8	45.5	4.3	4.3
Mole percent	0.77	3.79	4.3	0.13

Table 2
Elemental analysis results for PPY/NiTsPc composite

Element	N	C	H	S
Mass percent	9.3	44.8	5.5	4.1
Mole percent	0.66	3.73	5.5	0.13

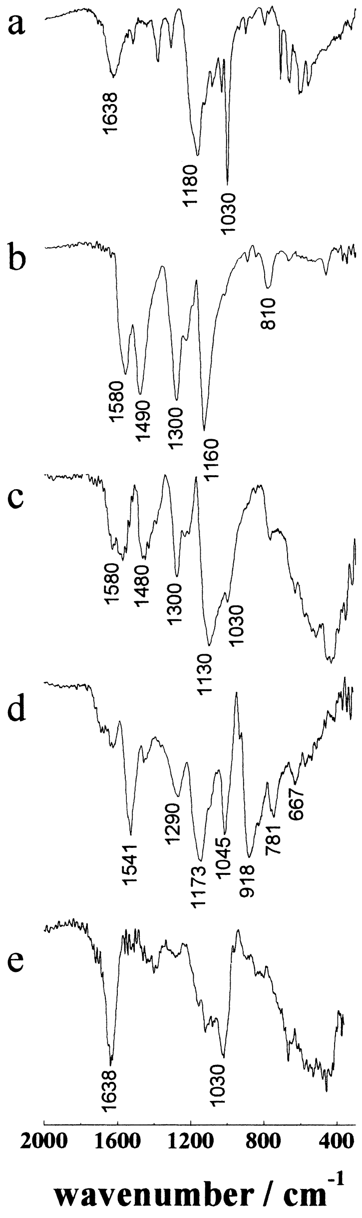

Fig. 3. FTIR spectra of NiTsPc (curve a), PANI (curve b), PANI/NiTsPc (curve c), PPY (curve d) and PPY/NiTsPc (curve e).

1490 cm^{-1} correspond to quinoid and benzenoid C=C stretches, respectively, and the bands at 1300 and 810 cm^{-1} to C–N and C–H bending, respectively. Curve c shows the spectrum for PANI/NiTsPc, where it can be seen that there is a superposition between the bands of the PANI and NiTsPc, but also the presence of bands at 1130 and 1030 cm^{-1} corresponding to the O=S=O stretching showing the signature of the NiTsPc incorporation into the polymeric matrix. These findings show the presence of the phthalocyanine and that it is immobilized in the polymer matrix even after cycling. Curve d shows the spectrum of PPY doped with chloride anions. The bands at 1541, 1290 and 1173 cm^{-1} correspond to ring stretching, the band at 1045 cm^{-1} corresponds to C–H and N–H bending and the bands at 918, 781 and 667 cm^{-1} to C–H bending; all bands assignation are in agreement with literature data [39]. Curve e shows the spectrum of PPY doped with the phthalocyanine. It is clearly seen that the bands at 1638 and 1030 cm^{-1} corresponding to C=N bending and O=S=O stretching, respectively.

The elemental analysis and FTIR results clearly show that the tetrasulfonated phthalocyanine is the dopant, that is to say that it is incorporated as counter-ion during polymerization in both cases and that stays immobilized in the polymer matrix even after the electrochemical cycling.

3.2. Redox process in PANI/NiTsPc modified electrode

Fig. 4 shows j/E and $\Delta m/E$ potentiodynamic profiles for PANI/NiTsPc modified electrodes in HCl (Fig. 4a) and HCSA (Fig. 4b) electrolyte solutions. These data are for steady state scans, i.e. voltammetric shape is invariant with respect to the cycle number. In both cases, voltammogram shows similar anodic and cathodic charges, evidencing the reversibility of the redox process in both electrolytic solutions. Oxidation and reduction current peaks are observed at ca. 0.2 and 0.05 V, respectively, in both cases. The $\Delta m/E$ potentiodynamic profiles also are very similar in both cases, but the total mass gain at the end of the positive going scan (0.5 V) is 0.86 and 0.5 μg cm^{-2} for modified electrodes cycled in HCl and HCSA electrolytic solutions, respectively. During the first stage of the oxidation process (positive going scan, −0.1 to 0.15 V) the mass is almost constant in both cases with only a small decrease in HCSA electrolytic solution of about 0.04 μg cm^{-2}. After c.a. 0.15 V, mass increases up to the end of the oxidation process and then decreases to the initial value during negative going scan (reduction process). As a whole, this behavior can be compared with previous data for PANI modified electrodes, where the electroneutralization process is first attained by the proton expulsion (mainly before the oxidation peak) and after by the anion insertion during oxidation process [26,40–44].

