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Influence of chloride anions on the electrodeposition and electroactivity of the polymer matrix in polypyrrole, poly(*N*-methylpyrrole) and polypyrrole derivatives functionalized by titanocene centers, in dry non-aqueous solutions

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Abstract We report electrochemical studies on the influence of a small concentration of chloride ions on the electroactivity of the polymer matrix of polypyrrole (PPy), poly(*N*-methylpyrrole) [p(*N*-MePy)] and a poly(titanocene-propyl-pyrrole) derivative, p(Tc3Py) [Tc(CH₂)₃NC₄H₄; Tc = CpCp'TiCl₂; Cp = C₅H₅; Cp' = C₅H₄] in acetonitrile (AN), tetrahydrofuran (THF) and *N,N*-dimethylformamide (DMF). The polymer films were obtained on Pt disc electrodes from AN solutions of the monomers containing 0.1 M tetrabutylammonium hexafluorophosphate (TBAPF₆) as the supporting electrolyte and then transferred to the corresponding monomer-free solution. Studies in Cl⁻-containing solutions have shown that the p(Tc3Py) matrix is very sensitive to the presence of Cl⁻ ions in all the above solvents, namely that it was subjected to electrochemical degradation at potentials above 0.1 V vs. a Ag/0.01 M Ag⁺ in AN reference electrode. Degradation of the p(Tc3Py) matrix was also observed in chloride-free DMF + TBAPF₆ solutions. Addition of chloride ions to the AN solution containing pyrrole, *N*-methylpyrrole or Tc3Py inhibits the deposition of the polymer films. On the other hand, we have found that PPy and p(*N*-MePy) matrices after their deposition in chloride-free AN solutions show much more stable redox

responses in contact with chloride and/or DMF solutions. Possible mechanisms of these effects are discussed.

Keywords Functionalized films · Immobilized titanocene · Polymer chlorination · Poly(*N*-methylpyrrole) · Polypyrrole

Abbreviations AN acetonitrile · Cp cyclopentadienyl · DMF *N,N*-dimethylformamide · *N*-MePy *N*-methylpyrrole · *p*(*N*-MePy) poly(*N*-methylpyrrole) · PPy polypyrrole · *p*(Tc3Py) poly[Tc(CH₂)₃NC₄H₄] · Py pyrrole · Tc titanocene = bis(cyclopentadienyl)titanium dichloride, Cp₂TiCl₂, or its radical CpCp'TiCl₂ (Cp' = C₅H₄) · Tc3Py titanocene-propyl-pyrrole, Tc(CH₂)₃NC₄H₄ · THF tetrahydrofuran

Introduction

Functionalization of conducting polymers attracts great interest because it is a powerful tool for the preparation of materials with very specific properties for many practical applications, such as chemical and biochemical sensors, catalysts or electrochromic devices.

In our previous papers we have reported the electrochemical behavior of polypyrrole (PPy) with bis(cyclopentadienyl)titanium(IV) dichloride, Cp₂TiCl₂ (Cp = C₅H₅), linked to nitrogen in the pyrrole ring via an aliphatic chain, (CH₂)₃ [1, 2]. Titanocene dichloride, Cp₂TiCl₂, in its free form is a well-known catalyst of many organic processes, including alkene polymerization as well as numerous organic reactions (isomerization, hydrogenation, C–C coupling, etc.) [3, 4]. Immobilization of titanocene (Tc) centers inside a porous polymer membrane opens the prospect of creating a heterogeneous catalyst, advantageous in some aspects with respect to its homogeneous analogue.

Electrodes modified with polymers with attached electroactive centers reveal the characteristic electro-

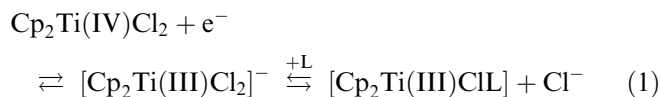
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Dedicated to the memory of Harry B. Mark, Jr. (28 February 1934–3 March 2003)

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chemical response both of the centers and the polymer matrix. In general, the reduction of titanocene in the film occurs according to a mechanism similar to that reported for this system in solution [5, 6, 7, 8, 9, 10, 11]. According to this scheme, one-electron reduction of the complex leads to the bis(cyclopentadienyl)titanium(III) dichloride radical anion, which is subject to a very rapid elimination of one of the Cl⁻ anions from the complex substituted by the solvent (L) molecule [12, 13, 14]:



The reversibility of the chemical step in reaction (1) depends on the experimental conditions, first of all of the solution composition (solvent, electrolyte). For certain solvents (acetonitrile, AN, *N,N*-dimethylformamide, DMF) the reduction is *electrochemically* irreversible if the electrolyte solution does not contain chloride [7, 14]. In contrast, a strong and quasi-reversible reoxidation peak is observed in cyclic voltammograms obtained in tetrahydrofuran (THF) without chloride, with tetrabutylammonium hexafluorophosphate (TBAPF₆) as the supporting electrolyte [14].

Our studies have revealed a profound parallel between the redox response of free and immobilized Tc complexes, in particular a much greater reversibility of their cyclic voltammetry (CV) response if the film is in contact with a chloride-free THF solution. However, consecutive scans of the electrode modified with titanocene-polypyrrole film in THF + 0.1 M TBAPF₆ show a gradual decrease of electroactivity of the titanocene centers, probably due to dissociation of the reduced titanocene complex followed by coordination of the solvent molecule. For sufficiently thick films, most of the thus-formed chloride anions are left inside the film so that they may return to the complex in the course of its reoxidation. However, a certain amount of "free" chloride anions is likely expelled from the polymer matrix to the solution and they diffuse away from the electrode. Most of them are lost for the reoxidation process since the electron exchange is accompanied mostly by the incorporation of background anions, PF₆⁻, instead of chloride, with the loss of the film electroactivity in this range of potentials.

This finding has led us to the idea of replacing the background electrolyte in solution by a chloride soluble in the corresponding solvent. This change resulted indeed in an essential improvement of the stability of the response of immobilized centers. However, the presence of chloride anions led also to certain harmful effects for the film response in the range of the polymer matrix (see below). This observation was unexpected since chlorides (mostly in aqueous medium) represent one of the most popular electrolytes for studies of electron-conducting poly-

mers, including polypyrrole and its derivatives [15, 16, 17, 18, 19, 20].