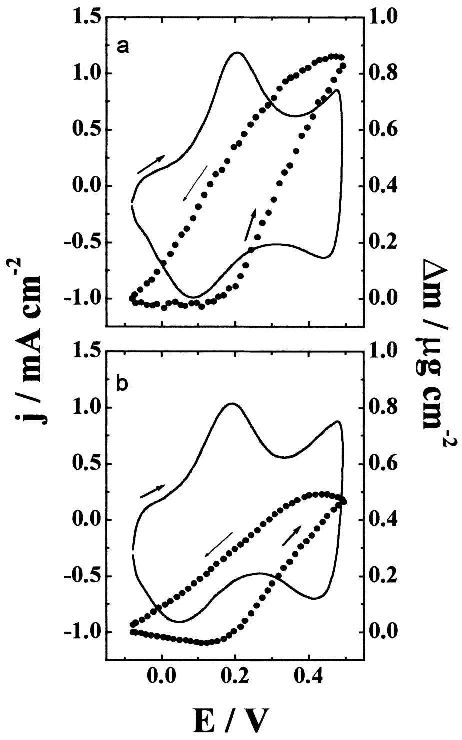

Fig. 4. Potentiodynamic j/E (line) and $\Delta m/E$ (full circle) profiles for PANI/NiTsPc films in (a) HCl and (b) HCSA electrolytic solutions. $v = 0.05$ V/s.

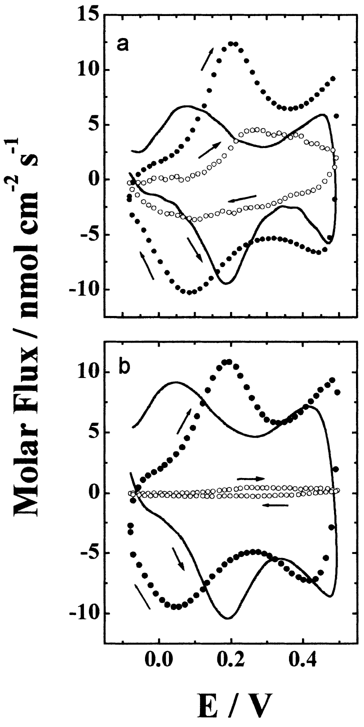

Fig. 5. Molar fluxes of proton + water (line), anion + water (open circle) and electron (j/F) (full circle) for PANI/NiTsPc films in (a) HCl and (b) HCSA electrolytic solutions. $v = 0.05$ V/s. Data calculated from Fig. 4.

In order to provide a better understanding of the ionic transport in PANI/NiTsPC modified electrodes, plots of molar fluxes obtained by using Eqs. (A7) and (A8) (see Appendix) are shown in Fig. 5. In a first glance, the role played by the NiTsPc incorporation becomes evident in these plots when one recalls similar plots for PANI films in the same conditions [42,45]. The main difference referred is associated to the increase of the protonic transport during the electroneutralization process when NiTsPc is incorporated into PANI matrix, since in both electrolytic solutions the proton + water molar flux is dominant in the whole process. As shown in Fig. 5, the proton + water molar fluxes are very similar to the electronic flux (j/F) with different sign, since positive current was adopted for oxidation process and species expulsion was adopted as being negative. When HCl is used (Fig. 5a) only a small anion contribution is observed, on the other hand, when the modified electrode is cycled in HCSA, the molar flux of CSA^- is very small during the whole process and can be neglected. Comparing electronic and protonic flux it can be seen that the whole process of charge compensation is mainly achieved by the participation of proton. Obviously, this dominant proton transport cannot be straightforwardly seen in a mass basis as in the $\Delta m/E$ plots due the difference in molar mass of anions and protons. The difference between Cl^- and CSA^- participation is rationalized in terms of the lower diffusion coefficient and mobility of CSA^- because of its size and polarizability [46–49] coupled with the steric hindrance of the entrapped NiTsPc. Therefore, positive charges created in the PANI chain during the oxidation process are partially compensated by the negative charge of the deprotoned sulfonated group in the NiTsPc, the extent of this protonic contribution to the charge compensation process will be fully discussed below.

In addition to the increase in the proton participation due to the NiTsPc incorporation, is the apparent absence of water participation during the redox process of PANI/NiTsPc modified electrodes in comparison to that observed in PANI films. This null (or very small) solvent participation can be conveniently justified by the absence of the sign inversion in the molar proton + water fluxes, like that observed in PANI films [33]. The small swelling is attributed to the reduction of the free volume creation during the oxidation process as result of the NiTsPc immobilized in the polymer matrix in a similar way when SO_3^- groups are incorporated in the polymer backbone. This conclusion is supported by recent results in our group [50] in which through in situ ellipsometric experiments was found that the sulfonic group incorporated in PANI backbone (sulfonated PANI, or SPAN) diminishes the film volume changes to less than 2% between reduced and oxidized states.