The influence of Cl⁻ ions on the electroactivity of polypyrrole is still a matter of controversy in the literature. It has been reported in some papers that Cl⁻ ions enhance the electrosynthesis of polypyrrole films in aqueous solutions [21] and increase the conductivity of the polymer [22, 23]. In contrast, according to some other authors, polypyrrole undergoes degradation because of a chemical reaction with electrolytically generated species in aqueous solutions containing Cl⁻ ions [24] or by hydroxylation of the chlorine-substituted polypyrrole [25]. Information on chloride effects in non-aqueous solutions is scarce. A "chlorination" of PPy but without a serious loss of electroactivity has been reported for AN solutions [26].

A specific feature of our studies was the use of distilled organic solvents necessary to observe a stable response of immobilized Tc centers in a monomer-free solution. In this paper we present results which demonstrate a strong influence of chloride anions both on the stage of electrodeposition of PPy, poly(*N*-methylpyrrole) [p(N-MePy)] or titanocene-polypyrrole films and on the p(Tc3Py) (poly [Tc(CH₂)₃NC₄H₄]) matrix response in the course of its cycling in the monomer-free solution in AN, THF and DMF. The found effects represent a serious problem for reaching a stable electrochemical behavior of the latter system in the Tc range of potentials that are essential for its further practical applications.

Experimental

All electrochemical experiments were done in a conventional, single-compartment cell with a platinum wire counter electrode (CE) and a Ag/(0.01 M AgNO₃ + 0.1 M TBAPF₆ in AN) double-junction reference electrode (RE). All potentials below are referred to this reference electrode. Electropolymerization of Tc3Py, N-MePy and Py was carried out on a Pt disc electrode with a surface area of 0.005 cm² or 0.02 cm² from the monomer solutions (1–5 mM) in AN containing 0.1 M TBAPF₆ as the supporting electrolyte, by means of an AUTOLAB potentiostat (Ecochemie, The Netherlands). The polymer films for studies in Cl⁻-containing solutions were formed potentiostatically, according to the procedure described previously [1, 2], by applying a potential step from 0 V to 0.78 V for preparation of p(Tc3Py), 0.72 V for p(N-MePy) and 0.71 V for PPy, with control of the polymerization charge to obtain films of reproducible properties. The influence of Cl⁻ on electrodeposition of the polymer films was studied by CV. The electrodes were cycled at a scan rate of 100 mV s⁻¹ within a potential range from -0.25 to 0.98 V in the solution of Tc3Py, from -0.25 to 0.82 V in N-MePy and from -1.0 to 0.82 V in Py solutions in AN containing about 0.02 M LiCl (saturated solution) and the supporting electrolyte (0.1 M).

All salts, TBAPF₆ (Fluka), LiCl (Fluka) and LiClO₄ (Aldrich), were dried under vacuum at 80 °C for several hours prior to use. THF (AnalytiCals, Carlo Erba) stabilized by hydroquinone was distilled over metallic Na + benzophenone (Merck). AN for polymerization was of spectroscopic grade (99.5%), with a water content < 0.03%. AN for CV studies of the films in monomer-free solution was HPLC grade (Carlo Erba) with initial water content < 0.02%, distilled before the use. All solutions were thoroughly deaerated by vacuum pumping and filling with dry argon prior to the experiments.

Results and discussion

Influence of a small amount of chloride on the redox behavior of Tc centers and the polymer matrix of p(Tc3Py) in THF + 0.1 M TBAPF₆

In order to compare the behavior of p(Tc3Py) in Cl⁻-free solution and in the presence of Cl⁻, two identical films were deposited on Pt electrodes at a charge density of 6 mC cm⁻² from 0.1 M TBAPF₆ + 0.001 M Tc3Py in AN. The qualitative identity of the films was confirmed by exactly the same CVs in the range of PPy electroactivity (from -0.7 to 0.55 V) in the monomer-free solution (besides, we have checked the reproducibility of the redox response of Tc centers for another series of such films). Then, the films were subjected to several consecutive scans in the "whole" potential range, i.e. between -1.6 and 0.55 V, one film being cycled in THF + 0.1 M TBAPF₆ while the second one in the same solution with a small addition of LiCl (well below 0.01 M in view of the low solubility of this salt in THF).

As visible in Fig. 1a, the presence of Cl⁻ improves a little the reversibility of the Tc redox reaction in the first cycle (the charge involved in reoxidation of the centers is about 22–25% higher than that in Cl⁻-free solution). However, the presence of chloride does not prevent a gradual decrease of the redox activity in the next cycles, but only decelerates this process (cf. curves 6' and 6 in Fig. 1a). This is not surprising because the chloride fraction in the solution is low with respect to that of PF₆⁻, and therefore it is the latter anions which compensate the electronic charge of the polymer and replace the chlorides in the matrix. At the same time, some additional undesirable changes occur in the polymer matrix upon treatment in Cl⁻-containing solution. Namely, a remarkable increase of the current, related to an irreversible faradaic reaction of the polymer matrix, is observed at the positive limit of the potential range. In effect, the reduction current in the reverse scan markedly decreases. Similar studies performed for a thicker film (obtained at a charge density of 25 mC cm⁻²) confirmed a marked destroying effect of chloride on the electroactivity of the polymer matrix (Fig. 1b).