Based both on the PANI/NiTsPc composition and on our findings in combined cyclic voltammetry/EQCM experiments it is possible to illustrate the discussion above in terms of the following mechanism for the charge compensation process,

$$\left[\mathrm{PANI} + \frac{1}{16}\mathrm{NiTsPc}^{4-} + \frac{1}{4}\mathrm{H}^{+}\right]_{\mathrm{film}} + y\mathrm{A}^{-} \rightleftarrows \left[\mathrm{PANI}^{x+} + \frac{1}{16}\mathrm{NiTsPc}^{4-} + \left(\frac{1}{4} - x + y\right)H^{+} + y\mathrm{A}^{-}\right]_{\mathrm{film}} + (x - y)\mathrm{H}^{+} + xe$$

In this mechanism, the reaction from left to right accounts to the oxidation process, and the reverse one to the reduction process, the brackets present the composite film as indicated and solvent transport is neglected. The presentation of the incorporated NiTsPc with four negative charges stands to the deprotonated state of its $-\mathrm{SO}_3^-$ groups (Fig. 1) most likely in self-doped conducting polymers as referred above in the case of SPAN. The stoichiometric number of 1/16 refers to the presence of 1 NiTsPc for 16 aniline rings as obtained by elemental analysis. In this schematic presentation, in its reduced state, film electroneutrality is provided by the presence of four positive charges (protons).

The main point to be stressed in this simplified mechanism is the dual feature of the compensating ions that takes place in the electroneutralization process. In fact, besides the proton uptake in the earlier stages of PANI oxidation, its participation can be increased by the NiTsPc^{4-} anion entrapped inside the films similarly to that observed when functioned negatively charged groups are attached to polymer backbone [42,45,48]. The fractional extent of the oxidation x can be estimated by the ratio between the actual oxidation charge (per mass) and the theoretical value of $1.036\ \mathrm{C\ mg}^{-1}$ that corresponds to the fully oxidized polymer (i.e. one electron per aniline ring). Following this procedure, the calculated x values are 0.30 and 0.28 for the PANI/NiTsPc modified electrodes cycled in presence of HCl and HCSA, respectively. Therefore, as suggested in the mechanism above, up to a doping level of about 25% ($x = 0.25$) it is possible to attain the electroneutrality only with proton expulsion/insertion in the course of positive/negative going scan without any anion transport to the film. Whereupon, the required anionic flux through the film/solution interface is smaller than in PANI films and corresponds to about 15% in a molar basis, i.e. y equal to about 0.05 and 0.03 in HCl and HCSA electrolytic solutions, respectively. In all cases just a small amount of anion moving to the film during the oxidation results in a mass increase due to the big difference in molar masses as already pointed out and proton transport can be observed only in a molar basis.

About the activity observed in PANI/NiTsPc films and discussed in the last paragraph its comparison with pure

PANI films can be understood as following. It is well known that in aqueous media, PANI films can be oxidized up to 50% (or, equivalently one oxidized ring per each two ones) without degradation due nucleophilic attack [40]. Therefore, since the doping level found here amounts to 0.30 and 0.28, the activity of the PANI/NiTsPc composite falls in the range of 58–60% of the maximum activity for pure PANI films cycled in aqueous media. Such activity can be considered high and presents a very important feature for a potential candidate in energy storage applications. Moreover, such activity was found to be almost independent upon the nature of the anion present in solution. In contrast to that observed in pure PANI films, in which the activity can decrease up to around 3% when cycled in HCSA solution in respect to when cycled in HCl [45,51]. Finally, when compared with another PANI/phthalocyanine composite (namely phthalocyanine oligomer with carboxyl terminals), the material presented here presents a higher activity [52]. This higher activity can be related with the fact that the $NiTsPc^{4-}$ is electroactive in the potential region used in this work. However, electrochemical response expected for the $NiTsPc^{4-}$ is not readily observed for PANI/NiTsPc and PPy/NiTsPc (as it will be shown further on); this fact can be related with the composite composition, the amount of NiTsPc is several times smaller than the polymer amount. It must be mentioned that the redox reaction of the phthalocyanine can modify the participation of ions in the charge compensation process in comparison with other big inactive counter-ion. Even considering the electro-activity of the phthalocyanine, the global behavior of the composites are similar to that of self-doped polymers, clearly showing that negative charges of the sulfonate produce the marked influence on the way to achieve electroneutrality.