According to the literature, film stability and conductivity may be influenced not only by anions compensating the positive charge of the polymer matrix but also by cations which may change the electronic interaction between the polymer chain and the anions and/or the ion pairs [21, 27]. Therefore, in order to separate the influence of Cl⁻ and Li⁺ ions on the electroactivity of the p(Tc3Py) matrix, a series of redox cycles in the range of the PPy matrix of the thicker polymer film was repeated subsequently in several electrolytes in THF. Firstly, the film was cycled in the monomer-free solution of TBAPF₆. After three cycles with a stable voltammetric response, the polymer was transferred to 0.1 M LiClO₄ in THF and submitted again to several subsequent scans. Finally, a small amount of LiCl was

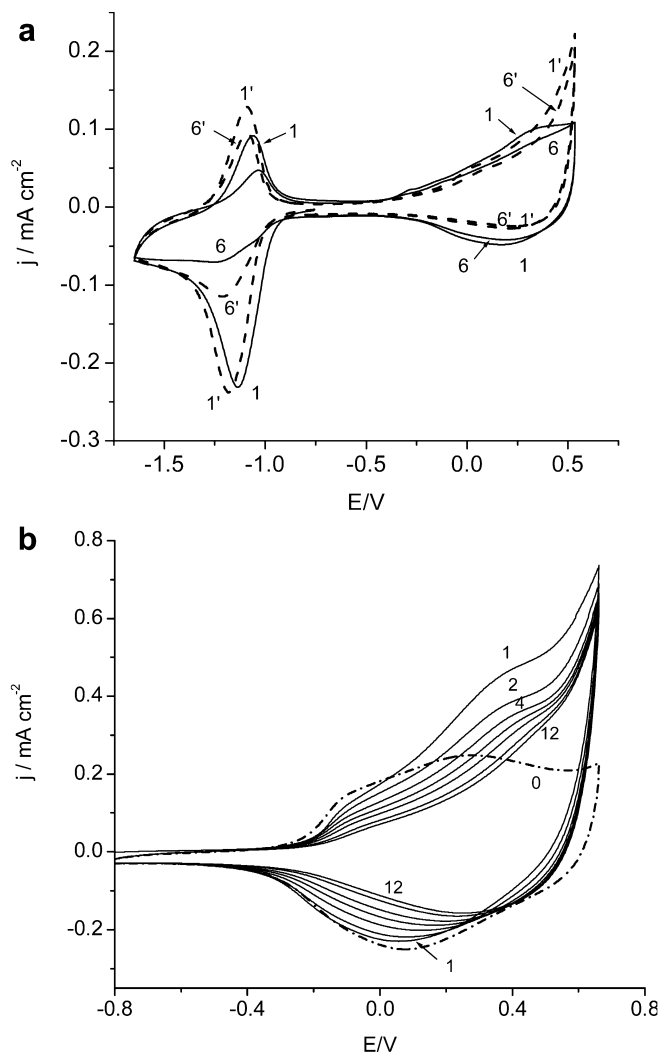


Fig. 1 (a) Influence of chloride ions on the electroactivity of titanocene centers and the polymer matrix for thin polymer films (deposition charge density: 6 mC cm⁻²). Numbers 1 and 6 correspond to the 1st and 6th scans in THF solutions of PF₆⁻ without Cl⁻ ions (solid line) and in the presence of a small addition of Cl⁻ ions (<0.01 M) (1' and 6', dashed lines). (b) Consecutive scans in the range of the PPy matrix for a thicker p(Tc3Py) film (25 mC cm⁻²) in THF + 0.1 M TBAPF₆ in the presence of a small amount of Cl⁻ ions. The dashed line corresponds to the curve obtained in the supporting electrolyte before the Cl⁻ treatment

added to the solution of 0.1 M LiClO₄ and a series of potential scans was performed in the same potential range (-0.8 V, 0.7 V). The first and tenth scans in each electrolyte studied are compared respectively in Fig. 2a and 2b. As can be seen, replacement of TBAPF₆ by LiClO₄ did not influence the behavior of the film. The redox charge density (of about 1.8 mC cm⁻²) was stable in the subsequent voltammetric scans. In contrast, the addition of even a small amount of Cl⁻ ions gave rise to significant changes in the voltammograms.

A significant increase of the anodic current, starting from 0.1 V, followed by the decrease of the reduction current in the backward scan and a progressive loss of the film electroactivity in the subsequent cycles, indicate

that a faradaic process involving Cl^- ions occurs in the polymer film at $E > 0.1$ V.

The destroying effect of a small amount of chloride on the electroactivity of the p(Tc3Py) matrix seems to be stronger than that reported in the literature for unsubstituted PPy film in AN + 0.1 M TEACl [26]. One of the reasons for this difference between the two polymers may be an electronic effect of the alkyl spacer between the Py ring and the titanocene center, which may change the charge distribution in the Py ring, enhancing the "chlorination" of the polymer matrix. Another possibility is some distortion from co-planarity in the polymer chain due to the presence of the bulky titanocene substituent. This may enhance nucleophilic attack of

Cl^- ions on radical cations created along the polymer chain, owing to their better accessibility. A strong distortion from planarity and conjugation between the pyrrole units have been also postulated in the literature in the presence of a much smaller *N*-methyl substituent [28, 29].

Therefore, in order to check the role of *N*-substituents on the electrochemical behavior of the polymer matrix, namely on the polymer stability in Cl^- -containing solution, we performed a series of studies on the polymerization and redox activity of PPy and another PPy derivative substituted with a relatively small methyl group, p(N-MePy), in a pure supporting electrolyte (0.1 M LiClO_4 or 0.1 M TBAPF₆) and in the presence of a small amount of chloride.