3.3. Redox process in PPY/NiTsPc modified electrode

Following a similar strategy to that adopted above, properties of the PPY/NiTsPc composite were investigated by cycling the modified electrodes in presence of different aqueous electrolyte solutions. Fig. 6 shows j/E and $\Delta m/E$ potentiodynamic profiles for this electrode in different chloride salts solutions: LiCl (Fig. 6a), NaCl (Fig. 6b), CsCl (Fig. 6c), and $BaCl_2$ (Fig. 6d). In all cases, the shapes of the voltammograms are very similar and the ratios between oxidation and reduction charges are close to 1 and no difference in the overall activity is observed in respect to the cation nature. Oxidation current peak occurs at −0.3 V and the reduction one at −0.4 V with only small variations comparing different electrolytic solutions. Analyzing the mass change profiles, it can be seen that in all cases a mass decrease/increase is observed in the positive/negative going scans. Therefore, it is completely plausible to infer that the electroneutralization is dominated by the cation expulsion/insertion during oxidation/reduction process on a mass basis. The total mass decrease (at 0.2 V) was found to follow this sequence NaCl < LiCl < $BaCl_2$ < CsCl considering the electrolytic solution used. This sequence is evidence that other species together with cations participate in the whole electroneutralization process, since the mass decrease in the oxidation process was not found to be proportional to the molar mass of each cation.

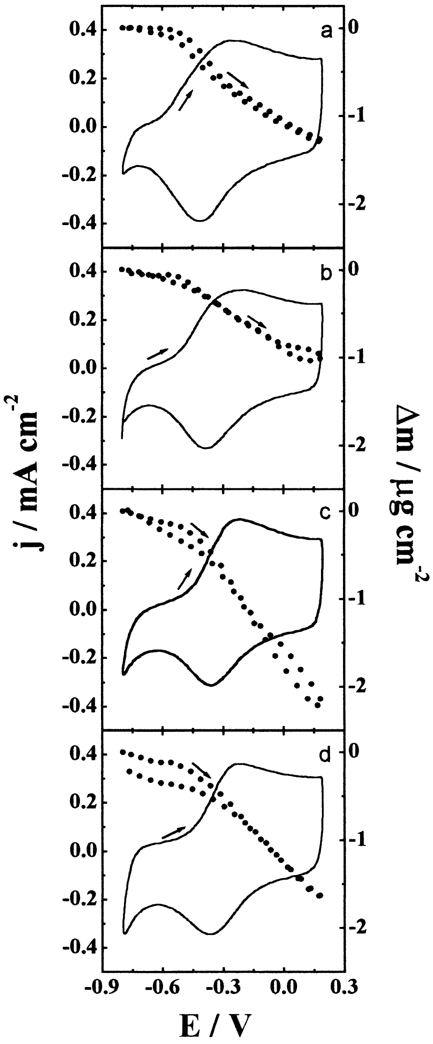

Fig. 6. Potentiodynamic j/E (line) and $\Delta m/E$ (full circle) profiles for PPY/NiTsPc films in (a) LiCl, (b) NaCl, (c) CsCl and (d) $BaCl_2$ electrolytic solutions. $v = 0.05$ V/s.

As a first approximation, the nature of compensating species can be discussed in terms of the mass to charge ratios during the redox process. To this purpose, Table 3 shows the experimental mass/charge ratios, $(\Delta m/\Delta q)_{exp}$ in

Table 3
Comparison between calculated ($(\Delta m/\Delta q)_{theor}$) and obtained ($(\Delta m/\Delta q)_{exp}$) mass to charge ratios considering exclusive cations in the course of the oxidation process of PPY/NiTsPc in different electrolyte solutions

Salt	$(\Delta m/\Delta q)_{theor,C^+}$ (mg C^{-1})	$(\Delta m/\Delta q)_{exp}$ (mg C^{-1})
LiCl	−0.07	−0.28
NaCl	−0.24	−0.23
CsCl	−1.38	−0.44
$BaCl_2$	−0.71	−0.36

the oxidation process for PPY/NiTsPc modified electrodes. For comparison, theoretical values for mass/charge ratios were calculated considering that the electroneutralization process is achieved only by cations expulsion during the oxidation process, $(\Delta m/\Delta q)_{\mathrm{theor,C^+}}$ and are also shown.

In LiCl electrolyte solutions, the $(\Delta m/\Delta q)_{\mathrm{exp}}$ value (-0.28 mg C^{-1}) is four times greater than that expected if only Li^+ expulsion takes place (-0.07 mg C^{-1}). This fact is a strong hint that in this case, no anion participation is observed and the difference observed between $(\Delta m/\Delta q)_{\mathrm{exp}}$ and $(\Delta m/\Delta q)_{\mathrm{theor}}$ values is due to water molecules participation during the charge compensation process in the same direction than that for Li^+. Considering that there is only lithium cation and water exchange between the polymer and the electrolytic solution, and the experimental value on mass/charge (-0.28 mg C^{-1}), it is possible to determine that for 1 mol of Li^+ there is 1 mol of accompanying H_2O molecules. This value is in good agreement with that previously reported (1.2 mol of H_2O per mol of Li^+) by Yang et al. [30] for PPY/CuTsPc modified electrodes by using electrochemical impedance spectroscopy measurements.