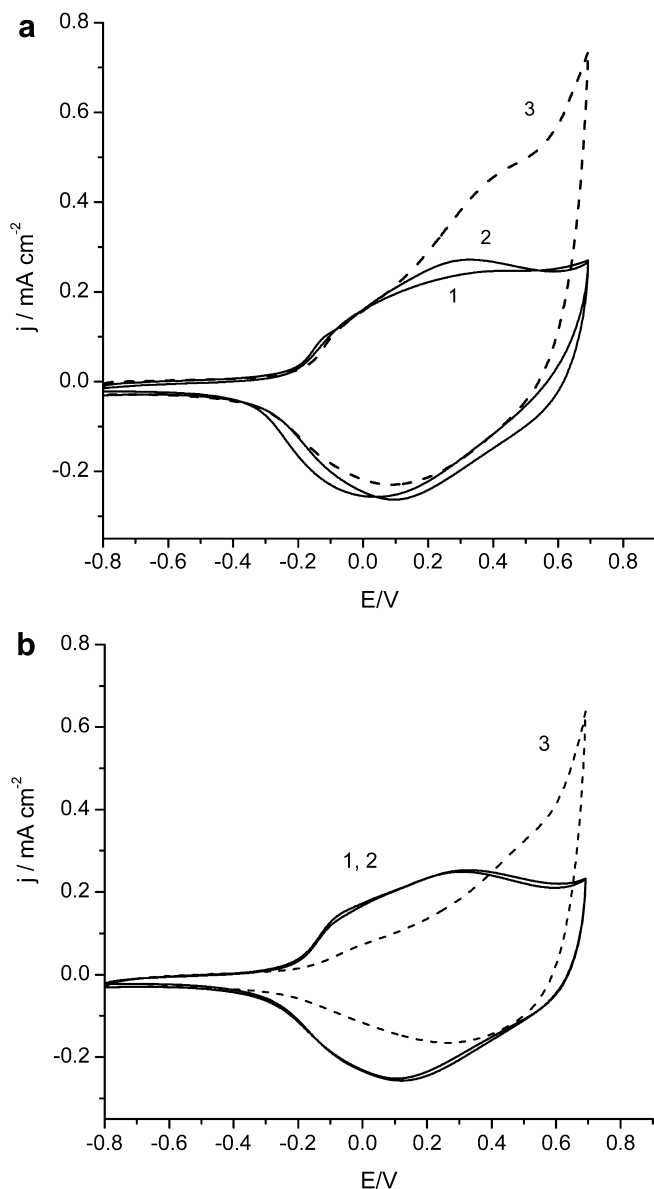


Fig. 2 Cyclic voltammograms corresponding to the 1st (a) and 10th (b) scans of p(Tc3Py) film in THF containing 0.1 M TBAPF₆ (curve 1), 0.1 M LiClO_4 (curve 2) and 0.1 M LiClO_4 with a small amount of LiCl (curve 3)

Influence of small amount of LiCl (about 0.02 M) on the electrosynthesis of PPy and p(N-MePy) in AN + 0.1 M TBAPF₆

Figure 3a and 3b present voltammograms of pyrrole polymerization by cycling at a Pt electrode in AN solution of 0.005 M Py + 0.1 M TBAPF₆ and in the same solution after addition of a small amount of Cl^- ions. As may be seen in Fig. 3a, in the solution without chloride the polymer easily formed on the electrode. The charge yield of electropolymerization, γ , characterized by the ratio of the reduction charge of the polymer in the monomer-free solution to the charge involved in oxidation of the monomer during polymerization, 10.5%, is close to the theoretical limit, about 11%. For comparison, the value of γ for electrodeposition of p(Tc3Py) was not especially lower, about 8–10% [2].

A comparative experiment on pyrrole polymerization was performed under similar conditions but with a small addition of LiCl to the polymerization bath. As visible in Fig. 3b, the current corresponding to oxidation of the monomer decreased cycle by cycle. Moreover, the voltammograms shift to more positive potentials and no reduction wave for the polymer appears (cf. Fig. 3a). Thus, one can conclude that, during potential cycling in the monomer solution containing a small amount of Cl^- , the electrode surface is covered with a highly resistive layer which impedes charge transfer between the electrode and the solution and inhibits the formation of a conducting polymer film.

Comparison of the first cycles for a clean Pt surface in the three solutions presented in Fig. 3c shows that oxidation of Cl^- in the monomer-free solution starts in the same potential range as monomer oxidation. On the other hand, addition of a small amount of chloride to the Py solution gives rise to a shift of the oxidation current of the monomer to less positive potentials. Thus, it seems probable that the Cl_2 molecules (or the intermediate species, chemisorbed chlorine atoms) which are formed at the electrode initiate the chlorination of the monomer and/or react with the already deposited polymer, leading to its degradation. Another possible

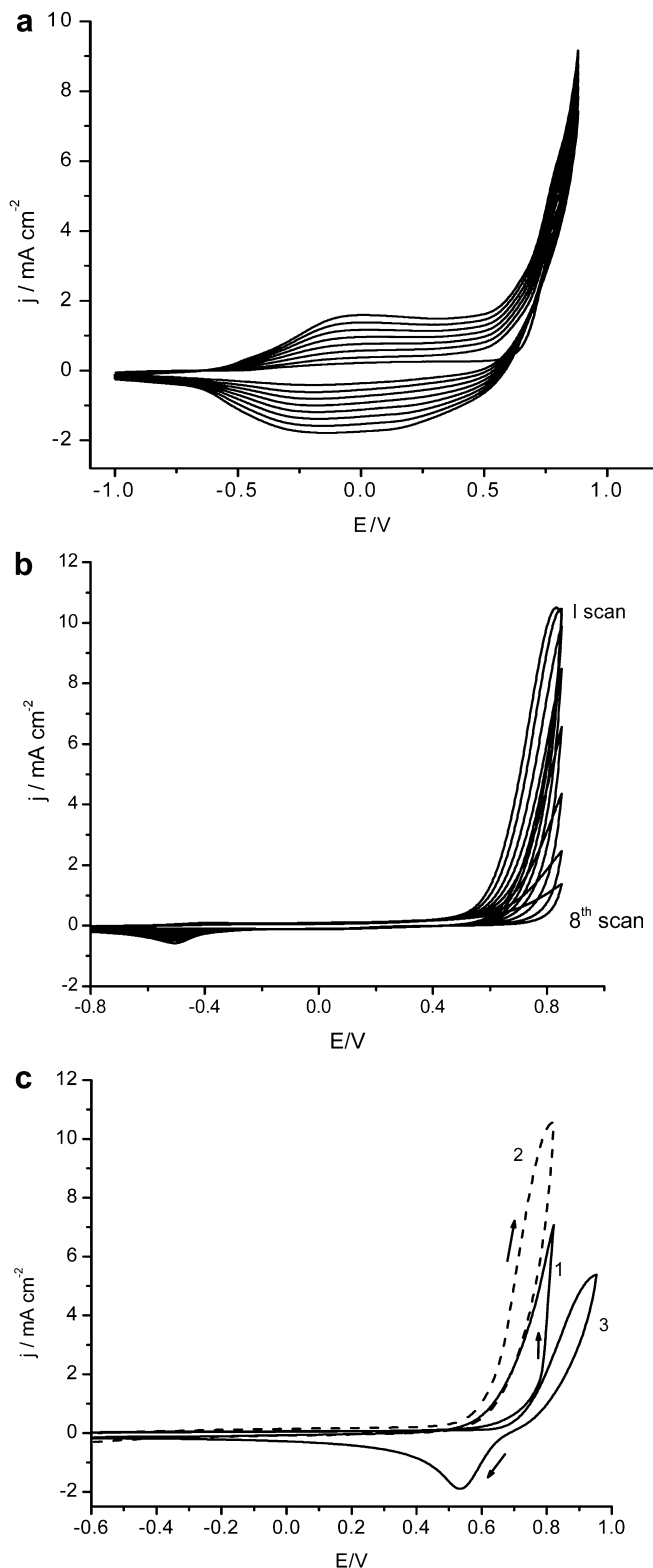


Fig. 3 Cyclic voltammograms for a Pt electrode in AN solution containing: (a) 0.1 M TBAPF₆+0.005 M pyrrole; (b) 0.1 M TBAPF₆+0.005 M pyrrole+ca. 0.02 M LiCl (saturated solution). (c) Comparison of first voltammetric scans for a Pt electrode in pyrrole solution+0.1 M TBAPF₆ in AN without Cl⁻ ions (curve 1) and in the presence of Cl⁻ (curve 2). Curve 3 was recorded on a bare Pt electrode in the monomer-free solution of TBAPF₆ containing 0.02 M LiCl

mechanism is reaction between the generated pyrrole cation-radicals and chloride anions. These experimental observations lead to the conclusion that electroactive polypyrrole films cannot be formed in AN solutions (with a relatively low content of water) containing even a small amount of chloride ion.

The same experiments were performed for electro-deposition of p(N-MePy) and p(Tc3Py) films. In both cases, no films were formed on the electrodes after addition of chloride to the monomer solutions. The subsequent voltammograms, different from either those obtained in pure monomer solution or those in the monomer-free 0.02 M LiCl (Figs. 4 and 5), suggest that the reaction between chloride and monomer occurs but without formation of a film on the electrode. The increase of the monomer or chloride concentrations does not influence the shape of the resultant voltammograms, only the current intensity.

Influence of a small amount of LiCl (about 0.02 M) on the electroactivity of PPy and p(N-MePy) films in AN+0.1 M LiClO₄

In order to check whether chloride ions, due to strong nucleophilic properties, may also react irreversibly with radical cations or dications generated at the polymer chains, we compared the electroactivity of PPy and p(N-MePy) (already deposited from a chloride-free solution) in acetonitrile solutions with or without Cl⁻. Qualitatively, the results were similar to those presented by Pickup and co-workers [26].

As shown in Fig. 6, cycling in the Cl⁻ solution did not influence noticeably the electroactivity either of PPy or p(N-MePy). The principal effect of chloride ions on the charging curve of the PPy or p(N-MePy) films, the appearance of a drastic increase of the anodic current above 0.1 V (curves 1–5), is qualitatively similar to that for p(Tc3Py) films (Figs. 1 and 2). However, contrary to p(Tc3Py), the unsubstituted polypyrrole and p(N-MePy) do not show any indication of serious *irreversible* deactivation of the polymer. The voltammograms after the back transfer into Cl⁻-free solution are very similar to those before the treatment in Cl⁻ (cf. curves 6 and 0, respectively). The oxidation peaks after the cycles in Cl⁻-containing solutions became a little flattened but the overall charge involved in the redox reaction of the polymer decreased only by about 4% in the case of PPy and 7% for p(N-MePy). Extension of the positive potential to 1.0 V did not affect markedly the electroactivity of these two polymers. At the same time, the decrease of the redox charge of p(Tc3Py) after the treatment in Cl⁻ solution was 35–40%.

Thus, one may conclude that the higher sensitivity of p(Tc3Py) films to chloride than PPy and p(N-MePy) is not due to the electronic effect of the alkyl substituent which separates the titanocene centers from the pyrrole ring, but probably a consequence of the presence of a bulky titanocene group. This may lead to a marked non-

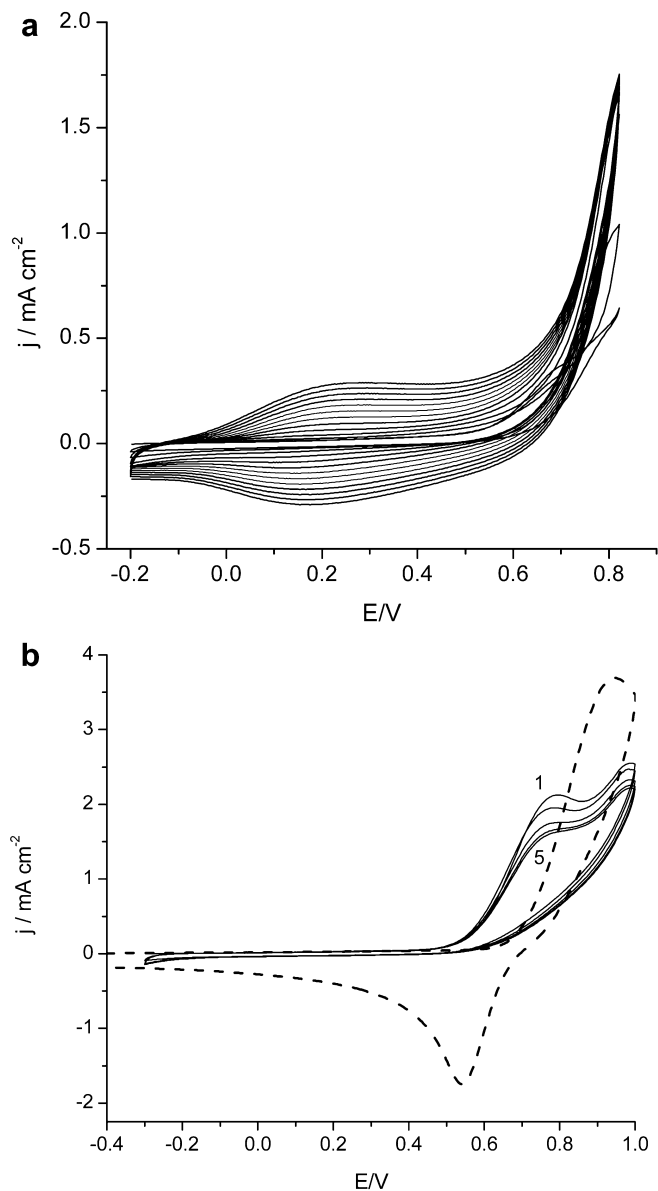


Fig. 4 Cyclic voltammograms for a Pt electrode in AN solution containing: (a) 0.1 M TBAPF₆+0.001 M N-MePy; (b) 0.1 M TBAPF₆+0.001 M N-MePy+ca. 0.02 M LiCl (saturated solution). The *dashed line* corresponds to the curve obtained in the solution without any monomer

coplanarity of the polymer chain and an easier reaction of radical cations with chloride ions due to better accessibility of electroactive centers in the polymer matrix.