In NaCl electrolyte solution, the $(\Delta m/\Delta q)_{\mathrm{exp}}$ was found to be almost the expected one if only Na^+ participates in the charge compensation process. However, it is not possible to say if Cl^- species are participating or not, since the mass/charge ratio presents a global mass balance during the oxidation process. In other words, the mass change during the whole oxidation process can be considered a balance between cation expulsion and anion incorporation, plus water transport. This fact will be further discussed below. In the CsCl and BaCl_2 electrolytic solutions the $(\Delta m/\Delta q)_{\mathrm{exp}}$ values are lower than the theoretical one for exclusive cation participation, and in these cases one can stress that both cation and anion contributions may be taken into account when analyzing the electroneutralization process.

In order to analyze the ion and water fluxes in a quantitative way, plots of both fluxes were build by using Eqs. (A9) and (A10) (see Appendix) for PPY/NiTsPc modified electrodes in LiCl electrolytic solution, which are shown in Fig. 7. As discussed above, the molar flux of water molecules occurs in the same direction of Li^+ species and both fluxes present a very similar dependence with the potential, when the maximum for oxidation and reduction processes occurs in the same potential range. In fact, previous workers have been discussed the solvent transport accompanying the cation transport in PPY modified electrodes as being dependent on the nature and concentration of the electrolytic solution as well as the applied potential in both aqueous [53] and organic [54] media.

The anion participation is important when CsCl and BaCl_2 electrolytic solutions are used and may be better investigated in the case of NaCl electrolytic solution. So, in order to clarify this mixed cation and anion participation, henceforth the analysis will be carried out considering the flux of charged species by using of Eqs. (A5) and (A6) (see

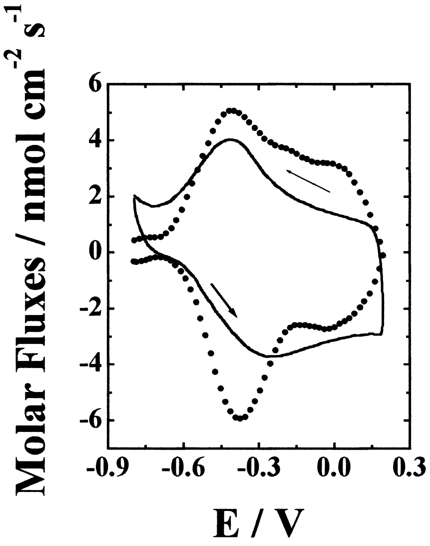

Fig. 7. Molar fluxes of lithium (line) and water (full circle) for PPY/NiTsPc films in LiCl electrolytic solutions. $v = 0.05$ V/s. Data calculated from Fig. 6a.

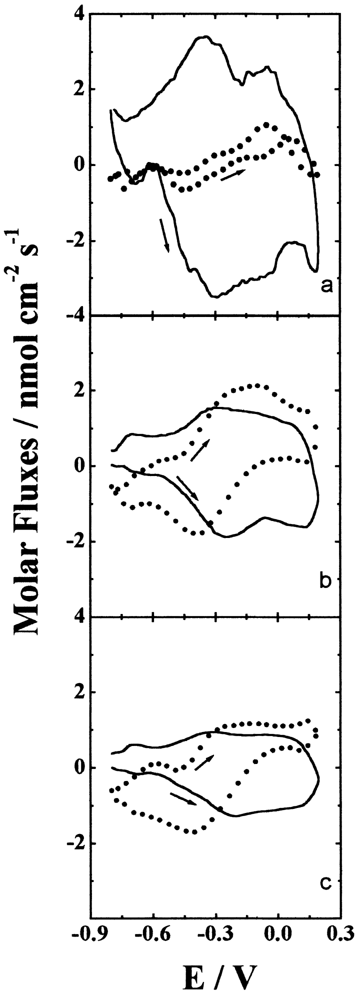

Fig. 8. Molar Fluxes of cation + water (line) and anion + water (full circle) for PPY/NiTsPc films in (a) NaCl, (b) CsCl and (c) BaCl_2 electrolytic solutions. $v = 0.05$ V/s. Data calculated from Fig. 6b–d.