As a practical consequence, we have to keep in mind that studies of the electroactivity of Tc centers immobilized in a polypyrrole matrix in Cl⁻-containing solutions should be carried out in a potential range limited to about 0.1 V, to avoid the degradation of the polymer matrix. This restriction represents a serious problem since the *complete* reoxidation of Tc centers after their reduction requires passing the prepeak located within the potential range of the polymer matrix [2].

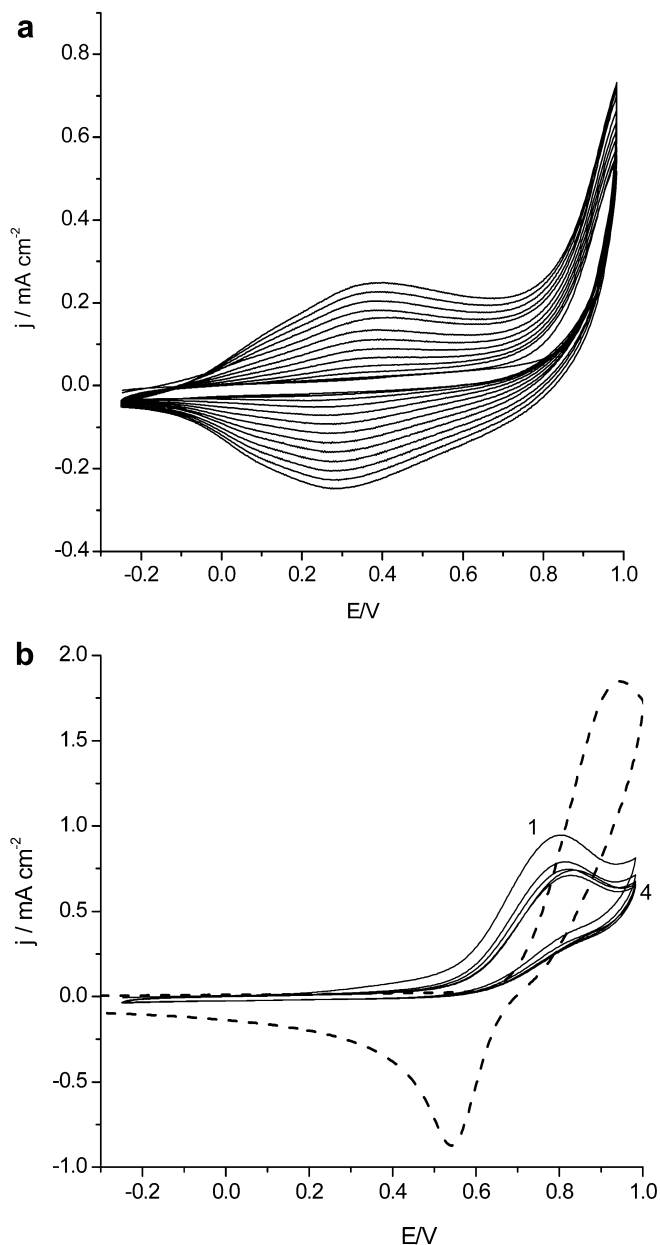


Fig. 5 Cyclic voltammograms for a Pt electrode in AN solution containing: (a) 0.1 M TBAPF₆+0.001 M Tc3Py; (b) 0.1 M TBAPF₆+0.001 M Tc3Py+ca. 0.02 M LiCl (saturated solution). The *dashed line* corresponds to the curve obtained in the solution without any monomer

Electrochemical properties of p(Tc3Py) and PPy in DMF in pure 0.1 M LiClO₄ and in the presence of a small amount of LiCl

The properties of PPy and p(Tc3Py) films were also examined in DMF. This solvent is attractive due to the high solubility of lithium chloride. For comparison, the solubility of LiCl is about 0.02 mol dm⁻³ in AN, well below 0.01 mol dm⁻³ in THF but 2.6 mol dm⁻³ in DMF [30]. Therefore, in the latter solvent, studies of the chloride influence on the reversibility of the redox