Appendix). Plots of molar fluxes for PPY/NiTsPc modified electrode in NaCl, CsCl, and $BaCl_2$ electrolytic solutions are depicted in Fig. 8a–c, respectively. In NaCl electrolytic solution (Fig. 8a), the charge compensation process is achieved mainly by cation participation during the first stages of oxidation process (-0.8 to -0.3 V), after c.a. -0.3 V the flux corresponding anion + water becomes representative, but its contribution is small when compared to that of cation + water flux. Therefore, considering the whole process it can be observed that the charge compensation is mainly achieved by cation participation in NaCl electrolytic solution. Fluxes of charged species for PPY/NiTsPc modified electrodes in CsCl, (Fig. 8b) and $BaCl_2$ (Fig. 8c) are very similar in shape, and show participation of both charged species in about the same potential range. In these two cases, the anion participation was found to be responsible to 50% of the electroneutralization process, in contrast when solutions with small cations (Li^+ and Na^+) are used. In addition, it must be stressed that the mass decrease in the positive going scan showed above, (Fig. 6) corresponds to the *net* mass transport across the film/solution interface and, in the last two cases (CsCl and $BaCl_2$ electrolytic solutions), must be interpreted in terms of cation/anion uptake/intake during oxidation process. This fact shows the relevance of the analysis of fluxes in order to calculate the contribution of each species.

Comparing cycling properties of PPY/NiTsPc modified electrodes as a function of different electrolytic solutions it can be concluded that the electroneutralization is achieved by exclusive cation participation in the case of LiCl. The extent of anion participation during the charge compensation process increases from a small contribution in the case of NaCl electrolyte solution to a high one (about 50% as discussed above) when CsCl and $BaCl_2$ are used.

This fact can be discussed in terms of the inverse dependence between diffusion coefficient (or even mobility) and the ionic radius (like for example in the case of the Stokes–Einstein relationship for diffusion in an ideal solution). In fact, considering the ionic radius of each cation in aqueous solutions as being 3.82, 3.58, 3.29, and 4.04 Å for Li^+, Na^+, Cs^+, and Ba^{2+}, respectively [55], it can be expected that small cations like Li^+ and Na^+ (considering that these cations do not move with all hydration sphere, as was discussed above) can move faster than big cations like Cs^+ and Ba^{2+} through the polymer matrix in order to compensate the charge created during the cycling. However, in the case of Cs^+ and Ba^{2+} species the difference in ionic radius is not exactly reflected in their participation during the charge compensation process. In both cases, the cation contribution is about 50%. Since Ba^{2+} is smaller than Cs^+ it can be expected greater cation participation when Ba^{2+} is present. This apparently controversial behavior is explained taking into account that the two positive charges of Ba^{2+} make the movement of this cation more difficult in the polymer chain because of its stronger interaction with the negative charge inside the film (SO_3^- from the tetrasulfonated group in the NiTsPc and/or Cl^- compensating ions and consequently ion pairing).

The charge compensation during the redox process in PPY modified electrodes has been studied by several groups [56–59]. Considering the size influence on the redox behavior, G. Maia et al. [60] have studied PPY modified electrodes in several aqueous solutions and they have found a greater participation of Cs^+ than that of Na^+ species, they have attributed this behavior to differences in electrostatic interaction of the positive charge of these cations with the positive charge created in the polymer chain, and the discussion was carried out in terms of the Lewis acid strength. As discussed above, in the case of PPY/NiTsPc modified electrodes the participation of monovalent cation (like Li^+, Na^+, and Cs^+) during the electroneutralization process is determined only by the cation size. This fact can be explained if one consider the volume occupied by the big NiTsPc species inside the film, in comparison with PPY matrix; this is the same explanation used to explain the difference between chloride and camphorsulfonate anions in the case of PANI/NiTsPc modified electrodes.

Following the same strategy adopted above in the case of PANI/NiTsPc composite, the following equation accounts to the proposed electroneutralization process in PPY/-NiTsPc modified electrodes,

$$\left[\mathrm{PPY} + \frac{1}{12}\mathrm{NiTsPc}^{4-} + \frac{1}{3}\mathrm{C}^{+}\right]_{\mathrm{film}} + y\mathrm{A}^{-} \leftrightarrow \left[\mathrm{PPY}^{x+} + \frac{1}{12}\mathrm{NiTsPc}^{4-} + \left(\frac{1}{3} - x + y\right)\mathrm{C}^{+} + y\mathrm{A}^{-}\right]_{\mathrm{film}} + (x-y)\mathrm{C}^{+} + xe$$

In this case, up to an oxidation level of 33% ($x = 0.33$) the charge compensation can be attained only by cation expulsion/insertion during oxidation/reduction process due the negative charges provided by $NiTsPc^{4-}$ in both oxidation states. Therefore, the extent of the anion participation will depend mainly on cation mobility through the polymer matrix as already stressed above. Small cations like Li^+ and Na^+ can move easier than big ones like Cs^+ and Ba^{2+} through the polymer matrix, and their contribution is more important that anion one. As a consequence, the coefficient y in the suggested mechanism is null in the case of LiCl solution and very small in NaCl. In the case of Cs^+ and Ba^{2+} containing solutions, the electroneutralization is attained by about the same contribution for cations and anions, therefore y can be approximately 0.07 (i.e. half of the oxidation level x in these cases, see Fig. 8).