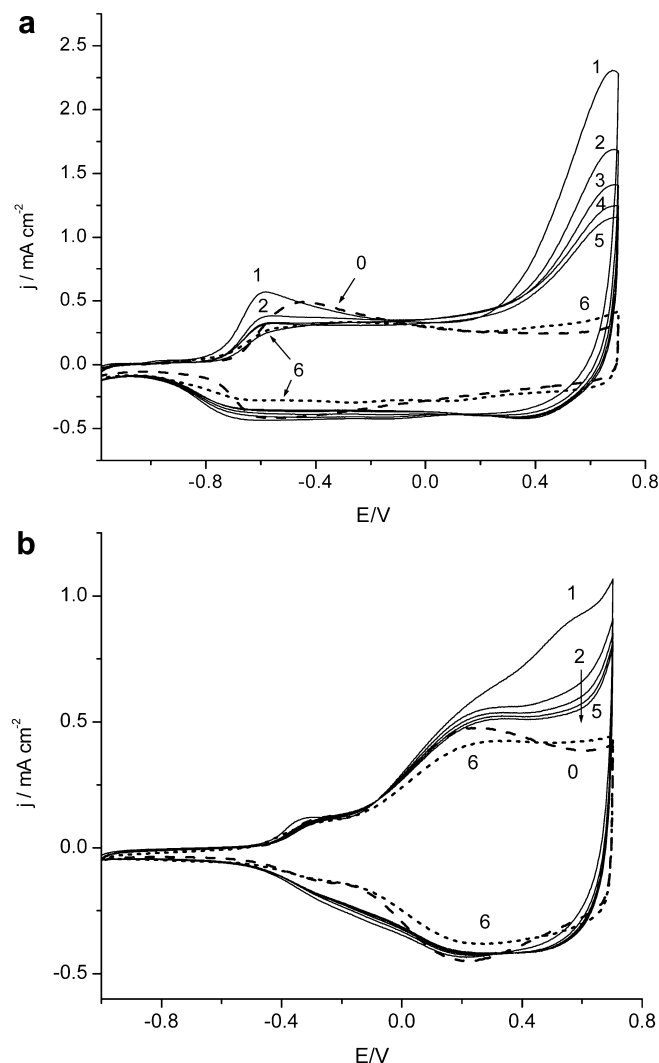


Fig. 6 Cyclic voltammograms of PPy (a) and p(N-MePy) (b) films in AN + 0.1 M LiClO₄ (curves 0), then after the transfer of the films into an AN solution of 0.1 M LiClO₄ + 0.02 M LiCl (curves 1–5) and back into the LiClO₄ solution (curves 6)

reaction of Tc centers immobilized in the polymer matrix may be performed in a wide range of Cl⁻ concentrations and even in pure chloride solutions, as has been reported in the literature for solutions of free Cp₂TiCl₂ [7]. The CVs for the redox reaction of p(Tc3Py) film in a chloride-free solution of DMF + 0.1 M LiClO₄ are presented in Fig. 7a. A comparison with the reference curve obtained in THF solution for the same electrolyte (dashed line) reveals that the polymer oxidation in DMF starts at a much more positive potential than in THF, but then the current achieves values markedly higher than those observed in THF. Moreover, the consecutive scans performed in DMF lead to a gradual irreversible decrease of the polymer electroactivity (curves 1–5 in Fig. 7a). The charge consumed in the polymer reduction decreases from a value of 1.8 mC cm⁻² in THF to 1 mC cm⁻² for the first scan carried out in DMF and 0.84 mC cm⁻² for the fifth

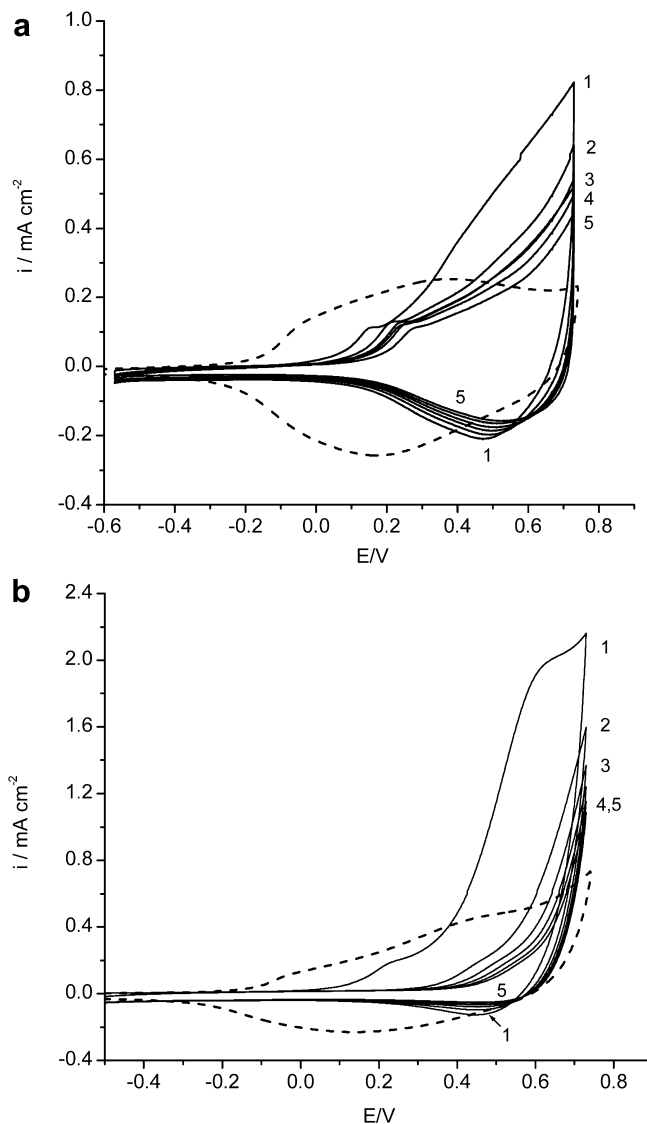


Fig. 7 Cyclic voltammograms of p(Tc3Py) films (deposition charge 25 mC cm⁻²) in the range of electroactivity of the PPy matrix in DMF solutions containing 0.1 M LiClO₄ (a) or 0.1 M LiCl (b) as supporting electrolyte. The dashed curves correspond to the CV obtained for similar films in THF containing 0.1 M LiClO₄ (a) and 0.1 M LiClO₄ + 0.01 M LiCl (b)

scan in this solvent. This clearly indicates that DMF itself has a harmful effect on the electroactivity of the polymer matrix. The loss of polymer activity is likely a consequence of a faradaic reaction of DMF with charges at the matrix.

As shown in Fig. 7b, degradation of p(Tc3Py) is strongly enhanced after replacement of LiClO₄ by LiCl supporting electrolyte.

As has been reported in the literature [31], DMF also deactivates the unsubstituted polypyrrole matrix during polymerization in this solvent. PPy films electrosynthesized in DMF contained an appreciable amounts of C=O groups due to overoxidation and revealed a lowered conductivity, presumably because of disruption of

the conjugated structure. We found that even a drop of DMF added to 10 mL of the acetonitrile bath for p(Tc3Py) electrodeposition prevented formation of the polymer film on the electrode.

In contrast, the results presented in Fig. 8 demonstrate that PPy films deposited from AN solution and then transferred into DMF + 0.1 M LiClO₄ are resistant to attack by DMF molecules. These results are consistent with those presented by Otero et al. [32] in their study of solvent influence on the storage ability of polypyrrole. Our CV recorded in DMF (Fig. 8) differs only slightly from the curve obtained for the same film in AN solution with the same supporting electrolyte (cf. curves 1 and 2). Analogous data [32] show a greater difference between the redox properties of PPy in these two solvents.