The fractional extent of the oxidation x was estimated considering the value of 1.438 C mg^{-1} for the fully oxidized polymer. The values for x were found to be 0.15 (LiCl), 0.13 (NaCl), 0.14 (CsCl) and 0.14 ($BaCl_2$). Considering the maximum extent of the oxidation as being about 30% in the case of PPY films [27,60,61], the activity found was about 44–50%. Such activity is considered relatively high considering that the activity decrease accompanying either the polymerization in presence of big anions or the polymer chain substitution. To give just one example, Lee et al. [54] have been studied the redox process in poly(*N*-methylpyrrole) modified electrodes and they found a decrease of about three times in its activity when compared with non-substituted PPY cycled in the same conditions (namely $LiClO_4$/acetonitrile electrolyte solution).

4. Conclusions

PANI/NiTsPc and PPY/NiTsPc composite films were electrochemically obtained and characterized by elemental analysis and FTIR. The obtained composites presented ratios of 1/16 and 1/12 NiTsPc per aniline and pyrrole ring, respectively; the incorporated species stay entrapped inside the film after long term cycling in monomer free solutions. The obtained modified electrodes were found to be stable and no activity decrease was detected. The impact of the NiTsPc incorporation upon the charge compensation process was studied in several electrolytic solutions under potentiodynamic conditions by using an EQCM apparatus.

On one hand, the activity of PANI/NiTsPc composite showed a weak dependence upon the electrolytic solution and proton transport was found to be the main responsible to the maintenance of the electroneutrality inside the film during cycling. The composite activity was found to be between 58 and 60% than that observed for pure PANI films. On the other hand, the charge compensation process in PPY/NiTsPc modified electrodes showed to be dependent on the cation size. However, in the case of LiCl, the electroneutrality was attained only by Li^+ transport. The film activity for PPy composites is 43–50% of that for PPY films.

In both cases the ionic exchange was rationalized in terms of a participation of cations (or protons in the case of PANI/NiTsPc films) and anions considering the film composition and EQCM data.

The high activity associated to its high proton/cation participation in the electroneutralization process gives new perspectives to the application of such materials as cation selective membranes. In addition, the negligible water exchange phenomena (swelling) during the cycling in the case of PANI/NiTsPc and the lithium participation in the case of PPY/NiTsPc films strongly credence these composites for high performance cathodic materials energy storage devices.

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Appendix A

EQCM data analysis

The use of EQCM data to extract the contributions of anions and cations to the observed mass changes during a given EQCM voltammetric scan have been previously described elsewhere [60]. The treatment begins from the global mass and charge balances during the charge compensation process. Thus, the global mass change during a given voltammetric scan ($\Delta m_{(E)}$) can be written as

$$\Delta m_{(E)} = W_{C^+}\xi_{C^+(E)} + W_{A^-}\xi_{A^-(E)} + W_s\xi_{s(E)} \qquad (A1)$$

where W is the molar mass of cations (C^+), anions (A^-) or solvent molecules (s) and ξ is the number of moles of cations, anions or solvent molecules undergoing transport. Considering the requirements of electroneutrality within the bulk of the film, the charge involved in the redox process can be related to the number of moles of ionic species in the following way

$$q_{(E)} = -z_{C^+}F\xi_{C^+(E)} + z_{A^-}F\xi_{A^-(E)} \qquad (A2)$$

where F is the Faraday constant. By combining Eqs. (A1) and (A2), one obtains the amount of cations and anions, each one with a contribution from solvent (left hand side of Eqs. (A3) and (A4), respectively), as a function of the charge density and mass,

$$\xi_{C^+(E)} + \frac{W_s}{\gamma}\xi_{s(E)} = \frac{1}{\gamma}\Delta m_{(E)} - \frac{W_{A^-}}{\gamma z_{A^-}F}q_{(E)} \qquad (A3)$$

for cation + solvent, and

$$\xi_{A^-(E)} + \frac{z_{C^+}W_s}{z_{A^-}\gamma}\xi_{s(E)} = \frac{z_{C^+}}{z_{A^-}\gamma}\Delta m_{(E)} + \frac{1}{z_{A^-}F}\left(1 - \frac{z_{C^+}W_{A^-}}{\gamma z_{A^-}}\right)q_{(E)} \qquad (A4)$$