Moreover, we have found that even these small changes in the redox response of PPy in DMF compared to AN are reversible. When the film is transferred back into AN solution, after a few cycles the shape of the voltammograms becomes again similar to the initial curve recorded in this solvent (Fig. 8a, curves 3 and 1, respectively).

Addition of LiCl to DMF does not lead to a marked degradation of PPy electroactivity during redox cycling. In spite of some changes in the shape of subsequent scans in DMF + 0.1 M LiClO₄ + 0.01 M LiCl (Fig. 8b), the initial redox behavior is nearly restored when the polymer is transferred back into AN + 0.1 M LiClO₄ (cf. curves 4 and 1 in Fig. 8a). After polymer treatment in Cl⁻-containing DMF solution, the redox peaks became broader but the overall charge density involved in the polymer oxidation is only a little smaller than that for the fresh film (3.8 and 4 mC cm⁻², respectively). This leads to the conclusion that the behavior of PPy in DMF solution containing Cl⁻ is similar to that observed in the presence of Cl⁻ in AN.

Conclusions

This study has shown that the addition of even a small amount of chloride (of the order of 0.01 M or even lower) to solutions of 0.1 M TBAPF₆ in dry THF, AN or DMF has two opposite effects on the electroactivity of p(Tc3Py) film. One can observe some improvement of the reversibility of the redox reaction of Tc centers (in the negative potential range -1.6, -0.5 V), in combination with a decrease of the electroactivity of the polypyrrole matrix (in the potential range -0.5, 0.7 V). Therefore, in order to avoid the degradation of the polymer matrix, investigations of the electroactivity of immobilized Tc centers in Cl⁻-containing solutions should be performed in the potential range limited to about 0.1 V.

The electroactivity of the p(Tc3Py) matrix is destroyed not only by chloride but also by DMF itself, used as a solvent in the polymer studies. In contrast, unsubstituted PPy and p(N-MePy), deposited from a

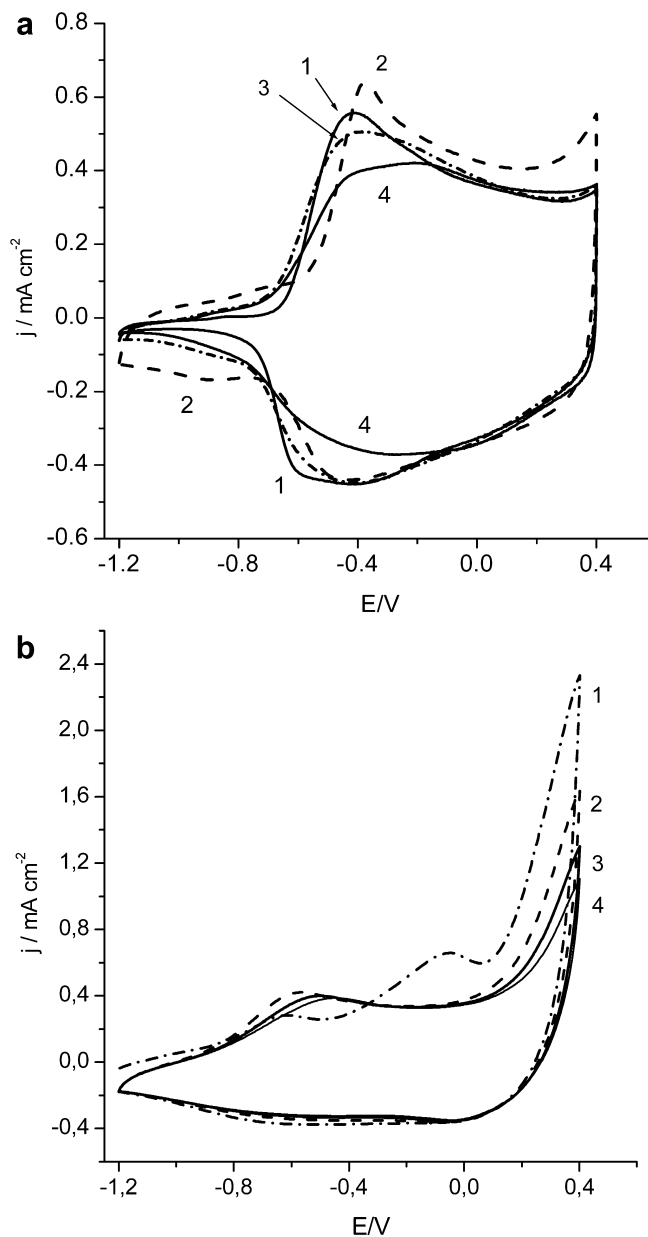


Fig. 8 (a) Cyclic voltammograms of PPy film (deposition charge 25 mC cm⁻²) in a 0.1 M solution of LiClO₄ in: AN (curve 1), DMF (curve 2), in AN after cycles in DMF (curve 3) and in AN after treatment in DMF + LiCl (curve 4). (b) Consecutive cyclic voltammograms of PPy film in DMF containing 0.1 M LiClO₄ + 0.01 M LiCl

background AN solution and then transferred into a solution containing these agents, chloride and/or DMF, are relatively resistive in the course of cycling within the range of the polymer redox activity.

The deposition process is more sensitive to the action of chloride, which shows a harmful effect even for polymerization of unsubstituted pyrrole in a dry AN solution. A small amount of Cl⁻ lead to the formation of a highly resistive layer on the electrode, which impedes the charge transfer between the electrode and the solution and prevents the formation of a conducting

polymer film. Similarly, addition of Cl^- to the electro-deposition bath of p(N-MePy) or p(Tc3Py) prevents formation of the film on the electrode.

The observed low electrochemical stability of the p(Tc3Py) matrix in AN, THF and DMF solutions containing Cl^- ions is probably a consequence of the presence of the bulky substituent attached to the PPy ring. This may cause some distortion of co-planarity of the polymer chain, likely enhancing the reaction of the oxidized polymer matrix with Cl^- ions.

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