for anion + solvent, where $\gamma = (z_{A^-}W_{C^+} + z_{C^+}W_{A^-})/(z_{A^-})$. After differentiation of Eqs. (A3) and (A4), the fluxes for cations and anions with solvent contribution can be given as a function of current density and mass flux

$$\frac{\mathrm{d}\left(\xi_{C^+(E)} + \frac{W_s}{\gamma}\xi_{s(E)}\right)}{\mathrm{d}t} = \frac{1}{\gamma}\frac{\mathrm{d}(\Delta m_{(E)})}{\mathrm{d}t} - \frac{W_{A^-}}{\gamma z_{A^-}F}j_{(E)} \qquad (A5)$$

and

$$\frac{\mathrm{d}\left(\xi_{\mathrm{A}^-(\mathrm{E})} + \frac{z_{\mathrm{C}^+}W_\mathrm{s}}{z_{\mathrm{A}^-}\gamma}\xi_{\mathrm{s}(\mathrm{E})}\right)}{\mathrm{d}t} = \frac{z_{\mathrm{C}^+}}{z_{\mathrm{A}^-}\gamma}\frac{\mathrm{d}(\Delta m_{(E)})}{\mathrm{d}t} + \frac{1}{z_{\mathrm{A}^-}F}\left(1 - \frac{z_{\mathrm{C}^+}W_{\mathrm{A}^-}}{\gamma z_{\mathrm{A}^-}}\right)j_{(\mathrm{E})} \qquad (\mathrm{A6})$$

For (1:1) electrolyte ($z_{\mathrm{A}^-} = z_{\mathrm{C}^+} = 1$), the term γ becomes W_{ca} (molar mass of the salt) and flux of both charged species will be given as,

$$\frac{\mathrm{d}\left(\xi_{\mathrm{C}^+(\mathrm{E})} + \frac{W_\mathrm{s}}{W_\mathrm{CA}}\xi_{\mathrm{s}(\mathrm{E})}\right)}{\mathrm{d}t} = \frac{1}{W_\mathrm{CA}}\frac{d(\Delta m_{(\mathrm{E})})}{\mathrm{d}t} - \frac{W_{\mathrm{A}^-}}{W_\mathrm{CA}F}j_{(\mathrm{E})} \qquad (\mathrm{A7})$$

and

$$\frac{\mathrm{d}\left(\xi_{\mathrm{A}^-(\mathrm{E})} + \frac{W_\mathrm{s}}{W_\mathrm{CA}}\xi_{\mathrm{s}(\mathrm{E})}\right)}{\mathrm{d}t} = \frac{1}{W_\mathrm{CA}}\frac{\mathrm{d}(\Delta m_{(\mathrm{E})})}{\mathrm{d}t} + \frac{W_{\mathrm{C}^+}}{W_\mathrm{CA}F}j_{(\mathrm{E})} \qquad (\mathrm{A8})$$

Negative flux values refer to ejection and positive values to incorporation of species in the film. Note that both ionic fluxes contain contributions from solvent; this is because the set of simultaneous expressions given by Eqs. (A1) and (A2) is underdetermined. However it is often the case that certain assumptions can be made about these solvent contributions. For example, when the sign of the flux for a given ionic species is contrary to expectations, it can sometimes be assumed that solvent transport is contributing significantly to the overall mass change. Also, it is often the case that assumptions can be made as to the degree of swelling (either from solvent or ion incorporation) that can be achieved for a given type of film, based on previous experimental studies of the material (e.g. ellipsometric film thickness measurements in different redox states, expected degree of cross-linking, etc.). Note also that equations for molar fluxes represent quantitative calculations of ionic fluxes, so they can be compared directly to the currents/F in cyclic voltammetric experiments.

In this case where only cation and water molecules participation are observed during the redox process, the molar fluxes for these both species can be derived from the reorganization of Eqs. (A7) and (A8), resulting in

$$\frac{\mathrm{d}\xi_{\mathrm{C}^+(\mathrm{E})}}{\mathrm{d}t} = -\frac{1}{F}j_{(\mathrm{E})} \qquad (\mathrm{A9})$$

for cations, and

$$\frac{\mathrm{d}\xi_{\mathrm{s}(\mathrm{E})}}{\mathrm{d}t} = \frac{1}{W_\mathrm{s}}\frac{\mathrm{d}(\Delta m_{(\mathrm{E})})}{\mathrm{d}t} + \frac{W_{\mathrm{C}^+}}{W_\mathrm{s}F}j_{(\mathrm{E})} \qquad (\mathrm{A10})$$

for solvent molecules.

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